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Polymer 40 (1999) 1159–1165

polymer

D.s.c studies of states of water, hydrazine and hydrazine hydrate in ethylcellulose membrane[1]

R. Ravindra[a], Kameswara R. Krovvidi[a], A.A. Khan[a,]*, A. Kameswara Rao[b]

[a]Membrane Separations Group, Chemical Engineering Division, I.I.C.T., Hyderabad 500 007, India
[b]Department of Polymer Science and Technology, S. K. University, Anantapur 515 003, India

Received 1 May 1997; revised 9 February 1998; accepted 23 March 1998

Abstract

Studies of the states of water, hydrazine and hydrated hydrazine in ethylcellulose membrane were made for various mass fractions of solvents using differential scanning calorimetry (d.s.c.). Four or five energetically distinct states of these species in the membrane were identified and their quantitative estimations made. A new peak of enthalpy of mixing was identified at higher temperatures. Such a significant peak has not been previously recorded or discovered by d.s.c. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: States of solvent; Ethylcellulose; Water

1. Introduction

The states of a solvent in a polymer constitutes an important and interesting field of study for membrane separation processes. Sometimes separation mechanisms can be identified by estimating the states of solvent in the membrane [1]. The solvent which swells but does not dissolve the polymeric membrane exists in three or four states throughout the membrane matrix. These are free, interacting or adsorbed and bound states. These states will also have different thermal transitions and hence their quantitative estimation is possible by using differential scanning calorimetry (d.s.c.). The bound state of the solvent in the membrane will often govern the separation process. Normally, the bound state will exist in two forms: freezable and non-freezable. The former is estimated from the thermal transitional calorimetric data and the latter is obtained by difference or other indirect methods.

Quantitative measurements of water or other components in the membrane can be made by Fourier transform infrared [2–4] and nuclear magnetic resonance spectroscopy [5–7], d.s.c [8,9] and Raman spectroscopic [10,11] methods. Among the available procedures d.s.c. gives greater accuracy and ease of compilation of data.

Hydrazine (N_2H_4) is a well-known liquid propellant. It forms an azeotrope with water at a composition of 71.5 wt% N_2H_4 and it also forms the hydrate with a molecular formula N_2H_5OH [12]. Hydrazine has many other important applications such as oxygen scavenger for boiler feed water. It is used in the preparation of drug intermediates and in polymerization reactions. We found that ethylcellulose (EC) is a chemically resistant polymer suitable for the separation of water from the azeotrope by the pervaporation method [13]. Interaction, diffusion and ageing studies of water, hydrazine and hydrazine hydrate with the EC membrane have also been made [14]. The present paper discusses the states of water, hydrazine and hydrazine hydrate in EC as studied by analysing data obtained from the d.s.c. analysis.

2. Experimental

2.1. Materials

The polymer used in the study was 48–49% ethoxy content ethylcellulose from Loba Chemie (Bombay, India). Its M_n (63 156) and M_w (89 448) were determined by gas permeation chromatography using polystyrene as the standard. Toluene, a solvent for EC, was also purchased from Loba Chemie, India, and was used as received without any further purification. Hydrazine and hydrazine hydrate were kindly supplied by VSSC (ISRO), Thiruvananthapuram, India. Double distilled deionized water was used in the experiments.

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* Corresponding author.
[1] I.I.C.T. Communication No. 3752

PII S0032-3861(98)00274-2

Table 1
Amounts and various states of water in ethylcellulose membrane

Sorption of membrane (%) (1)	Freezable bound state of water (mg/wt%) (2)	Freezable intermediate state of water (mg/wt%) (3)	Free state of water (mg/wt%) (4)	Non-freezing water (mg/wt%) (5)
2.44	0.0245/10.00	0.0392/14.79	0.0221/9.02	0.1593/65.00
4.38	0.0991/28.55	0.0362/10.35	0.1024/29.27	0.114/31.83
6.10	0.1447/30.10	0.0393/08.35	0.1470/31.18	0.1423/30.27
10.83	0.1621/24.94	0.0341/05.25	0.2977/45.80	0.1561/24.03
15.49	0.1711/20.08	0.3421/04.02	0.4981/58.46	0.1571/18.44
50.00	← 1.0906/87.25[a] →			0.1594/12.75

[a] Sum of bound, freezing intermediate and free water in the membrane

2.2. Film preparation

Clear polymer solution (15 wt% dissolved in toluene) was used for casting a membrane of the desired thickness on a clean glass plate. The solvent was evaporated at room temperature for 10 h, and then the plate was kept under vacuum at 60°C for complete removal of the solvent. The thickness of the dry membrane was found to be 80 μm (measured with a micrometer, accuracy: ±1 μm), and pieces of the same membrane were used in the experiments.

