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Pervaporation of ketazine aqueous layer in production of hydrazine hydrate by peroxide process

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Abstract

Hydrazine hydrate is now produced worldwide by an ecofriendly process using ammonia and hydrogen peroxide as reactants, with methylethylketone (MEK) and acetamide being other active ingredients. Ketazine is an intermediate product during the formation of which, phase separation occurs between an upper organic layer enriched in ketazine and lower aqueous phase containing substantial amounts of acetamide (30 wt.%) and methylethylketone (5%) which have to be recycled in the form of a concentrated solution after partial removal of water (60%). The membrane based pervaporation (PV) technique has been successfully applied using the chemically compatible and highly hydrophilic chitosan membrane to dehydrate the highly alkaline aqueous layer. The effect of operating parameters such as feed composition and barrier thickness on membrane performance with respect to acetamide separation and water flux has been evaluated. High degree of acetamide separation was achieved along with reasonably good water flux and MEK separation.
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1. Introduction

Hydrazine hydrate ($N_2H_4 \cdot H_2O$) is a very important chemical which finds application as blowing agent in plastic industry, reducing agent, oxygen scavenger for boiler feed water, starting material for dye intermediates, catalyst for polymerization reactions, etc., besides fuel for rockets and space crafts in the form of pure hydrazine [1,2]. The present technology for worldwide production of hydrazine hydrate employs the environmentally clean peroxide-ketazine process wherein ammonia and hydrogen peroxide (oxidizing agent) are the major reactants [3] (Fig. 1). The reaction is carried out in the presence of methylethylketone (MEK) at atmospheric pressure. Initially MEK reacts with ammonia to form Schiff's base while acetamide reacts with hydrogen peroxide forming iminoperacetic acid. Schiff's base and iminoperacetic acid further react together to produce oxaziridine as well as acetamide which is thus regenerated. The overall reaction results in the formation of key intermediate methyl ethyl ketazine in high yield along with 4 mol of water for every mole of peroxide consumed.

This intermediate product is distributed amongst an upper organic-rich (ketazine-enriched) layer and a lower aqueous phase which is lean in ketazine (1–2%) but contains substantial amounts of acetamide (30%) and MEK (5%) in water. The organic-rich layer undergoes distillation followed by hydrolysis to give hydrazine hydrate while the aqueous layer has to be dehydrated in order to recycle the expensive acetamide (along with MEK) back to the reactor in the form of a 65–70 wt.% acetamide solution in water. Conventional dewatering by energy intensive evaporation is disadvantageous since the recovered reactants develop coloration at temperatures above 45 °C when the aqueous layer is heated to remove water. The coloration leads to excess consumption of hydrogen peroxide which is a well known decolorizing agent thus reducing the product yield. Moreover, acetamide sublimes at high temperatures and is prolific in its presence in the water vapor resulting in losses. In order to avoid the above discrepancies, alternate separation methods devoid of heating such as membrane technology were considered.

Membrane separation techniques such as reverse osmosis (RO), electrodialysis (ED), nanofiltration (NF) and pervaporation (PV) yield excellent results for conventionally difficult separations when applied judiciously. RO and ED membranes are damaged by the high pH (13–14) of the ketazine

