Processing of Liquid Propellant Reaction Liquors by Pervaporation

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ABSTRACT: Unsymmetrical dimethylhydrazine and monomethylhydrazine are the two well-known liquid propellants. Substantial amounts of sodium chloride present in the aqueous unsymmetrical dimethylhydrazine and monomethylhydrazine reaction liquors. Pervaporation experiments have been conducted using dense chitosan membrane for desalting of these reaction liquors. The effect of membrane thickness, salt concentration in the feed, and permeate pressures on flux and % rejection have been studied and discussed to optimize the conditions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 141–149, 1999

Key words: liquid propellant; pervaporation; monomethylhydrazine; unsymmetrical dimethylhydrazine; chitosan

INTRODUCTION

Hydrazine, unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH) are well-known liquid propellants and oxygen scavengers with $pH > 12.^{1}$ These liquids are highly reducing, as well as hydrolyzing in nature. The following industrial procedures are outlined to indicate the composition of reaction liquors (RLs) and the components present in addition to the desired product.

Ammonia is reacted with NaOCl to produce chloramine. This reaction yields NaOH as a by-product.

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$

Chloramine RL is reacted subsequently with dimethylamine (DMA) in the presence of NaOH to produce UDMH.

$$H_2NCl + HN(CH_3)_2 + NaOH →$$

 $H_3NN(CH_3)_2 + NaCl + H_2O$

Similarly, chloramine liquor is reacted with monomethylamine (MMA) to produce MMH.

$$\label{eq:hamiltonian} \begin{split} H_2 NCl + HN \ CH_3 + NaOH \rightarrow \\ H_2 NNHCH_3 + NaCl + H_2 O \end{split}$$

Yields of the overall reactions are of the order of 7% in both the processes of preparation. As can be seen from the above procedures, the resulting reaction liquors will consist of UDMH or MMH, NaCl, unreacted ammonia (NH₃), and unreacted DMA or MMA, as the case may be with a typical composition in the liquor as indicated in Table I. The presence of alkalies imparts high pH (>12) to the liquors.

NaCl needs to be removed first, because it causes severe corrosion problems. Presently, flash vaporization, followed by extractive distillation, is

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Compound	Wt %
UDMH/MMH NH ₃ DMA/MMA NaCl Water	<1-2 <2 pprox 1.5 pprox 8 Balance

Table ITypical Compositions of the UDMHand MMH RLs

used in the purification of these RLs. As can be expected, this entails huge requirements of steam (210 kg of steam/kg of UDMH and 410 kg of steam/kg of MMH) in the process of purification.

To reduce the severe energy (steam) requirements, our group has begun exploring alternative technologies. One such technology is based on membrane separation processes. As compared with other methods, membrane technologies have far less energy requirements, they are clean, efficient safe, and easy to operate. Also, they are economical, environmentally safe, and do not create waste disposal problems.

Applied Membrane Technologies

There are basically two proven routes currently practiced in the industry for demineralization of aqueous solutions, which can be equally useful for the treatment of UDMH and MMH RLs. They are reverse osmosis (RO) and electrodialysis (ED).

RO

The presence of salt and other components in an aqueous solution causes reduction in solvent chemical potential.² When such solution is separated from pure solvent (water) with a semipermiable barrier in between, solvent will flow from the pure solvent to the solution side due to the gradient in chemical potential of the solvent until the two sides reach the same osmotic pressure. To cause a reversal in flow (i.e., to make solvent flow from the solution side), a pressure greater than the osmotic pressure of the solution has to be applied. In principle, salts should be completely rejected in RO but, in reality, rejection tends to be low (<95%) due to leakiness of membranes. The main energy consumption is in the high-pressure pumping of feed. The membranes in use for desalting globally are based on cellulose esters and polyamides, with rejection capabilities² in the range of 80 to 90%. These membranes are known

to be chemically less tolerant toward chlorides and organic, which are essential components in the present case. The membranes made of cellulose acetate or polyamide indigenously developed by Bhaba Atomic Research Centre (Bombay, India) have been used. Accordingly, experiments had been performed to check the viability of RO for desalination of UDMH/MMH liquors. The RO membranes were found to be not compatible with the organic present in liquors and were subjected to chemical attack. This resulted in degradation and poor performance. Furthermore, an approximate calculation shows that osmotic pressure in excess of 60 atm will be required for desalination in the present case.