2.3. Sample preparation

The thermal properties of the solvents in the EC membrane were measured on a Perkin-Elmer (USA) DSC-7 model instrument. Membranes with different amounts of residual solvent can be prepared either by drying the presoaked wet membrane under vacuum for a set time (for this the membrane should be initially in steady state equilibrium with the solvent), or by immersing an initially totally dry membrane in the solvents for different times. The membrane is taken out and the excess adhering solvent removed by blotting with a filter paper. For the present work, the former procedure was adopted. The solvent containing the membrane was transferred into an aluminium sample pan with a lid, and was hermetically sealed to prevent leakage. The pan had been boiled previously for several hours in distilled water to eliminate any possibility of the formation of aluminium oxides during the experiment.

D.s.c. scans were taken from sub-ambient temperatures starting from −60°C. The head-space over the sample holder was maintained in a flowing pure nitrogen atmosphere. The rate of heating was kept at 5°C min^{-1}. The maximum temperature was set at 25°C. Samples were kept initially at −60°C for 10–15 min before starting the scans to create identical conditions to those in the instrument chamber.

3. Results

It is a general observation that solvents which do not swell the polymer appreciably are characterized by interactions with low energetic states [15]. Likewise, the mutual interactions of solvent molecules are characterized by exchange of higher quanta of energy, and the bulk solvent melts at higher temperatures than the solvent present in the membrane. This state of the solvent in the polymer matrix is referred to as the *free state of the solvent* and is marked as (C) in the d.s.c. spectra (column 4 in Tables 1 and 2). A large number of investigators have concluded that the structure of the solvent inside the membrane was slightly clustered and weakly hydrogen bonded to the surface hydroxyl groups [11,16], and that the interacting or adsorbed solvent melts at somewhat lower temperatures than in the bulk. This state is identified as the *freezing intermediate state of the solvent*, and is represented as (B) in the d.s.c. spectra (column 3 in Tables 1 and 2). Diffusion of solvent molecules in the

Table 2
Amounts and states of hydrazine in ethylcellulose membrane

Sorption of membrane (%) (1a)	Hydrazine content at sub-ambient temperature (mg/wt%) (1b)	Freezable bound state of hydrazine (mg/wt%) (2)	Freezable intermediate state of hydrazine (mg/wt%) (3)	Free state of hydrazine (mg/wt%) (4)	Non-freezing hydrazine (mg/wt%) (5)
5.91	0.007/01.51	0.023/5.00	← 0.0338/75.00[a] →		0.083/18.49
17.54	0.1648/20.29	0.0487/6.00	0.175/21.5	1.287/35.33	0.136/16.88
47.19	0.1472/05.75	← 1.975/77.16[b] →			0.147/05.75

[a] Sum of interacting and free hydrazine in the membrane
[b] Sum of bound, intermediate and free hydrazine in the membrane

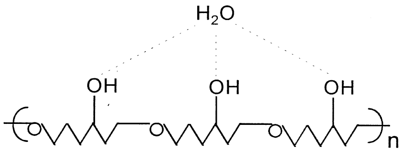

Fig. 1. Non-freezable bound state of water in EC membrane matrix.

amorphous regions of the polymer represents the least energy variation region and the energy exchanged during their melt transition is lower than in the transitional states B and C and is called the *freezable bound state of the solvent* (column 2 in Tables 1 and 2). This state is identified as (A) in the d.s.c. transitional spectra [1,17].