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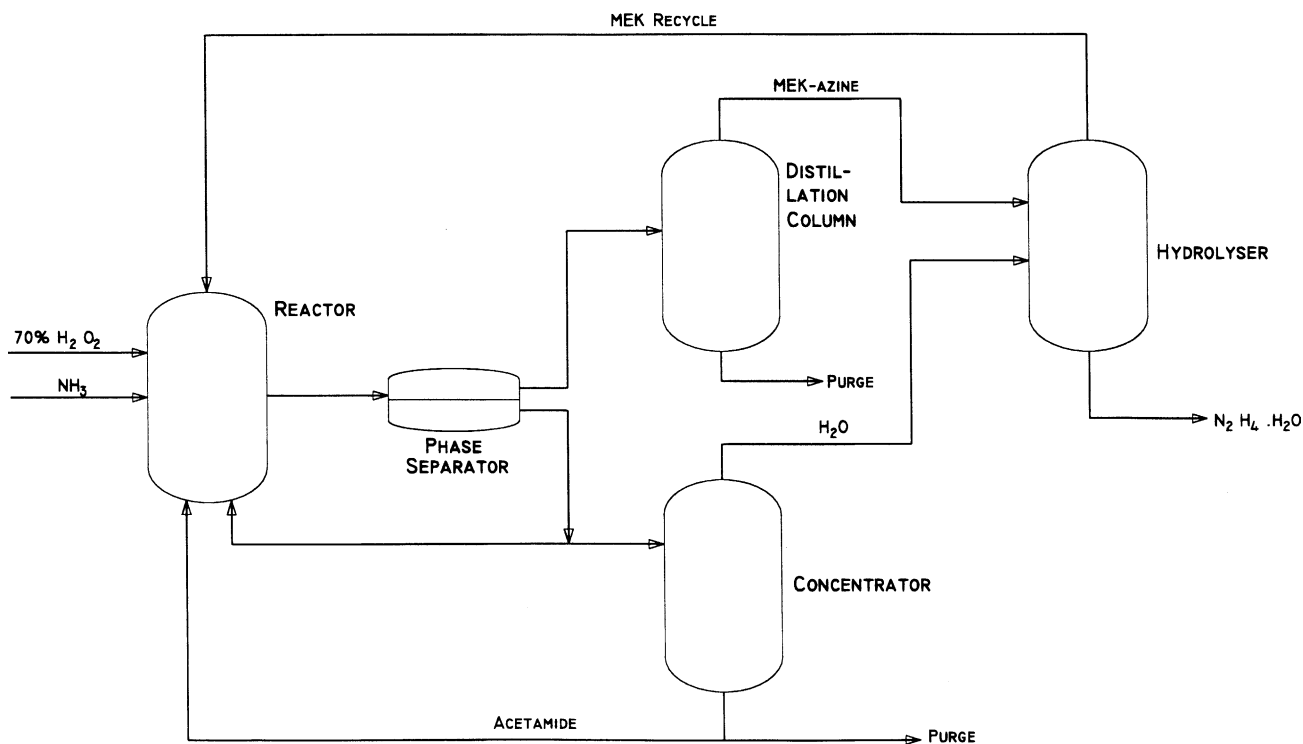*E-mail address:* aakhan_iict@rediffmail.com (A.A. Khan).

Fig. 1. Process flow sheet of peroxide-ketazine process for hydrazine hydrate production.

aqueous layer whereas in contrast, pervaporation offers a wider range of membrane materials capable of withstanding highly alkaline solutions besides being an economical, ecofriendly and safe process as compared to other separation processes. PV has so far been successfully applied for industrial applications involving separation of azeotropes, dehydration of alcohols, ketones and esters besides hazardous and heat-sensitive compounds [4–9]. The authors have previously carried out dehydration of highly alkaline aqueous solutions of hydrazine and monomethyl hydrazine liquid propellants using ethylcellulose membranes [10,11].

Pervaporation has so far been restricted to separation of azeotropes and solvent dehydration and hence it is worth mentioning that this technique has been applied for the first time in the present study to concentrate a multicomponent mixture inclusive of a dissolved solid. The chemically compatible and highly hydrophilic chitosan membrane was selected with the help of Hansen's solubility parameter [12,13] for dehydrating the ketazine aqueous phase. Chitosan is a very promising membrane material for pervaporation and has so far been applied successfully on the bench-scale for dehydration of ethanol [8] and isopropanol [9]. The polymer's ability to form highly selective and permeable blend membranes with polyvinyl alcohol, sodium alginate, etc., has been exploited significantly in the past [14]. Influence of process parameters such as feed composition and membrane thickness on separation performance of chitosan membrane has been extensively investigated.