ED

Due to poor chemical tolerance of the RO membranes as previously explained, trial runs have been performed with ED. In this case, the ions present in the RL are removed across the porous ion-permeable membranes with the application of an electric field potential.³ In the present case, NaCl has to be removed from the reaction liquid. This requires the use of cationic and anionic permeable membranes for the removal of Na⁺ and Cl^- ions, respectively. ED membrane stack with 13 cell pairs in which the anion and cation exchange membranes (Selemion AMV and CMV membranes, respectively, obtained from Asahi Glass Co., Ltd., Japan) are placed alternately was used.

Experiments were conducted by taking the RLs having 5.68-8.166 wt % and 6.17-8.224 wt % of NaCl present in UDMH and MMH, respectively. The final NaCl compositions were determined after 15–20 h of continuous runs; they were found to be 0.11-1.51 and 0.126-4.54 in wt % with UDMH and MMH RLs, respectively. Experimental results of ED clearly indicated that this could not remove the salts completely from RLs. The advantages of ED over RO techniques are that the chemical tolerance of the membranes is generally excellent, and operating conditions are not severe.

Both ED and RO failed to remove the salts completely from the RLs of MMH and UDMH. Hence, the objective of the present study is to find an alternative and more efficient membrane technique for desalting the liquid propellant RLs. For this purpose, pervaporation (PV) technique has been investigated.

PV is an economical technique to separate of $azeotropes^4$ and isomers,⁵ and for the removal or

recovery of trace substances,⁶ compared with the conventional methods of separation. Because of its good separation efficiency and flux rates, PV results in savings in energy costs. Most of the research and industrial applications use this technique for the dehydration of alcohols,^{7,8} separation of isomeric compounds^{9,10} for separation of mixtures of chlorinated solvents,¹¹ for the separation of ketones and esters,¹² and in the separation of saturated hydrocarbons.¹³ In the PV process, the feed mixture is contacted with a nonporous permselective membrane. Separation is in general explained by the steps of sorption into, diffusion through, and desorption from the membrane. The first and the last steps are usually considered to be fast and taking place at equilibrium. Diffusion is a kinetically controlled and slower process. The U.S. Department of Energy identified "pervaporation membrane for organicorganic separation," is the highest ranking research priority.¹⁴

Experiments were continued with a benchscale PV unit. The aim was restricted initially to removal of the salts or salt and water from the RLs. To make this technique more economical, fluxes of the membranes have to be reasonable. A very important consideration has been to obtain a permeate with the same or even higher concentration of the UDMH or MMH than the feed. In general, membranes should have high sorption capacity (for higher flux) either for UDMH, MMH, and water such that there should be no trace of UDMH or MMH left at the salt-enriched feed side.

During the experimental studies, chitosan membranes have shown excellent chemical resistance in all liquid propellants and with water. The sorption capacity of these membranes is found to be >100% for all the liquids mentioned herein. With UDMH and MMH, it is higher than water. This clearly indicates that the membrane is more selective to UDMH and MMH components. Hence, the permeate after salt rejection will have a larger amount of UDMH/MMH, or utmost it may have same composition of water and UDMH/MMH present in the feed.

Based on these observations, the PV experiments for the removal of salts present in RLs were conducted with chitosan membranes. It was established subsequently that no other hydrophilic membranes, such as PVA or cellulose acetate, can serve better than chitosan because of mechanical instability or rejection of UDMH/ MMH from the feed.

EXPERIMENTAL

Materials

RLs of UDMH and MMH were supplied by VSSC-ISRO (Thiruvananthapuram). Chitosan was purchased locally in Andhra Pradesh and chitosan was purified by dissolving in 2% aqueous acetic acid solution and precipitating in 10 wt % NaOH solution. The precipitate was first washed with distilled water to neutrality and then rinsed with acetone. The residue was then vacuum-dried at 70°C for \sim 8 h. HCl was purchased from Merck (India) Ltd. Double distilled water was used throughout the experimental work. Chitosan, a biopolymer of N-deacetylated chitin, has drawn more attention than other biopolymers because of its ability to form specific complexes with the number of ions or dyes, as well as specific complexes with organic molecules.^{15,16} Its degree of deacetylation, determined by the infrared spectroscopy method,¹⁷ was found to be 64%. It's viscosity average molecular weight M_{ν}^{18} was found to be $\approx 500,000$.

