

**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY  
(KNUST), KUMASI**

**SCHOOL OF GRADUATE STUDIES**

**PERVAPORATIVE SEPARATION OF ETHANOL-WATER MIXTURES  
USING GHANAIAN ZEOLITE-CLAY FILLED PVA COMPOSITE  
MEMBRANE**

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requirement for the award of the degree**

**Of**

**MASTER OF SCIENCE  
IN  
CHEMICAL ENGINEERING**

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## CERTIFICATION

I, Mohammed Nafiu Zainudeen, hereby declare that this thesis, “Pervaporative Separation of Ethanol-Water mixture using Ghanaian Zeolite-clay filled PVA Composite Membrane”, consists entirely of my own original work produced from research undertaken under supervision of the undersigned and that no part of it has been published or presented for another degree elsewhere, except for the permissible excerpts/references from other sources, which have been duly acknowledged.

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## ABSTRACT

A pervaporative separation of ethanol-water mixture was successfully performed using a PVA based composite membrane filled with zeolites made from Ghanaian clay. The substrate for the ultra-thin PVA composite membrane was made of polysulphone. The pervaporation cell was fabricated locally from scrap aluminium and feed concentrations of ethanol-water mixture ranging from 60 to 90 v% were separated.

The clay samples used in the development of the membranes were obtained from Abonku, Anfoega and Teleku-Bokazu. The effective surface area of the membranes for separation was  $0.007854 \text{ m}^2$ . The experiments were carried out at room temperature of  $30^{\circ}\text{C}$ . For each run, a feed concentrations of 60 v%, 70 v%, 80 v% and 90 v% ethanol was used and respective permeate concentrations were measured accordingly. The pressure at the feed was kept at atmospheric while that at the permeate side was kept at vacuum pressure in the range of 0.10 to  $0.15\text{kg/cm}^2$ .

For all the feed concentrations, the final retentate concentrations after 10 hours of experiment produced relatively higher concentrations of ethanol, signifying separation of the mixture. For a feed concentration of 90 v %, the mixture was enriched to concentrations more than 95 v% and a separation factor of 85.09 and more was obtained.

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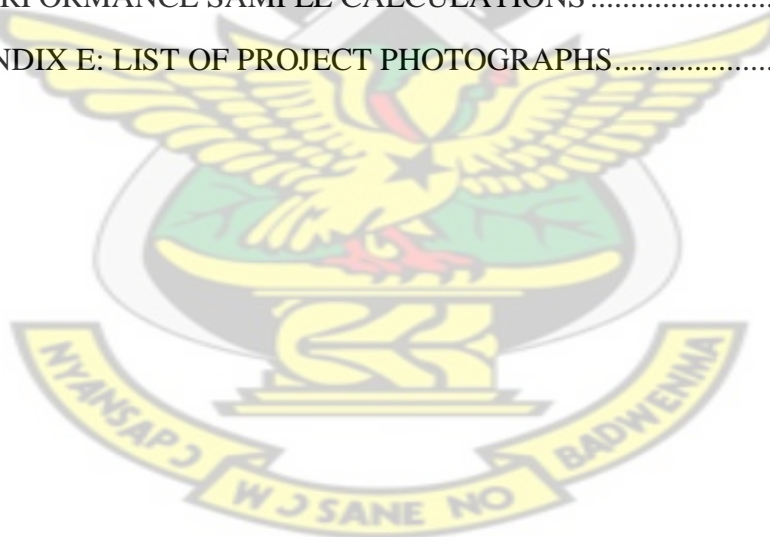
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## GLOSSARY

### Alphabetical abbreviations

$A_e$	Effective membrane area
ABK	Abonku zeolite clay filled membrane
$C_{A,M}$	Concentration profile of the diffusing molecule, A, in the separating layer
$C_{A,V}$	Concentration of the more permeating molecule in the permeate chamber of the Pervaporation cell
$C_{A,1}$	Concentration of the more permeating molecule at the upstream surface of the separating layer
$C_{A,2}$	Concentration of the more permeating molecule at the upstream surface of the support
DMAc	Dimethyl acetamide
DMF	Dimethyl formamide
FAU	faujasite (mineral group in the zeolite family of silicalite minerals)
$F_D$	total amount of feed prepared
FG	Anfoega zeolite clay filled membrane
$F_{NP}$	Unused amount of feed
GC	Gas Chromatograph
hrs	hours
J	mass flux through a membrane
$l_m$	Membrane thickness
LP	Lower permeate pressure
$L_{R/P}$	Amount lost from retentate and permeate
LTA	Linde Type A zeolite
$m$	mass
Max.	maximum
$m_e$	mass of ethanol
MFI	Mordenite Framework Inverted zeolite
Min.	minimum

MOR	Mordenite zeolite
$m_w$	mass of water
$M_w$	molecular weight
$N_i$	molar transmembrane flux of species i
NMP	N-methyl pyrrolidone
$P$	Pressure of the system
$P_{oi}^*$	Vapour pressure of pure alcohol
$P_{Mi}$	Permeability of species i
$\check{P}_{Mi}$	Permeance of species i
PSf	Polysulphone
PVA	Polyvinyl alcohol
$P_{H_2O}^*$	Vapour pressure of pure water
Q	Amount (mass) of permeate
$R_6$	Total amount of retentate after separation
$r_e$	mass fraction of ethanol in retentate
$r_w$	mass fraction of water in retentate
$t$	permeation (diffusion) time
$T_g$	Glass transition temperature of polymer
TKB	Teleku-Bokazu zeolite-clay filled membrane
$T_m$	Melting temperature of polymer
$T_P$	total mass of permeate
UP	Upper permeate pressure
$v$	volume
$v_e$	volume of ethanol
$v_w$	volume of water
v%	composition based on volume
wt %	composition based on mass (weight)
$X$	Thickness of support layer of composite membrane
$x_A$	mass fraction of the more permeating molecule in the feed



$x_B$	mass fraction of the less permeating molecule in the feed
$x_E$	mass fraction of ethanol in feed
$x_w$	mass fraction of water in feed
$y_E$	mass fraction of ethanol in permeate
$y_A$	mass fraction of more permeating component in the permeate
$y_B$	mass fraction of more permeating component in the permeate
$y_w$	mass fraction of water in permeate

### Greek abbreviations

$\alpha$	separation factor
$\alpha_{A/B}$	selectivity of A with respect to B
$\delta_M$	thickness of the thin membrane separating layer
$\rho$	density
$\rho_E$	density of ethanol
$\rho_w$	density of water
$\gamma_i$	activity coefficient of species $i$

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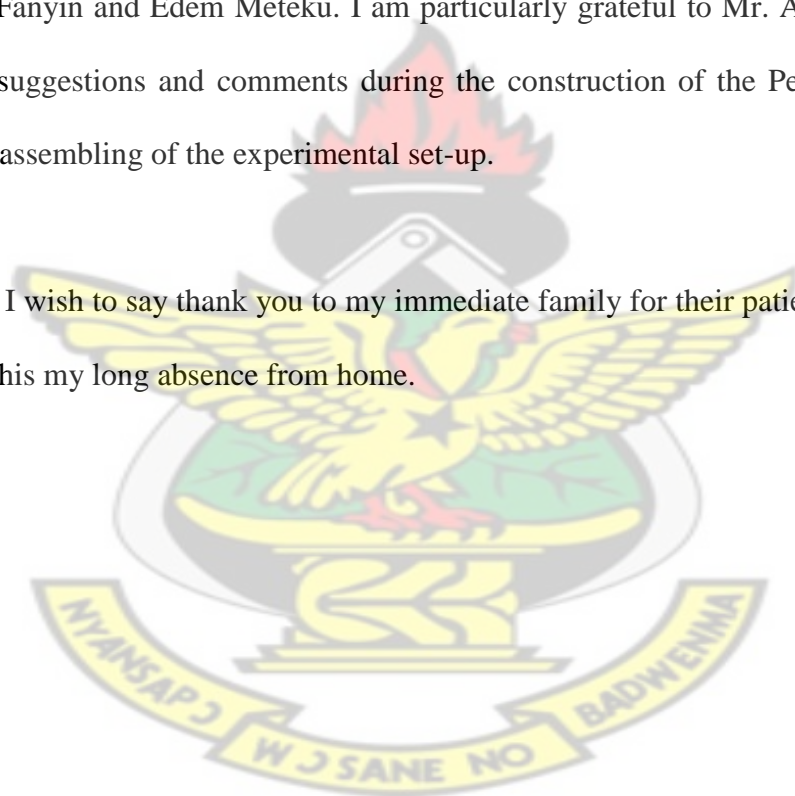
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## DEDICATION

This work is dedicated to the memory of my mother and father who did not live to see and reap the fruit of their toil.

Madam Hajara Barmo

And

Mallam Mohammed Zainudeen

KNUST



## CHAPTER 1

### 1.0 INTRODUCTION

#### 1.1 Production, purification and use of alcohol as fuel

The rate of usage of traditional petrochemical energy resources for meeting the world's chemical and energy needs is expected to lead to global energy shortage in the future (Austin, 1984:46). Moreover as nations search for methods to reduce greenhouse gas emissions, there is a renewed focus on alternate production of organic solvents and transportation fuel, such as ethanol, biodiesel, and butanol from biomass and other organic sources to be used as fuel or chemical feedstock (Rhim & Huang, 1993). Although several of these fuels have a long history of production, they have not been widely adopted due to the expensive nature of production of fuel-grade alcohols and biodiesel generally. For an alternate transportation fuel to displace conventional oil derivatives such as gasoline and diesel there must be reasonable probability that the fuel can become competitive in total costs including production, distribution, and consumption and must comparatively be environmentally friendly.

Alcohols are primarily used as industrial solvents. For example, ethanol and butanol are widely used as solvent in the chemical, pharmaceutical and cosmetic industries. The respective energy contents per litre of butanol, ethanol as shown in Table 1.1 below, are comparable to that of gasoline, making them attractive bio-fuel replacement for petroleum based fuel. As a result, a potential exists for a cost competitive bio-fuel with alcohols as the feedstock.

**Table 1.1 Energy content of selected liquid fuels**

Fuel Type	Energy Content (kJ/litre)
Unleaded Gasoline	26,478
Butanol	24,387
Ethanol	19,510

(Source: Law *et al.*, 2008)

Distillation is by far the most widely used method for the purification of alcohols from the fermentation broths (Mulder, *et al.*, 1983; Austin, *supra cit.*). However, it is an energy intensive operation especially when the components being separated are close boiling-point liquid mixtures or when they form azeotropes. When membrane technology is coupled with distillation in this purification, the energy consumption could be reduced drastically (Mulder *et al.*, *supra cit.*). In one such work it was observed that pervaporative separation, which is the membrane process capable of breaking the azeotrope, is efficient when coupled with distillation in a hybrid process (Mulder *et al.*, *supra cit.*). According to Rhim & Huang, *supra cit.*, for example, the separation of ethanol-water mixtures from the fermentation broths to concentrations closer to 100 wt % ethanol could be more efficient when distillation is used in the preliminary stage to concentrate the product from the broth to about 90 wt%. This latter product could then serve as feed for the pervaporation unit to further separate the mixture to fuel-grade concentrations of 99.5 wt% ethanol or more (Mulder *et al.*, *supra cit.*).



### 1.1.1 Alcohol Purification

Alcohol (butanol, ethanol or methanol) production from fermentation has been practiced commercially for over a century. In the process, the alcohol inhibit the micro-organisms (enzymes) which facilitate the fermentation process, when at low concentrations of between 4-6 g/l and occasionally halts the growth of the micro-organisms (El-Zanati *et al.*, 2006) resulting in low productivity and yield. The traditional method of purification of alcohol has been the energy intensive azeotropic distillation, liquid-liquid extraction, rectification, stripping and/ or adsorption (Seader & Henley; 2001:528-529).

Alcohols normally form azeotrope with water; a condition which make their separation more challenging. While butanol has recently been recognized as a commercially viable bio-fuel, ethanol has long attracted attention as a transportation fuel additive (Law *et al.*, 2008). Even with this potential, substantial technical challenges remain with regard to commercial implementation.

For industrial and fuel uses, ethanol which is produced from fermentation broth at a concentration of only 5-10 wt % must be purified. But due to the formation of azeotrope which boils at 78.2<sup>0</sup>C, its purification goes no further than 96 % by weight ethanol via fractional distillation (Ling *et al.*, 2008). To circumvent this azeotrope during separation, significant economic capital and energy are required. In order for the production of this fuel-grade alcohol to be cost effective, a membrane separation process with capability of circumventing the azeotrope is suggested. Pervaporation, which is a membrane separation technique with an added advantage of requiring less energy, has been the most justified technique for adoption (Baker, 2004:355).

### 1.1.2 Pervaporation process in Alcohol purification

Pervaporation is a separation process in which a binary or multi-component liquid mixture is separated by partial vaporization through a dense non-porous membrane (Kujawski *et al.*, 2009). The feed mixture is in constant contact with one side of a liophilic or liophobic membrane whereas permeate is removed in the vapour state from the opposite side into a vacuum or sweeping gas and then condensed. Pervaporation is a combination of membrane permeation and evaporation. In the process, generally the component in the mixture with smallest weight fraction, like water in these alcohol-water mixtures, should preferentially be transported across the membrane. This is because when the molecule with smallest weight fraction has affinity towards the membrane material (hydrophilic), the sorption of the feed liquid by the membrane decreases resulting in reduction of polymer swelling. By rejecting more of the molecules in higher fraction (ethanol), the molecules in less quantity (water) tend to diffuse with ease through the membrane and hence increase in the selectivity (Seader and Henley, 2001: 531).

As an energy efficient process, pervaporation could serve as alternative to the already existing processes of alcohol purifications, like distillation, extraction and sorption. The advantage of pervaporation is in separating azeotropes, close boiling mixtures, and thermally sensitive compounds, while removing species present in low concentrations. Another advantage is that only a fraction of feed is vapourised and the operating temperatures are mostly lower than those required for distillation. The challenges in pervaporation have however been the search for suitable membranes with good separating properties of permeation rate and separation factor in order to minimize concentration polarization.

The use of a highly hydrophilic membrane in pervaporation favours the transport of the higher boiling water while the use of highly hydrophobic membrane, will favour the transport of the lower boiling ethanol (Baker, 1991) for ethanol-water mixtures. The efficiency of the pervaporation is highest near the azeotropic composition of ethanol-water system (Kujawski, 2000), where the concentration of the permeating molecule (water) is less than 5 wt %.

### **1.1.3 Membranes and membrane materials for alcohol-water separation**

Membranes separate mixtures by discriminating between components in a mixture on the basis of their physical or chemical properties such as molecular size, charge and solubility. Membranes normally permit smaller species to pass through them while larger ones are retained. However, with the development of composite and asymmetric membranes, the separation of mixtures is based on the affinity of the species towards the membrane material and the solubility of the species in the membrane material. A separation technology based on membranes can be developed to increase the concentration of ethanol and butanol in the feed to distillation columns to reduce the energy consumption. According to Rhim & Huang, (1993), alcohol recovery by membranes lead to low energy consumption compared to distillation resulting in reduction in overall processing cost.

Dehydration of alcohol is one of the most important developed areas in pervaporation separation process. The element contributing to the success of this separation technology is the development and fabrication of suitable membranes, with high permeability, good selectivity and proper mechanical strength. This implies synthesizing new inorganic-organic composite polymeric materials with good pervaporation performance. The use of zeolites which have constant crystal structure

and molecular sieving effects as fillers in such membrane forming polymers has been reported (Ling *et al.*, 2008; Yeh *et al.*, 2002; Mulder *et al.*, 1983).

Zeolites have been found to be very suitable adsorbents for the separation of ethanol-water mixtures (Atta *et al.*, 2007 and Igbokwe *et al.*, 2008). Natural zeolites such as clinoptilolite, phillipsite and chabazite among others, as well as clays are found to be suitable adsorbents for ethanol-water separation (Ivanova *et al.*, 2009) because of their heterogeneous crystal structure, molecular sieving properties, uniform pore size distribution, high thermal resistance, high chemical inertness and high mechanical strength (Kazemimoghadem *et al.*, 2004). However, zeolites can also be formed synthetically with same characteristics as mentioned above (Atta *et al.*, 2007; Baker; 2004 and Igbokwe *et al.*, 2008) from clay resources. The advantage here is the formation of tailor-made zeolites which are highly replicable and could be used for specific purposes like dehydration of ethanol-water mixtures.

Polyvinyl alcohol (PVA) is one of the most widely used polymers in membrane separation technology. It is used in the fabrication of membrane for the dehydration of ethanol due to its hydrophilic properties. Pervaporation is performed better when the concentration of the permeating component of the mixture is less than 10 wt% (Mulder *et al.*, *supra cit*). When pervaporation has to be performed for a feed with low ethanol concentration, it has to be performed with ethanol permeable membranes while for high ethanol concentration in feed, water permeable membrane must be utilized.

## 1.2 Problem Statement

There are large deposits of clay as well as abundance of alcohol producing capacity in the country. Due to dearth in less energy consuming and cost effective separation technology, distillation is the purification method used in the alcohol producing

industries in the country. As a result, most of the highly concentrated alcohols produced in the country are not to the satisfaction of consumers in for example, the pharmaceutical and cosmetic industries. It is therefore no wonder that most of the highly concentrated alcohols used for various purposes in the country are imported. The inability to purify ethanol beyond the azeotropic composition by distillation means no fuel grade alcohols are produced in the country.

In order to reverse this trend, a new and novel method of separation using local materials is suggested that will not only separate the aqueous mixture effectively, but also reduce the cost of production. Pervaporation process, being a membrane separation process that has gained worldwide acclamation for separating close-boiling point liquids or mixtures with azeotropic compositions is being proposed to be applied in separating ethanol-water mixtures.

The separation capacity of a given membrane, for example in pervaporation process, toward a given feed mixture is determined solely by the permeabilities of the respective components, in that it is the solubility of a component in the membrane material, together with diffusivities that govern mass transport across the membrane (Hennepe *et al.*, 1990). This makes pervaporation a nonequilibrium dynamic process where transport phenomena determine separation efficiency.

Among the materials used in fabricating and developing membranes for effective separation are zeolites. In this research, hydrophilic zeolites will be produced from Ghanaian clay deposits. This hydrophilic zeolite would be introduced as filler in order to enhance the separation and also strengthen the PVA base membrane matrix, thereby prolonging the membrane's life.



### 1.3 Aims and Objectives

The aim of this work is to separate alcohol-water mixtures by pervaporative separation technique using membranes with additives made from Ghanaian Clay deposits. The specific objectives are;

1. To produce zeolites from suitable local clays
2. To use the zeolite so formed as fillers in the formulation of the membranes based on PVA.
3. To design and fabricate a pervaporation cell from aluminium metal scraps.
4. To use the pervaporation cell for separation experiment using different ethanol-water concentrations.

### 1.4 Scope and Justification of the Research

The suitability for the formation of zeolite supported composite membranes from clay resources is well documented (Atta *et al.*, 2007; Igbokwe *et al.*, 2008; Ivanova *et al.*, 2009; Ling *et al.*, 2008 and Nawawi *et al.*, 2008). The clay resource in Ghana is estimated at between 500-600 million cubic meters (Hammond, 1997). Currently, the utilization of clay in Ghana has been in the production of bricks, tiles and other ceramic materials (Hammond, 1997 and Kokoroko, 1993). The exploitation and utilization of clay in this new field of membrane technology has the potential of boosting the country's economy.

In this research, zeolites will be produced from Ghanaian clay deposits mined at Anfoega from Volta region, Abonku from Saltpond in the Central region and Teleku-Bokazu in the Western region. The choice of these locations is due to the fact that earlier beneficiation and characterization of clay samples have been carried out with the exception of clay from Teleku-Bokazu (Kokoroko, 1993). With success of this



project, it would be possible to produce alcohols locally to any required purity for consumers in the country and beyond.

# KNUST



## CHAPTER 2

### 2.0 LITERATURE REVIEW

#### 2.1. Production and Properties of Alcohols

Alcohols are compounds with a general formula  $C_nH_{2n+1}OH$  (Dean, 2010), where  $n$  is the number of carbon atoms. Examples are methanol, ethanol, propanol, butanol and pentanol. There are two opposing solubility tendencies for alcohols; the tendency of the polar OH group to promote solubility in water and that of the carbon chain to resist it. Thus, methanol, ethanol, and propanol are miscible with water. While butanol, with a 4-carbon chain is moderately soluble, alcohols with 5 or more carbons are insoluble in water because of the hydrocarbon chain's dominance. Due to the presence of hydrogen bonds, alcohols tend to have higher boiling points than comparable hydrocarbons.

Alcohols are generally produced by fermentation using glucose (produced from sugar in the hydrolysis of starch) in the presence of yeast and at temperatures less than  $37^{\circ}C$ . The most commonly used alcohol is ethanol which has been produced and consumed by humans for millennia in the form of fermented and distilled alcoholic beverage. For example, fermentation of barley produces beer while fermentation of grapes produces wine. The maximum ethanol concentration from these fermentation processes is normally in the order of 15 wt % or less. This is because the higher concentrations inactivate the enzymes, thus halting fermentation (Rhim & Huang, 1993). Ethanol is a clear, flammable liquid that boils at  $78.4^{\circ}C$  with many uses as industrial solvent and raw material in the chemical industry.

Propanol, on the other hand is prepared commercially from petroleum by hydration of propene and has a boiling point of  $82^{\circ}C$ . Isopropyl alcohol is the major component of

rubbing alcohol. It possesses weak antibacterial properties and is used to maintain medical instruments in sterile condition and to clean the skin before minor surgery.

Of the alcohols mentioned above, methanol, ethanol and butanol have been found to be useful as fuel while propanol is mostly used as solvent in industry. Among the 3 alcohols, ethanol and butanol have been successfully used as transportation fuel additives mostly in Brazil and United States of America (Sheehan *et al.*, (1998)).

### **2.1.1 Ethanol as Fuel**

Ethanol is used as transportation fuel mainly as biofuel additive in gasoline. The use of ethanol as fuel is well documented in the US and Brazil. As such these countries are responsible for over 89% of ethanol production in 2009. Most cars on the road today in US and Brazil can run on blends of up to 10% ethanol (Sheehan *et al.*, (1998)).

Bio-ethanol, unlike petroleum, is a form of renewable energy that can be produced from agricultural feed stocks. It can be made from very common crops such as potato, cassava and maize. In Ghana however, it is mostly produced from sugarcane. There has been considerable debate about how useful bio-ethanol will be in replacing gasoline. This is due to the fact that the raw materials also serve as food for humans, hence the likelihood of increased food prices globally. In contrast, the need for clean environment which will be enhanced when ethanol blended gasoline (gasohol) is utilized as transportation fuels, is gaining a lot of attention.

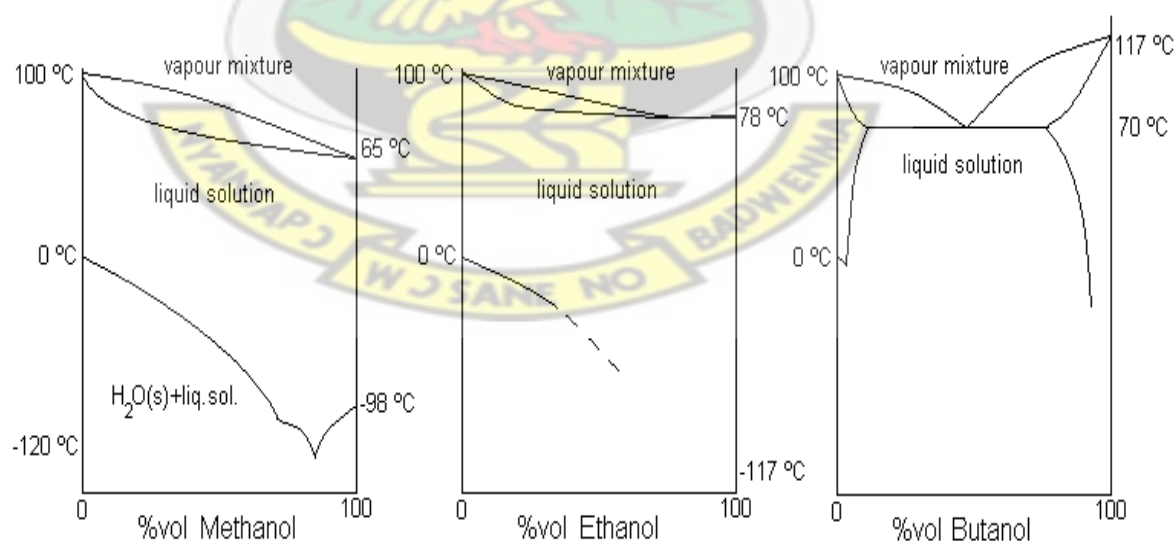
### **2.2 Purification of Alcohols**

Alcohols produced from fermentation broths are normally of low concentration; not exceeding 15 wt% (Rhim & Huang, 1993). The use of alcohol as fuel additive and

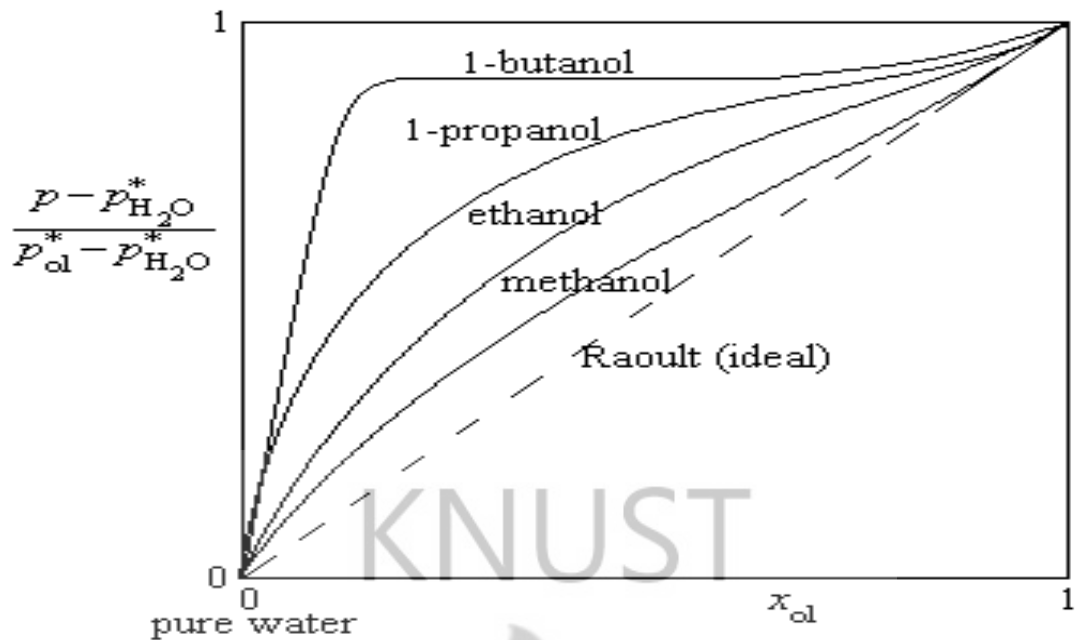
substitute demand a higher concentration. This means the product from the broth need to be purified to the acceptable ethanol concentrations of 98-99.5 wt%.

The conventional method of purification of ethanol has been distillation technique which relies on the differences in the volatilities of the components in the mixture. This separation technique is however limited to ethanol purity of 95-96 wt% due to the formation of low boiling ethanol-water azeotrope. In order for ethanol to be used as a fuel in internal combustion engines, water must be removed so that the required ethanol concentration of 99.5 wt% or higher would be attained. The azeotrope provides a barrier to further purification by distillation as the vapour composition is the same as that in the liquid state, hence behaving like a pure substance. In purifying therefore, significant economic capital and energy are required for success of such separations to concentrations above the 95.6 wt% ethanol.

The phase diagrams shown on Figure 2.1 depict the various forms of azeotrope formed during phase transition of methanol, ethanol and butanol respectively.