2. Experimental

2.1. Materials

Chitosan flakes of 84% degree of deacetylation were purchased locally while glacial acetic acid was purchased from Ranbaxy, Mumbai. Acetamide and MEK were purchased from Loba Chemie, Mumbai. Non-woven membrane support fabric was supplied by Veratec, USA. Distilled water was utilized to prepare the synthetic mixtures.

2.2. Membrane synthesis

Membranes were prepared by solution casting and solvent evaporation technique. A 2 wt.% solution of chitosan in aqueous acetic acid (2% (v/v) in distilled water) was prepared, stirred and filtered to remove undissolved matter. Air bubble-free solution was cast on a non-woven membrane support fabric of 100 μm thickness which was fixed onto a clean glass plate. The film was initially dried in atmosphere at room temperature followed by vacuum drying for a period of 5 h at elevated temperature (50 °C) in a closed oven to remove the remaining traces of solvent. Chitosan membrane thus prepared was dense (nonporous) and it penetrated about 40% of the non-woven support thickness. The thickness of the membrane was controlled by adjusting the gap between casting blade and membrane support fabric keeping viscosity of the solution constant.
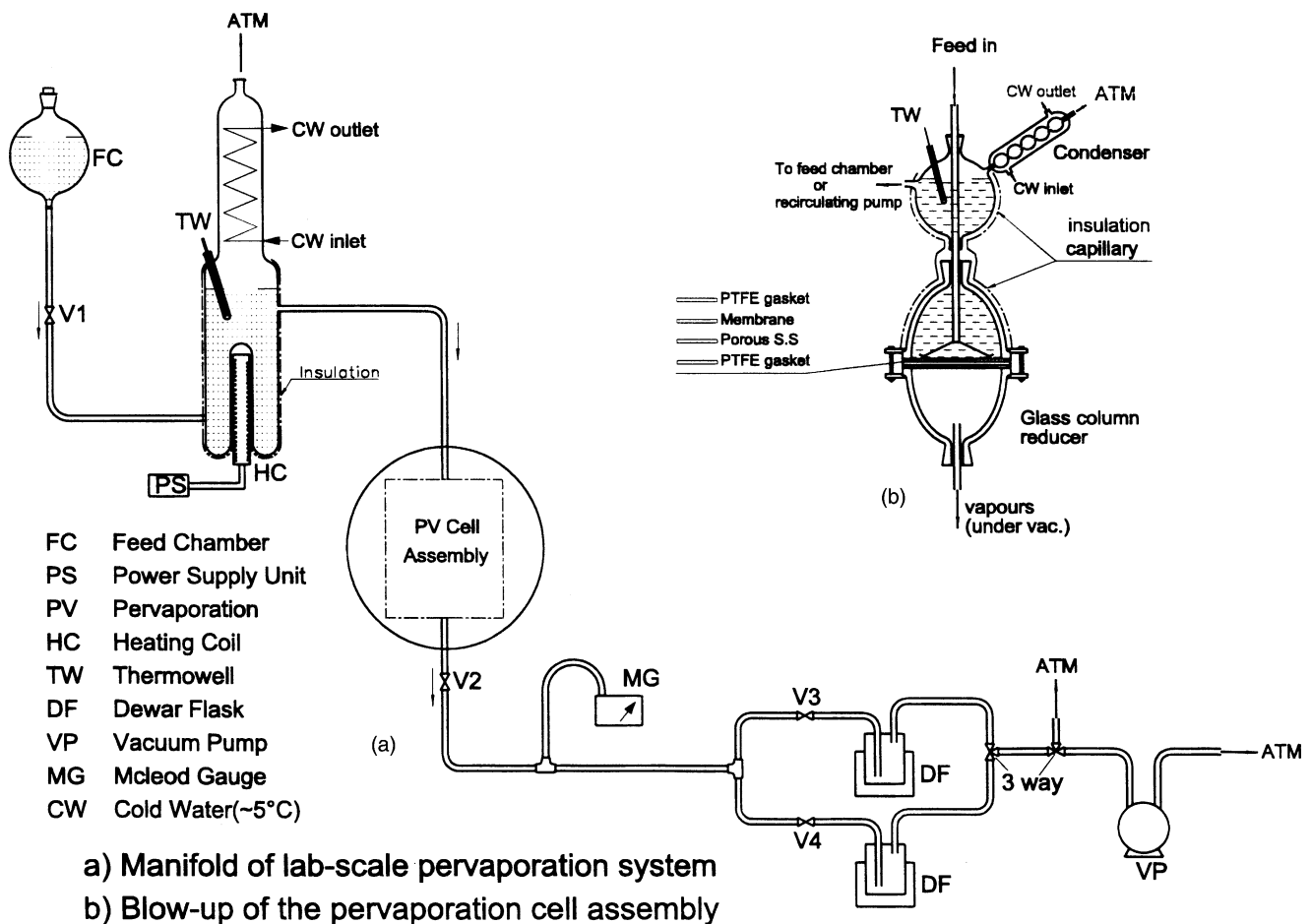
Fig. 2. Schematic of pervaporation experimental setup.