Membrane Preparation

A 3 wt % of chitosan was dissolved in 100 mL of 2 wt % of aqueous HCl solution by continuous stirring to get a clear homogeneous polymer solution. The solution was cast on a clean glass plate to a desired thickness, and the solvent was allowed to evaporate initially at room temperature and then the residual solvent was removed by vacuum-drying. The membrane was peeled off from the glass plate and vacuum-dried at ambient temperature.

Selection of the polymer materials for separation is based mainly on three important aspects: the polymer should have high chemical resistance (compatibility), sorption capacity, and good mechanical strength in the solution. It should have good interaction, preferably with one of the components of the mixture for separation.

PV Experiments

A schematic of the bench-scale PV unit is shown in Figure 1. The membrane was supported by a stainless steel screen embedded in a stainless steel porous plate. Gaskets were placed on either side of the membrane, and the sandwich was kept between the glass column couplers and clamped together with external padded flanges. The top half was used as the feed chamber, and the bottom one worked as the permeate chamber. Teflon



Figure 1 Schematic of laboratory PV unit. (a) Manifold of lab scale PV system. (b) Blow-up of the PV cell assembly.

gaskets were used to prevent any leakage. Feed solution flowed from an elevated vessel (A) by gravity. Provision was also made to preheat the feed solution to study the temperature effect. At the beginning of each run, dry membranes having an effective area of 19.4 cm^2 was mounted in the cell. Feed (150 mL) was placed on the top, and this was kept under constant stirring throughout the experiment by applying vacuum from the opposite side. The separation takes place by sorption, diffusion, and desorption steps.¹⁹ The permeate vapors were collected in a cold trap (B)filled with a dry ice-acetone mixture after the membrane was in a steady-state condition. The collected permeate was weighed after allowing it to attain room temperature. The sample was analyzed to estimate the salt content by titration methods. The permeate pressure was measured with an Edward's McLeod gauge.

Generally, in an RO separation process, the reduction in the concentration of salt in permeate, compared with the feed, is expressed in terms of % rejection (% R),²⁰ which is represented as

$$\%R = \left[1 - \left(\frac{C_p}{C_f}\right)\right] 100 \tag{1}$$

where C_p and C_f are concentrations of salts present in permeate (p) and in feed (f), respectively. Similarly, in PV, the difference in salt concentrations of feed and permeate is expressed in % R. The amount of permeate collected per unit area of the membrane per unit time per unit thickness is expressed as the "total flux."

PV runs were performed with the chitosan membrane. Effects of membrane thickness and permeate pressures on the % R of the salts in RL and total flux were studied. Similarly, the effect of salt concentration in feed on flux and rejection were recorded. For all the experiments, the permeate pressure was maintained at 10 mm Hg. The RLs consists of 2 wt % of UDMH/MMH, 8 wt % of NaCl, 2 wt % ammonia, and 1.5 wt % of DMA/MMA. Fresh solutions were used in every experiment. No permeate was analyzed for the first 1 h. By that time, the membrane comes to steady state. Only steady-state permeate fluxes



Figure 2 Effect of membrane thickness on % R. Permeate pressure, 10 mm Hg; NaCl, 7 wt %.

were analyzed by titration methods. Experiments were repeated at least three times, and the average result is reported.

RESULTS AND DISCUSSION

Effect of Variable Parameter

Membrane Thickness

Membrane thickness varied from 25 to 150 μ m. UDMH or MMH RLs were continuously circulated over the membrane.