**Figure 2.1 Phase diagram for several alcohol water solutions at 100 kPa: From left methanol, ethanol and butanol (Source: Martinez, 2011).**



**Figure 2.2 Deviation from ideal mixture of several alcohol solutions: vapour-liquid equilibrium curve of alcohols (Source: Martinez, 2011)**

By superimposing the vapour-liquid equilibrium curves of the alcohols on the same graph, the same shape and form of the azeotrope is vividly depicted as in Figure 2.2. The graphs show the vapour-liquid equilibrium curves of the alcohol-water mixtures with a total vapour pressure of the solution,  $P$ . It shows the deviation from Raoult's law by the alcohols. The symbols  $P_{ol}^*$  and  $P_{H_2O}^*$  represent the vapour pressures of pure alcohol and pure water respectively. The ordinate is the mole fraction of the most volatile component (alcohol) in the vapour phase, while the abscissa represents the mole fraction of the alcohol in the liquid phase of the mixture. The diagonal shows the situation where the mole fraction of the components in the vapour is the same as that in the liquid phase.

There are three major dehydration processes used to purify ethanol-water mixtures beyond the azeotropic composition. They are distillation (azeotropic distillation and extractive distillation), adsorption through bed of molecular sieves (zeolites) and

membrane separation process of pervaporation. Of these processes, adsorption through molecular sieves and pervaporation are more promising in that the technology can account for energy saving of 3,000 Btu/gallon (840 kJ/L) compared to distillation (Law *et al.*, 2008).

### **2.2.1 Distillation**

It is a separation process in which one component of a binary mixture is made to boil and the vapour made to condense separately. For complete separation of liquid mixtures by distillation, the vapour that condenses first may only contain few particles (molecules) of the component with the lowest boiling point in the mixture (Seader & Henley; 2001: 256). Even if this condition is met, the distillate will contain particles (molecules) of the less volatile component and the separation is never complete. The extractive and azeotropic distillations are methods where a third component is introduced into the distillation process to offset the main barrier to the separation. This entrainer affects the volatility of one of the azeotropic constituents more than the other. For example in the ethanol-water azeotrope with 95.6 wt% ethanol and 4.4 wt% water which boils at  $78.2^{\circ}\text{C}$ , benzene or cyclohexane could be added as entrainers. When Cyclohexane is used as entrainer in azeotropic distillation, just enough of it is added to the ethanol-water azeotrope to form a ternary azeotrope of 7% water, 17% ethanol and 76% cyclohexane that boils at  $62.1^{\circ}\text{C}$ . When the mixture is then boiled, the cyclohexane- water azeotrope vaporizes leaving a residue almost entirely of ethanol.

### **2.2.2 Adsorption through Molecular Sieve**

The use of molecular sieves as adsorbents is another technique used in the purification of alcohols to concentrations above the azeotropic compositions (Ivanova *et al.*, 2009 and Igboke *et al.*, 2008). The hybrid process is such that the fermentation process is



coupled with the conventional distillation processes by allowing the distillate to pass through beds of molecular sieves to adsorb the water. (Igbokwe *et al.* 2008 and Ivanova *et al.*, 2009).

Zeolite is the general name given to molecular sieves (Seader & Henley, (2001: 554) and Igbokwe *et al.*, 2008). Depending on the type of zeolite, as will be explained in section 2.8.2, either water or the alcohol would be adsorbed. For example, zeolite 3A, which has a pore size of not more than 0.3nm, have crystal structure which allows only water molecules to penetrate into its micro pore volume. On the other hand, dealuminated zeolites like silicalites or NaZSM-5, preferably adsorb ethanol (Ivanova *et al.*, 2009). There are other zeolites, such as zeolite 5A (pore size 0.5nm), however, which do not separate ethanol-water mixtures because both molecules (molecular size of water is 0.265nm while that of ethanol is 0.446nm) could enter the pore volume and be equally adsorbed. Therefore, for effective dehydration of alcohol-water mixtures the characteristics of the molecular sieve, thus the Si:Al ratio, need to be ascertained (Ivanova *et al.*, (2009). This will inform the proper protocol to be followed for the kind of hydrophilic zeolite to be formed.

The uptake of water or other species in zeolites functions on the basis of physical adsorption and the main driving force is the highly polar surface within the pores of the zeolite which enables an extremely high adsorption capacity for water and other polar components even at very low concentrations (Igbokwe *et al.*, 2008). In addition to the polarity, the size and shape of the molecules to be separated play important roles as molecules larger than or of different shape to the pore opening of the molecular sieve cannot be adsorbed whereas smaller or same shape molecules can (Igbokwe *et al.*, 2008 and Ivanova *et al.*, 2009).

### 2.3 Membrane Separation Process

By definition, a membrane is a structure, having lateral dimensions much greater than its thickness, through which mass transfer may occur under a variety of driving forces (Koros *et al.*, 1996). Thus, a membrane is a selective barrier that separates components in a fluid by differences in one or more properties of the components such as size, shape, electrical charge, solubility, and diffusion rate. It can selectively separate components over a wide range of particle sizes (of about  $1\text{-}10^7\text{\AA}$ ) and molecular weights. In the process, the feed mixture is contacted on one side of a membrane barrier through which the molecules of the individual components in the mixture diffuse to the other face of the membrane. Separation is then accomplished by the ease with which one component travels the thickness of the membrane relative to the other species in the mixture to be separated. The part of the feed that is separated by permeating through the membrane is called the permeate while the bulk portion rejected by the membrane and in most cases recycled back into the feed stream is called the retentate (Mulder *et al.*, 1983 and Baker, 2004:370).

There are two proposed models for the mechanism of membrane separation namely; the Solution-diffusion model and the Pore-flow model. In the solution-diffusion model, the permeate dissolves in the membrane materials and then diffuse through the membrane. The separation is achieved because of the differences in the amounts of permeates dissolving in the membrane and the rates at which the permeate species diffuse through the membrane (Lipnizki *et al.*, 1999). Since the solubility and diffusivity of permeating species in the membrane are difficult to determine accurately, the application of the solution-diffusion model often depends on empirical solubility and diffusivity calculations (Shao & Huang, 2007).

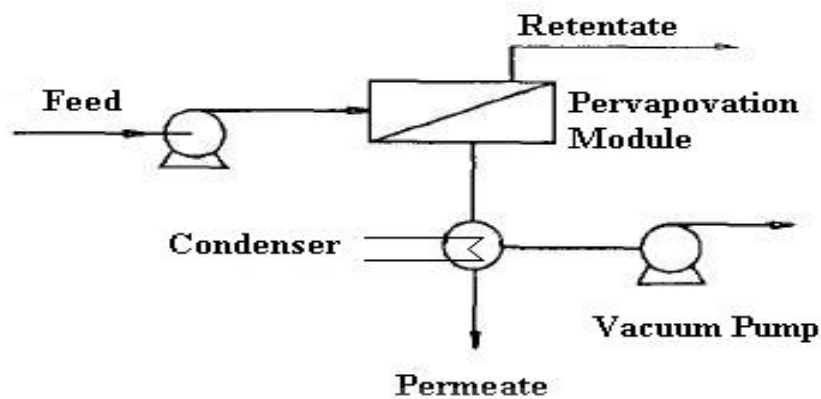
On the other hand, in the pore-flow model, permeates are separated by a pressure-driven convective flow through tiny pores. The separation is achieved because one of the permeate species is excluded from some of the pores in the membrane through which other permeate species transfer. The pore-flow model is thus a good mechanism for porous membrane but not for non-porous dense membranes.

Dialysis, Reverse Osmosis, Micro-filtration, Ultra-filtration, Gas permeation and Pervaporation are some of the most prominent applications of membrane separation processes. Of these, pervaporation is applied for the effective separation of closely boiling liquids and azeotropic mixtures, for example, alcohol-water mixtures (Seader & Henley; 2001: 527).

### **2.3.1. Pervaporation Process and Pervaporation Membrane**

The term “pervaporation” was introduced in membrane technology to describe the phenomenon that a liquid could evaporate through a non-porous barrier material (Zhu, 2006). Theoretically, pervaporation, can be used for three types of separation:

1. The removal of a small amount of water from organics (dehydration),
2. The removal of a small amount of organics from water and
3. The separation of organics from organics.



**Figure 2.3 Schematic of a typical pervaporation system (Source: Zhu, 2006)**

A simple pervaporation system consists of a pervaporation module, a condenser and a vacuum pump, as shown in Figure 2.3. The liquid mixture to be separated is introduced to a pervaporation module and is separated into two streams; one of which is the retentate which contains the components rejected by the membrane and the other is the permeate which consists of the components that passed through the membrane. Inside the module, as shown in Figure 2.5 on page 21, the feed mixture is in contact with one side (the active side) of the membrane while some components will dissolve in the membrane and then diffuse through it.

The driving force for the separation is maintained by the chemical potential differential, in this case, the vapour pressure differential across the membrane. In contrast to distillation, pervaporation relies on the differences in solubility and the diffusivities of the components in the membrane. The solubility of species however, may cause membrane swelling and enhance cross-diffusion effects (Wijmans & Baker, 1995).

Though different species permeate through the membrane at very different rates, a substance at low concentration in the liquid feed can be highly enriched in the vapour

permeate. Thus the pervaporation efficiency is strongly determined by the physico-chemical nature of the membrane and by the kind of feed mixture to be separated.

Compared with distillation, pervaporation has the following advantages:

1. It is difficult to use distillation to separate components in azeotropic mixtures or close boiling point mixtures. In using distillation to break these types of mixtures, some entrainers have to be used. Pervaporation, on the other hand, can easily break an azeotrope or separate the components from a close-boiling-point mixture. Thus pervaporation can be used for the separation of mixtures that conventional distillation cannot separate effectively.
2. Pervaporation is an energy efficient process for liquid separation, especially when the feed mixture contains one component that is in low concentration and more permeable than other components in the mixture. In pervaporation, only the permeate needs latent heat to evaporate, while in distillation, almost all components in the feed undergo phase changes back and forth. As such, distillation consumes much more energy than pervaporation.
3. Pervaporation can be performed at a relatively low temperature, and this is important for the separation of some temperature-sensitive materials such as biomaterials.
4. A pervaporation system is small and compact with very little capital cost relative to a distillation system.

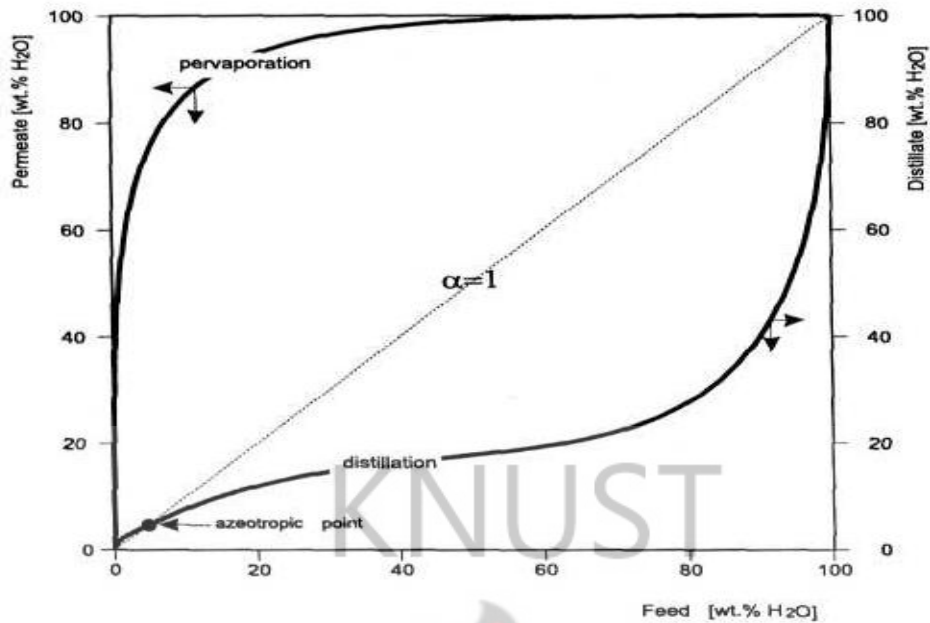
Figure 2.4 depicts the comparison of a typical distillation and pervaporation separation techniques of water-alcohol mixtures. The diagram was obtained when a 50-50% alcohol-water mixture was separated via pervaporation and distillation under the same operating conditions (Kujawski, 2000). While the lower part shows the liquid-vapour equilibrium curve for alcohol-water mixture during distillation, the



upper portion shows the curve for pervaporation. The diagonal represents azeotropic composition for which separation does not take place. At this azeotropic feed compositions, the separation factor,  $\alpha$ , has a value of 1. The diagram shows how pervaporation separation circumvents the azeotrope of ethanol-water mixtures as against distillation which is incapable of further separation beyond the azeotropic point. The same mechanism and hence the diagram for the azeotropes of other alcohols follow similar pattern (Kujawski, 2000).

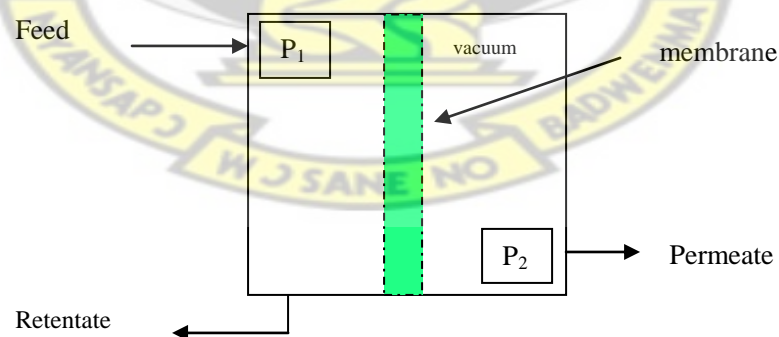
In spite of the advantages mentioned above, applications of pervaporation are very limited as traditional liquid separation technologies are still dominant due to non availability of appropriate membranes. In order to make pervaporation more competitive, it is necessary to improve the engineering design of pervaporation, including module configuration, module fabrication and optimization of operating conditions and more importantly, development of high performance membranes (Mulder *et al.*, (1983); Seader & Henley, (2001: 228-229)).





**Figure 2.4 McCabe-Thiele separation diagram. Comparison of pervaporation selectivity with distillation selectivity. System: ethanol-water. Membrane: PVA composite hydrophilic membrane.**

The operation of a pervaporation cell (or module) is illustrated in Figure 2.5. The two functions of the membrane in the pervaporation process are to keep the two phases from remixing and to control the selectivity of components in the mixture.



**Figure 2.5 Inside pervaporation unit**

Essentially, pervaporation differs from other membrane separation processes in that the phase on one side of the membrane is different from that on the other side. The feed to the membrane module as shown in the figure is a binary liquid mixture of components A and B. The feed pressure,  $P_1$ , is maintained at a relatively high value such that the feed remains in a liquid phase. The permeate pressure,  $P_2$  on the other hand is maintained low enough such that a substantial pressure driving force is generated across the membrane for the feed to be depleted of species A and B to produce the product retentate on the upstream of the membrane.

In a typical process, the membrane used must be selective for species A, which is of low concentration, while the species with highest concentration, B, usually has some finite permeability thereby rendering the retentate enriched in species B. The permeate on the other hand then becomes rich in species A. The permeate pressure which is near vacuum, is maintained at or below the dew point of the permeating species such that the mixture at that point would be in the vapour phase.

Pervaporation is effective when the applied feed solution is dilute in the main permeant such that relatively little energy in the form of sensible heat of the feed mixture would provide the enthalpy of vaporization of the relatively small permeant (Mulder *et al.*, 1983). This is because if the feed is rich in the main permeant, a number of membrane stages may be needed, with a small amount of permeant produced per stage while the retentate is reheated between stages.

Depending on the applications, it was reported by Lipnizki *et al.*, (1999) that three different kinds of pervaporation membranes can be distinguished as hydrophilic, hydrophobic and target-organophilic membranes. A hydrophilic membrane is used in pervaporation when the mixture to be separated is dilute in a polar component. When

the mixture, however, is dilute in an organic component, a hydrophobic membrane is used. Target organophilic membranes are used in the separation of mixtures made of only organic components. In this case a polymer membrane is selected such that it has higher affinity towards the dilute organic component in the mixture.

For example, in the pervaporation of ethanol-water mixture, when the feed has low ethanol concentration, then ethanol must be the permeating component and as such a hydrophobic membrane should be used. On the other hand when the ethanol is the component with higher concentration, then a hydrophilic membrane made of PVA for example, must be used for water to be preferentially removed as permeate.

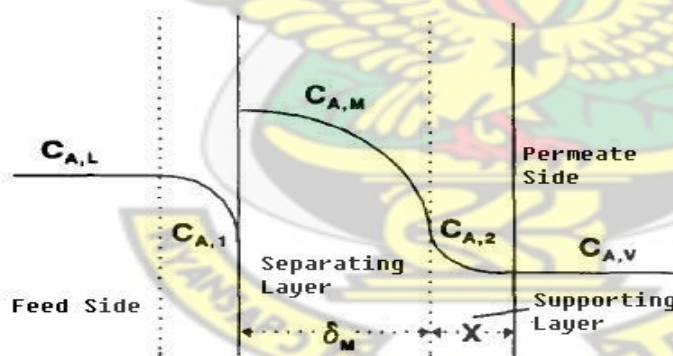
### **2.3.2 Mechanism of Pervaporation within Membranes**

Pervaporation membranes generally have three different structures: symmetric, asymmetric and composite membranes. Symmetric membranes are produced from a single polymer material with uniform pore structure. Asymmetric membranes are also made from a single polymer material, but the method of production is such that two different types of layers are formed. A composite membrane on the other hand is formed from different polymer materials in different layers of the membrane. Thus a composite membrane can have a separating layer made from a polymer with inorganic filler without support or be made of a separating layer and a support layer from different polymer material. These composite membranes offer the possibility of having an effective separation layer, which leads to flux increase, and a support layer which gives mechanical strength to the thin separating layer. Since a single polymer usually does not have the optimum separation capability and mechanical stability at the same time, asymmetric membranes are hardly used for pervaporation effectively (Baker, 1991).

The solution-diffusion model is commonly used to describe the mass transport through the membrane by pervaporation. Accordingly, Mulder *et al.*, (1983) and Kazemimoghadam *et al.*, (2004), have reported the mechanism of the solution diffusion model as consisting of three steps:

- (i) Sorption of the permeable component into the separating layer of the membrane,
- (ii) Diffusive transport of the substance across the membrane and
- (iii) Desorption of the substance at the permeate side of the membrane.

Figure 2.6 shows the concentration profile of the more permeable component in a pervaporation system with a composite membrane. The molecules of the more permeable component A (water molecules), at concentration,  $C_{A,L}$ , sorbs onto the surface of the separating layer (PVA/ zeolite composite membrane) where its concentration is  $C_{A,1}$ .



**Figure 2.6 Concentration profile of the more permeable component in a pervaporation system (Source: Zhu, 2006)**

Due to its high affinity (of the water molecules) towards the separating layer, it dissolves in the layer much faster than B (ethanol molecules), after which its molecules diffuse towards the downstream side of the membrane. The concentration,  $C_{A,M}$ , is the concentration profile as A diffuses through the separating layer with

thickness,  $\delta_M$  to the upstream surface of the support (porous polysulphone substrate). The decrease in the concentration of  $C_{A,M}$  to  $C_{A,2}$  is due to the resistance to flow in the separating layer. After passing through the supporting layer with thickness,  $\chi$ , the concentration does not change much as negligible separation takes place within the support layer. The molecules of A which finally desorb as vapour from the downstream side of the composite membrane has concentration of  $C_{A,v}$ . The permeate concentration of  $C_{A,v}$ , is always higher than  $C_{A,L}$ , the feed concentration in terms of A.

#### 2.4 Construction of the Pervaporation Unit.

The most common material of construction of pervaporation cells is steel (Buckley-Smith, (2006); El Zanati *et al.* (2006)). This is because steel can withstand harsh conditions of the feed of highly corrosive liquid mixtures at elevated temperatures (Kazemimoghadam; 2007). Apart from the inertness to most liquid mixtures even at elevated temperatures as mentioned above, steel is also durable. Therefore, since Pervaporation cells are fabricated so that it would be used for several other feed mixtures over and over again steel is the preferred material of construction.

In Ghana, steel is relatively expensive and the use of other suitable materials was considered. The criteria used in this case for qualified materials are abundance and inertness of the material to any of the components in the mixture at various concentrations and at different temperatures. With the added desire to reduce cost of the whole project and the fact that it is abundant, aluminium was selected as the best material for the construction. The cell could be fabricated by molding a molten aluminium scrap to specified design dimensions comparable to that given by Buckley-Smith, (2006). This decision was informed by the fact that aluminium is inert to the intended mixture under the operating conditions of pressure and temperature



(Tsuchida; (2004) and <http://www.usmotor> , (2011)). The main overriding principle considered in the design must be whether the concentration polarization would be at the barest minimum.

Concentration polarization is a membrane process phenomenon that adversely affects the performance of pervaporation. As the separation process proceeds, the more permeating molecule become depleted at the upstream surface of the membrane while at the same time gets enriched at the downstream surface. The two surfaces are then said to be polarized. Polarization reduces the available driving force across the membrane, since the permeating molecule's mass transfer rate is controlled by the difference between chemical potentials (approximated by concentrations) in the boundary layers at both sides of the membrane. In order to remedy this situation, turbulence at the upstream surfaces of the membrane has been suggested (Liu *et al.*, 2003). Concentration polarization was reported however as insignificant especially for the pervaporation of organic solvent-water mixtures (Psaume *et al.*, (1988); and Karlsson & Tragardh, (1993) as cited by Buckley-Smith, (2006).

## **2.5 Membrane Materials and their Properties**

The key to an efficient and economical membrane separation process is the membrane and the manner in which it is packaged and modularized. Some of the most desirable attributes of a membrane are:

1. Good permeability
2. High selectivity
3. Chemical and mechanical compatibility with the processing environment
4. Stability, freedom from fouling and reasonable useful life
5. Amenability to fabrication and packaging and



6. Ability to withstand large pressure differences across the membrane thickness.

The main forming materials are made from natural or synthetic polymers (macromolecules). Natural polymers include wool, rubber, and cellulose, while synthetic polymers include polyethylene, polybutadiene, phenolformamide or butyl rubber.

The main property of polymers exploited in membrane application is the arrangement or conformation of the polymer molecules in terms of being glassy or crystalline at temperatures below 100°C (Baker, 2004). By increasing the temperature of a glassy polymer, its glass transition temperature,  $T_g$ , is reached where the polymer becomes rubbery. However when the temperature of crystalline polymer is increased a melting temperature,  $T_m$ , is reached where the polymer becomes a melt. Thermosetting polymers on the other hand do not form melt. Membranes made of glassy polymers can operate below or above  $T_g$ . But membranes of crystalline polymers must operate below or above  $T_m$ .

### **2.5.1 Membrane Performance**

For membrane performance evaluation, the most important parameters are; productivity, selectivity, and stability (Baker, (1991) & (2004: 361)). When the permeate stream is the product, membrane productivity is characterized by permeation flux (moles, volume, or mass) of a specified component per unit time passing through a unit membrane surface area. The permeation flux is influenced by the driving force, the membrane permeability, the membrane thickness, and the concentration polarization phenomenon. For example in the separation of a binary mixture of components A (water) and B (alcohol), the membrane selectivity is related to the relative permeate fluxes of A and B. As the flux of the feed components on the

membrane decreases, the selectivity increases and vice versa (Rhim & Huang, (1993); Seader & Henley, (2001:531); Shao & Huang, (2007) and Ling *et al.*, (2008)). When the pervaporation membrane is hydrophilic, and the feed concentration increases in B, the sorption of the feed then decreases as A diffuses through the membrane while B is rejected. Conversely, when the feed concentration increases in A, the amorphous region of the membrane matrix gets swollen such that the restriction to diffusion for both components decreases. As a result the membrane selectivity increases.

To be effective for separating a mixture of chemical components, a polymer membrane must possess high permeance and a high permeance ratio for the two species being separated by the membrane. The permeance for a given species diffusing through a membrane of a given thickness is analogous to a mass transfer coefficient, which is defined as the flow rate of that species per unit cross sectional area of membrane per unit driving force (concentration, partial pressure etc) across the membrane thickness (Seader & Henley, 2001: 530).

The molar transmembrane flux of species,  $i$ , is defined as

$$N_i = \left( \frac{P_{M_i}}{l_M} \right) (\text{driving force}) \quad (2.1)$$

$$= \check{P}_{M_i} (\text{driving force})$$

Where  $\check{P}_{M_i}$  is permeance, defined as the ratio of  $P_{M_i}$ , the permeability to  $l_M$ , the membrane thickness.

Apart from permeability, selectivity is also used in defining the performance of membranes. The permeability for a penetrant A is defined as;

$$P_{MA} = \frac{N_A l_M}{\Delta P_A} \quad (2.2)$$

Where  $N_A$  is the molar amount of component A passing through the membrane,  $l_M$ , the membrane thickness and  $\Delta P_A$ , the pressure difference driving force between the upstream and the downstream sides of the membrane.

Permeability, which is also called the flux of the permeating species, can also be defined in terms of the mass of component A passing through the membrane, with units in  $\text{kg/m}^2\text{hr}$ .

Permeability is usually given in units of Barrer, defined as:

$$\text{Barrer} = 1 \times 10^{-10} \frac{\text{cm}^3 (\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}}$$

Selectivity reflects the efficiency of a membrane to separate one component from another in a given mixture. The ideal selectivity, or permselectivity, of a membrane for penetrant A relative to penetrant B is the ratio of the permeabilities of the two penetrants.

$$\alpha_{A/B} = \frac{P_{MA}}{P_{MB}} \quad (2.3)$$

The permeability of the slower component is used as the denominator, hence conventionally ideal selectivity is greater than or equal to one.

The productivity of a pervaporation membrane is represented by the permeation flux,  $J$ , ( $\text{kg/m}^2\text{hr}$ ) which is mathematically defined as

$$J = \frac{Q}{A_s t} \quad (2.4)$$

Where  $Q$  is the amount of permeate collected (kg),  $A_e$  the membrane area ( $m^2$ ), and  $t$  the time to collect permeate (hr).

The selectivity of a membrane can be expressed in different ways. Most commonly, the selectivity is expressed by the separation factor which for a binary mixture system is defined as:

$$\alpha_{A/B} = \frac{\left[ \frac{y_A}{y_B} \right]_P}{\left[ \frac{x_A}{x_B} \right]_F} \quad (2.5)$$

where  $y$  is weight fraction in vapour phase and  $x$  is weight fraction in the liquid phase;  $P$  represents the permeate side and  $F$  the feed phase;  $A$  is the component that is more permeable through the membrane than component  $B$ . For a fixed feed composition, the selectivity of a pervaporation membrane can be simply expressed by the concentration of the more permeable component in the permeate. A high concentration of the more permeable component in the permeate means a high selectivity of the membrane.

Another performance parameter is the Pervaporation Separation Index (PSI) that is calculated from the values of  $J$  and  $\alpha$  discussed above is defined as;

$$PSI = J(\alpha - 1) \quad (2.6)$$

This is used to determine the overall pervaporation membrane factor. The higher the value of PSI, the better the performance of the membrane provided the separation factor is equally high (Lai *et al.*, (2003); Li & Lee, (2006); Ling *et al.*, (2008)). When

the separation factor is low for a high PSI, the performance is poor since the purpose of separation is not achieved with the membrane.

## **2.6 Types of Membrane and their Support**

There are two main types of membranes; namely the non-porous dense and the micro-porous membranes. The non-porous dense membranes are free of defects, have well-defined pores or voids and their effectiveness depends on the nature of the materials, the species to be separated and the type of interaction of the species with the membrane. These dense membranes are normally made very thin and in most applications are supported with substrates in order to prevent rupture or collapse during the separation upon the application of the driving force (pressure). The substrate used must however not interfere in any way with the separation mechanism. As reported by Baker, (2004:121), the porosity of this substrate must be more than 90% of that of the dense selective layer. And in most cases most of the supports (substrates) are themselves porous membranes (Hennepe, 2006).

On the other hand, the porous organic membranes are constituted by a discrete and well-defined pore size distribution. Compared to dense membranes they usually offer higher permeabilities. In general terms, as the pore size of the membrane increases, its permeability also increases although the membrane becomes less selective as species being separated could both diffuse through the pores without any resistance. Depending on the mode of preparation, membranes can be classified as symmetric, asymmetric and composite membranes.