2.3. Laboratory pervaporation unit

This section describes the experimental setup that was used to carry out pervaporation studies for dehydration of ketazine aqueous layer. A schematic diagram of the experimental facility is shown in Fig. 2 which includes the pervaporation manifold (Fig. 2a) and blowup of the permeability cell assembly (Fig. 2b). The pervaporation cell consisted of two bell-shaped B-24 size glass column reducers/couplers clamped together with external padded flanges by means of tie rods to give a vacuum tight arrangement. The top half was used as the feed chamber and the bottom one worked as the permeate chamber. The membrane was supported by a stainless steel porous plate which was embedded with a mesh of the same material to provide a smooth uniform surface. Teflon gaskets were fixed by means of high vacuum silicone grease on either side of the membrane and the sandwich was placed between the two glass column couplers and secured tightly. The effective area of the membrane in the PV cell was 20 cm^2. After fixing the membrane, the cell was installed in the manifold and connected to the permeate line by means of a B-24 glass cone which was fixed on one side to a high vacuum glass valve followed by a glass con-

densor trap which consisted of a small detachable collector. The trap was placed in a Dewar flask containing liquid nitrogen for condensing the permeate vapors. A 0.75 hp rotary vacuum pump was used to maintain the permeate side pressure which was measured with an Edward's Mcleod gauge of scale in the range 0.01–10 mmHg (1333–13.33 Pa). High vacuum rubber tubing was used to connect the various accessories to the experimental manifold. All glass cone–socket joints were fixed with good quality high vacuum grease (Dow Corning).

2.4. Pervaporation procedure

Dry membrane film was fixed over the porous stainless steel support and the pervaporation cell assembly was clamped and installed in the manifold. Initially no feed solution was introduced in the cell and the vacuum pump was turned on to detect the presence of pinholes in the membrane or any other leakage present in the manifold and cell assembly. Experiments were begun only after a steady vacuum of at least 0.05 mmHg (6.65 Pa) could be obtained with the system. The vacuum pump was then switched off and a known volume of feed liquid (70 ml) was poured into the top

Table 1
Composition (wt.%) of various aqueous layer feed mixtures

Feed mixture (MX)	Water	Acetamide	MEK	Ammonia	Ketazine
MX1	60.32	29.1	5.81	2.86	1.91
MX2	54.23	33.59	6.65	3.31	2.22
MX3	45.76	39.8	7.87	3.94	2.63
MX4	37.11	46.11	9.14	4.56	3.08
MX5	25.21	54.86	10.84	5.44	3.65
MX6	14.73	65	11.27	5.9	4.1