In brief, at low concentrations, the solvent molecules in polymers will exists in an unassociated (non-clustered) bound form and many authors [18,19] showed that the solvent molecule in the polymer is in an unassociated form up to a concentration of one solvent molecule per two to three functional groups present on the repeating units as shown in Fig. 1. Such a state is referred to as the non-freezing bound state of the solvent. Above a characteristic concentration of solvent for each polymer, a number of molecules (≥ 1) are attached to sites of the polymer and thus form a solvent (water-like) cluster, pictorially represented in Fig. 2, where the ethylcellulose repeating unit is shown loosely bound to water molecule with X varying from 1,2,…. This state is referred to as the freezing intermediate state of the solvent. As the concentration increases, further sorbed solvent forms bridges in between the previously clustered form in the freezing intermediate state as shown in Fig. 3, and this state is referred to as the freezable bound state of the solvent. Naturally, the unassociated solvent molecules require less energy compared to the energy required by solvent existing in the form of clusters and bridged clusters and hence the former will melt at lower temperatures and the latter at higher temperatures.

Representative d.s.c. heating curves for the water/EC and hydrazine/EC systems are shown in Figs. 4 and 5 respectively. In each spectrum, the solvent content is different and is defined as

$$W_c = (W_w/W_s) \times 100 \quad (1)$$

where W_c is the percentage weight of solvent in the membrane and W_w and W_s are the weights of the solvent in the wet and dry EC membrane respectively. In each spectrum the letters A, B, C represent melting endotherms of bound, interacting or adsorbed, and free states of solvent respectively.

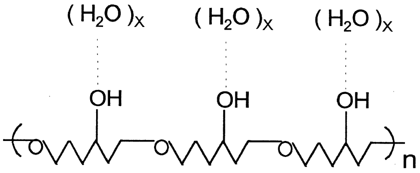

Fig. 2. Freezable intermediate state of solvent in EC membrane matrix.

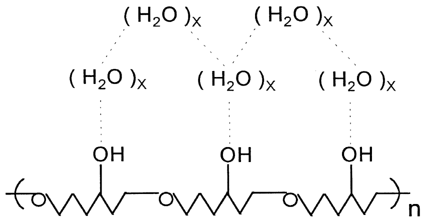

Fig. 3. Freezable bound state of solvent in EC membrane matrix.

Quantitative estimation of each state of freezable solvent can be made from the melting curves by [17].

$$W_i = 100(Q_i/H_f) \quad (2)$$

where W_i is the percentage weight of the state of water in the individual peaks (A, B, C), Q_i is the total measured heat of transition under the peak, and H_f is the enthalpy of solid–liquid transition of pure liquid (hydrazine or water). The amount of non-freezing solvent (W_{nf}) can be obtained from

$$W_{nf} = W_T - (W_f + W_{fb} + W_{ad}) \quad (3)$$

where W_f, W_{fb} and W_{ad} are the free, freezable bound and freezable intermediate (interacting) components of the solvent in percentage weight respectively. W_T, the total solvent content in the membrane, can be determined by Eq. (1). The values in Eq. (1) are determined by puncturing the initially pre-weighed pan with the wet sample used in the experiment, and removing the residual solvent by vacuum-drying for several hours and noting the weight of pan without any solvent. (The weight of empty pan is very important and is to be accurately measured for the exact W_T).

In the hydrazine/EC system, it can be seen from Fig. 5 that some transitions occur at sub-ambient temperatures around −55°C. These peaks are the melt transitions of hydrazine coupled with traces of water, i.e. less than 4%.

Fig. 6 shows the d.s.c. spectrum of the hydrazine hydrate/EC system. This has transitional states in the range −5 to 5°C as well as at −60 to −45°C. The former are due to melting of both water and hydrazine, and the latter are the melting transitions of the hydrazine–water mixture.

4. Discussion

4.1. States of water

State C in Fig. 4 represents the free water content in the EC membrane. The peak is sharp and shifts towards lower temperatures with increase in percentage of water. When the water present is in excess, the free water behaves like bulk water and the melting transition shifts towards 0°C (the melting temperature of pure water) from 5°C at the initial transition. This state exists only when the water content is above the equilibrium percentage of sorption (which is 3.4 wt% for EC/water) and hence it was not observed for