Figure 2 is a graphical representation of the effect of membrane thickness on % R of UDMH and MMH RLs. This clearly indicates that the % Ris steadily increasing with an increase in membrane thickness, and it reaches maximum for membranes having a thickness $>125 \ \mu m$. Earlier results concluded that chitosan membrane swelled excessively with all these liquids, even though it does not disintegrate like poly (vinyl alcohol). As thickness decreases, % swelling would be even more, and swelling is uniform across its thickness. Membrane behavior is isotropic across the thickness. This isotropic nature of swelling will allow all components to diffuse in freely without any restriction. Because of its larger size, salts do not diffuse as freely as the other liquid components. Hence, relatively salts

should have some restricted movements in the membrane. In PV experiments, membrane facing the permeate side will be in dry condition because the vacuum is continuously applied for desorption of liquid passing through the membrane, and the other side is in equilibrium with feed liquid and will be in wet condition. An isotropically swollen membrane would not restrict complete movement of the salts in it. However, swelling behavior is unisotropic. In the dry part of the membrane, facing the permeate side, salts already diffuse through the swollen upper part of the membrane cannot have free movement and will be retained. As anticipated, because salt does not have any vapor pressure, it does not appear at all in the permeate. But, it can bind with either MMH/ UDMH/hydrazine or water molecules due to the salvation and hydration effects, and lowers the activity of the components in the solution and their vapor pressures. Furthermore, as solution is absorbed within the membrane and remains in the liquid state over a major part of the thickness of the membrane, except near the permit face where vaporization takes place, salt can also diffuse to the depth and may get precipitated out due to saturation. This whole mechanism may have resulted in reduced performance and permselectivity of the membrane. Furthermore, when the membrane thickness increased, the dry part of the region will increase, and it goes on increas-



Figure 3 Effect of permeate pressure on % R. Membrane thickness, 150 μ m; NaCl, 7 wt %.

ing with the increase in membrane thickness. The thickness of the dry portion is that it will decide the characteristics of the permeant. As it goes on increasing, the % R will also increase. After reaching a certain thickness, rejection reaches 100%, and further increase has no effect on rejection. This could even reduce the passage of other liquid components, hence resulting in reduction of the flux. In PV at 10 mm Hg permeate pressure, the optimal thickness of the membrane to get 100% rejection is 135 μ m. But, it is more advisable to run the experiment with a membrane slightly thicker than 135 μ m. It is mentioned that the flux will come down with membrane thickness; but, in the present study, and more because of higher sorption capacities of membranes with the liquids, no major changes in the fluxes were observed. Hence, the results relating the flux versus membrane thickness are not reported. Experimental results of MMH and UDMH show similar trend.

Permeate Pressures

Earlier experiments concluded that the membranes >135 μ m gave 100% rejection. To optimize experimental conditions, the present study was continued with fresh chitosan membrane of 150 μ m thickness. For this set of experiments, the permeate pressure varied from 0.05 to 12 mm Hg. No changes were made in the feed RL compositions. The effect of permeate pressures on % R is shown in Figure 3.

Figure 3 shows that the % R has a direct relation with permeate pressure. It reaches maximum at ~ 8 mm Hg of permeate pressure. At lower pressures, the influence of the driving force for the diffusing molecules in the membrane is high with the result that the components were swept out immediately from the permeate side. This implies that the swelling nature of the membrane is isotropic throughout its thickness, it does not seem to have a dry portion that restricts the movement, and salt molecules pass freely along with the other liquid components. These differences in diffusion rates is a major driving force for the initial rejection of the salts. Hence, initially, membrane gave $\approx 20\%$ rejection at 0.05 mm Hg permeate pressure. The influence of the driving force on diffusing molecules is reduced with increasing permeate pressure. Beyond a certain state, the effect of pressure on diffusing molecules will be negligible. Such a stage cut was observed here at 8 mm Hg of permeate pressure, above which the membrane showed 100% rejection capacity. Similar type of observations were made with UDMH, MMH, and RLs.