half chamber of the cell allowing it to soak the membrane. Table 1 provides the list of feed mixtures containing varying concentrations of acetamide, MEK, ketazine, ammonia and water, which have been subjected to pervaporation. Mixture MX1 relates to the initial composition of the lower aqueous phase generated during the formation of the key intermediate ketazine. MX1 contains only 29% acetamide and has to be concentrated to 65–70% acetamide before recycle to the reactor. The other feed mixtures in Table 1 relate to subsequent compositions encountered during the course of concentration of the aqueous layer from 29% to a minimum of 65% for recycle. Evacuation was again applied and data collection started once steady-state concentration profile was attained. The experiments were carried out with the feed stirred continuously throughout the experiments to reduce concentration polarization. Same volume of the feed material was introduced in each run to avoid any inconsistencies. Permeate was collected for a duration of 10–12 h. Tests were carried out at room temperature (30 ± 2 °C) and repeated twice using fresh feed solution to check for reproducibility. The effect of operating parameters such as feed composition and membrane thickness on the separation performance and flux of the membrane was studied in detail. The collected permeate was weighed in a Sartorius electronic balance (accuracy: 10^{-7} kg) after allowing it to attain room temperature to determine the flux and then analyzed by gas chromatography to evaluate the separation characteristics.

2.5. Analytical

The feed and permeate ketazine aqueous layer samples (size: 0.2 μl) were analyzed using a Shimadzu 17 A gas chromatograph installed with a Tenax column and thermal conductivity detector (TCD). Hydrogen at 80 Pa pressure was used as the carrier gas and the oven temperature was programmed at 160 °C for 3 min followed by an increase to 190 °C at the rate of 10 °C/min. Both the TCD and injection port temperatures were maintained at 220 °C.

3. Results and discussion

Chitosan membrane was selected for dehydrating the ketazine aqueous layer on the basis of the close proximity of its

Hansen's solubility parameter value [12] (43.04 $J^{1/2}/cm^{3/2}$) to that of water (47.9) [13]. Moreover, the highly hydrophilic chitosan is also chemically compatible with strongly alkaline medium such as the one in the present case. The effect of feed concentration on the separation characteristics of the membrane was evaluated by experimenting with different compositions of feed solution as shown in Table 1. Variation of acetamide concentration in permeate and corresponding water flux was studied at different membrane thickness. The absolute pressure on the permeate side was maintained constant at 0.1 mmHg (13.33 Pa) throughout the studies.

3.1. Acetamide separation

Fig. 3 depicts the effect of acetamide feed concentration on separation performance of chitosan membrane of 50 μm thickness in terms of the permeate concentration obtained. Initially, at 29% acetamide feed concentration, complete separation was achieved but with increasing feed content of acetamide from 33.6 to 65%, the acetamide content in permeate increased gradually from 0.06 to 2.5%, respectively. Pervaporation is the only membrane-based process in which a phase change from liquid state to vapor occurs on the permeate side of the barrier. Only volatile components are solubilized and transported across the dense membrane due to their ability to vaporize at lower pressures. Therefore, solids cannot penetrate through a pervaporation membrane due to their nonvolatile nature. However, rising feed concentration of acetamide resulted in increasing percentage of the same in the permeate. The reasons for these observations could be attributed to the fact that acetamide is a strongly hydrogen bonding molecule and is involved in extensive inter- and intra-molecular H-bonding with the amine (–NH$_2$) and hydroxyl (–OH) functional groups of chitosan polymer [14]. The extensive interaction enables acetamide to penetrate the selective dry downstream face of the membrane especially at higher feed concentrations when the membrane matrix gets saturated with the amide. Under such conditions, feed solution is absorbed within the membrane and acetamide remains in dissolved state over a major part across the thickness, during which it can diffuse to the depth due to interaction, and get precipitated out owing to saturation at the
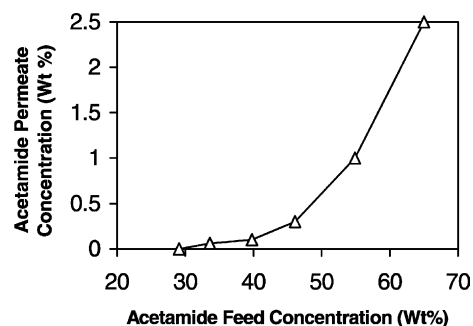