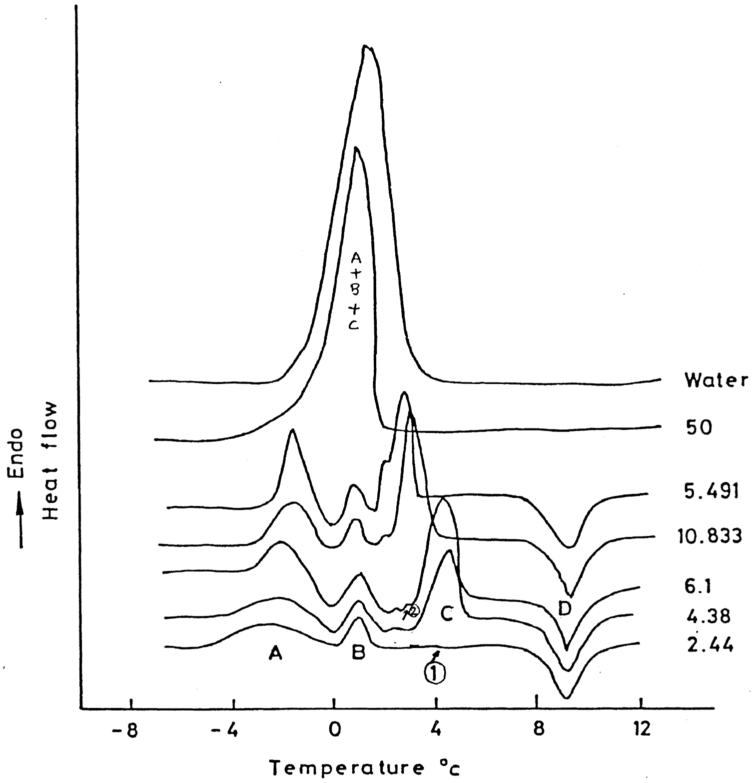

Fig. 4. D.s.c. spectra of ethylcellulose–water system. Number at right side is wt% of water in membrane.

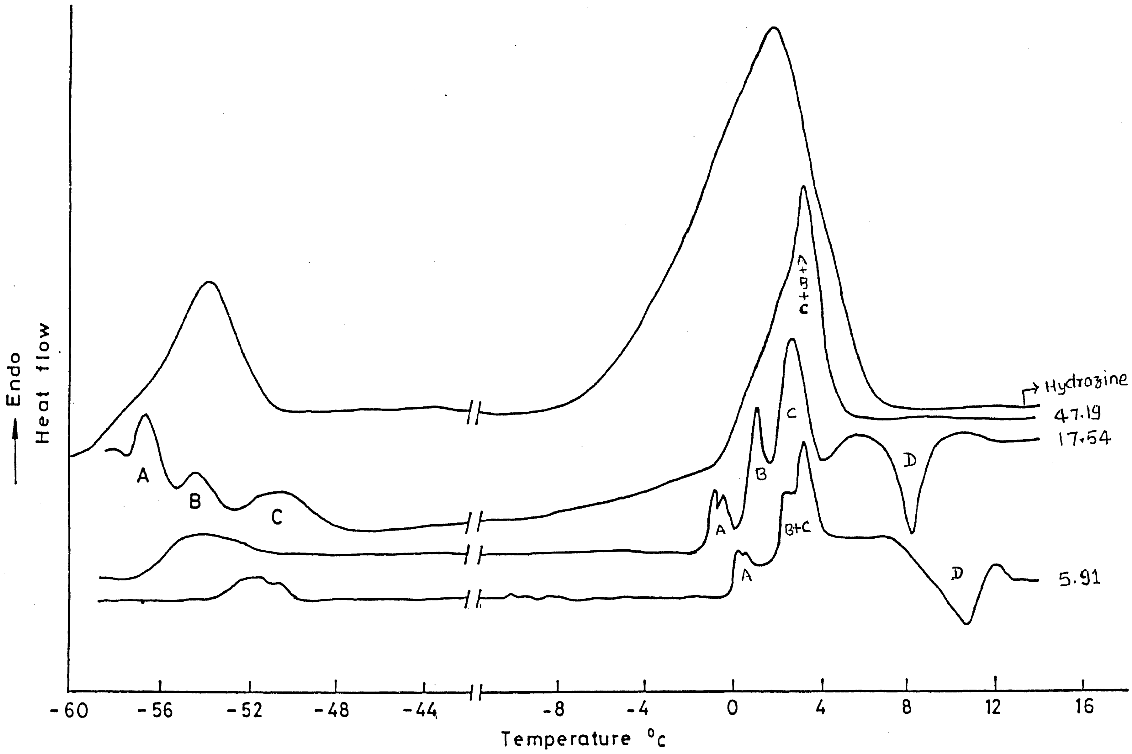

Fig. 5. D.s.c. spectra of ethylcellulose–hydrazine system. Number at right side is wt% of hydrazine in membrane.