### **2.6.1 Symmetric Membrane**

These membranes have a uniform composition and structure throughout and they are also called isotropic membranes. They can be porous or dense. They can be directly prepared, without a support or onto a provisional support which is removed after the



synthesis. The applications of symmetric membranes are currently limited because of their small dimensions and low mechanical resistance. Therefore they are normally supported by a more porous and tough substrate in order to offset these disadvantages.

### **2.6.2 Asymmetric Membrane**

These types of membranes consist of a number of layers each with different structures and permeabilities. A typical asymmetric membrane has a relatively dense, thin surface supported on an open, much thicker micro-porous substrate. The surface layer performs the separation and is the principal barrier for flow through the membrane. Indeed the porosity of the substrate before it qualifies as support for the very thin separating layer must be about 90% of that of the thin separating layer (Baker, (2004:121); Shao & Huang, (2007)).

These types of membranes are synthesized onto flat or tubular polymeric or inorganic micro filtration or ultra filtration supports. The thickness of the layer varies from a few nanometers (thin layers) to a few microns (thick layers). For the separation of ethanol-water mixtures Polysulphone (PSf) has been the most preferred type of material for the support fabrication. The polysulphone film does not exhibit any selectivity in the ethanol-water system, and it also possess micro-porosity which results in a large flux of about  $50 \text{ l kg/m}^2 \text{ h}$  (Niedlinger *et al.*, 1987).

In preparing asymmetric membranes for pervaporation purposes as given by Baker, (2004:104), the polymer concentration in the casting solution should be in the range 15 wt% - 20 wt% while the solvent-nonsolvent interaction should be low in order to obtain a smooth membrane surface. Apart from the thermodynamic factors mentioned above, kinetic factors such as nonsolvent flow into nascent membrane and solvent



flow into the coagulation bath, together with the gelation and crystallization kinetics, also play an important role in membrane formation (Mulder *et al.*, 1983).

### **2.6.3 Composite Membrane**

The materials used for fabrication are not uniform but made from a combination of two or more in the same separating layer. The top layer and sub-layer (support) always originate from different polymeric material. An example is a membrane made of PVA and nanoparticles like clay material. The incorporation of nanoparticles strengthen and prolong the life span of membranes (Yeh *et al.*, (2003); Lai *et al.*, (2003)), by reducing swelling as a result of the cross links it forms by dispersion within the matrix of the membrane material (Ling *et al.*, 2008). The other sub-layer in this case could be a porous support made of PSf.

### **2.7 Pervaporation Membrane Preparation for Alcohol Dehydration**

Several factors contribute to the successful fabrication of a high performance membrane module. The criteria for the choice of the membrane materials with the appropriate chemical, mechanical and permeation properties must be process-specific. This criteria depends on the polarity of the component in the mixture with low concentration, as it becomes the most permeating component. When this component is nonpolar, an organophilic material is chosen while hydrophilic material is chosen for a polar component (Baker, 2004:364).

There are several methods of preparing membranes; the most common used in preparing small samples of membrane for laboratory characterization experiments being the solution casting method. In this method, an even film of an appropriate polymer solution is spread across a flat plate with a casting knife. The casting knife consists normally of a steel blade, resting on runners, arranged to form a precise gap

between the blade and the plate onto which the film is cast. After casting, the solution is left to stand, and the solvent evaporates to leave a thin, uniform polymer film.

Another method is dip coating where the substrate on to which the thin separating layer must be supported, is dipped into the polymer solution of the separating layer and allowed to dry in the ambient. There is also the hand coating or lamination with the help of a dropper and glass rod after which normal ambient drying is allowed (Ling *et al.*, 2008).

The polymer solution used for solution casting should be sufficiently viscous to prevent it from running over the casting plate. A typical polymer concentration has been reported to be in the range 15-20 wt% (Baker, 2004:99). When the solvent has completely evaporated, the dry film can be lifted from the glass plate.

### **2.7.1 Anisotropic Membrane as Support**

Anisotropic membrane support is made from a homogeneous polymer material but having two layers, each with its own porosity. While the top layer is dense, the sub (bottom) layer is very porous. The technique used in the production of such membranes is called phase inversion technique. Anisotropic membranes made by this technique are called phase inversion membranes and are of order of magnitude more permeable than the isotropic membranes produced from the same materials.

The phase inversion process or polymer precipitation process involves the precipitation of a casting solution by immersion in a non-solvent like water in a bath. A non-solvent is a solvent which cannot dissolve the membrane polymer but is miscible with a solvent capable of dissolving the polymer. For example water cannot dissolve polysulphone (PSf) yet is miscible with Dimethyl acetamide (DMAc), which dissolves PSf completely.

A liquid polymer solution is precipitated into two phases; a solid, polymer-rich phase that forms the matrix of the membrane and a polymer-poor phase that forms the membrane pores. In this process after casting the film, it has to stand for about 1 to 3 minutes to allow some of the solvent to evaporate, after which the film has to be immersed in a water bath to precipitate the film and form the membrane.

Generally, the best casting solution solvents are aprotic solvents such as Dimethyl formamide, (DMF), N- methyl pyrrolidone (NMP) and Dimethyl acetamide (DMAc). These solvents dissolve a wide variety of polymers including polysulphone, and casting solutions based on these solvents precipitate rapidly when immersed in water to give porous, very anisotropic membranes. In the work of Ling *et al.*, (2008), however, DMF was found to dissolve PSf completely only after the addition of some amount of Ethylene glycol mono- methyl ether (Methyl cellosolve). When the amount of the polymer in the casting solution is high, the porosity and flux of the membrane is reduced. As a result, the amount of polymer used for anisotropic support membranes must be controlled in order for the porosity to be high enough (over 90% more porous than that in the separating layer) in conformity with its non-participation in the separation process.

### **2.7.2 Composite Membrane Preparation**

For dehydrating alcohols, polyvinyl alcohol (PVA) has been found to be a very effective polymer for the thin and dense separating barrier. However, the abundant hydrophilic moiety in the polymer chain induces an excessive swelling during pervaporation process, thus rendering the membrane unstable (Yeh *et al.*, 2003). As a result, attention has been focused on improving the stability of PVA through a physical and chemical reaction cross-linking (Yeh *et al.*, *loc. cit.*). The organic feed mixtures are directly in contact with the polymer membrane in pervaporation, hence

the physical and chemical properties of the membrane are often influenced by the feed mixtures via effects of swelling or shrinking.

In order to overcome this membrane disadvantage, a new area of research attracting interest is the use of inorganic hybrid nano-particles, for example clay powder, Chitosan-clay and zeolite-clay, that are dispersed as fillers in the organic polymer matrix. This inorganic material has been found to improve the physical and mechanical properties of the polymer (Aouinti *et al.*, 2009; Ling, *et al.*, (2008); Yeh *et al.*, (2003) and Nawawi *et al.*, (2008)). The resulting polymer nanocomposite exhibits higher heat distortion temperatures, a decreased thermal expansion coefficient and better barrier properties as reported by Giannelis, (1996) and Yeh *et al.*, (2003). Moreover there is the advantage of reduction in swelling and an added advantage of high membrane permselectivity and long-term stability (Lai *et al.*, 2003). With this combination of polymer-nanoparticle as casting solution for the thin separating layer, the resulting membrane though composite may not be able to withstand the pressure difference driving force. In order to mitigate the possibility of rupture during usage, a support made of a polymer material that is tougher and forms more porous membrane like polysulphone, is normally used as substrate.

The procedure is based on the solution coating or lamination of a given substrate or support with the solution of the thin separating layer. One or more thin, dense polymer layers are solution coated onto the surface of a micro-porous support made earlier by phase inversion technique. The combined membrane is then placed either vertically or at 45<sup>0</sup> angle to the vertical (Cadotte, (1975 & 1977) and Vankelecom *et al.*, (2007)) to drain excess thin film solution in the atmosphere until it is dried. When this final separating thin layer is laminated onto the support membrane, the residual water is removed by heat treatment.

## 2.8 Production of Zeolites from Clays

Zeolites are crystalline aluminosilicates containing pores and channels of molecular dimensions that are widely used in industry as ion exchange resins, molecular sieves, sorbents, catalysts and in detergent applications. Generally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores.

### 2.8.1 Zeolite Production

Clays contain an amorphous framework structure, and their use in the production of molecular sieves is well documented (Haden *et al.*, 1961; Howell *et al.*, 1963; Koegher *et al.*, 2004; Atta *et al.*, 2007 and Igbokwe *et al.*, 2008). It has been reported that some clay types, principally those of kaolin type are used in synthesizing crystalline aluminosilicate zeolites by treatment with caustic solutions namely; Potassium hydroxide, Sodium hydroxide and Calcium hydroxide (Haden *et al.*, 1961). Such clays are known to have the general molar compositions  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$  and therefore act as the source of Si and Al, the two key ingredients for zeolite formation.

The silica to aluminium ratio in this inorganic clay is the indicator that determines the type of zeolite that can be formed from the clay; thus either hydrophilic or hydrophobic zeolite. This ratio may vary from 0.06 to 3.4 (Milton, (1959); Howell *et al.*, (1963)). For example when the Si:Al ratio is less than 2, a hydrophilic zeolite can easily be prepared by treating appropriately with the caustic solution. On the other hand when a hydrophobic zeolite is the primary target for this range of ratio, the aluminium content in the clay is reduced in a process termed dealumination. By so doing, the silica content of the raw material is increased from low content to high silica content. A typical Si:Al ratio ranges for the formation of a hydrophobic zeolite is given by Ivanova *et al.*, (2009); Titus, (2006) as;



- i. Si:Al < 4      low silica content for hydrophilic
- ii. Si:Al < 20    intermediate silica for larger pore hydrophilic (zeolite Y) or dealuminated to form hydrophobic zeolites.
- iii. Si:Al < 200    high silica for hydrophobic.

The concentrations of the caustic solution necessary for the preparation of a hydrophilic zeolite varies from 20 wt% to 55 wt% and preferably ranges between 45 wt% and 50 wt% (Haden *et al.*, 1961; Howell *et al.*, 1963; Koegher *et al.*, 2004). The process is began by conditioning the clay into a reactive form called metakaolin, by calcining in a furnace at temperatures between 550<sup>0</sup>C to about 830<sup>0</sup>C for a period of not more than 2 hours (Atta *et al.*, 2007; Igbokwe *et al.*, 2007 and Kokoroko, 1993). The aggregation of the clay with respect of being a powder or pellet is of no consequences of the type of zeolite to be formed (Haden *et. al. infra*; and Howell *et al.*, (1963)). However the type of zeolite produced depends on the reaction conditions of temperature, duration for which the amorphous mixture is in contact with the caustic solution (pore-forming directing agent) and type of agitations employed.

Haden *et al.*, (1961) have patented the use of dehydrated kaolin clay into type A zeolite, by treating with a relatively concentrated caustic solution at low temperature. Another process of zeolite A formation entails digesting an aqueous reactant mixture containing reactive kaolin at a temperature of 20<sup>0</sup>C to 55<sup>0</sup>C for 2 hours. This is followed by crystallizing sodium zeolite A in the digested reactant mixture in a temperature range of about 75<sup>0</sup>C to 100<sup>0</sup>C. After about two hours within this temperature range, the crystalline zeolite A is then recovered as the product (Koegher *et al.*, 2004). In order to complete the zeolite production procedure, the crystals formed are to be filtered of any excess caustic solution. Further washing of the crystal



must be carried out such that the pH of the effluent filtrate is in the range 9 to 12 (Milton, 1959) after which drying is carried out at room temperature. The crystals obtained could be left as pellets or pulverized. Before utilizing this zeolite, the prepared crystals need to be calcined or activated at temperatures between 300<sup>0</sup>C and 500<sup>0</sup>C (Haden *et al.*, 1961; Howel *et al.*, 1963 and Atta *et al.*, 2007).

### 2.8.2 Types of Zeolites

Zeolites are classified based on several features. Some of the features are pore dimensions, Si:Al ratio, and aperture type like single 4 ring, single 6-ring, double 4 ring and double 6 ring. For instance, the various types of zeolite structures, like the super cages and cylindrical structured pores differ not only in type and dimensionality of the pore system but also in the size of the pore apertures (Titus, 2006). According to the pore apertures, zeolites are classified as shown in Table 2.1.

**Table 2.1 Types of zeolite with respect to pore dimensions**

Zeolite type	Pore aperture	Dimension (nm)
Sodalite, Zeolite A	Narrow pore	0.30-0.45
ZSM-5 (MFI)	Medium pore	0.45-0.60
X, Y (FAU), Mordenite (MOR)	Wide pore	0.60-0.90

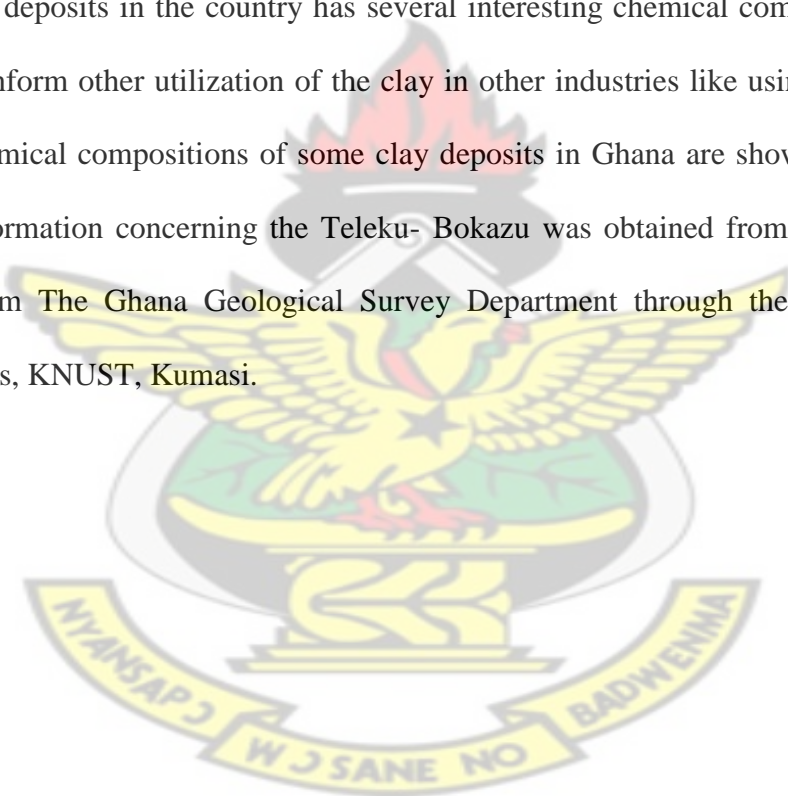
When the dimensions of these apertures are of the same order of magnitude as the kinetic diameter of other molecules, it enables zeolites to behave as molecular sieves. This unique property is what gives zeolites the quality of being selective adsorbents for separating substances and as shape-selective catalysts.

### 2.8.3 Clay Deposits in Ghana

The clay resource in Ghana is estimated at between 500-600 million cubic meters (Hammond, (1997). Some of the settlements where these deposits have been

identified are Abonku, Anfoega, Ekon, Fomena, Kibi, Kpeve and Teleku-Bokazu. Currently, the utilization of clay in Ghana has been in the production of bricks, tiles and ceramic industries (Hammond, 1997; Kokoroko, 1993).

Physical and chemical constituents of these clay raw materials are essential for efficient processing techniques in production. The exploitation of the clay in these industries has not been satisfactory due to inadequacy of information on the chemical and physical properties of the clay deposits. From the work of Kokoroko, *supra cit.*, the clay deposits in the country has several interesting chemical compositions which would inform other utilization of the clay in other industries like using it as zeolites. The chemical compositions of some clay deposits in Ghana are shown in Table 2.2. The information concerning the Teleku- Bokazu was obtained from an unpublished data from The Ghana Geological Survey Department through the Department of Ceramics, KNUST, Kumasi.



**Table 2.2 Chemical composition of some selected clay deposits (Ghana)**

<b>Component</b>	<b>Abonku Clay (%)</b>	<b>Anfoega Clay (%)</b>	<b>Teleku-Bokazu Clay (%)</b>
<b>SiO<sub>2</sub></b>	59.8	69.2	71.14
<b>Al<sub>2</sub>O<sub>3</sub></b>	21.3	19.8	19.75
<b>Fe<sub>2</sub>O<sub>3</sub></b>	7.2	0.5	0.24
<b>CaO</b>	0.2	0.5	0.17
<b>MgO</b>	0.4	trace	0.73
<b>K<sub>2</sub>O</b>	0.8	1.1	0.70
<b>Na<sub>2</sub>O</b>	0.4	1.1	-
<b>TiO<sub>2</sub></b>	1.0	0.6	-
<b>Ignition Loss</b>	8.4	6.6	4.94
<b>TOTAL</b>	99.5	99.4	97.67
<b>SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub></b>	<b>2.808</b>	<b>3.177</b>	<b>3.602</b>
<b>Na<sub>2</sub>O:SiO<sub>2</sub></b>	<b>0.00669</b>	<b>0.0159</b>	-
<b>H<sub>2</sub>O:Na<sub>2</sub>O</b>	-	-	-

The suitability for the formation of zeolites supported composite membranes from clay resources is well documented (Atta *et al.*, 2007; Igbokwe *et al.*, 2008; Ivanova *et al.*, 2009; Ling *et al.*, 2008 and Nawawi *et al.*, 2008). When the zeolite is hydrophilic, it helps in the separation by adsorbing polar components preferentially in the separation of organic-inorganic liquid mixtures like ethanol-water mixture. In addition, when the nanocomposite form is well-dispersed in a membrane polymer matrix as filler, it causes an improvement in the physical and mechanical properties of the polymer (Yeh *et al.*, (2002); Ling *et al.*, (2008)).

According to Table 2.2 above, clay materials from Abonku, Anfoega and Teleku-Bokazu can be used as raw materials in the formation of successful hydrophilic zeolites due to their respective Si:Al ratio being below 4. In fabricating a composite PVA-base membrane for the pervaporation separation of ethanol-water mixture therefore, anyone of them could be used as filler to limit the extent of swelling and dissolution of the PVA.

## CHAPTER 3

### 3.0 METHODOLOGY

#### 3.1 Equipment and Materials

##### 3.1.1 Equipment needed for the experimentation

**Table 3.1 Apparatus needed**

Equipment	Model	Source
ASTM E11mesh No: 35 and 70	-----	-----
Condenser	Improvised	-----
Drawing paper	Ordinary	-----
Filter paper	Ordinary	-----
Furnace	Electric Muffle Chamber Furnace	Vecstar, United Kingdom
Gardener's knife	Improvised	-----
Gas Chromatograph	Perkin Elmer DSC-7	Denmark
Mortar and pestle		
Oven	Gallenkamp Hotbox size 1	United Kingdom
Pervaporation cell unit	-----	Magazine, Kumasi
pH meter	Orion 3-Star Plus pH Benchtop Meter	Germany
Polypropylene mesh	-----	-----
Pressure gauge		
Vacuum pressure gauge	BAPHA VARNA	Bulgaria
Vacuum pump	Edwards' Model 5	United Kingdom

### 3.1.2 Materials needed

**Table 3.2 Chemicals needed**

Chemical	Source
Clay	Abonku-Central Region Anfoega-Volta Region Teleku-Bokazu- Western Region
DMAc	Merck Schuchardt, Germany
Ethanol (96.1 v%)	UK Chemicals, UK
NaOH pellets	UK Chemicals, UK
Polysulphone (PSf) MW=35,000	Aldrich, USA
Polyvinyl alcohol (98% hydrolyzed) MW 16,000	Acros Organics, USA

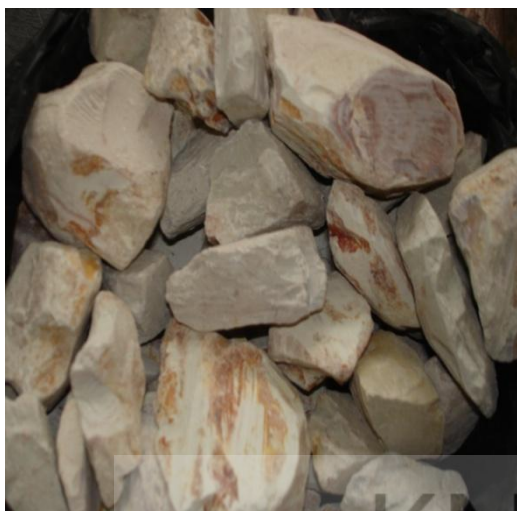
### 3.2 Hydrophilic Zeolite-A Formation.

Clay samples were obtained from 3 different locations of Abonku, Anfoega and Teleku-Bokazu. The sample from Abonku was wet and contained lots of debris that were removed as explained below. It dried out after 3 days in transit to Kumasi. Those from Anfoega and Teleku-Bokazu were already dry and contained no debris. Pictures 1.0, 2.0 and 3.0 below are photographs of the three raw clay samples



**Picture 1.0 Raw Abonku Clay**





**Picture 2.0 Raw Anfoega Clay**



**Picture 3.0 Raw Teleku-Bokazu**

### **3.2. 1 Conditioning of the raw clay samples**

For the clay to be suitable for zeolite formation, it must be free from contaminants, must have appropriate Si:Al ratio and be free of any water of hydration. Therefore the following conditioning procedure was followed.

#### **a. Cleaning of the clay**

The raw Abonku clay was left on the ground for two weeks in the ambient. It was then soaked in ordinary water for 24 hours until slurry was formed. The debris of trees, leaves and other suspended foreign matter was scooped from the surface of the mixture. The solution was then sieved to remove larger undissolved clay particles together with some particles of stones that came with it with a 500 microns mesh sieve (ASTM-E11 mesh No:35). The slurry was allowed to settle for 36 hours and the surface water was poured off. The cake was dried in the open atmosphere for 72 hours.

## b. Calcination



**Picture 4.0 Calcined clay samples**

The clay samples from Anfoega, Abonku and Teleku-Bokazu were pulverized by using mortar and pestle and all three clay samples were sieved with a 212 microns wire mesh. Based on the procedure followed by Haden *et al.*, (1961); Howel *et al.*, (1963) and Atta *et al.*, (2007) on the formation of metakaolin, the pulverized samples were calcined at a temperature of 700 °C in a laboratory type Muffle Chamber Furnace for two hours. After cooling, the three types of the metakaolin were stored in polypropylene containers under ambient condition for later use. The appearance of the calcined clays is shown in Picture 4.0.

## c. Composition of clay

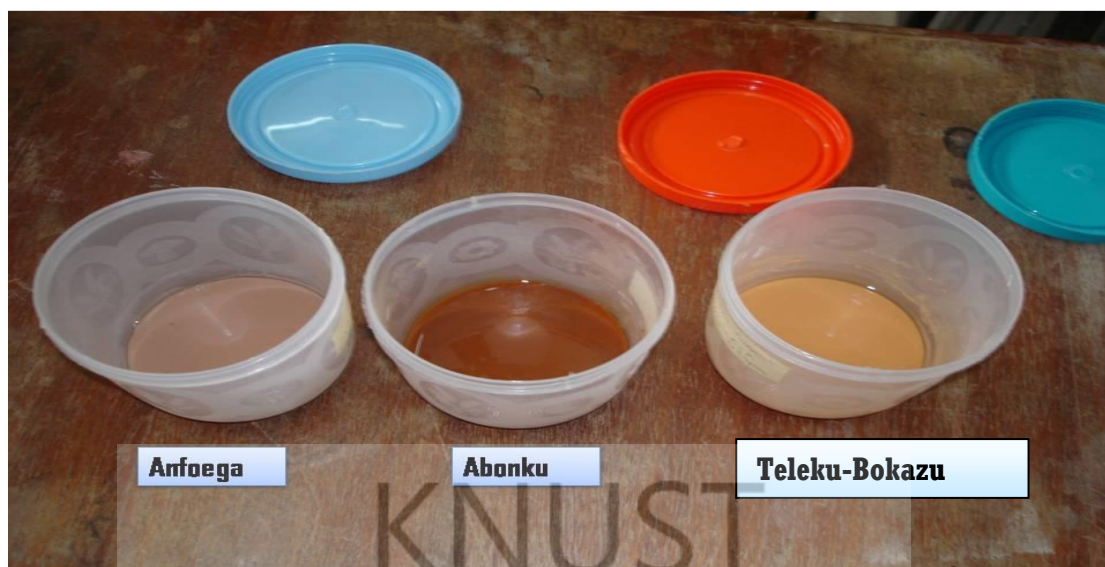
The composition of the different clay samples is given by Kokoroko , (1993) and shown in Table 2.2. Based on the Si:Al ratio from this table, the following procedures was followed in the zeolite preparation.

### 3.2.2. Inorganic micro-pore forming directing agent and its preparation

The inorganic micro-pore forming agent is NaOH. From the guiding work of Ling *et al.*, (2008), less than 1.0g of the Zeolite would be required. It was decided therefore that about 50g of the pulverized calcined clay was to be converted as described in the next section so that part could be kept for later use and analysis. In line with the patented works of Haden *et al.*, (1961) and Koegher *et al.*, (2004), a solution of the NaOH with a concentration of 45% by weight was prepared. The method of preparation is given in Appendix D.

### 3.2.3. Zeolite preparation from the calcined clay

35g each of the metakaolin powder from the 3 clay samples was separately mixed in a polypropylene container with 33.5 cm<sup>3</sup> of 45% NaOH solution. While the mixture containing clay from Abonku and Anfoega were in slurry forms, that containing Teleku-Bokazu was a gel-like mass. The reaction mixtures for Abonku, Anfoega and Teleku-Bokazu clays were dark chocolate, light mauve and yellow respectively. The closed containers were maintained at room temperature without stirring for a digestion period of approximately 165.5 hours (about 6½ days) to age as a way of insuring completion of the reaction (Milton, 1959).



**Picture 5.0 Near-completion reaction mixture of zeolite formation**

The samples were then placed in a water bath at  $85^{\circ}\text{C}$  for another 2 hours without opening the container to ensure complete formation of the polycrystalline aggregate of the required zeolite. This crystalline aggregate was then separated from the mother liquor by filtration and subsequently the residue (crystals) was washed with excess distilled water until the pH of the filtrates were between 9 and 12 during washing period as explained by Milton, (1959) and Howell *et al.*, (1963).

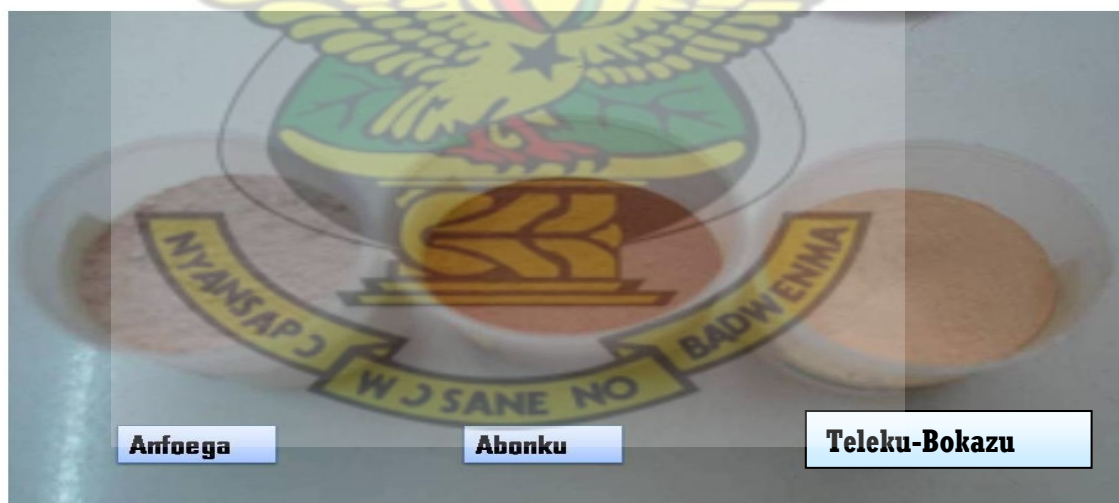
The pHs of the filtrates from the formed zeolites were 11.4 for Abonku, 12.0 for Anfoega and 11.7 for the Teleku-Bokazu samples. The formed aggregated crystals as shown in Appendix E were left at room temperature to dry for 3 days. In order to ensure complete drying, the semi-dried solids were subjected to heating in an oven at  $90^{\circ}\text{C}$  for an hour (Igbokwe *et al.*, 2008). The products are shown in Picture 6.0.