Fig. 3. Effect of acetamide feed concentration on separation performance of chitosan membrane.
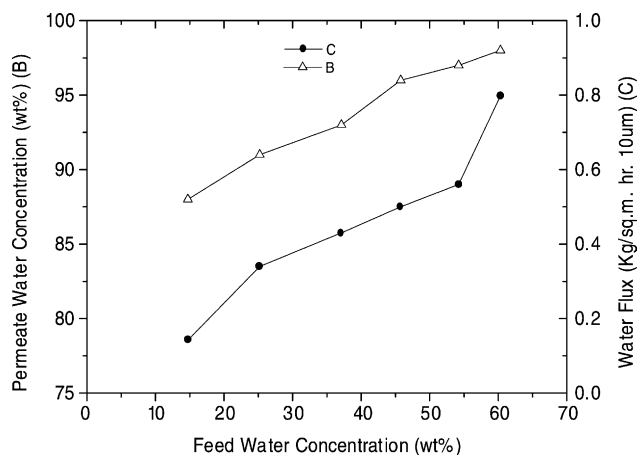
Fig. 4. Variation of permeate concentration and flux of water with feed composition.

Fig. 5. Variation of MEK permeate concentration and flux with feed concentration.

downstream face. However, the amounts of acetamide found in permeate are very small (Fig. 3) and hence the extent of separation achieved in the present case appears to be promising enough for pervaporation to be applied on an industrial scale for treating or concentrating high pH and heat-sensitive solutions of solid compounds.

3.2. Permeation characteristics of water

The effect of feed composition on permeate concentration and flux of water is represented by Fig. 4. Very high permeate concentrations of 98–96% were obtained for high feed water concentrations upto 45.76%. The corresponding flux values were also reasonably high and varied from 0.8 to 0.5 kg/(m^2 h). In pervaporation, the permeability of water or any other liquid component depends upon the concentration of the component inside the membrane which in turn is related to its vapor pressure or activity in the feed mixture as well as its affinity towards the membrane [14,15]. Chitosan membrane shows preferential affinity for water which was proven by sorption studies that revealed a high equilibrium sorption value of 176% for water compared to a low value of <2% for MEK. The solubility and consequently the membrane swelling progressively increases with increasing concentration of water due to rising vapor pressure or activity leading to plasticization of membrane matrix and enhanced flux. Water is also a smaller molecule (MW = 18) compared to acetamide (59) and MEK (72) because of which its diffusion coefficient would be relatively much higher [16]. At lower feed water concentrations the activity is already low and is further reduced due to the increasing concentration of solute (acetamide) which binds with water and lowers its vapor pressure resulting in reduction of flux.

3.3. Separation of methylethylketone

Fig. 5 depicts the variation of permeate MEK content with increasing feed concentration of the liquid (as per Table 1).
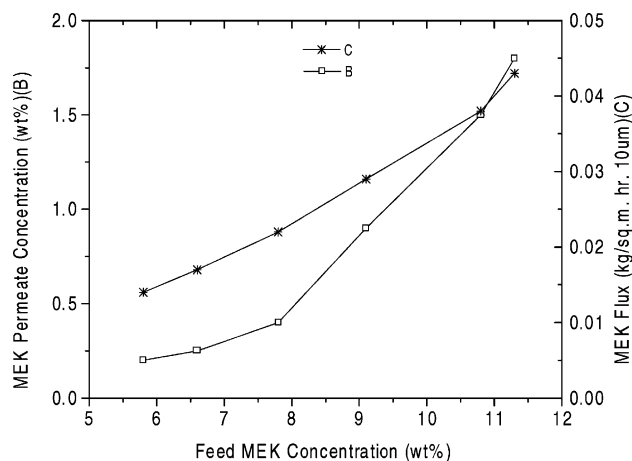
The permeate concentration and flux of MEK increased progressively from 0.2 to 1.8% and 0.014 to 0.043 kg/(m^2 h), respectively, with increasing feed concentration from 5.8 to 11.3% because of rising vapor pressure and activity of MEK in feed as discussed in Section 3.2. However, the permeation rate of MEK was generally poor due to lack of affinity between the hydrophilic membrane and the ketone which is a relatively nonpolar molecule and weak hydrogen bonding agent compared to water.