example at 2.44 wt% water in the EC membrane where only a small shoulder appears shown by an arrow and number 1 in Fig. 4. A small hump at just the beginning of the free water transition, represented by the arrow and numbered 2 may be due to cold crystallization of the water/polymer system [9].

The melting of the freezing intermediate state of water in EC is seen at about 1°C. The peak B is well defined and has not been influenced by the total water content in the membrane, i.e. the position and area of its appearance is the same at all concentrations. In general, as reported by some authors [18], the amount of water present in this state increases with the increase of total percentage of water in the membrane. This statement may be true for the polymers having considerable hydrophilicity. In the present case the amount of water present in this state does not seem to vary appreciably (Table 1, column 3) since the membrane used in the present study absorbs relatively less water, interacts with water only through hydroxyl (OH) functional groups freely and no other functional groups are available (only the water concentration is varying but not the membrane area or volume and hence a fixed number of OH only are present) to interact with the extra water molecules. The replacement of water molecules by more of the same is possible but still the total amount remained the same.

A crucial state of water in the membrane can be seen between -4 to 0°C, the so-called freezing bound state of water. When the total water content in the membrane increases, this peak A becomes sharper and the water content present in this state also increases. The peak is present at all concentrations of water in the membrane except at very high concentrations. This trend is shown in Fig. 4 where at 50% total water, the peaks of bound and interacting or sorbed states lose their identity (but each state will never lose its significance) and merge with the peak of the free transitional state of water. The quantities of various states of water at different total water contents are shown in Table 1.

4.2. States of hydrazine

The EC membrane with hydrazine concentrations slightly below 5.91 wt% and much above 17.54 wt% (the equilibrium sorption is 7.96 wt%) and extremely high amounts, i.e. up to 47.19 wt%, are tested by d.s.c. The resulting spectra are shown in Fig. 5. The peak represented as C indicates the free state of hydrazine in the membrane. This thermal transition exists even below the equilibrium sorption percentage and has not been observed in the case of the water/EC system even below its equilibrium sorption level. The reasons for this phenomenon are discussed as follows.

In our experiments, vacuum-dried (sorbed) membranes were used. During the drying process, the permeability of the component controls transport of solvent molecules across the polymer matrix. The permeability coefficient is defined as the product of sorption (S°) and diffusion (D°) coefficients given by

$$P^\circ = S^\circ \times D^\circ$$

The overall selectivity (α), a relative permeability term, is given by

$$\alpha = P^\circ_1/P^\circ_2 = (S^\circ_1 \times D^\circ_1)/(S^\circ_2 \times D^\circ_2)$$

where subscripts 1 and 2 represent water and hydrazine respectively. From pervaporation experiments, the value of α for the hydrazine–water system is 3.94. However, since $S^\circ_1 < S^\circ_2$, and $P^\circ_1 > P^\circ_2$ (because $\alpha > 1$) this implies that $D^\circ_1 > D^\circ_2$. Kinetic sorption experiments were performed to prove this by plotting reduced sorption curves [20] and the values of D° were found to be 2.57×10^{-8} and $0.28 \times 10^{-8}\ \mathrm{cm^2\,s^{-1}}$ for water and hydrazine respectively. Because of the smaller diffusivity value of hydrazine in the membrane, it diffuses relatively slowly from bulk solution and exists at the surface layers of the membrane. This may explain the appearance of the free state of hydrazine below the equilibrium sorption percentage. The fact that the membrane should contain less bound hydrazine is borne out by the calculated amounts of hydrazine in bound transitional states (A). Initially, this peak is broad and becomes sharper with excess hydrazine. The results are given in Table 2. The results also confirm the above proposition that less hydrazine will diffuse inside the membrane and larger amounts will remain in the free state.