**Picture 6.0 Dried zeolites from the oven**

The dried aggregated crystals were pulverized by the use of mortar and pestle and later sieved with 212 mesh sieve size. This powdered zeolite was then calcined at  $180^{\circ}\text{C}$  for a period of 2 hours and stored in air-tight polypropylene containers as shown in Picture 7.0 for later use as filler in the membrane formation



**Picture 7.0 Pulverized and calcined zeolite samples**

### **3.3 Membrane Support Preparation**

In order to adopt the phase inversion technique which assures the formation of asymmetric micro-porous membrane, the casting solution was prepared based on the recipe given by Baker, (2004), which was in a range of 15 -20 wt% concentration of



the polymer in the casting solution. Due to the variable average molecular weights of the polymers it was important to ascertain the quality of the resulting supports by varying the concentration of the Polysulphone (PSf) used in this work. The calculations required for the preparation of the support casting solution are shown in Appendix D.

### **3.3.1 Preparation of the support casting solution**

2g of PSf were dissolved in equivalent volume of Dimethyl acetamide (DMAc) at 50°C. It took approximately 2 hours for complete dissolution of the PSf pellets. The final gel-like solution was transparent and colourless. Trial solutions were prepared for polymer concentrations of 14wt%, 16wt%, 17 wt%, 18 wt% and 20 wt%. After casting these solutions on a flat plate with gardener's knife, 16 wt% PSf-DMAc cast solution produced a more suitable smooth-surfaced micro-porous support membrane. The results of this observation are shown in Appendix B.

### **3.3.2 Fabrication of the Porous PSf support membrane by Phase Inversion**

#### **Technique**

A sheet of white paper was wetted with distilled water and placed on a hard flat surface for it to be well-aligned. The polysulphone solution was cast onto the paper fabric by pouring it carefully at the upper edge of the paper. With the aid of glass rod and a Gardener's knife that was pre-adjusted to ½ a millimeter thickness the solution was spread evenly on the paper fabric (Ling *et al.*, (2008) and Nawawi *et al.*, (2008)). One of the micro-porous cast films is shown in Picture 8.0.



**Picture 8.0 Evenly cast polysulphone support**

The film was allowed to stand for a period of between 3 and 4 minutes at room temperature to allow some of the DMAc solvent to evaporate from the surface, after which the film, together with the plate was immersed in distilled water at room temperature. The flat plate was then carefully removed and the paper and membrane support floated on the water surface. After 2 minutes the paper finally got detached from the support membrane and subsequently removed from the inversion solution. The membrane floated on the water for about 10 minutes and sank to the bottom. It was allowed to stay in the bath for 18 hours. The final support membrane was opaque and whitish in colour. Picture 9.0 shows the porous support immersed in distilled water.



**Picture 9.0 Immersed porous support in the inversion solution**

The resulting porous support was removed from the solution and then dried in air at room temperature for 24 hours.

### **3.4 Preparation of the Thin film Membrane**

The polymer material selected for the thin membrane film was Polyvinyl alcohol (PVA). It is unstable in aqueous solutions and needed to be cross-linked with zeolite powder made from the 3 different Ghanaian clay deposits from Abonku, Anfoega and Teleku-Bokazu. The calculations for the preparation of the 5 wt % PVA Zeolite-clay solution are shown in Appendix D.

#### **3.4.1 Preparation of PVA Zeolite-Clay Composite Membrane**

The composite membrane was prepared by laminating the top surface of the prepared PSf porous support with the 5 wt% PVA zeolite-clay solution. Before coating, the porous support was spread on the flat plate after which it was heated in an oven at 85°C for 10 minutes to bring it closer to the temperature of the casting solution of 95°C. The 5 wt % PVA zeolite-clay solution was slowly and carefully poured onto the porous support and spread uniformly with glass rod (Ling *et al.* (2008). This lamination procedure is a modification of the method described by Forester, (1970) and Baker, (2004). The resulting supported thin composite membranes were hanged

vertically to drain all excess polymer solution and maintain uniform film thickness as depicted in Picture 10.0. The membrane was then dried in air at room temperature for 15 hours.

In order to coat about 3 of the PSf micro-porous membranes that were supposed to act as substrate for the PVA composite membranes, 20 g of the 5 wt% PVA zeolite clay solution for each of the zeolite powder was observed to be just enough. The fabricated composite membranes were stored in a polypropylene container at room temperature.



**Picture 10.0 Composite thin layer membrane laminated on PSf support.**

### **3.5 Pervaporation Experiment**

In the experiment, several concentrations of ethanol were to be dehydrated above the azeotropic concentrations. In order to achieve this objective, an ethanol solution of concentration 96.1 v% was accordingly diluted to specific concentrations for onward purification above the azeotropic concentration levels. The selected concentrations of the ethanol-water mixture for the five runs were 60 v%, 70 v%, 80 v% and 90 v%. Due to the capacity of the feed compartment of the Pervaporation cell unit, a volume

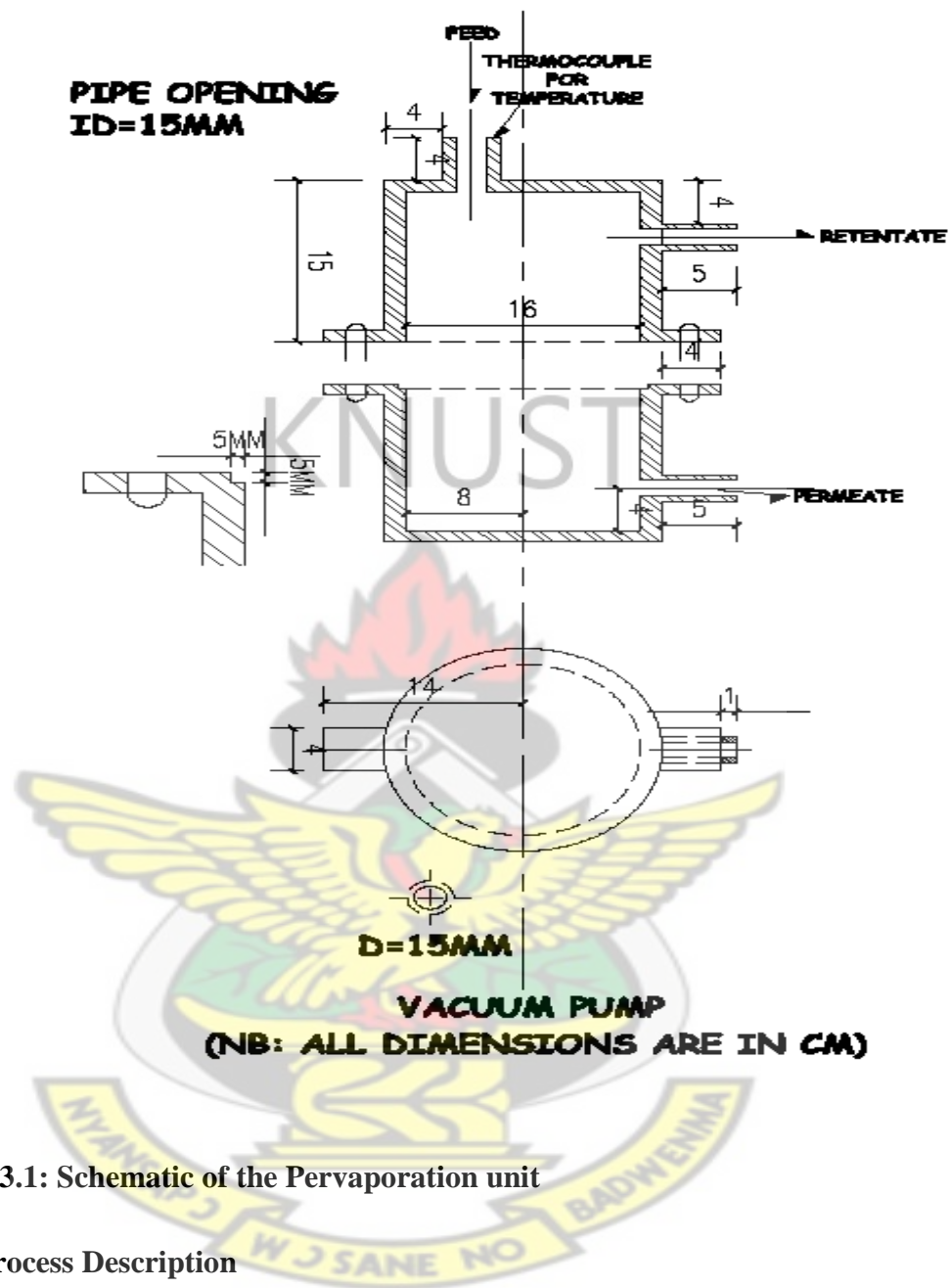
of 50cm<sup>3</sup> of each concentration were prepared. Table B-8 in Appendix B gives the results of the preparations made.

### 3.5.1 Pervaporation cell

A pervaporation cell unit was built using recycled aluminium metal scraps that was melted and the ingot cast into required shape in a workshop at Suame-magazine in Kumasi, Ghana. The technical engineering design diagram for the cell is shown as in Figure 3.1. The top portion is the feed chamber while the lower part is the permeate chamber. In between the 2 chambers is an indentation for the membrane, its perforated metal support that prevents membrane rupture or collapse and finally a propylene wire mesh that keeps the permeate flow channel opened. The pictorial diagrams are shown in Appendix E.

The limitation to this particular cell is that experiments cannot be carried out at temperatures above 70<sup>0</sup>C as ethanol may react with the aluminium to form alkoxides. With this formation therefore, the main purpose of the purification of ethanol from ethanol-water mixtures will then be defeated.



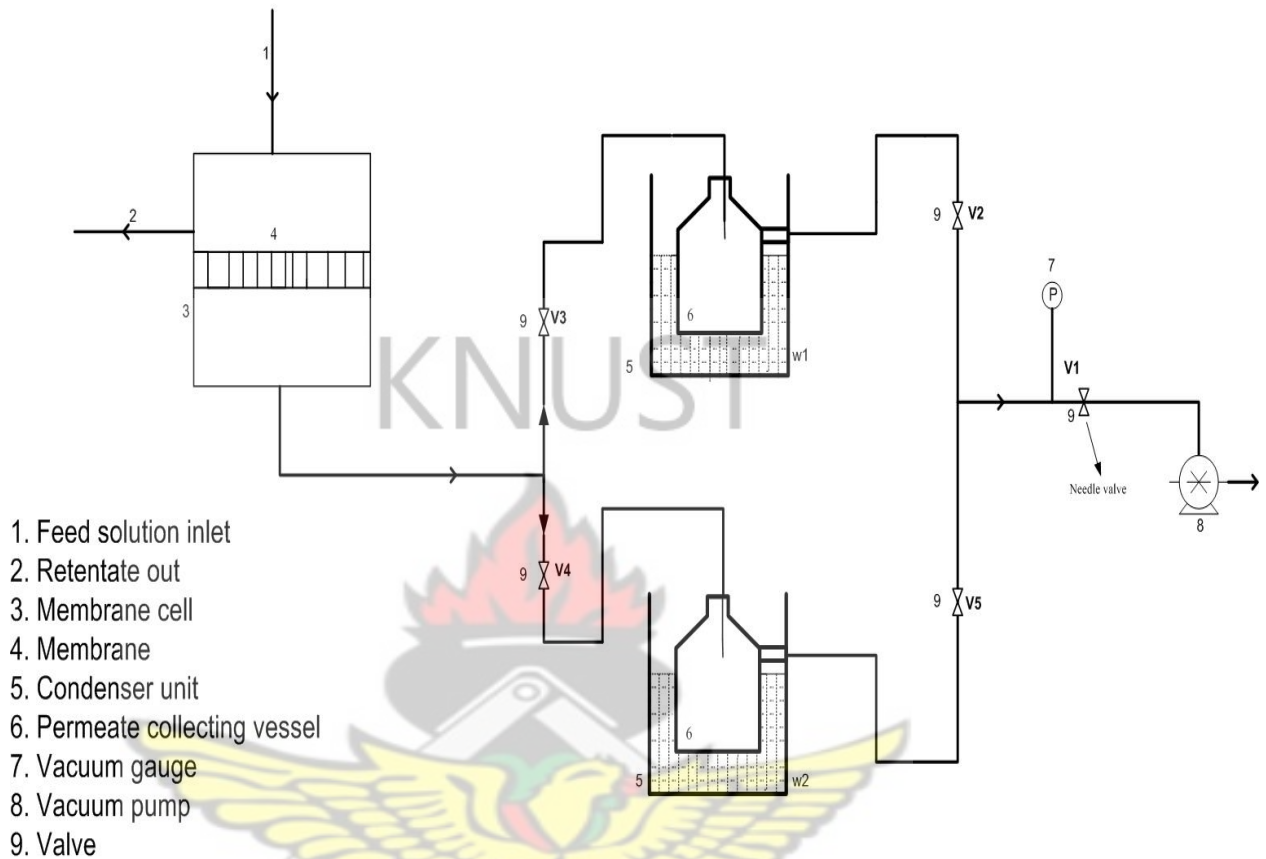


**Figure 3.1: Schematic of the Pervaporation unit**

### 3.5.2 Process Description

The flow sheet for the experimentation is shown in Figure 3.2 and the set-up shown in Picture 11.0. It consists of the pervaporation cell unit, condenser unit and the vacuum unit. The 3 units are connected to one another by vacuum hoses and valves. The pervaporation unit is made up of the feed and permeate chamber. The membrane is placed in between the chambers to separate the feed from permeate with the help of a perforated metal plate support to avoid membrane rupture during the operation.

## PERVAPORATION SET- UP FLOW DIAGRAM



**Figure 3.2: Pervaporation process flow-diagram**

Two condenser units were each placed on the two flow lines through which the permeate passes. Line 1 consists of condenser W<sub>1</sub>, valves V<sub>2</sub> and V<sub>3</sub>. Line 2 on the other hand consists of condenser W<sub>2</sub>, valves V<sub>4</sub> and V<sub>5</sub>, via vacuum hose with valves V<sub>3</sub> and V<sub>4</sub> respectively. A vacuum pump, pressure gauge for the feed chamber and a vacuum pressure gauge for the vacuum together with 4 ordinary valves and a needle valve for the vacuum gauges were provided as well. The vacuum unit consists of the vacuum pump that was used to create a near-vacuum condition in the whole system by the adjustment of a needle valve V<sub>1</sub>. The level of vacuum is indicated by P<sub>6</sub>.

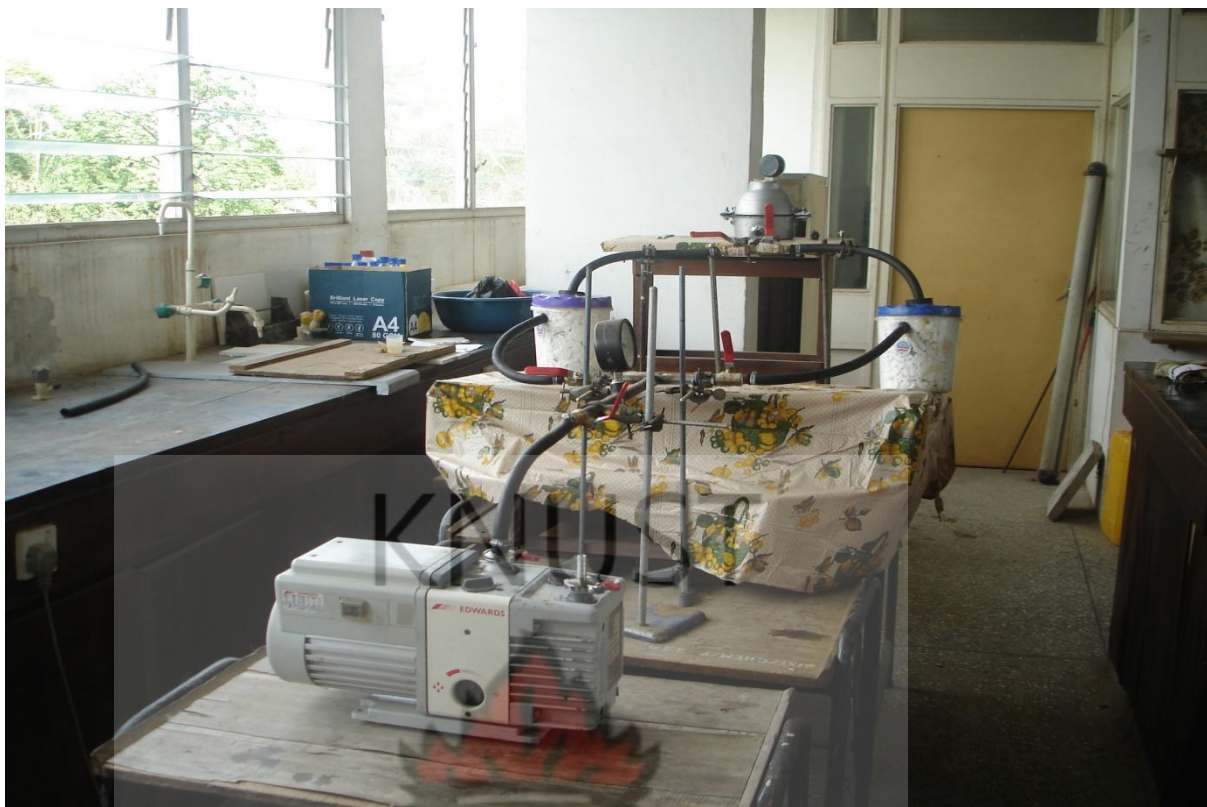
### 3.5.3 Operation procedure

Initially the perforated metal plate was placed in between the 2 chambers followed by a polypropylene mesh of same diameter as the plate. The zeolite filled membrane with the same diameter as the metal plate was then put on the mesh after which the Teflon O-ring was put in place. The two chambers were then bolted together. The steps that were followed until completion of the experiment have been detailed below.

1. The feed was introduced into the chamber in order to wet the membrane for about 15 minutes.
2. Iced blocks were then introduced into condenser  $W_1$  to a level far below the outlet of the collecting vessel
3. Valve  $V_1$  was opened while the vacuum pump was switched on.  $V_1$  was then adjusted until the reading of the vacuum pressure was between 0.10 to 0.15  $\text{kg/cm}^2$ . Then  $V_2$  was opened to further create same pressure range in the condenser  $W_1$ . When the pressure range was satisfied,  $V_3$  was then opened. By adjusting the needle valve  $V_1$  carefully the required pressure of about 0.15  $\text{kg/cm}^2$  was obtained throughout line 1 within 15 minutes. Immediately the reading of pressure  $P_6$  stayed constant, the timing of the experiment was started using an alarm clock for a 2 hour duration after which the permeate condensate sample was taken and analysed.
4. At about 10 minutes prior to the sample collection, condenser  $W_2$  was opened and iced blocks introduced to the same level as in  $W_1$  above. As soon as it was time, valve  $V_2$  was closed simultaneously as valve  $V_5$  was opened.

5. At this point valve  $V_3$  was closed simultaneously as  $V_4$  was opened, thus making the operation pseudo-continuous in nature.
6. At predetermined time intervals, the trapped and condensed permeate was removed from its pre-weighed permeate vessel, weighed and emptied into a sample bottle for later analysis with Gas chromatography. Iced blocks were replenished intermittently into the condensation vessel with fresh ones in order not to loose permeated vapour.
7. Steps 2 to 6 were followed until 5 different samples were taken for a total duration of 10 hours for each feed concentration.
8. At this point the vacuum pump was switched off and then  $V_1$  closed. After closing  $V_3$ , the sample was again left to stay inside the condenser for an hour before emptying into the sample bottle after its weight had been determined. The resulting retentate was also removed and weighed accordingly.
9. At the end of the each experiment the membrane was dried while the lines were cleaned of traces of the experimental components by running distilled water through for about 15 minutes. The system unit was then left opened overnight for all parts to be dry and free of any contaminant.
10. The experiment was performed for ethanol concentrations of 60 v%, 70 v%, 80 v% and 90 v%.
11. The procedure was repeated for the other membranes from the other clay samples.





**Picture 11.0 Process set up showing the 2 condensers and the vacuum pump with vacuum level gauge.**

### **3.5.4 Method of Analysis**

The liquid permeate was analysed with a Gas Chromatograph that is equipped with Flame Ionisation Detector (GC-FID) with operating conditions given below.

Gas flow rates:  $N_2 = 25\text{ml/min}$ ,  $H_2 = 40\text{ml/min}$

Temperature : Injection =  $200^{\circ}\text{C}$ , Column =  $150^{\circ}\text{C}$

Sample injector =  $1\mu\text{L}$  syringe

The liquid permeate sample was injected manually using  $1\mu\text{L}$  syringe. It took a retention time of 3 minutes for each sample. Each sample was injected twice and the average peak height was taken as representative of the sample concentration.



Two different concentrations of the standard ethanol aqueous solution of known concentrations were used as standards. An average of the peak heights of each sample was compared with that of the standard and the concentrations determined from the calibration curve. A sample output of the peak heights is given in Appendix A while the calibration method is in Appendix D.

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## CHAPTER 4

### 4.0 RESULTS AND DISCUSSIONS

#### 4.1 Experimental results, Operating conditions and Concentration profiles of Permeate

##### 4.1.1 Permeate Samples Collected

In all, 5 samples were taken for each of the feed ethanol concentrations of 60 v%, 70 v%, 80 v% and 90 v%. For each membrane type, there were 20 permeate samples. A total of 60 permeate samples were therefore generated from the use of Abonku zeolite, Anfoega zeolite and Teleku-Bokazu zeolite filled membranes. The pervaporation experiments were run for 10 hours in each case and the results are presented in Appendix B.

##### 4.1.2 Operating conditions

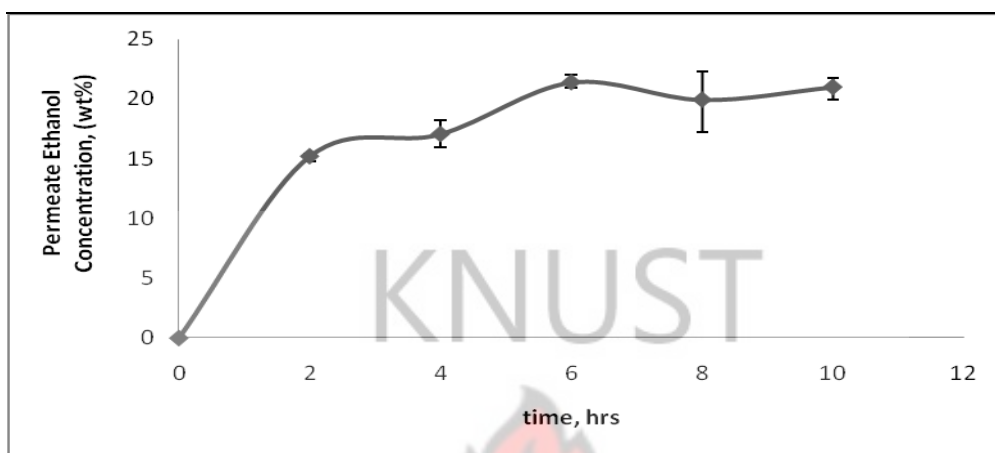
1. The permeate pressure was selected such that it was always between 0.10 kg/cm<sup>2</sup> and 0.15 kg/cm<sup>2</sup> (73.6 mmHg and 110.3 mmHg) vacuum at the operating temperature of 30<sup>0</sup>C. This is because according to Mulder *et al.*, (1983); Seader & Henley, (2001:530) and Baker, (2004) at any point in the pervaporation, the partial vapour pressure of the individual components in the permeate must be less than their respective saturated vapour pressures.
2. In all the relevant calculations however, the average of these two pressures, 0.125 kg/cm<sup>2</sup> (92.028 mmHg), was taken as the permeate pressure.

##### 4.1.3 Concentration profiles of the Permeate mixtures for constant feed compositions

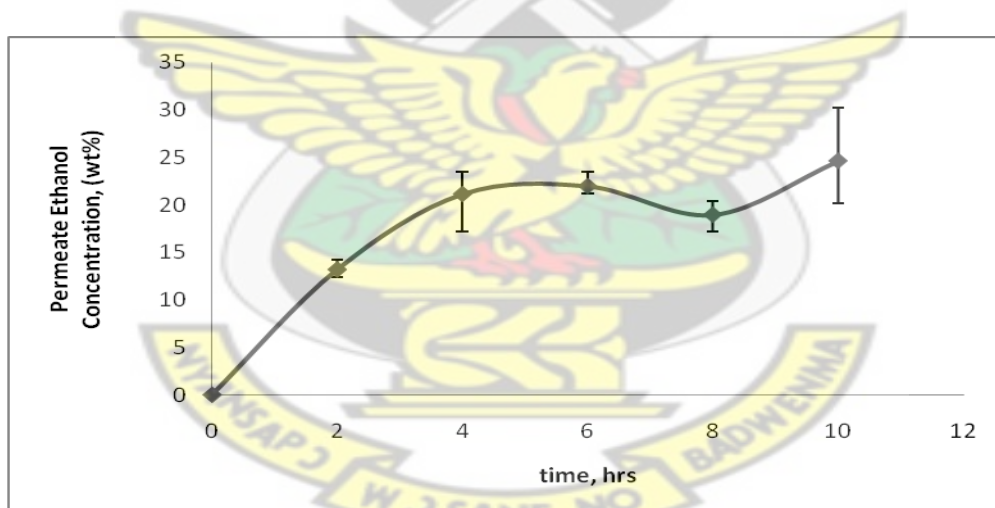
The concentration profiles are shown in Figures 4.1 to Figure 4.16. In general, the concentration of ethanol in the permeate increased steadily to a constant value within

ten hours for all the three types of zeolite-clay filled membranes for each of the given feed concentrations.