3.4. Effect of membrane thickness

The effect of membrane thickness on water flux and permeate acetamide concentration is shown in Fig. 6. The membrane thickness was varied from 25 to 200 μm with the feed composition fixed at an average composition (MX4) of ketazine aqueous layer (Table 1) and permeate vacuum maintained constant at 0.1 mmHg (13.3 Pa). In pervaporation, the upstream face of the membrane is in a swollen state due to constant contact with the feed liquid mixture while the other
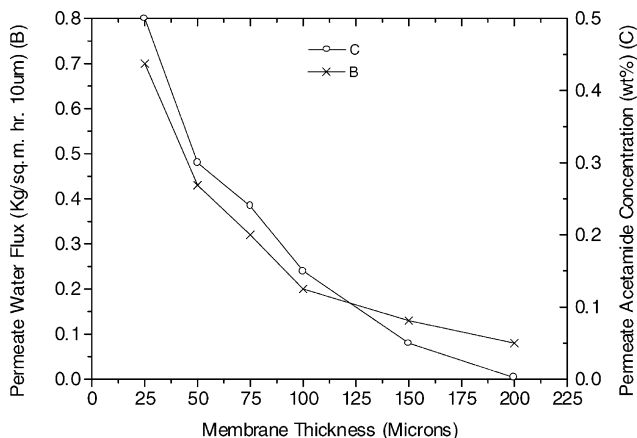

Fig. 6. Effect of chitosan membrane thickness on water flux and acetamide separation.

side is in dry state due to continuous evacuation, i.e. the membrane is always in pseudo equilibrium condition [14]. The swollen membrane portion acts like a fluid and allows all the permeating components to diffuse through whereas the dry layer is the selective face which restricts the flow of the penetrants. Every dense (nonporous) pervaporation membrane possesses a dry downstream layer during operation and the thickness of this dry layer increases with increasing total membrane thickness causing a rise in resistance to mass transfer. Due to these reasons, the quantity of acetamide in permeate decreased from 0.5% at 25 μm membrane thickness to 0.05% for 150 μm and became negligible at 200 μm. Expectedly, the water flux reduced from 0.7 initially to 0.08 kg/(m² h) due to increasing resistance to flow of water.

Water is also a carrier for acetamide. As the water flux decreased the transport of acetamide to the downstream layer decreased proportionately.

4. Conclusions

The study reveals that pervaporation has very good potential for concentrating multicomponent solutions containing dissolved solids as well as volatile liquids. Pervaporation through chitosan membrane appears to be a promising alternative process for dehydration of ketazine aqueous liquor formed in the peroxide process for production of hydrazine hydrate. High degree of separation was obtained for acetamide over its entire feed concentration range since it is a nonvolatile solid at room temperature. Reasonable separation of MEK was observed owing to the inability of the ketone to interact substantially with the separating phase. Increasing amounts of acetamide and MEK were found in permeate at higher feed concentrations due to increasing activity of the solutes in the feed. The high selectivity and flux achieved with respect to water are due to hydrophilic nature of chitosan membrane and high activity of water which also has strong tendency to form extensive inter- and intra-molecular hydrogen bonds with amine and hydroxyl functional groups of the polymer. The results are substantiated by pure component sorption studies and the fact that water is a relatively small molecule compared to acetamide and MEK which enables the former to diffuse more rapidly through the barrier. The extent of acetamide separation improved with increasing membrane thickness which causes a corresponding rise in the thickness of the selective dry downstream membrane layer. To achieve greater flux pervaporation could be considered at higher temperatures (40–45 °C) where discoloration does not occur.

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