If the permeate pressure is increased further, the effect of driving force reduces, and drastically



Figure 4 Effect of permeate pressure on total flux. Membrane thickness, 150 μ m; NaCl, 7 wt %.

decreases, the flux. The results pertaining to the same are shown in Figure 4. In actual practice, it was proved that the sorption value of UDMH in chitosan membrane is greater than MMH, hence, UDMH RL should give higher flux. This apparent discrepancy is mainly explained by the fact that MMH has higher vapour pressures and diffusion coefficient than UDMH, because of its lesser molecular size than that of UDMH. Results reported by several researchers clearly state that permeability is a product of sorption and diffusion coefficients. Species having higher sorption and the lower diffusion rates cannot pass as freely as the other species having medium sorption and higher diffusion rates. In the present case, MMH has a higher diffusion coefficient (because of its smaller size) that results in increased flux with MMH RL, than that of UDMH. The same reasons can be extended for the deviations in rejection values with MMH and UDMH. However, because the concentrations of UDMH and MMH in the RLs are low (≈ 2 wt %), the deviations in experimental results are small.

Salt Concentration

Figures 5 and 6 are graphical representations of the effect of the salt concentration on both the % R and flux, respectively, for UDMH and MMH RLs. In this study, membranes used were 150 μ m thickness, and the permeate pressure was main-

tained at 10 mm Hg. Earlier experiments confirmed that these are the optimal conditions in obtaining 100% rejection. As shown, % R reduces with an increase in the concentration of the salt in feed. When the salt concentration was < 10 wt %, as stated in the previously described sections, the membrane gave 100% rejection. As concentration increases above 10 wt %, the rejection starts decreasing. The flux decreased steadily up to 17 wt % of the salt content and more sharply beyond this value.

As shown in Figure 6, the flux decreases with an increase in salt content of feed plausibly due to concentration polarization. At higher concentrations, the salts diffusing along with the other components first block the channels from where the liquid molecule are entering the membrane, thereby reducing the flux. After initial blocking, most of the available free spaces on the surface of the membrane salt molecules start moving further and facilitate transfer of incoming molecules. In this way, the transport of salt molecules continues until the "front" reaches the other side of the membrane, where it gets desorbed. If this understanding is correct, one would observe the deviations in fluxes even before the drop in the % R. Experimental results confirm this. The flux values for UDMH and MMH constantly decrease as the salt content of feed increases. A slight improvement in the rejection and flux were ob-



Figure 5 Effect of salt concentration in the feed on % R. Membrane thickness, 150 μ m; permeate pressure, 10 mm Hg.

served when an additional stirring arrangement was made at just above the membrane in the feed chamber. This hinders the rapid settling of salt component over the membrane.

Maximum deviation in the rejection was found only when the salt concentration exceeds 17 wt %, but a sharp decrease in flux was observed at the salt concentrations of ≈ 15 wt % and above. Another observation from Figure 6 is that the flux varies steadily with feed concentration, whereas the rejection varies starting from 10 wt % of the salt content. Below this concentration, 100% rejection was observed. These two experimental observations from the figures support the comments made previously on flux. Based on flux response, it should be possible to predict deviations on % R.



Figure 6 Effect of salt concentration in the feed on total flux. Membrane thickness, 150 μ m; permeate pressure, 10 mm Hg.

CONCLUSIONS

Chitosan membrane is most suitable for the desalting of the UDMH and MMH RLs. RO and ED techniques failed to separate salts completely from these RLs, hence an attempt was made with PV membrane separation process. % R, for both UDMH and MMH RLs, increases with the membrane thickness, and it reaches a maximum at 135 μ m. Due to excess swelling of the membrane, maximum deviations in the PV fluxes were not observed. At a constant membrane thickness, the % R has a direct relation with the permeate pressure until it reaches maximum. Flux is inversely proportional to the permeate pressure. It decreases steadily with an increase in permeate pressure. Due to concentration polarization, both flux and % R decrease with the increase in salt concentration in feed. Experimental results with the chitosan membrane clearly proved that, at 10 mm Hg permeate pressure, a membrane with 150 μ m thickness gives 100% rejection, with the RLs containing 2 wt % of UDMH or MMH and 10 wt % of NaCl salts in it. Hence, PV is more suitable than RO and ED membrane techniques. Higher concentrations of the salts in the feed RLs effect both the overall flux and salt rejection. Flux is more sensitive to the salt concentration at feed side, and rejection does not vary below the 10 wt % salt concentrations.

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