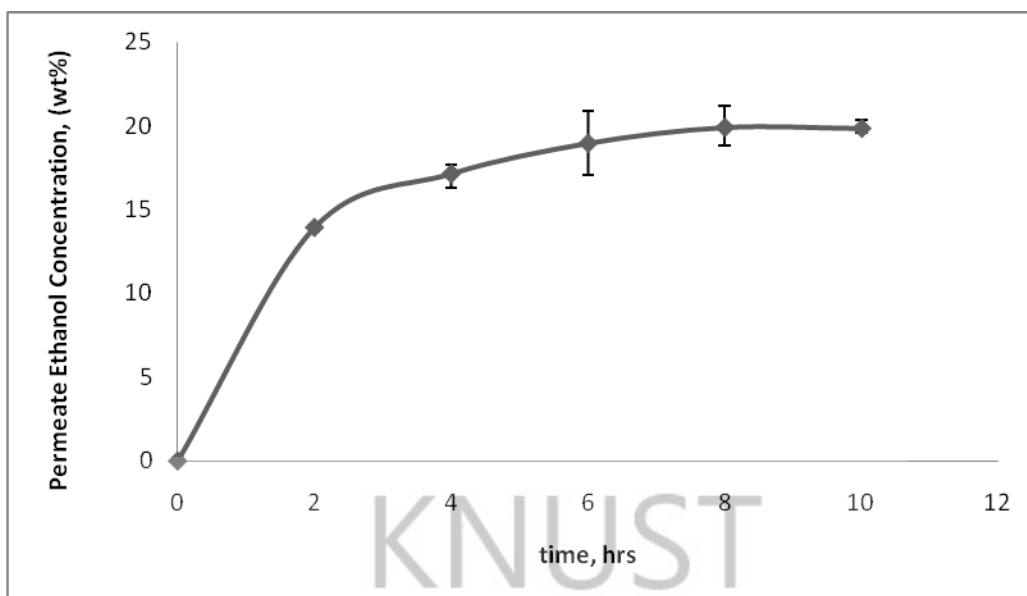
**a. Feed Ethanol concentration of 53.9 wt%**



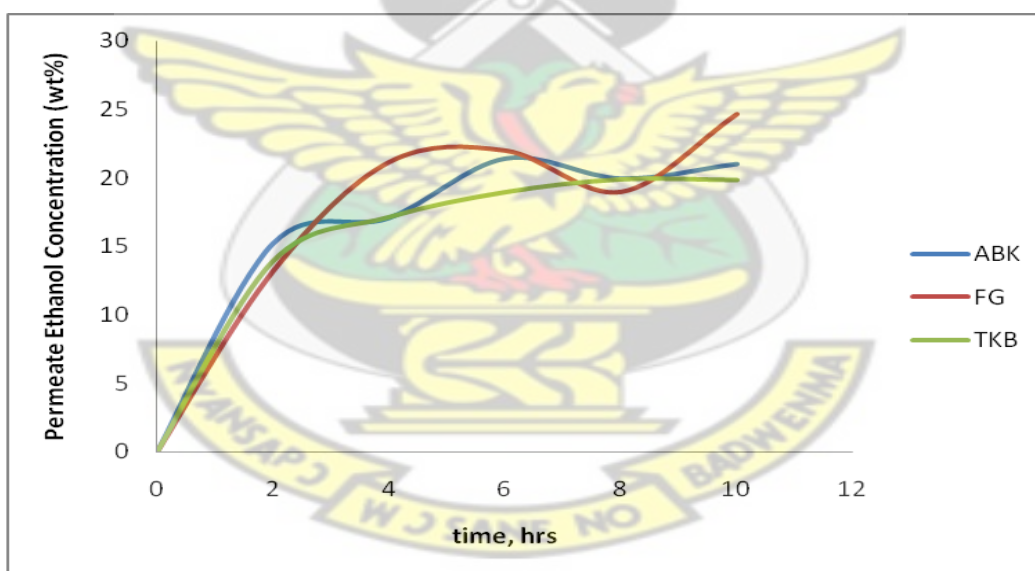
**Figure 4.1 Concentration profile of permeate for 53.9 wt% Ethanol in feed mixture versus diffusion time for Abonku membrane**



**Figure 4.2 Concentration profile of permeate for 53.9 wt% Ethanol in feed mixture versus diffusion time for Anfoega membrane**



**Figure 4.3** Concentration profile of permeate for 53.9 wt% Ethanol in feed mixture versus diffusion time for Teleku-Bokazu membrane



**Figure 4.4** Combined concentration profiles of permeate for 53.9 wt% Ethanol in feed mixture against diffusion time

At a feed concentration of 53.9 wt%, the concentration of ethanol in the permeate increased exponentially to a steady value for all three membranes types as shown in Figures 4.1, 4.2 and 4.3. When the 3 graphs are plotted on the same axes, Figure 4.4 is

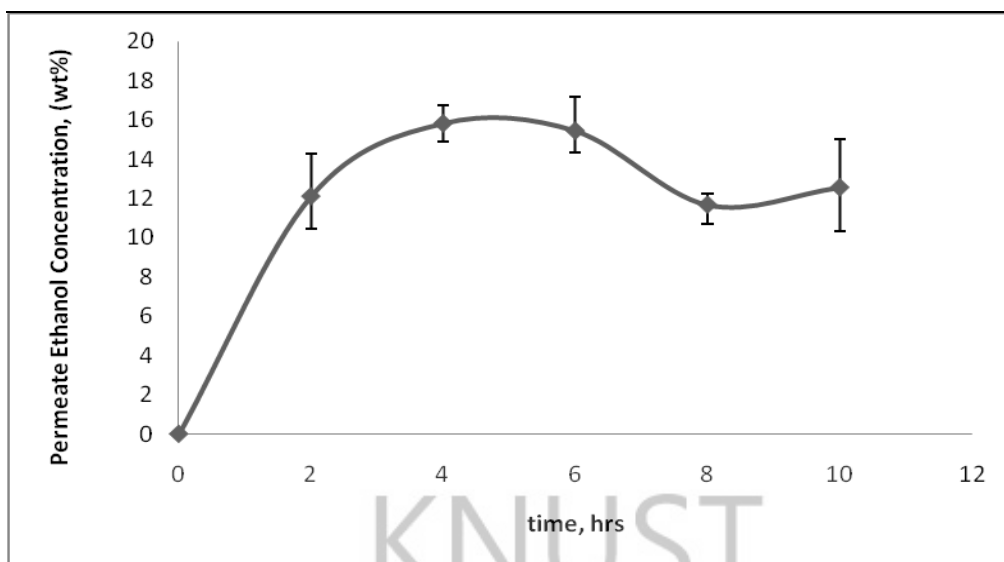
obtained and it shows how the ethanol concentrations varied for the different membranes.

While the steady value for Abonku membrane was 23.0 wt%, that for Anfoega membrane was 20.0 wt% and that for Teleku-Bokazu membrane was 18.0 wt%. These values implied that at the given feed concentration, the flux of ethanol through the Abonku membrane is more than that through the Anfoega membrane. There was least diffusion of ethanol molecules through the Teleku-Bokazu membrane. This suggests that using ethanol feed concentration of 53.9 wt%, Teleku-Bokazu membrane could give a better separation, followed by the Anfoega and the Abonku membranes in that order.

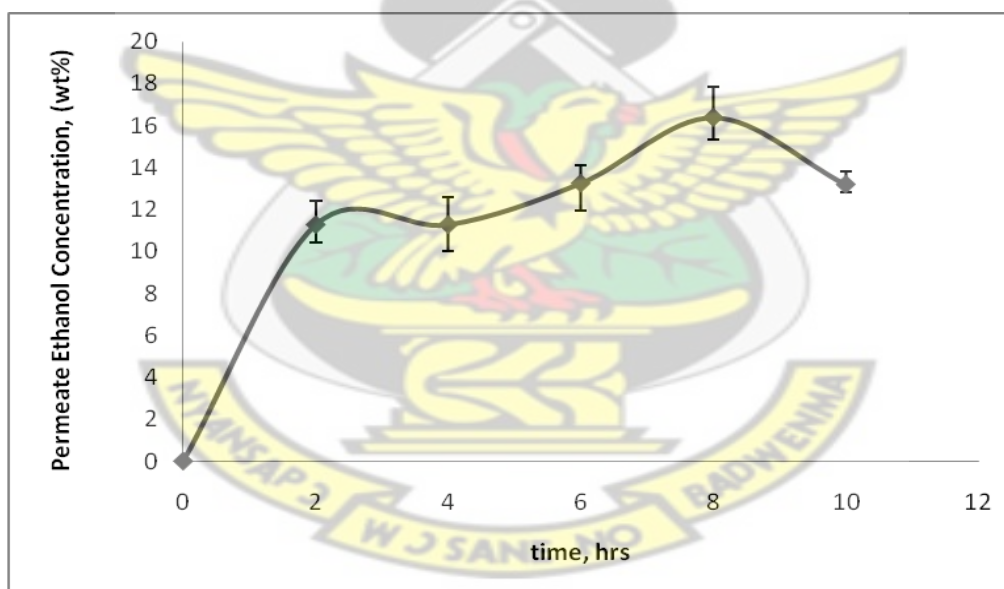
#### **b. Feed Ethanol concentration of 64.6 wt%**

The results for the feed concentration of 64.6 wt% ethanol are shown in Figures 4.5, 4.6 and 4.7 respectively for the individual zeolite-clay membranes. Figure 4.8 shows the combination of the concentration profiles of each membrane types on the same axes. The behavior of the curves indicates that the ethanol concentration in the permeate rose exponentially to a steady value for the three membrane types to different levels. The maximum concentrations of the ethanol in the permeate at this feed concentration were lower than the values at a feed concentration of 53.9 wt%. For the Abonku membrane the steady value was 13.6 wt%, while that for Anfoega was 13.1 wt% and Teleku-Bokazu, 12.9 wt%. These values again suggests that while Abonku zeolite-clay filled membrane allows more ethanol molecules to permeate through it, the Teleku-Bokazu zeolite-clay filled membrane allows the least ethanol molecules to permeate through it.

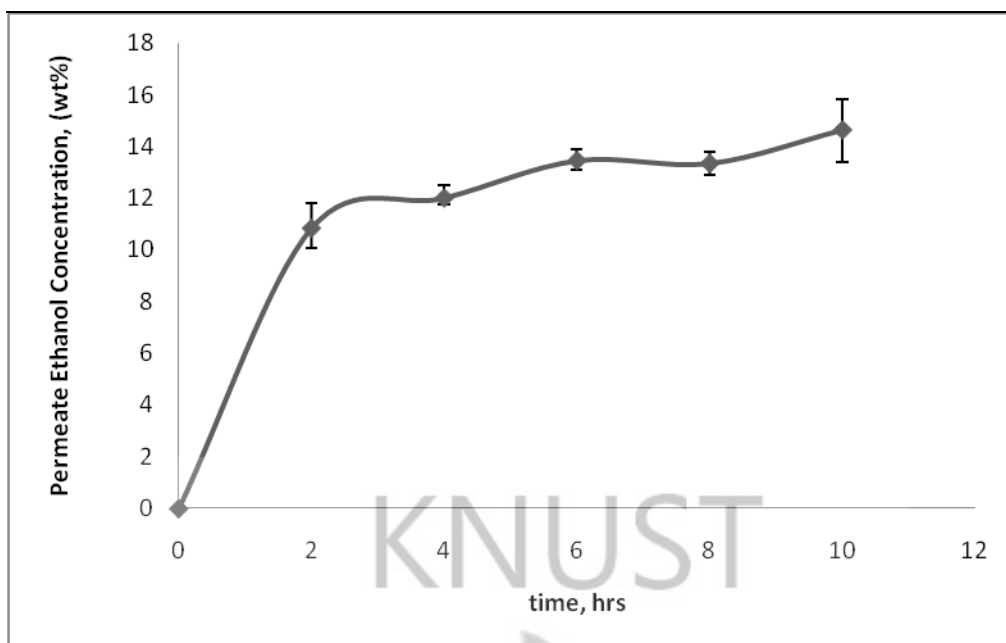




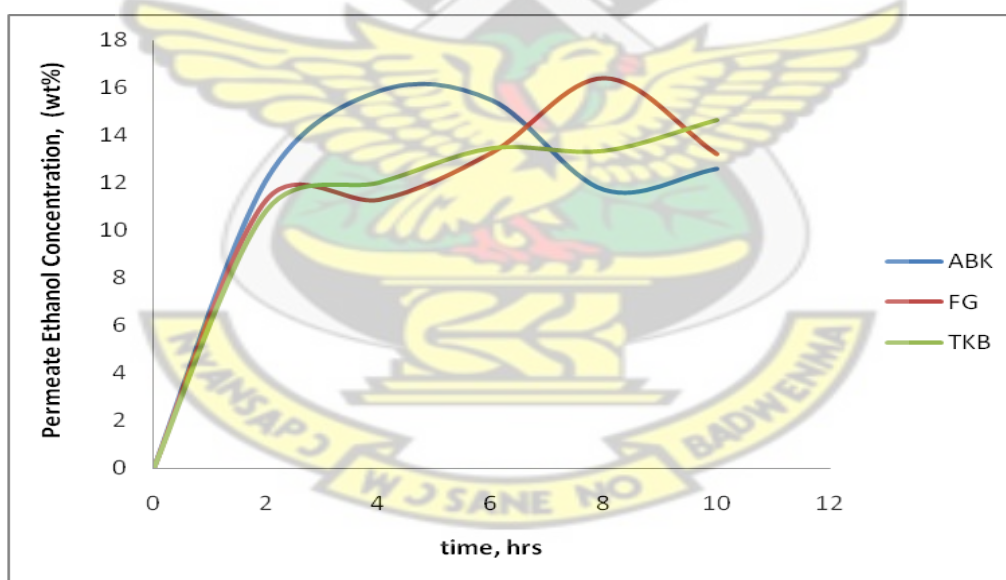
**Figure 4.5** Concentration profile of permeate for 64.6 wt% Ethanol in feed mixture versus diffusion time for Abonku membrane



**Figure 4.6** Concentration profile of permeate for 64.6 wt% Ethanol in feed mixture versus diffusion time for Anfoega membrane



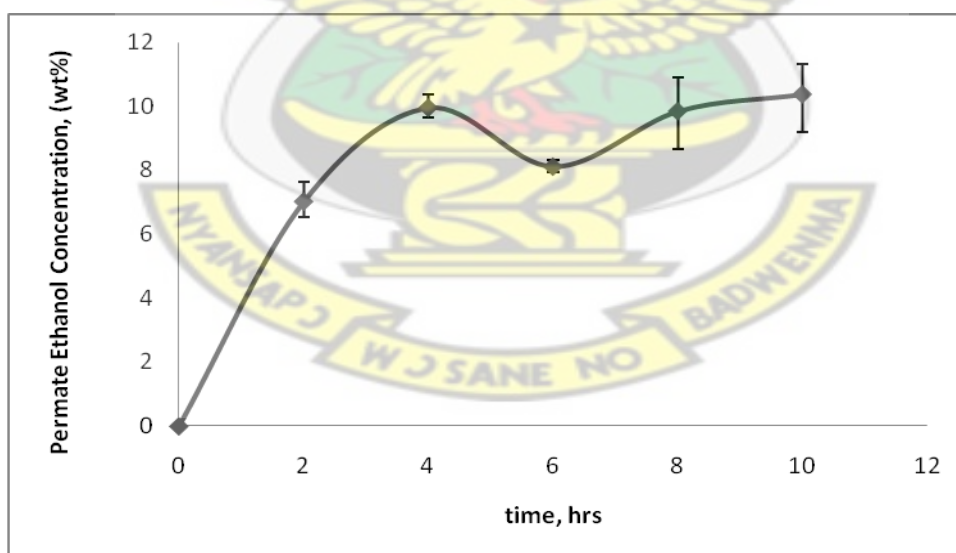
**Figure 4.7** Concentration profile of permeate for 64.6 wt% Ethanol in feed mixture versus diffusion time for Teleku-Bokazu membrane



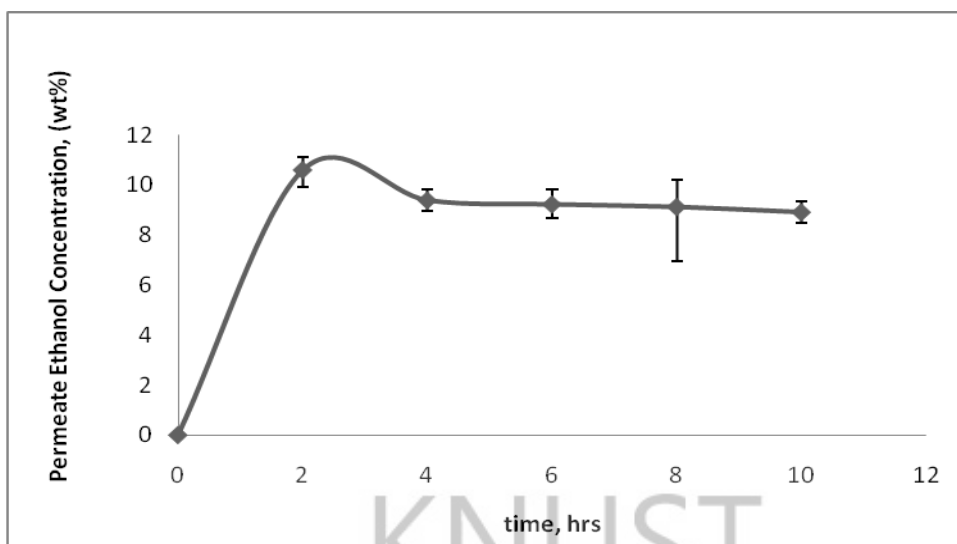
**Figure 4.8** Combined concentration profiles of permeate for 64.6 wt% Ethanol in feed mixture against diffusion time

**c. Feed Ethanol concentration of 75.7 wt%**

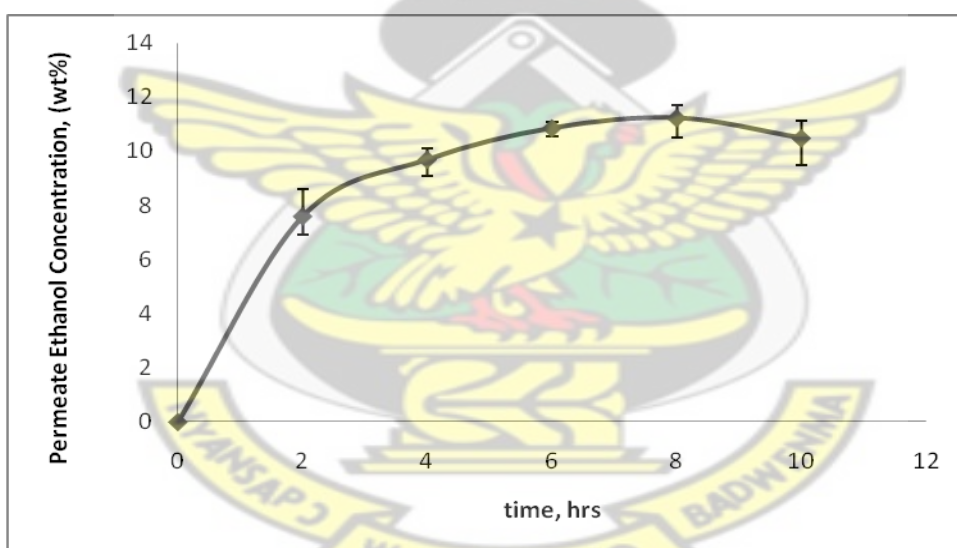
Figures 4.9, 4.10, 4.11 are the results of the ethanol concentrations in the permeate when the ethanol concentration in the feed mixture was 75.7 wt% for the various zeolite-clay filled membrane types. They all show another exponential rise to a steady value and Figure 4.12 is the combination of the 3 curves on the same graph. The steady values are 9.1 wt%, 9.4 wt % and 10.0 wt% for the Abonku, Anfoega and Teleku-Bokazu membranes respectively. The trend here seems to suggest that at ethanol feed concentration of 75.7 wt%, Abonku membrane allows less ethanol molecules to permeate through it while the Teleku-Bokazu membrane allows more ethanol molecules to permeate. This trend is the reverse of the trend observed when the feed ethanol concentration was 64.6 wt%. In those instances, Teleku-Bokazu zeolite-clay filled membrane allowed less permeation of ethanol, while the Abonku zeolite-clay membrane allowed more permeation of the ethanol molecules.



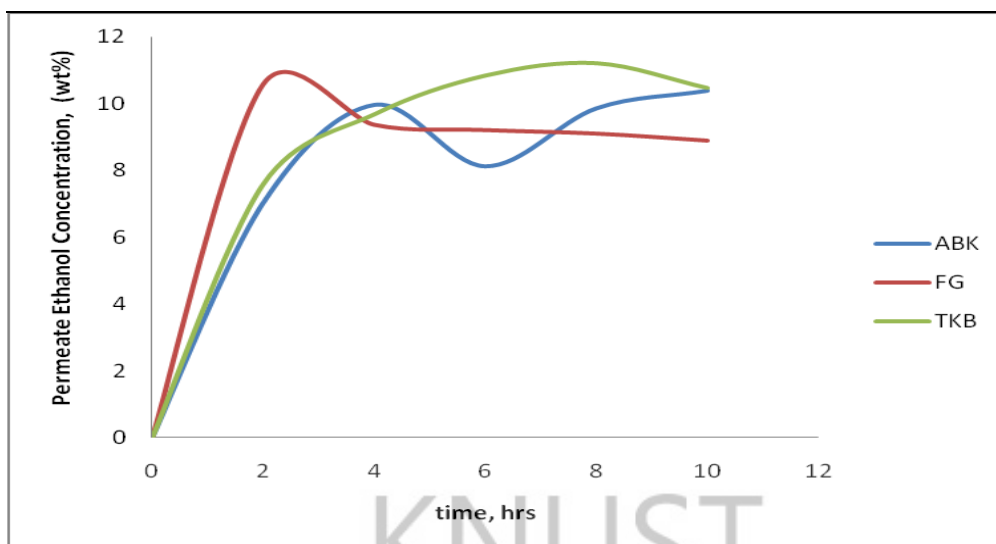
**Figure 4.9 Concentration profile of permeate for 75.7 wt% Ethanol in feed mixture versus diffusion time for Abonku membrane**



**Figure 4.10** Concentration profile of permeate for 75.7 wt% Ethanol in feed mixture versus diffusion time for Anfoega membrane



**Figure 4.11** Concentration profile of permeate for 75.7 wt% Ethanol in feed mixture versus diffusion time for Teleku-Bokazu membrane

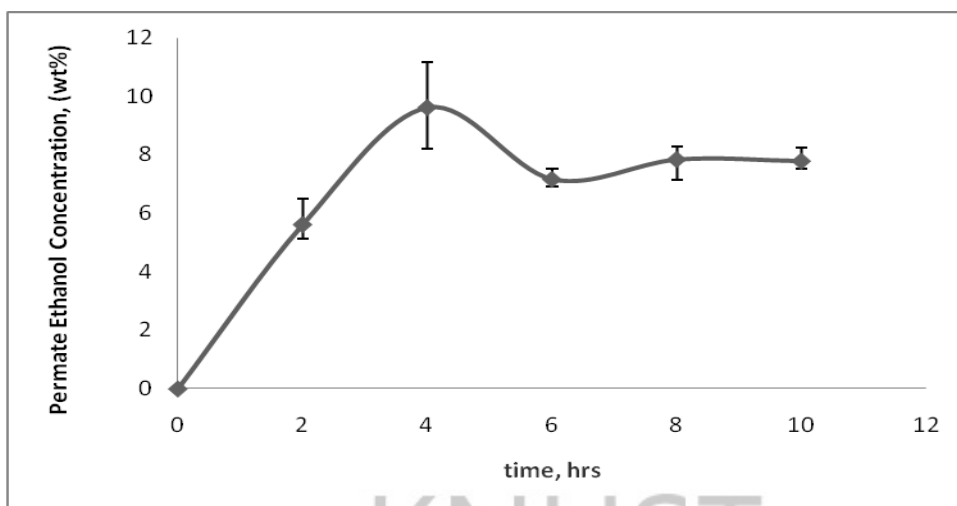


**Figure 4.12 Combined concentration profiles of permeate for 75.7 wt% Ethanol in feed mixture against diffusion time**

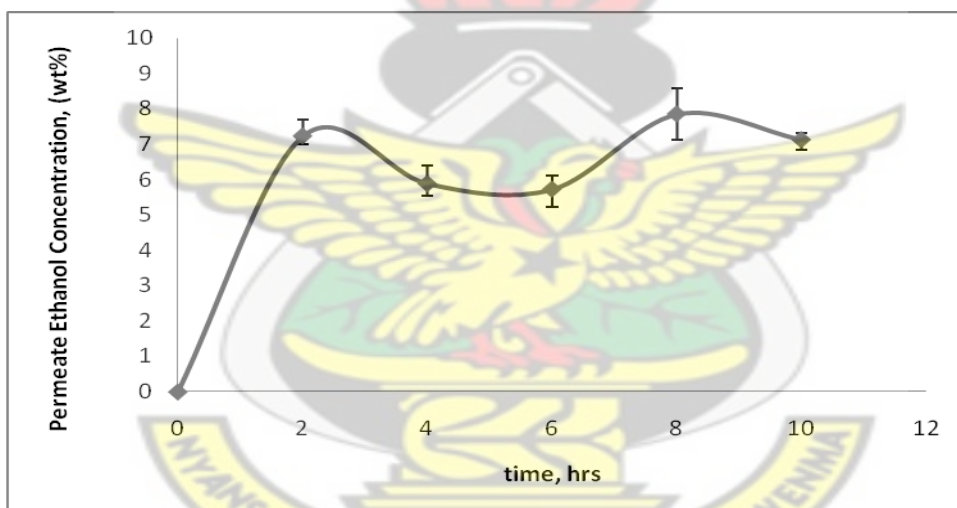
**d. Feed Ethanol concentration of 87.5 wt%**

The results shown in Figures 4.13, 4.14 and 4.15 are the permeate concentrations for the different zeolite-clay filled membranes when the feed concentration of ethanol was 87.5 wt%. They show exponential increase in ethanol concentration to again steady values. These steady ethanol concentrations are 7.6 wt%, 6.8 wt% and 6.0 wt% for ABK, FG and TKB respectively. From the combined graphs in Figure 4.16, the maximum steady value for Teleku-Bokazu zeolite-clay membrane is lower than the steady permeate ethanol concentrations for both the Abonku and Anfoega zeolite clay membranes. This lower value of 6.0 wt% for TKB means that membrane rejects ethanol more than FG and ABK.

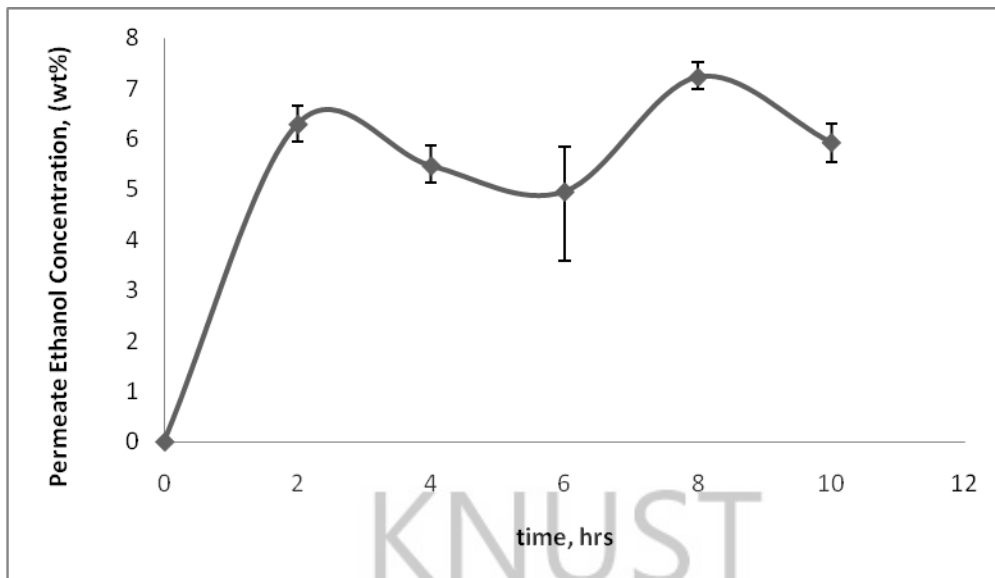




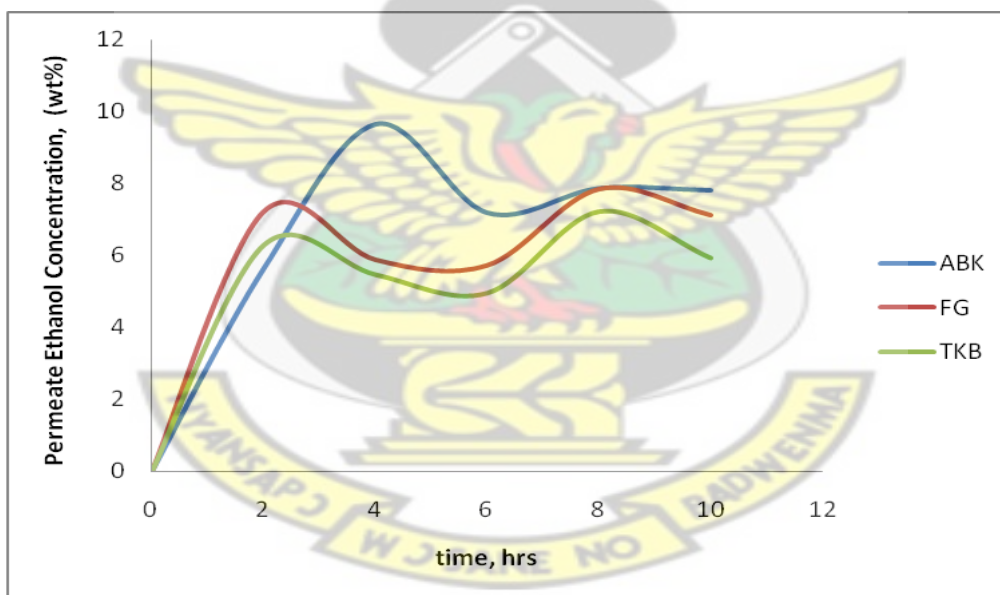
**Figure 4.13** Concentration profile of permeate for 87.5 wt% Ethanol in feed mixture versus diffusion time for Abonku membrane



**Figure 4.14** Concentration profile of permeate for 87.5 wt% Ethanol in feed mixture versus diffusion time for Anfoega membrane

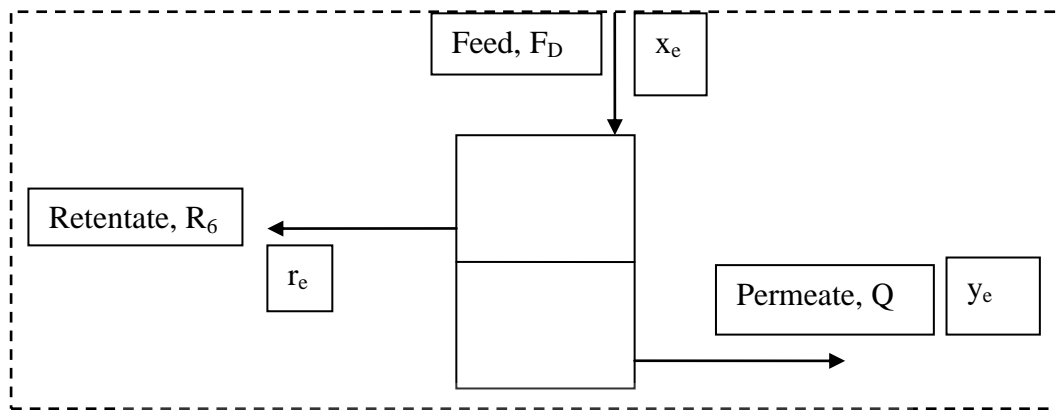


**Figure 4.15** Concentration profile of permeate for 87.5 wt% Ethanol in feed mixture versus diffusion time for Teleku-Bokazu membrane



**Figure 4.16** Combined concentration profiles of permeate for 87.5 wt% Ethanol in feed mixture against diffusion time

## 4.2 Material Balance



**Figure 4.17** Diagram for material balance around Pervaporation cell

The following equations were used to account for all the materials used in the experiment in terms of the masses of ethanol and water introduced into the system.

### a. Overall balance

$$F_D - F_{NP} = R_6 + Q + L_{R/P} \quad (4.1)$$

Rearranging

$$\Rightarrow L_{R/P} = F_D - F_{NP} - R_6 - Q \quad (4.2)$$

Where  $F_D$  is the total amount of feed prepared,  $F_{NP}$  the unused amount of feed,  $L_{R/P}$  the amount of product lost from retentate and permeate,  $Q$  the total amount (mass) of permeate and  $R_6$  the total amount of retentate after separation.

### b. Ethanol balance

$$(F_D - F_{NP}) \times x_e = R_6 \times r_e + (Q + L_{R/P}) \times y_e \quad (4.3)$$

Where  $r_e$  is the mass fraction of ethanol in retentate,  $x_e$  the mass fraction of ethanol in feed and  $y_e$  the mass fraction of ethanol in the permeate.

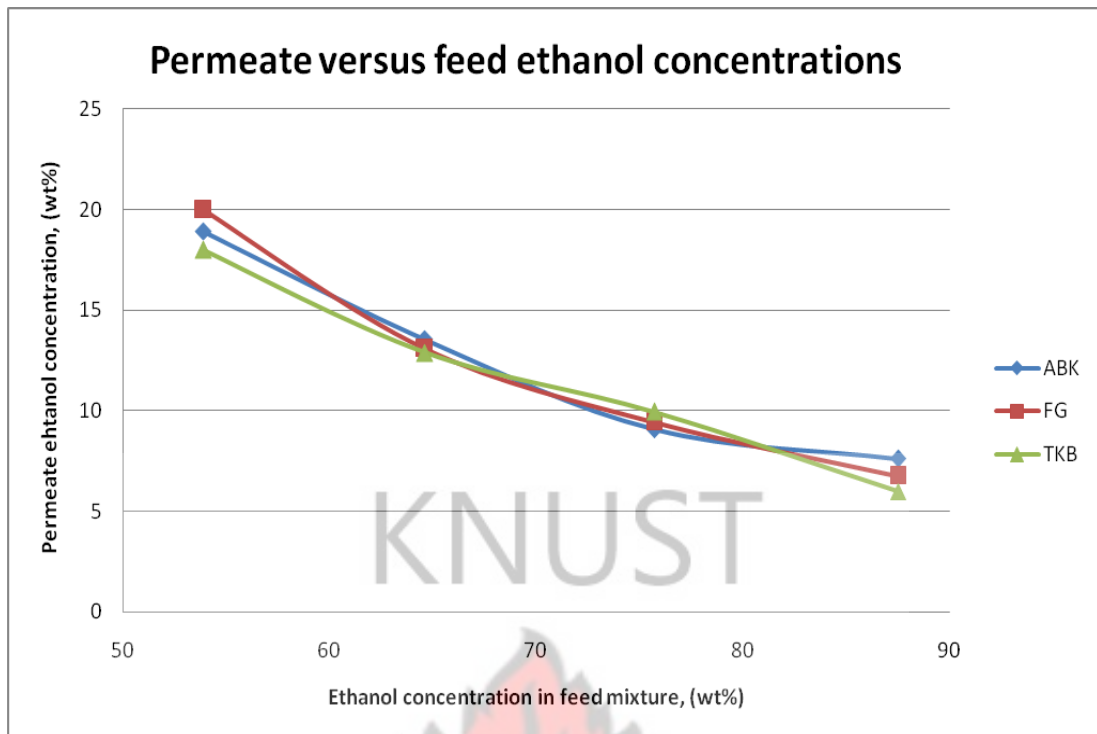
#### 4.2.1 Feed analysis

The amount and compositions of ethanol and water in the feed mixture for all three membrane types are given in Table B-8 in Appendix B.

#### 4.2.2 Permeate analysis

The composition of the permeate was calculated in order to ascertain whether the partial pressures of the components in the permeate conformed with theoretical expectations of being below the vapour pressures of both ethanol and water respectively in the feed. The respective partial vapour pressures for the permeate components were calculated for all the membrane types. The results showed that the partial pressures were below the respective saturated vapour pressures of the ethanol and water in the feed, indicating the presence of a mixture of ethanol-water vapour in the permeate chamber before condensation. By using the average permeate pressure of  $0.125 \text{ kg/cm}^2$  (92.028 mmHg) vacuum, a driving force was obtained which was used in subsequent calculations of the permeance of the components in the mixture.

For the same duration of the separation experiments, Table 4.1 shows the feed ethanol concentrations versus the average permeate ethanol concentrations. The numerical values suggest that as the feed ethanol concentration is increased, the permeate ethanol concentration reduced for all the clay type membranes. The trend follows the theory where the concentration of the least permeating molecule decreases in the permeate as its concentration in the feed increases especially when the feed concentration of the less permeating component is above 50 wt%. The graph showing this trend for all the three membrane types is shown in Figure 4.18.



**Figure 4.18 Variation of Permeate concentrations with Feed Ethanol concentrations for the three membrane types**

At ethanol feed concentration below 50 wt%, the concentration of permeants in the polymer could just be enough to cause polymer swelling and cross-diffusion effects, resulting in non ideal effects of increase in concentration of the less permeating component in the permeate with increase in its concentration in the feed (Seader & Henley (2001:530)). For example, at 50 wt% of ethanol in the feed, Rhim & Huang, (1993) found out that the sorption capacity of the membrane on the components is not different from each other. However, when the concentration in the feed is more than 50 wt% in ethanol, the sorption of the feed on the hydrophilic membrane reduces, causing increase in separation factor (Ling *et al*, (2008); (Rhim & Huang, (1993)). Similar effect is shown in Figure 4.18 where the concentration of ethanol in the permeate decreases with increase in ethanol concentration in the feed.



**Table 4.1 Average amount and concentrations of Permeate mixture for different zeolite clay-filled membranes.**

Ethanol feed concentration (wt%)	Average amount and concentration of Permeate collected					
	ABK		FG		TKB	
	Mass (g)	Conc. (wt%)	Mass (g)	Conc. (wt%)	Mass (g)	Conc. (wt%)
53.9	3.18	18.9	2.00	20.0	2.20	18.0
64.6	2.72	13.6	2.27	13.1	2.50	13.0
75.8	1.94	9.0	2.04	9.4	3.05	10.0
87.5	2.90	7.6	2.69	6.8	3.17	6.0

With respect to amount of permeate collected as shown on Table 4.1, there is a slight decrease in the amount of permeate as the amount of ethanol in the feed is increased for the Abonku membrane. However at concentrations above 80 wt% in the feed there is an increase in the amounts of permeates obtained. This may be due to excess swelling of the membrane matrix such that both the ethanol and water molecules diffused through the pores. Thus the cross-linking of the PVA by the Abonku zeolite clay which is supposed to reduce swelling may be ineffective when the ethanol feed concentration is above 80 v%. This is due to the fact that, cross-linking a membrane matrix to limit swelling reduces the flux of the least permeating component that diffuses through the membrane (Ling *et al.*, 2008).

For the Anfoega clay type membrane, the results show an increase in the total amount of permeate with increase in the feed ethanol concentration with the exception of a

slight decrease when the feed concentration was 80 v%. This could also be attributed to the swelling of the membrane because there was increase in the amount of water that sorbs onto the membrane.

An increase in the total amount of permeate was observed with an increase in the feed ethanol concentration throughout the experiment for the Teleku-Bokazu zeolite-clay membrane. In theory, there is supposed to be a decrease in the amount of permeate as the concentration of ethanol in the feed increases because the membrane is hydrophilic. However, since the feed was in constant contact with the membrane surface, there was a possibility of excess swelling which allowed both the ethanol and water molecules to permeate the membrane pores. Nevertheless the amount of ethanol decreased consistently in accordance with theory where least permeating molecules are rejected when their concentrations are increased in the feed. This suggests that when the feed ethanol concentration increases, there is better separation as the ethanol molecules allowed to permeate the membrane decreases. This trend suggests probably that the cross-linking of the PVA with Teleku-Bokazu zeolite clay controlled the swelling of the membrane during the dehydration separation.

Another possible reason could be due to a relatively higher Si:Al ratio of the Teleku-Bokazu zeolite clay compared to the Abonku and Anfoega zeolite clays. High Si:Al ratio is indication of larger pores as well as inclination towards hydrophobicity. When the filler in a hydrophilic membrane has hydrophobic tendencies, like zeolite ZSM-5 used as filler in a PVA based composite membrane, it allows both the ethanol and water to permeate through it without much restrictions, thereby causing an increase in flux and is also reported by Chan *et al.*, (2008).

### 4.2.3 Retentate analysis

In order to find the amount of product lost ( $L_{R/P}$ ) through removal of retentate, spillage or the clinging of permeate in the tubes, equation (4.2) above was used. Tables 4.2, 4.3 and 4.4 below give the masses of the retentates and the respective ethanol concentrations for the three membrane types.

### 4.2.4 Abonku material balance

**Table 4.2: Results of material balance for Abonku membrane**

Feed			Product			Retentate	
Ethanol concentration $x_e$ , (wt%)	Total feed prepared $F_D$ (g)	Unused feed $F_{NP}$ (g)	Ethanol concentration $y_e$ (wt%)	Mass of permeate $Q$ (g)	Lost $L_{R/P}$ (g)	Mass obtained $R_6$ (g)	Ethanol concentration $r_e$ (wt%)
53.9	42.0	0.57	18.90	3.2	1.58	36.61	58.45
64.6	41.6	3.17	13.54	2.7	1.11	34.60	70.20
75.7	40.6	1.14	9.06	1.9	1.85	36.55	80.84
87.5	40.0	1.83	7.62	2.9	0.456	34.82	95.17

The results obtained by the use of equations (4.1), (4.2) and (4.3) for the Abonku type membrane is in Table 4.2. From the results, there were losses of material. For example when the feed mixture was 53.9 wt% of ethanol, the loss of material was 1.58g from a total feed mass of 41.4g. This is equivalent to about 3.8% of the feed. This loss could be due in part to either the absorbed retentate on the membrane which was not initially considered and or the possible vaporization of the volatile component or the possible condensation of the permeate material within the tubes that was not accounted for during the mass measurements.

Taking into consideration the challenges mentioned above, the concentrations of the lost product was assumed to be that of the permeate. The results of the material balance show a substantial separation has taken place. The results also indicates that with time, there were increases in the concentration of ethanol in the retentate. The increase was more pronounced when the feed concentration was higher at 87.5 wt% in ethanol. For example, the retentate concentration when the concentration of ethanol in the feed was 87.5 wt% is 95.17 wt% .This follows the theory that dehydration is enhanced when the ethanol concentration in the feed is higher to about 90 wt% and is also reported by Ling *et al.*, (2008).

#### 4.2.5 Anfoega material balance

**Table 4.3: Results of material balance for Anfoega membrane**

Feed			Product			Retentate	
Ethanol concentration $x_e$ , (wt%)	Total feed prepared $F_D$ (g)	Unused feed $F_{NP}$ (g)	Ethanol concentration $y_e$ (wt%)	Total mass of permeate $Q$ (g)	Lost $L_{R/P}$ (g)	Mass obtained $R_6$ (g)	Ethanol concentration $r_e$ (wt%)
53.9	43.0	1.12	19.99	2.00	1.78	38.05	57.27
64.6	41.7	2.20	13.07	2.3	1.55	35.65	70.13
75.7	40.4	1.10	9.43	2.1	1.18	36.05	81.63
87.5	40.0	9.37	6.76	2.7	0.20	27.73	95.89

The losses of the material in the case of the FG membrane were comparable to the experiment with ABK membrane. From the results of the material balance, some level of separation has taken place. From Table 4.3, the feed with 53.9 wt% ethanol got enriched to 57.27 wt% while for a feed of 64.6wt% the retentate concentration was 70.13 wt%. The result portray a trend that when the concentration of ethanol in the feed increases, the retentate concentration is higher. It also means that when the

separation is carried out for a very long period of time the concentration of the mixture could go beyond the azeotropic concentration. For example for a feed concentration of 87.5 wt% ethanol, the retentate obtained had ethanol concentration of 95.89 wt%.

#### 4.2.6 Teleku-Bokazu material balance

**Table 4.4: Results of material balance for Teleku-Bokazu membrane**

Feed			Product			Retentate	
Ethanol concentration $x_e$ , (wt%)	Total feed prepared $F_D$ (g)	Unused feed $F_{NP}$ (g)	Ethanol concentration $y_e$ (wt%)	Total mass of permeate $Q$ (g)	Lost $L_{R/P}$ (g)	Mass obtained $R_6$ (g)	Ethanol concentration $r_e$ (wt%)
53.9	42.6	2.10	17.97	2.2	1.20	37.00	57.2
64.6	41.6	1.38	12.87	2.5	1.04	36.68	69.59
75.7	39.8	1.94	9.96	3.1	0.86	33.96	83.25
87.5	39.3	0.53	5.98	3.2	0.70	34.86	96.53

The results of the material balance for the TKB is given in Table 4.4. The results show an increase in the concentration of the retentate as a result of the separation, when the feed ethanol concentrations were also increased. At the highest concentrations studied, the results show a retentate concentration of 96.53 wt%.

#### 4.3 Membrane performance

As a measure of the performance of the membrane, the permeability, separation factor, total flux and the pervaporation separation index were evaluated from;



i. The Ethanol permeability:  $J_{\text{ethanol}} = \frac{Q}{A_e \times t}$

ii. Separation factor  $\alpha_{A/B} = \frac{\left[ \frac{y_A}{y_B} \right]_{\text{Permeate}}}{\left[ \frac{x_A}{x_B} \right]_{\text{Feed}}}$

iii. Permeation rate or total flux  $J_{\text{Total}} = \frac{Q}{A_e \times t}$  and finally

iv. The pervaporation separation index:  $\text{PSI} = J(\alpha - 1)$

Where  $A_e$  is the effective membrane area for permeation, calculated as  $0.007854 \text{ m}^2$ ,  $\alpha_{A/B}$  the selectivity (separation factor) of A with respect to B,  $\alpha$  the separation factor,  $J$  the flux through a membrane,  $t$  the permeation (diffusion) time,  $x_A$  the mass fraction of the more permeating molecule in the feed,  $x_B$  the mass fraction of the less permeating molecule in the feed,  $y_A$  the mass fraction of more permeating component in the permeate,  $y_B$  the mass fraction of the more permeating component in the permeate and PSI the Pervaporation separation index.

As different membranes with different characteristics have been fabricated, the pervaporation behaviour of each may be different. This is because the characteristics of the sorption as reported by Bartels *et al.*, (1992), depended on the difference between the affinity of the components towards the polymer, the mutual interactions of the components, and the way the interactions with the polymer of each component affects the interactions of the other penetrants with the polymer.

#### 4.3.1 The permeation rate of ethanol in the permeate

**Table 4.5: Mass of Ethanol and Ethanol permeability in the membrane**

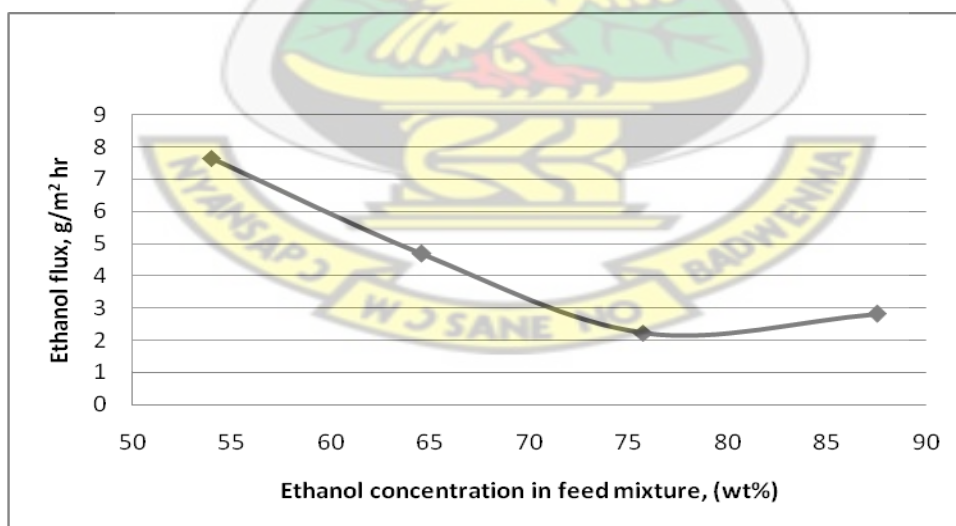
Feed Ethanol (wt%)	Abonku		Anfoega		Teleku-Bokazu	
	Mass of Ethanol (g)	Permeation rate (g/m <sup>2</sup> hr)	Mass of Ethanol (g)	Permeation rate (g/m <sup>2</sup> hr)	Mass of Ethanol (g)	Permeation rate (g/m <sup>2</sup> hr)
53.9	0.60	7.65	0.40	5.07	0.40	5.04
64.6	0.37	4.69	0.30	3.78	0.32	4.09
75.7	0.18	2.23	0.19	2.45	0.29	3.74
87.5	0.22	2.81	0.18	2.37	0.19	2.41

The permeation rate of ethanol was calculated and results tabulated in Table 4.5.

These results show a decrease in ethanol permeability with increase in ethanol concentration in the feed and could be attributed to the highly water selective ABK, FG and TKB membranes. As observed by Nawawi *et al.*, (2008), under high ethanol concentration, especially above 50 wt%, (Rhim &Huang, 1993), the molecular structure of PVA zeolite-clay membranes was packed much more tightly and restricted the diffusion of permeants. This could also be due to the decrease in the sorption of the feed onto the membrane surfaces when the concentration of ethanol is higher in the feed. As a result the ethanol permeability decreases with increase in ethanol concentration in the feed and is expected to increase the selectivity of the membranes.

#### 4.3.1.1 Ethanol flux through ABK membrane versus feed concentration

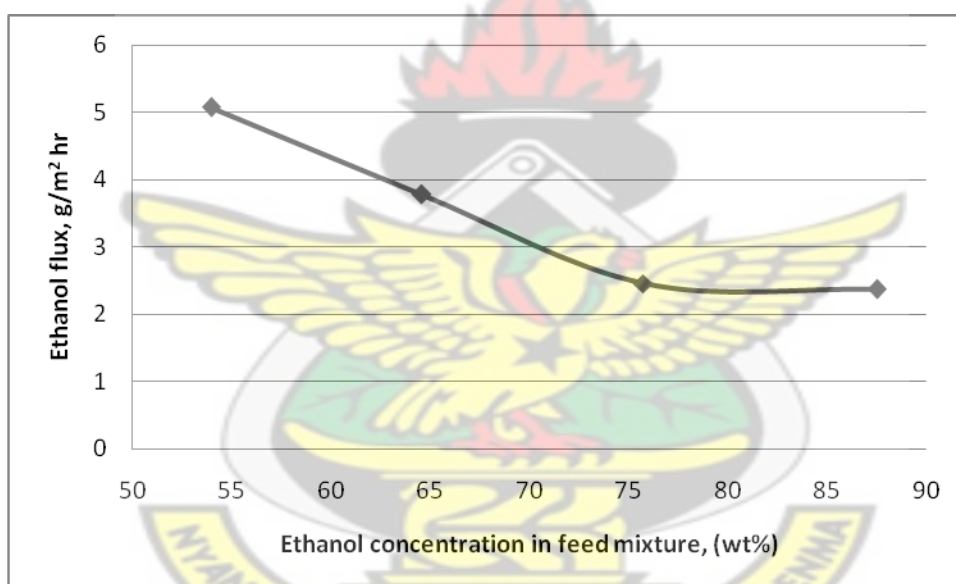
From Table 4.5 above, it can be inferred that ethanol concentration in permeate reduced drastically as the concentration of same was increased in the feed. In pervaporation with hydrophilic membrane, there must always be rejection of the organic component relative to the polar component (Mulder *et al.*, 1983). It is expected as theory suggests that at higher concentrations of ethanol, there must be reduction in sorption of the feed by the hydrophilic membrane and that should lead to reduction in ethanol concentration. From Figure 4.19, when the feed ethanol increased above 75 wt% to 87 wt%, however, there was slight increase in the ethanol permeability. But from theory, increase in swelling results in flux increase and hence permeability increase. Thus during swelling, the membrane matrix is stretched such that both molecules in the permeate mixture diffuse through the membrane with less restriction. And in this case both the water and ethanol molecules diffused through the membrane as the ethanol concentration increased beyond 75 wt% in the feed.



**Figure 4.19 Effect of feed ethanol concentration on permeation rate of ethanol for ABK**

#### 4.3.1.2 Ethanol flux through FG membrane versus feed concentration

From Figure 4.20, when the Anfoega zeolite-clay membrane was used, the ethanol flux decreased gradually as the feed ethanol concentration was increased. Again the membrane being hydrophilic gradually allowed the permeation of water molecules while rejecting ethanol molecules from diffusing through as the ethanol concentration increased in the feed. Rhim & Huang, (1993) and Ling *et al.*, (2008) have also reported similar results on other composite hydrophilic membranes. When the feed concentration was increased above 75 wt% however, the reduction in permeability was not significant as shown on Table 4.5.

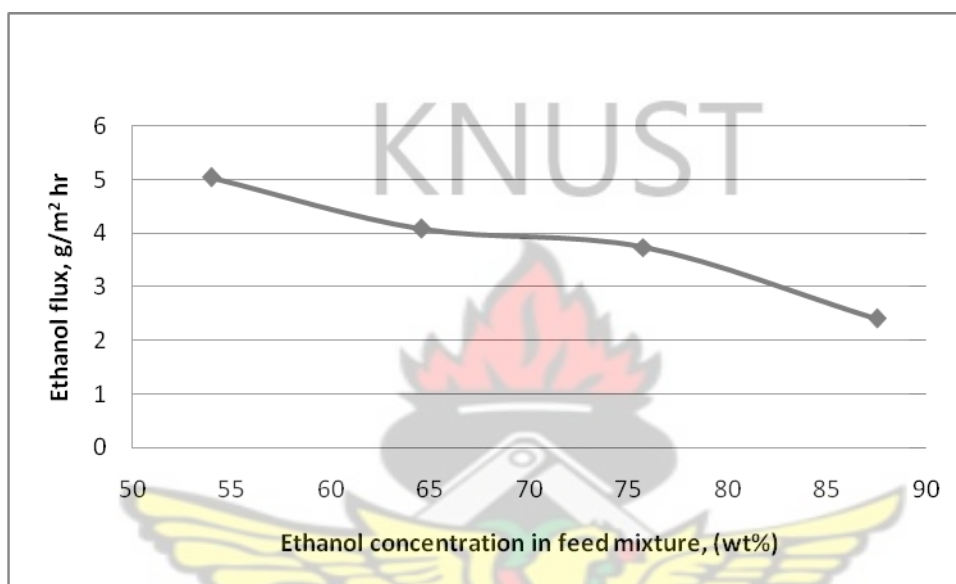


**Figure 4.20 Effect of feed ethanol concentration on permeation rate of ethanol for FG**

#### 4.3.1.3 Ethanol flux through TKB membrane versus feed concentration

From Figure 4.21, the behaviour of the ethanol flux when the Teleku-Bokazu membrane was used, showed decrease in the ethanol flux with increase in the ethanol concentration in the feed. Again this is due to the rejection of the organic component of the feed by the hydrophilic TKB membrane due to the reduction in sorption of the

feed when the ethanol concentration is increased. This conforms to the work by Nawawi *et al.*, (2008) and Rhim & Huang, (1993) who reported similar behavior of ethanol flux as the feed ethanol concentration was increased especially above 50 wt%. This is in agreement with theory where cross-linking of the hydrophilic membrane reduces swelling leading to eventual decrease in permeation of the ethanol molecules.



**Figure 4.21 Effect of feed ethanol concentration on permeation rate of ethanol for TKB**

#### 4.3.2 Selectivity of water relative to ethanol

**Table 4.6: Separation factor for the different types of Zeolite-clay membranes**

Feed Ethanol Concentration (wt%)	Separation factor		
	ABK	FG	TKB
53.9	5.03	4.69	5.35
64.6	11.63	12.11	12.34
75.7	31.35	29.99	29.26
87.5	85.09	96.71	110.35

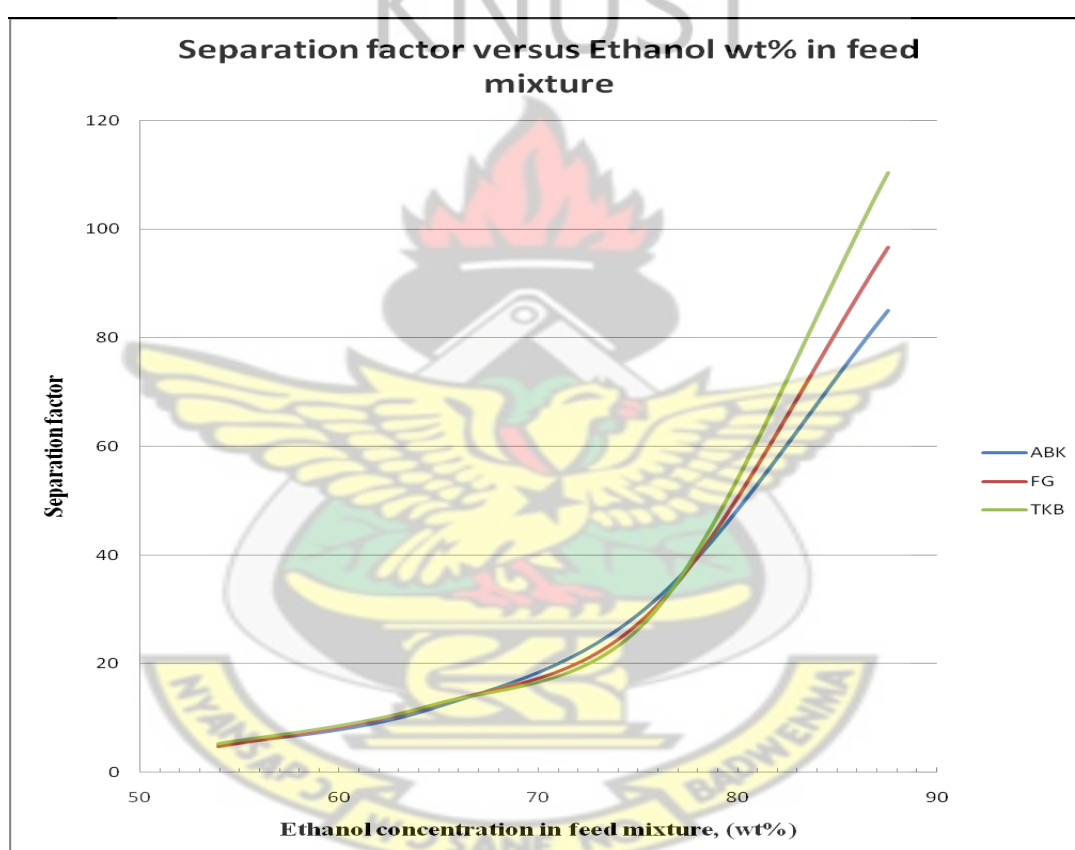


The results of calculations of the separation factor of water relative to ethanol for the pervaporation experiments carried out is shown on Table 4.6. From theory of separation with hydrophilic membrane, there must be increase in the separation factor with increase in concentration of ethanol in the feed. The plotted results on Figure 4.22 show increase in the separation factor with increase in feed ethanol concentration. Thus as the concentration of the ethanol in the feed liquid increases, there is increase in the rejection of the ethanol molecules which results in the reduction of the sorption of the feed liquid by the membranes. The effect is that separation is enhanced as more water molecules then diffuse through the pores of the membrane, resulting in increased separation factors.

The gradual initial increase up to feed concentration of 78 wt% could be due to the reduction in the plasticizing effect of the water molecules. As the water concentration in the feed decreases the amorphous regions of the polymer become less swollen and the polymer chains become less flexible, thus increasing the energy required for diffusive transport through the membrane. This therefore reduces the possibility of the permeation of the bulky component molecules through the membrane, hence reduction in permeation rate leading to the high membrane selectivity.

The fact that when the feed ethanol concentration is beyond about 80 wt%, a higher separation factor was obtained for all the 3 membrane suggests that any coupling of pervaporation with fermentation broth must be made such that the feed to the Pervaporation cell must be above 80 wt% when very hydrophilic membranes are used. The reason for this sudden increase could be due to the solubility of the feed mixture being saturated in the separating layer of the composite membrane at that concentration. Therefore molecules of the less permeating component in any feed with concentrations higher than 78 wt% ethanol is rejected by the membrane as no

more dissolution would take place. As a result, a sharp increase in selectivity of the composite membranes with respect to water is observed since the hydrophilicity of the PVA-zeolite clay membrane would still attract water molecules into its pores. The general behavior of increase in selectivity with increase in ethanol concentration in the feed mixture agrees with the findings of Ling *et al.*, (2008); Rhim & Huang, (1993) and Li & Lee, (2006), where the selectivity increased with increase in feed ethanol concentration.



**Figure 4.22 Effect of feed ethanol concentration on selectivity for different membranes**

From Figure 4.22, the separation factor for the ABK was higher between the feed concentrations of 68 wt% to 78 wt% ethanol, while it is lower when the concentrations of ethanol in the feed mixture was above 78 wt%. This could probably be due to some abnormality, with the ABK membrane as it gets excessively swollen

after 78 wt %. The cross-linking then becomes ineffective and the membrane allowed both molecules to permeate without much restrictions. The behaviour for the TKB membrane on the other hand could be due to the fact it does not get excessively swollen throughout but follow the theory where the higher the concentration of the less permeable component, the higher the separation factor. This indicates the possibility of the TKB membrane being more rigid than the rest due to the cross-linking effect of the Teleku-Bokazu zeolites on the PVA separating layer.

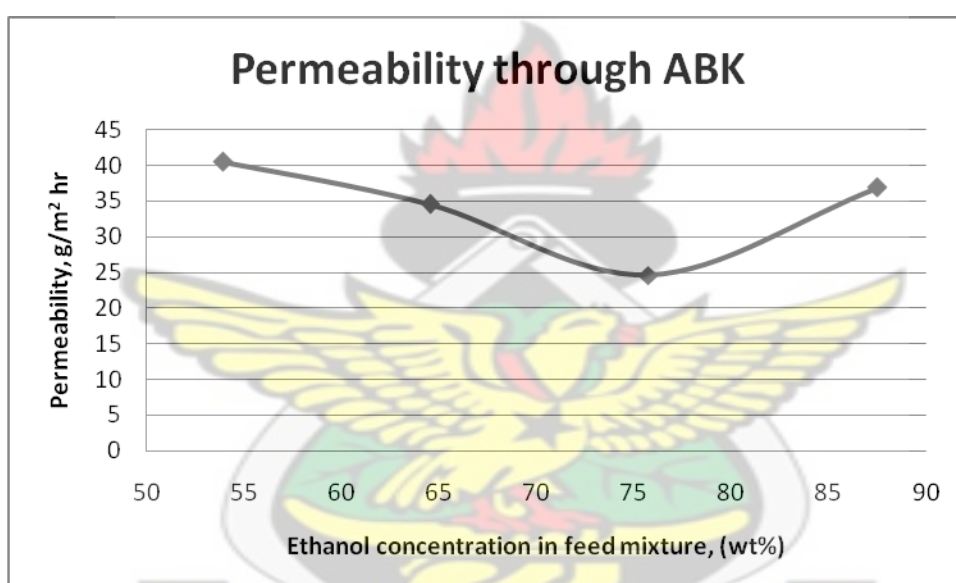
#### 4.3.3 Permeation rate

**Table 4.7: Permeability and Pervaporation Separation Index for the different types of membrane**

Feed Ethanol Concentration (wt%)	Permeation rate (g/m <sup>2</sup> hr)			Pervaporation Separation Index (PSI) (g/m <sup>2</sup> hr)		
	Abonku	Anfoega	Teleku-Bokazu	Abonku	Anfoega	Teleku-Bokazu
53.9	40.48	25.39	28.04	163.00	93.65	121.88
64.6	34.56	28.90	31.77	367.46	321.18	360.18
75.7	24.62	26.00	38.77	747.45	753.66	1095.83
87.5	36.86	34.19	40.30	3099.61	3272.09	4406.72

The results of the permeation rate (permeability), for all the three membranes are tabulated in Table 4.7. The results show an increase in the flux with increase in ethanol concentration in the feed for the Anfoega and Teleku-Bokazu clay membranes. The Abonku clay showed a decrease up to some point before increasing at higher feed concentration of ethanol. From theory as the concentration of ethanol in the feed increases, the total flux must decrease for hydrophilic membranes. The converse is that as the water concentration in the feed increases, the total flux must

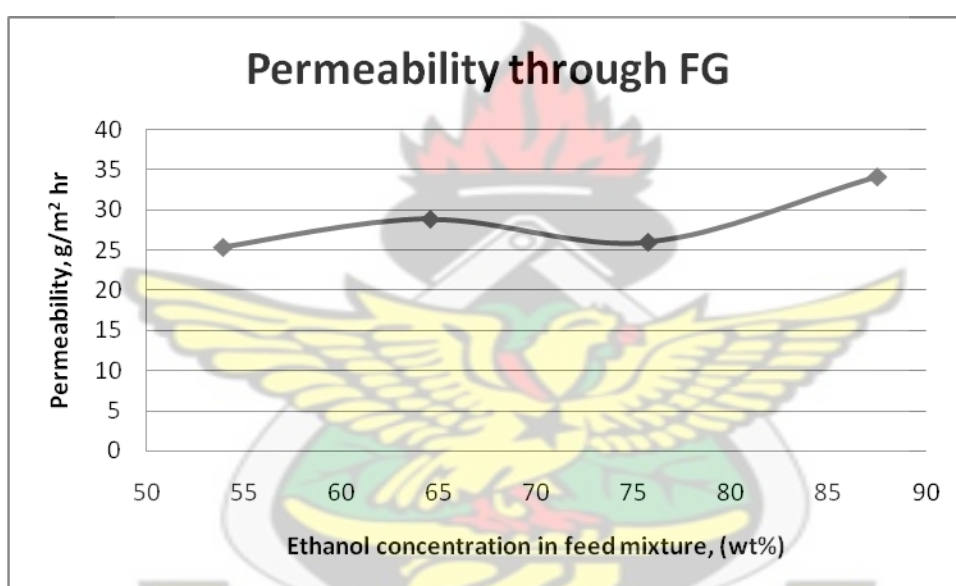
increase and has also been reported by Ling *et al.*, (2008); Nawawi *et al.*, (2008) and Rhim & Huang, (1993). However in this study, there has been increase in the flux as the feed concentration of ethanol increased contrary to theory. This may be due to the plasticizing effect of water, and probable flow coupling between water and ethanol. As the water concentration in the feed increases, the amorphous regions of the membranes swell, making the polymer chains more flexible and hence allowing ethanol molecules also to pass through in spite of its low affinity toward the membranes.



**Figure 4.23 Effect of feed ethanol concentration on the total flux for ABK membrane**

From Figure 4.23, the total flux decreased with increase in the ethanol concentration in the feed up to about 78 wt%, after which there was increase in the flux. This means up to the feed ethanol concentration of 78%, the Abonku zeolite clay membrane conforms to theory where the decrease must continue especially at higher ethanol concentration. When the concentration of ethanol in the feed increases, the sorption of the feed reduces since the membrane is hydrophilic. This eventually reduces swelling

of the amorphous region of the membrane and subsequently restricts the diffusion of the component with low affinity through the membrane. The behaviour of the flux in this instance is probably due to the fact that the ABK membrane though hydrophilic allowed both molecules to permeate. It could also be that due to excessive swelling by the persistent contact of the liquid feed with the membrane surface. The result is that the membrane might have lost its crystalline nature when the ethanol feed concentration increased beyond 80 wt%, thereby allowing both ethanol and water molecules to penetrate and hence increase the flux.

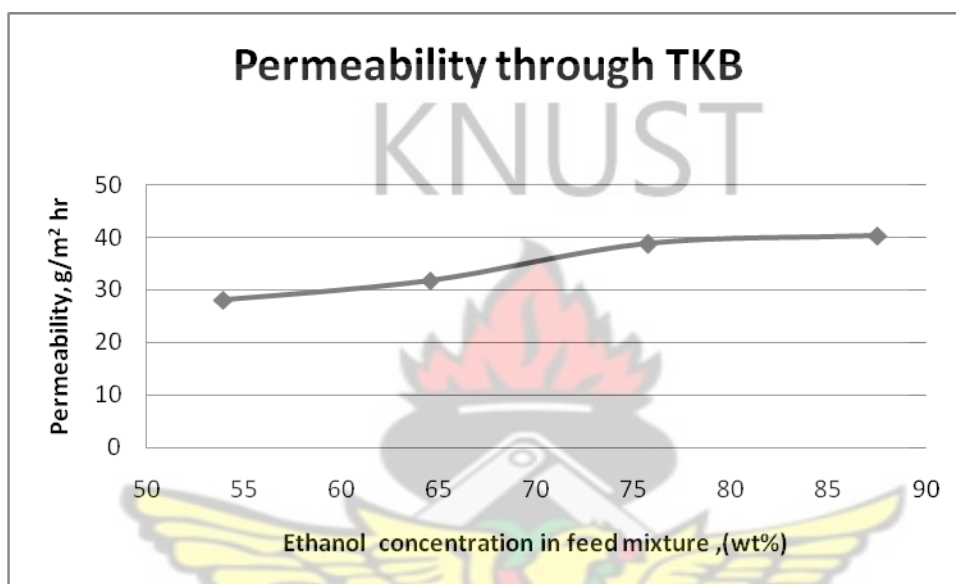


**Figure 4.24 Effect of feed ethanol concentration on the total flux for FG membrane**

The curve in Figure 4.24 shows the permeation flux versus concentration of ethanol in the feed when the Anfoega zeolite-clay filled membrane was used for the experiment. The shape of the curve appears to indicate a constant flux up to about 80 wt% followed by an increase in flux with increase in ethanol concentration in the feed. This unusual trend could probably be due to excess swelling which has made the polymer chains more flexible such that all the components diffuse through the



membrane without much restriction. There is also the possibility of increase in free volume due to the plasticizing effect of water molecules increasing when the ethanol concentration in the feed increases. This then results in decrease of energy required for diffusive transport through the membrane as reported also by Ling *et al.*, (2008) and Nawawi *et al.*, (2008).



**Figure 4.25 Effect of feed ethanol concentration on the total flux for TKB membrane**

The curve in Figure 4.25 shows an increase in the permeability with increase in the feed ethanol concentration. This is contrary to theory where for a hydrophilic membrane, the flux was expected to decrease with increase in ethanol concentration in the feed.

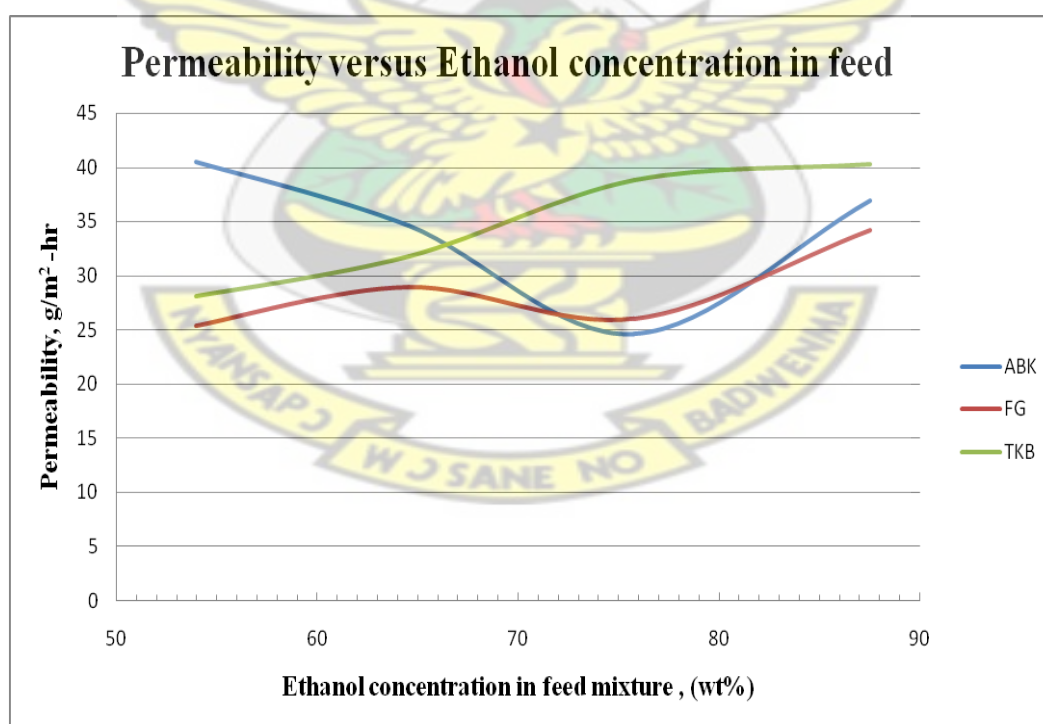
Generally an increase in flux means both components in a binary mixture diffuse through the membrane without much restriction. No restriction implies the membrane is less selective, and results in decrease in separation factor. However in this instance, the selectivity as well as the flux increased with increase in ethanol concentration in

the feed as shown in Figure 4.22. In terms of separation, there must be a decrease in separation factor. But for this membrane, the separation factor likewise increased. These findings are probably due to flexible linkages into the polymer backbone, thereby reducing its crystallinity and enhance the diffusion of both molecules as reported also by Li & Lee, (2006). It is also possible that for this TKB membrane the reduction in the diffusion of the ethanol is the overriding factor while at the same time sorbs more water molecules into its pores, hence increasing the flux as well as the separation factor. It is also possible that the hydrophilicity of the top separating layer of the composite membrane was influenced by the PSf supporting layer as reported by Sekulic, *et al.*, (2005). This is due to the fact that, Mulder *et al.*, (1983), found out that water permeates PSf preferentially in the presence of ethanol. Therefore when this effect of preferential sorption of water in the separating layer is reinforced with the preferential diffusion of water through the support, both the separation factor as well as the flux could increase with increase in ethanol feed concentration.

The permeability through the three membrane types is shown in Figure 4.26. The curves show different patterns. While at feed ethanol concentration of 50 wt% the permeability of Abonku membrane was decreasing up to a feed concentration of 78 wt%, that of Anfoega on the other hand was almost constant. After about 78 wt% of ethanol in the feed, the permeabilities of the two membranes increased with increasing feed concentration. However, the permeability when the Teleku-Bokazu membrane was used increased with increase in ethanol concentration in the feed throughout.

According to Yeh *et al.*, (2003), when the zeolite content of the composite separating layer membrane is 5wt % or more there is the possibility of formation of a micro-phase separation between the organic polymer (PVA) and the inorganic material

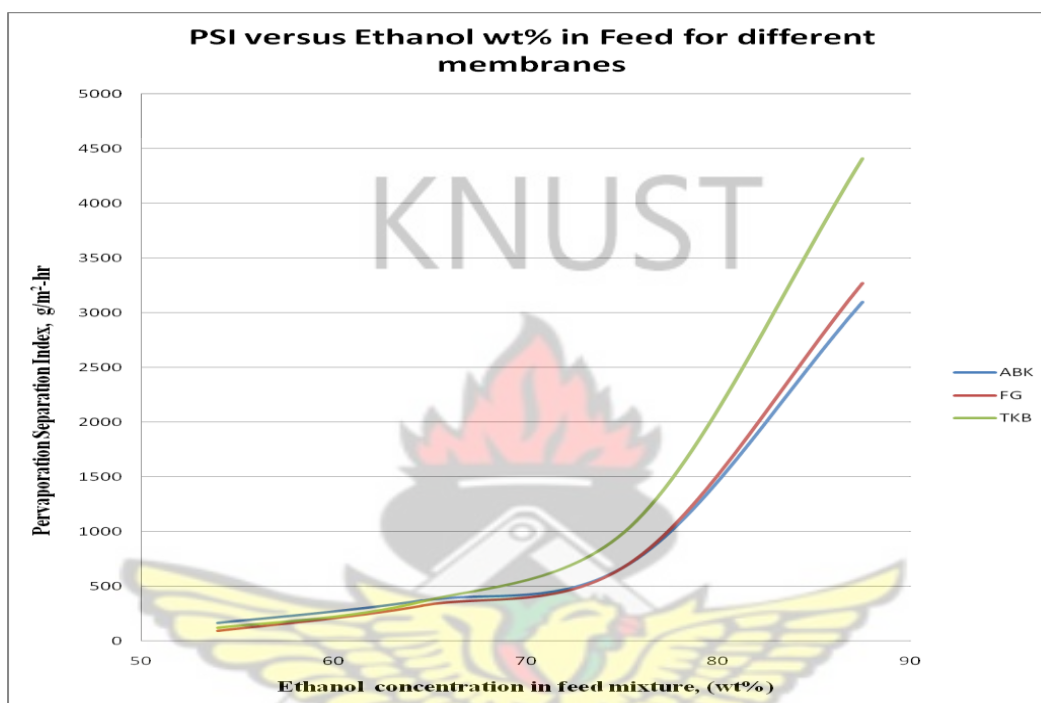
(zeolite-clay). Through the micro-phase separation the alcohol and water molecules permeate freely. The result is that permeability increases with increase in the less permeating molecule in the feed contrary to theory, especially when the feed concentration of ethanol is above 80 wt%. The selected concentrations in this project was based on an earlier work by Ling *et al.*, (2008) where 5 wt% PVA zeolite-clay solution was used for the PVA zeolite-clay composite membranes. Therefore the probable explanation to the behaviour found in Figure 4.26 for the three hydrophilic composite membranes may be due to the unique characteristics of the zeolite-clay in terms of their chemical constituents. As a result the limit to the concentrations of the nano-particles, made up of the three zeolite-clay types in the PVA cast solution of the separating layer to form the expected composite membrane, may not have to be the same.



**Figure 4.26 Effect of feed ethanol concentration on the Permeation rate for the three membranes**

Indeed the trend shown by the mass flux for all the three types of membrane is the same as that shown for the permeance of the components. The permeance results are in Appendix C in Tables C-2, C-3 and C-4.

#### 4.3.4 Pervaporation separation index (PSI)



**Figure 4.27 Effect of feed ethanol concentration on Pervaporation Separation Index for different membranes.**

The variation of Pervaporation Separation Index (PSI) with ethanol feed concentration is shown in Figure 4.27. The figure shows an increase in PSI with ethanol concentration in the feed. From theory, a high value of PSI could mean a higher flux with a higher separation factor. This is an indication of a good membrane for separation applications. On the other hand a high PSI value could also mean either a high flux with low separation factor or a low flux with high separation factor. The former is not good because it defeats the purpose of the separation since low separation factor indicates a longer time to achieve desired separation or none at all.

However, when a given membrane records low PSI value, it means the membrane does not perform well.

From the results above the Teleku-Bokazu zeolite-clay filled membrane achieved the highest PSI value among the three membranes as the ethanol concentration in the feed increases. There was gradual increase in PSI at ethanol concentrations up to about 64.6 wt%, then a sudden increase above that. The respective PSI values of the three membranes do not differ much at lower concentrations of ethanol in the feed. This could probably be due to the plasticizing effect of the hydrophilic membrane which gets swollen with increase in water. The lower concentrations of ethanol in the feed by inference relates to a relatively higher concentration of water. The effect is that the polymer chains become more flexible due to the amorphous region of the polymer matrix getting swollen. As a result, the restrictions to diffusion of both ethanol and water molecules are relaxed, hence an increase in the flux.

On the other hand the higher concentration of ethanol in the feed implies a relatively low water concentration. The effect is that the sorption of the feed by the hydrophilic membrane is reduced as ethanol molecules are rejected while water preferentially diffuses through. The result is a higher separation factor.



## CHAPTER 5

### 5.0 CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

Three different zeolite-clays were prepared from clay deposits at Abonku, Anfoega and Teleku-Bokazu. The zeolites were successfully used as fillers in hydrophilic PVA base composite membranes that were supported on polysulphone substrates. The membranes formed were used in the dehydration of ethanol-water mixture. The pervaporation cell used in the dehydration was successfully fabricated from scrap aluminium metal.

The pervaporation experiment using the prepared composite membranes showed some separation of water from the ethanol-water mixture took place. From the performance indices, the composite membrane with Teleku-Bokazu zeolite-clay filler gave the highest separation factors. It was followed by the membrane with Anfoega zeolite-clay and then the Abonku zeolite-clay in that order.

The results obtained with respect to selectivity and ethanol flux (permeance) followed theory for all the three membrane types. While the selectivity increased with increase in the concentrations of ethanol in the feed, the ethanol flux decreased with increase in the concentrations of ethanol in the feed mixture. The total flux (permeance), however did not follow theory wholly except when the membrane with Abonku zeolite-clay was used. With this membrane, there was a decrease in total flux (permeance) for ethanol feed concentrations up to 80 v%, then an increase when there was further increase in concentrations of ethanol. When the membrane with Anfoega zeolite-clay as filler was used, the total flux appeared constant for concentrations of ethanol increase up to 80 v% in the feed. Further increase of ethanol concentrations above the 80 v% resulted in increase in total flux. In the case of the Teleku-Bokazu

zeolite-clay filled membrane, the total flux increased with increase in the concentrations of ethanol in the feed.

From the results of the material balance for all the three membrane types, the ethanol-water mixture could be separated to ethanol concentrations higher than the azeotropic concentrations. This means it would be possible to use the Ghanaian clay deposits as an additive in the fabrication of composite membranes for dehydration of ethanol to higher concentrations above the azeotropic.

## **5.2 Recommendations**

One of the challenges encountered in the experimentation is that of the measurement of the weight of the permeates which were made after the collecting vessels were detached from the system after the duration of each test run. It is recommended that an online balance be used such that the weight could be measured before the sample is removed for the GC analysis. It is also recommended that the condenser unit be made such that the iced-blocks get introduced at one point and the melted ice drained at another point without necessarily opening the unit.

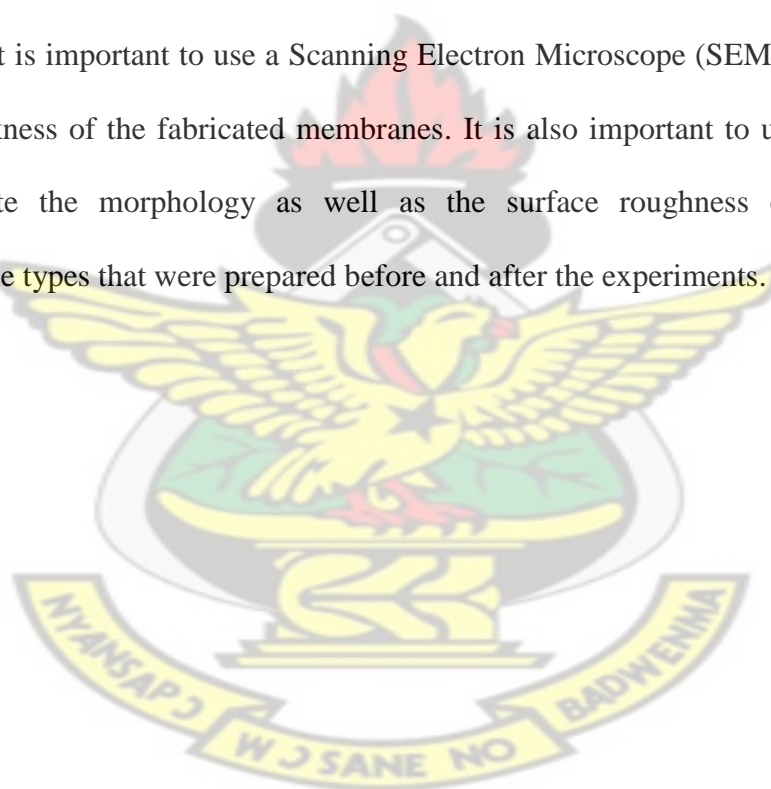
The feed to the feed chamber was introduced at inconsistent time intervals which could result in concentration polarization. In order to mitigate this polarization, it is recommended that a peristaltic pump be used between the feed tank and the feed chamber to increase turbulence at the upstream side of the membrane. Later research work must also consider similar experiments at temperatures above 30°C but below 70°C for periods longer than 10 hours to ascertain the durability of respective composite membranes.

It is also recommended that a higher molecular weight polymer be used in the membrane to ascertain if there would be any difference from the membrane

performance theory for the three composite membranes formed from PVA with a molecular weight 16,000. For example, the use of PVA with molecular weight 96,000 as the base polymer with the prepared zeolites as fillers in the formation of the composite membranes could be used for similar pervaporation process.

It is also recommended that tubes of smaller dimensions be used so that the vacuum pressure may not be so high before separation takes place. In addition the tubes must be transparent enough so that the process of permeate condensation within the tubes could be observed.

Finally, it is important to use a Scanning Electron Microscope (SEM) to ascertain the real thickness of the fabricated membranes. It is also important to use the (SEM) to investigate the morphology as well as the surface roughness of the different membrane types that were prepared before and after the experiments.



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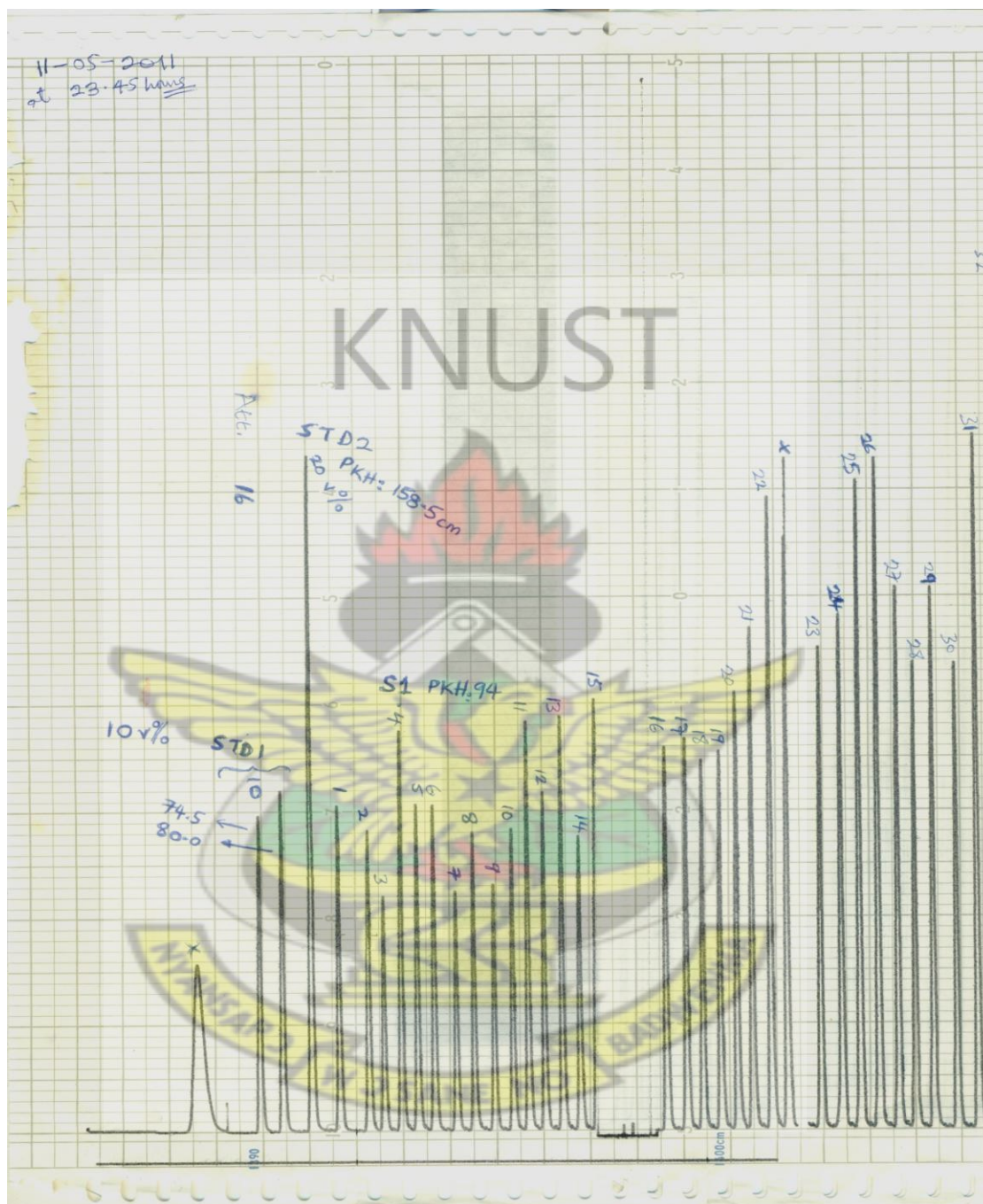
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## APPENDICES

### APPENDIX A: SAMPLE OUTPUT FROM THE GAS CHROMATOGRAPH



**Figure A-1: Peak heights for ethanol concentrations from the Gas Chromatograph**

**APPENDIX B: RAW DATA FROM THE PERVAPORATION EXPERIMENTS USING MEMBRANES WITH GHANAIAAN  
ZEOLITE-CLAY FILLERS**

**Table B-1 Dehydration of ethanol-water mixture using Abonku Zeolite clay filler**

Time (hrs)	60 v% (53.9 wt%) Feed Concentration of Ethanol						70 v% (64.6 wt%) Feed Concentration of Ethanol					
	Permeate concentration (wt %)			Deviation from mean			Permeate concentration (wt %)			Deviation from mean		
	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run	Mean Conc. (wt %)	Min.	Max.	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run	Mean Conc. (wt %)	Min.	Max.
0-2	15.42	14.73	15.42	15.189	0.459	0.230	14.26	11.68	10.43	12.123	1.693	2.136
2-4	15.99	16.91	18.23	17.042	1.050	1.182	16.76	14.92	15.84	15.841	0.921	0.922
4-6	20.95	22.00	21.14	21.364	0.414	0.636	17.14	14.33	14.91	15.461	1.131	1.682
6-8	22.29	17.24	20.22	19.913	2.673	2.372	10.73	12.11	12.24	11.693	0.964	0.547
8-10	21.28	21.71	19.93	20.973	1.040	0.737	15.01	10.34	12.38	12.577	2.237	2.434
<b>Total mass of permeate (g)</b>	<b>2.95</b>	<b>3.32</b>	<b>3.23</b>	<b>3.179</b>			<b>2.932</b>	<b>2.53</b>	<b>2.68</b>	<b>2.714</b>		



**Table B-2 Dehydration of ethanol-water mixture using Abonku Zeolite clay filler**

Time (hrs)	80 v% (75.7 wt%) Feed Concentration of Ethanol						90 v% (87.5 wt%) Feed Concentration of Ethanol					
	Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean		Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean	
	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.
0-2	7.62	6.51	6.93	7.021	0.508	0.598	5.11	5.29	6.48	5.626	0.518	0.854
2-4	9.83	10.38	9.64	9.949	0.309	0.431	11.16	9.53	8.21	9.633	1.420	1.529
4-6	8.08	7.94	8.32	8.113	0.173	0.207	7.07	7.53	6.93	7.174	0.244	0.350
6-8	8.64	10.89	10.00	9.844	1.202	1.046	8.28	8.13	7.15	7.852	0.702	0.423
8-10	11.32	9.21	10.58	10.371	1.161	0.952	7.62	7.53	8.25	7.798	0.268	0.452
<b>Total mass of permeate (g)</b>	<b>1.73</b>	<b>2.04</b>	<b>2.05</b>	<b>1.934</b>			<b>2.41</b>	<b>3.12</b>	<b>3.15</b>	<b>2.895</b>		

**Table B-3 Dehydration of ethanol-water mixture using Anfoega Zeolite clay filler**

Time (hrs)	60 v% (53.9 wt%) Feed Concentration of Ethanol						70 v% (64.6 wt%) Feed Concentration of Ethanol					
	Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean		Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean	
	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.
0-2	14.20	12.92	12.46	13.193	0.736	1.009	12.41	10.44	10.97	11.272	0.834	1.136
2-4	22.74	17.24	23.44	21.140	3.900	2.300	11.24	12.58	10.00	11.272	1.272	1.308
4-6	21.96	22.78	21.21	21.982	0.772	1.458	11.96	13.68	14.10	13.247	1.286	0.853
6-8	20.35	17.24	19.32	18.969	1.729	1.378	17.86	15.97	15.33	16.386	1.056	1.472
8-10	30.21	23.50	20.22	24.643	4.423	5.566	12.80	13.84	12.94	13.193	0.395	0.648
<b>Total mass of permeate (g)</b>	<b>1.58</b>	<b>2.41</b>	<b>1.99</b>	<b>1.994</b>			<b>1.98</b>	<b>2.52</b>	<b>2.31</b>	<b>2.270</b>		

**Table B-4 Dehydration of water-ethanol mixture using Anfoega Zeolite clay filler**

Time (hrs)	80 v% (75.7 wt%) Feed Concentration of Ethanol						90 v% (87.5 wt%) Feed Concentration of Ethanol					
	Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean		Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean	
	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.
0-2	9.93	10.69	11.13	10.583	0.654	0.547	7.01	6.99	7.69	7.228	0.237	0.456
2-4	9.31	8.96	9.84	9.370	0.41	0.47	5.72	6.39	5.54	5.883	0.341	0.507
4-6	8.66	9.13	9.84	9.211	0.548	0.629	5.87	6.1	5.22	5.728	0.508	0.372
6-8	6.95	10.16	10.21	9.107	2.156	1.103	8.58	7.12	7.86	7.852	0.732	0.725
8-10	8.85	9.35	8.49	8.897	0.407	0.453	7.21	6.85	7.32	7.125	0.275	0.196
<b>Total mass of permeate (g)</b>	<b>1.86</b>	<b>2.21</b>	<b>2.06</b>	<b>2.042</b>			<b>2.93</b>	<b>2.25</b>	<b>2.88</b>	<b>2.685</b>		

**Table B-5 Dehydration of ethanol-water mixture using Teleku-Bokazu Zeolite clay filler**

Time (hrs)	60 v% (53.9 wt%) Feed Concentration of Ethanol						70 v% (64.6 wt%) Feed Concentration of Ethanol					
	Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean		Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean	
	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.
0-2	14.03	13.71	14.10	13.946	0.236	0.154	10.66	11.81	10.08	10.848	0.768	0.962
2-4	17.49	16.32	17.65	17.152	0.832	0.498	11.80	11.77	12.48	12.016	0.246	0.464
4-6	20.86	19.00	17.05	18.969	1.919	1.888	13.37	13.91	13.11	13.462	0.352	0.448
6-8	18.80	19.73	21.21	19.912	1.116	1.298	12.87	13.4	13.79	13.354	0.482	0.436
8-10	19.57	19.65	20.35	19.857	0.286	0.493	15.82	14.75	13.38	14.648	1.268	1.166
<b>Total mass of permeate (g)</b>	<b>2.49</b>	<b>1.83</b>	<b>2.29</b>	<b>2.202</b>			<b>2.51</b>	<b>2.18</b>	<b>2.80</b>	<b>2.495</b>		

**Table B-6 Dehydration of ethanol-water mixture using Teleku-Bokazu Zeolite clay filler**

Time (hrs)	80 v% (75.7 wt%) Feed Concentration of Ethanol						90 v% (87.5 wt%) Feed Concentration of Ethanol					
	Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean		Permeate concentration (wt %)			Mean Conc. (wt %)	Deviation from mean	
	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.	1 <sup>st</sup> Run	2 <sup>nd</sup> Run	3 <sup>rd</sup> Run		Min.	Max.
0-2	8.61	6.93	7.24	7.592	0.662	1.014	6.65	6.31	5.94	6.295	0.361	0.352
2-4	10.09	9.88	9.09	9.686	0.596	0.402	5.43	5.86	5.13	5.471	0.347	0.389
4-6	11.08	10.93	10.54	10.848	0.308	0.226	3.59	5.44	5.85	4.957	1.371	0.888
6-8	10.50	11.45	11.71	11.219	0.722	0.491	7.16	7.53	7.00	7.229	0.229	0.303
8-10	9.46	10.84	11.13	10.477	1.016	0.653	5.97	5.54	6.29	5.934	0.394	0.356
<b>Total mass of permeate (g)</b>	<b>2.93</b>	<b>3.37</b>	<b>2.83</b>	<b>3.045</b>			<b>2.88</b>	<b>3.42</b>	<b>3.20</b>	<b>3.165</b>		



**Table B-7 Amount of PSf needed for given DMAc in micro-porous membrane formation**

Concentration of PSf (wt%)	Mass of PSf (g)	Mass of DMAc (g)	Vol. DMAc (cm <sup>3</sup> )	Observation of dry support cast on paper fabric
14	2.0	12.22	13.0	Smooth surface but folded with mottled paper base. This cast solution was not viscous enough hence rolled over the paper alignment.
16	1.0	5.25	5.59	<i>Wet paper alignment and came out nicely with smooth surface, as membrane support film was let to stand for about 3 minutes before submerging in water bath at room temperature overnight.</i>
16	2.0	10.50	11.17	Wet paper alignment and came out nicely with smooth surface, as membrane support film was let to stand for about 3 minutes before submerging in water bath at room temperature overnight.
18	2.0	9.11	9.69	Wet paper made to align well on the flat plate. Came out nice but the surface was rough.
20	2.0	8.0	8.51	Smooth surface rolled over when paper was being peeled off. Some solution precipitated as it was being removed from hotplate stirrer to the flat casting plate.

**Table B-8: Results of conversion calculations of Ethanol concentrations**

Concentration of solution (v %)	Volume of 96.1 v% Ethanol used (cm <sup>3</sup> )	Volume of distilled water used (cm <sup>3</sup> )	Concentration of solution (wt %)
60	31.25	18.75	53.94
70	36.46	13.54	64.56
80	41.67	8.33	75.75
90	46.88	3.13	87.54

**Table B-9: Mass and Compositions in terms of Ethanol in the Feed**

Composition of feed (wt) % ethanol	TOTAL MASS OF FEED PREPARED (g)		
	Abonku membrane	Anfoega membrane	Teleku-Bokazu membrane
53.9	42.94	42.94	42.60
64.6	41.59	41.67	41.60
75.7	40.63	40.37	40.80
87.5	40.00	39.98	39.25

## APPENDIX C: MEMBRANE PERFORMANCE

**Table C-1: Activity Coefficient of Ethanol and Water in Feed mixture**

Feed Ethanol Concentration (wt%)	Mole Fractions		Activity Coefficient	
	Ethanol	Water	Ethanol	Water
53.9	0.3139	0.6861	1.6466	1.2021
64.6	0.4166	0.5834	1.3757	1.3321
75.7	0.5494	0.4506	1.1783	1.5373
87.5	0.7326	0.2674	1.0491	1.8846

**Table C-2: Permeance results for ABK membrane**

Ethanol Concentration (wt %)		Total Flux $\frac{g}{m^2 - hr}$	Molar Flux $\times 10^{-2} \frac{g - mol}{m^2 - hr}$		Permeance $\times 10^{-4} \frac{g - mol}{m^2 - hr mmHg}$	
Feed	Permeate		Ethanol	Water	Ethanol	Water
53.9	18.896	40.476	16.63	182.38	34.58	165.0
64.6	13.539	35.536	10.47	170.79	20.88	153.3
75.7	9.060	24.624	4.85	124.41	8.97	112.5
87.5	7.617	36.860	6.11	189.18	9.70	179.9

**Table C-3: Permeance results for FG membrane**

Ethanol Concentration (wt %)		Total Flux $\frac{g}{m^2 - hr}$	Molar Flux $\times 10^{-2} \frac{g - mol}{m^2 - hr}$		Permeance $\times 10^{-4} \frac{g - mol}{m^2 - hr mmHg}$	
Feed	Permeate		Ethanol	Water	Ethanol	Water
53.9	19.985	25.3884	11.03	112.86	22.70	102.54
64.6	13.094	28.9025	8.22	139.58	16.40	125.04
75.7	9.434	26.0000	5.33	130.82	9.84	118.44
87.5	6.763	34.186	5.03	177.08	8.03	167.81

**Table C-4: Permeance results for TKB membrane**

Ethanol Concentration (wt %)		Total Flux $\frac{g}{m^2 - hr}$	Molar Flux $\times 10^{-2} \frac{g - mol}{m^2 - hr}$		Permeance $\times 10^{-4} \frac{g - mol}{m^2 - hr mmHg}$	
Feed	Permeate		Ethanol	Water	Ethanol	Water
53.9	17.967	28.037	10.951	127.77	22.97	115.20
64.6	12.866	31.767	8.89	153.79	17.84	137.70
75.7	9.964	38.771	8.340	193.93	15.49	175.6
87.5	5.972	40.298	5.23	210.51	8.40	198.9



## APPENDIX D: PREPARATIONS OF SOLUTIONS AND MEMBRANE PERFORMANCE SAMPLE CALCULATIONS

### *D1: Preparation of 45 wt% NaOH solution for zeolite A formation from Clay*

28.125 g of NaOH pellets were added to 34.36g of distilled water at room temperature. The mixture was stirred for 30 minutes until a clear homogeneous solution of the micro-pore forming directing agent was formed.

#### **Calculation:**

$M_w$  of NaOH =  $40\text{ g mol}^{-1}$  and Calcined clay to be used = 50g

36% alkali dosage means for a basis of 100 g clay-alkali mixture,

alkali content = 36g while the calcined clay content = 64 g.

using ratios

$$\frac{36\text{g NaOH}}{64\text{g clay}} = \frac{y\text{g NaOH}}{50\text{g clay}}$$

solving for y

$$y = 50\text{g clay} \times 36\text{g NaOH} / 64\text{g clay} = 50 \times 36 / 64 = \underline{28.125\text{g NaOH}}$$

**Moles of NaOH used:**  $28.125 / 40 = 0.703125\text{ g-mole}$

Utilizing 50 g calcined clay

$28.125\text{g NaOH} / (28.125 + z)\text{ g solution} = 0.45$  where z is the weight of distilled water used

$$\Rightarrow 28.125 \times (1 - 0.45) = 0.45 z \Rightarrow 15.46875 = 0.45 z.$$

$$\Rightarrow Z = 15.46875 / 0.45$$



$$\therefore Z = 34.375 \text{ g H}_2\text{O}$$

For density of water =  $1\text{g/cm}^3$ ,

$\therefore$   $34.375 \text{ cm}^3$  of water was used to dissolve the 28.125g of the NaOH to make 45% NaOH solution of the 3 different clay samples.

Volume of the solution taken as volume of solvent =  **$34.375 \text{ cm}^3$** .

**Molarity calculations:**  $0.703125 \text{ g-mol} \times 1000 \text{ cm}^3 \text{ l}^{-1} / 34.375 \text{ cm}^3 = 20.455 \text{ g-mol l}^{-1}$ .

$\therefore$  Molarity of the micro-pore forming directing agent =  **$20.455 \text{ M}$**

Preparations were made for 50g calcined clay in order to have excess for unforeseen losses. However the total calcined clay prepared was 35g and the volume used for it was  **$33.31 \text{ cm}^3$** . The 3 calcined clay samples needed 19.69g ( $0.49219 \text{ g-mol}$ ) of pore-forming directing agent.

### ***D2: Preparation of PSf-DMAc support casting solution.***

The goal is to prepare 20 wt% of PSf-DMAc solution using 2g of PSf

$$\frac{\text{mass PSf}}{(\text{mass PSf} + \text{mass DMAc})} \times 100 = \text{wt\% concentration}$$

$$\frac{2}{2 + y} = 0.20$$

Where

$y$  = mass of DMAc.

rearranging,

$$\Rightarrow 2 = 2 \times 0.2 + 2 \times y$$

$$\Rightarrow 2 - 0.4 = 0.2y \quad \Rightarrow \quad 1.6 = 0.2y \quad \therefore y = \frac{1.6}{0.2} = 8g$$

Density of DMAc is  $0.94g\text{-cm}^3$

For 8g DMAc, the volume is

$$volume = \frac{8}{0.94} = 8.5 \text{ cm}^3$$

Therefore 8.5cm<sup>3</sup> of DMAc added to 2g of the PSf to form the casting solution of the support. The rest of the weight percent compositions for the PSf casting solution for the support were calculated in the same manner.

Only one support could be made at a time, so the weight of the PSf used was halved to 1g resulting in the eventual use of half the required DMAc volume. For a concentration of the cast solution of 16 wt%, 5.6cm<sup>3</sup> of DMAc was added to 1g of PSf.

### ***D3: Preparation of 5 wt % PVA Zeolite-clay solution***

To be fabricated thin film and to cut down on waste, 1 gram of the PVA be used. This was done by carefully weighing 1gram of PVA crystals with molecular weight 16,000. It was put in a 250cm<sup>3</sup> beaker that was partially covered with a petri dish. 19 milliliters of distilled water was added and stirred using a hot-plate magnetic stirrer was set at 2.5 while the temperature was increased gradually for 50<sup>0</sup>C for 1hour. The temperature was increased to 70<sup>0</sup>C for another hour.

When the solution became clearer the temperature was further increased to 95<sup>0</sup>C while stirring continued for another hour until all the PVA crystals dissolved. The

solution was then filtered off of unwanted material and non-dissolved crystals with pump filter.

- **Calculation process**

Let  $y$  be the mass of water needed,

If  $1g \equiv 5\%$

$$y \equiv 95\% \quad \therefore y = \frac{95\% \times 1g}{5\%} = 19g$$

Since it is liquid, we need the volume equivalent.

$$\Rightarrow \text{volume} = \frac{19g}{1gcm^{-3}}$$

So 19cm<sup>3</sup> of distilled water was used to dissolve the 1g of the PVA pellet to form **5 wt% PVA solution.**

As the zeolite-clay sample must not be more than 0.2wt % of the casting solution (Ling *et al.*, 2008), the preparation was made on the basis of 20g PVA-water solution as;

let  $y$  be the necessary amount of zeolite powder needed

$$\Rightarrow \frac{y}{20 + y} = 0.2\%$$

$$\Rightarrow \frac{y}{20+y} = 0.002$$

$$y = 20(0.002) + 0.002y$$

$$y(1 - 0.002) = 0.04$$

$$\therefore y = \frac{0.04}{0.998} = 0.04008g$$

Therefore 0.04008g each of the zeolite powder was measured and added into the already prepared clear 5wt % PVA solution and stirred until complete dissolution.

The Abonku solution was reddish in colour and was foamy during stirring. The Anfoega and Teleku-Bokazu solutions were cloudy with greyish and yellowish colourations respectively. To ensure proper dispersion and homogeneity of the zeolite in the solution, stirring was restarted while the temperature was kept at 70°C for 20 minutes but later reduced to 50°C for duration of 2 hours by when the solution became clearer.

#### ***D4: Determination of Concentrations from Peak Heights of Chromatogram***

Assumption: Peak height of a given concentration is equivalent to the concentration.

Let **C**  $\equiv$  concentration, **STD**  $\equiv$  Standard solution and **PKH**  $\equiv$  Peak height

But  $PKH \propto C \Rightarrow PKH = K \times C$  (1)

Standard solutions used were Ethanol solutions of concentrations 10 v% and 20 v%

For the 10 v% STD,  $PKH_1 = 74.5 \text{ cm}$  and  $PKH_2 = 80.0 \text{ cm}$

$$\text{Average PKH} = PKH_{\text{average}} = \frac{74.5 + 80.0}{2} = 77.25 \text{ cm}$$

From (1)  $77.25 = K_1 \times 10 \Rightarrow K_1 = 7.725$

For the 20 v% STD,  $158.5 = K_2 \times 20 \Rightarrow K_2 = 7.925$

but  $K = \frac{K_1 + K_2}{2} = \frac{7.725 + 7.925}{2}$

$$\therefore K = 7.825$$

Equation (1) then becomes **PKH = 7.825C** or

$$C = \frac{PKH}{7.825} \quad (2)$$

To find any unknown concentration, the PKH is put into equation (2) and evaluated

For permeate sample S1, the chromatogram PKH = 94 cm,

$$\therefore C = \frac{94}{7.825} = 12.0128 \text{ v\% ethanol}$$

#### ***D5: Ethanol material balance***

Using equations ( 4.3) for the feed ethanol concentration of 53.9 wt% for Abonku Zeolite-clay filled membrane,

$$(F_D - F_{NP}) \times x_e = R_6 \times r_e + (Q + L_{R/P}) \times y_e \quad (4.3)$$

$$(41.937 - 0.566) \times 0.539 = 30.281 \times r_e + (3.179 + 7.911) \times 0.189$$

$$41.371 \times 0.539 = 30.281 \times r_e + (11.09) \times 0.189$$

$$22.29897 = 30.281 \times r_e + 2.09601$$

$$\Rightarrow 20.20296 = 30.281 \times r_e$$

$$\Rightarrow r_e = \frac{20.20296}{30.281} = 0.6672$$

$$\therefore r_e = 66.72 \text{ wt\%}$$



## D 6: Membrane performance

Sample calculations for the membrane performance are shown below:

For the concentration of permeate for a given feed concentration, the average value of the 5 samples were used as the representative concentration as reported by Yeh *et al.*, (2003). The results of the permeate concentrations for the Abonku membrane for a feed concentration of 53.9 wt% ethanol were 15.19 wt%, 17.04 wt%, 21.36 wt%, 19.92 wt% and 20.97 wt%. The average is 18.90 wt%. The procedure was used for all the representative permeates.

- **Mole % calculation**

Molecular weight :  $\text{H}_2\text{O} = 18\text{g/g-mole}$ ;  $\text{C}_2\text{H}_5\text{OH} = 46\text{g/g-mole}$

$$\text{Mole} = \frac{\text{mass}}{\text{molecular weight}}$$

The percent mole for permeate from 60 v% ethanol in feed was calculated as:

$$\text{Ethanol} = \frac{0.601}{46} = 0.013065 \quad \text{Water} = \frac{2.578}{18} = 0.143222$$

$$\text{Total mole} = \frac{0.601}{46} + \frac{2.578}{18} = 0.156287$$

$$\text{Percent mole of ethanol} = \frac{0.01306528}{0.156287} \times 100\% = 8.4 \%$$

$$\therefore \text{Percent mole of water} = 91.6 \%$$

### 1. Ethanol flux

The permeability (permeation rate) in the case of ABK at 64.6 wt% ethanol in the feed was calculated as

$$J_{\text{ethanol}} = \frac{0.368}{0.007854 \times 10} = 4.6855 \frac{\text{g}}{\text{m}^2 \text{hr}}$$

### 2. Total flux

The permeation rate (permeability), for the ABK at 64.6 wt% ethanol in the feed, was calculated as  $J_{64.6(\text{ABK})} = 2.714/0.007854/10 = 34.5556 \frac{\text{g}}{\text{m}^2 \text{hr}}$

### 3. Selectivity of water relative to ethanol

The separation factor in the case of ABK at 64.6 wt% ethanol in the feed, was calculated as

$$\text{Separation factor} = \frac{[0.86461/0.13539]}{[0.3544/0.6456]} = 11.633817$$

### 4. PSI

Using the formula earlier given somewhere, and knowing the selectivity and the permeability from previous calculations for the same ethanol wt% in the feed mixture of 64.6 wt% for ABK, the PSI is calculated as

$$\text{PSI} = 34.5556 \times (11.633817 - 1) = 367.441 \frac{\text{g}}{\text{m}^2 \text{hr}}$$

**5. Permeance** Let 1 designate ethanol and 2, water.  $\gamma_1$ ,  $\gamma_2$  are the activity coefficients of ethanol and water respectively. The permeate pressure was taken as  $0.125 \text{ kg/cm}^2$  (92.028 mmHg) vacuum.

i. Activity coefficient of Ethanol and water

Using Van Laar's equation of activity coefficient of binary mixtures, the following expression was used at the operating temperature of 30°C (Seader & Henley, (2001).

$$\ln \gamma_1 = 1.6276 \left[ \frac{0.9232 x_2}{1.6276 x_1 + 0.9232 x_2} \right]^2 \text{ and } \ln \gamma_2 = 0.9232 \left[ \frac{1.6276 x_1}{1.6276 x_1 + 0.9232 x_2} \right]^2 \text{ where } x_1 \text{ and } x_2 \text{ are the mole fractions of ethanol and water in the feed liquid mixture.}$$

$$\gamma_1 = \exp \left\{ 1.6276 \left[ \frac{0.9232 \times 0.2674}{1.6276 \times 0.7326 + 0.9232 \times 0.2674} \right]^2 \right\} = 1.0491$$

$$\gamma_2 = \exp \left\{ 0.9232 \left[ \frac{1.6276 \times 0.7326}{1.6276 \times 0.7326 + 0.9232 \times 0.2674} \right]^2 \right\} = 1.8846$$

ii. Molar flux =  $N_i = \frac{\text{mass flux} \times y_i}{Mw_i}$ , where  $Mw_i$  is the molecular weight and

$y_i$ , the mole fraction of species  $i$  in the vapour phase. For the ethanol concentration of 87.5 wt % in the TKB membrane, the results are,

$$N_1 = \frac{40.3 \times 0.059722}{46} = 0.05232 \frac{g}{hr-m^2} \text{ and } N_2 = \frac{40.3 \times (1 - 0.059722)}{18} = 2.10507 \frac{g}{hr-m^2}$$

iii.  $\check{P}_{M_i} = \frac{\text{molar flux}}{\gamma_i x_i P_i^0 - y_i P}$

$$\check{P}_{M_1} = \frac{0.05232}{1.0491 \times 0.7326 \times 78.154 - 0.024272 \times (-92.028)} = 8.398 \times 10^{-4} \frac{g-mol}{hr-m^2 mmHg}$$

$$\check{P}_{M_2} = \frac{2.10507}{1.8846 \times 0.2674 \times 31.8 - 0.975728 \times (-92.028)} = 19.893 \times 10^{-3} \frac{g-mol}{hr-m^2 mmHg}$$

## APPENDIX E: LIST OF PROJECT PHOTOGRAPHS



Picture 12.0 Filtered wet zeolites formed



Picture 13.0 Gardener's Knife on flat plate





**Picture 14.0 Pervaporation cell unit before fitting the hose and pressure gauge**



**Picture 15.0 Inside of the Pervaporation cell**





**Picture 16.0 Permeate chamber with perforated metal support and polypropylene wire mesh**



**Picture 17.0 Permeate chamber showing the membrane on the metal support; O-ring not fitted.**



**Picture 18.0 Permeate chamber showing the membrane and the O-ring well-fitted**



**Picture 19.0 Pervaporation cell with pressure gauge fitted on the feed chamber and retentate outlet closed.**





**Picture 20.0 Process set up showing the 2 condensers and the vacuum level gauge. Flow line 1 operational**



**Picture 21.0 Condenser with iced blocks around the permeate collecting vessel**