The thermal transitional peak (B) corresponding to interaction or adsorption layer is seen in the range of 1–2.5°C. In 5.91 wt% hydrazine containing membrane, this peak has less resolution and largely remains in a shoulder form and hence the quantitative estimation has not been made partly due to difficulties in drawing a baseline on the d.s.c. spectra. In a membrane containing 17.54% hydrazine a well-resolved peak (B) has been obtained. At this concentration the membrane has 0.2869 mg of interacting hydrazine which is higher than the interacting water content (0.0342 mg, Table 1) in the membrane having the 15.47% total water content. In brief, hydrazine is largely influencing the functional groups thereby channelling the water molecules to diffuse, which has been shown to be valid in an earlier study [13,14]. At the highest content of hydrazine (17.57 wt%), the peaks of bound and interacting states merge into the peak of free transitional states that results in the formation of a broad single peak.

A small peak at sub-ambient temperatures of -58 to -50°C is the melting transition of hydrazine coupled with some traces ($< 4\%$) of water, i.e. the responses are of water and hydrazine solution. Initially, it is very broad and becomes sharp with an increase of hydrazine, and at higher concentration, the single peak splits into three states but remains poorly resolved. This may be due to the re-formation of free, interacting, and bound states within the membrane at sub-ambient temperatures. This trend is in contrast to that taking place at 0°C. Quantitative evaluations of each peak at sub-ambient temperature are not possible. The

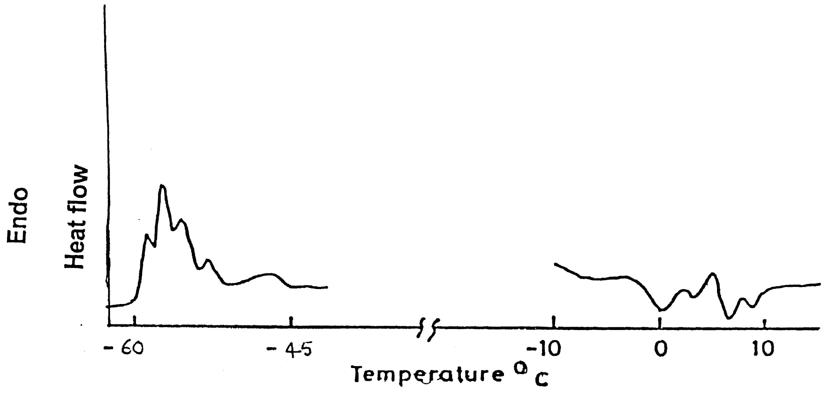

Fig. 6. D.s.c. spectra of ethylcellulose–hydrazine hydrate system.

reason is explained below for the hydrazine hydrate system. The amounts of hydrazine and water present in these regions are listed in Table 2.

Quantitative estimations for the hydrazine hydrate/EC system using the d.s.c. spectra shown in Fig. 6 are not possible at its equilibrium percentage of sorption because the actual melting temperatures of bulk water and hydrazine are 0 and 2°C respectively. In this temperature range the transitions for hydrazine hydrate/EC also occur, and hence characterization of individual peaks becomes problematic.

One of the most interesting observations we find from the d.s.c. spectra of pure water and pure hydrazine in EC is the appearance of a new exothermic transitional peak at around 8–10°C. Such a peak was not reported by others who have done extensive work on states of solvents in polymers using d.s.c [21–23]. To analyse the peak, we calculated the '$J\ g^{-1}$' values which are in the range −15 to $-8\ J\ g^{-1}$. These values are close to the heats of mixing [24]. The negative $J\ g^{-1}$ value increases as the amount of solvent in the polymer increases and attains a value of zero as the polymer is fully saturated with the solvent. This is expected because with large quantities available the solvent does not come into contact with any unsaturated parts of the polymer matrix and hence no thermal effects are observed. The extent of saturation of the polymer is very important in separation processes as the permeation of mixtures containing even one penetrant which swells the polymer is very complex. In the presence of the swelling penetrant the flux of other penetrants increases and may decrease or increase the selectivity. If the swelling component is also faster diffusing then the selectivity decreases. When it has lower diffusivity, it would interact more with the polymer functional group(s) and allow other penetrant to flow freely and the membrane is more selective towards the other component. The necessary condition for this is that the approximate percentage of swelling should be around 10. Beyond this percentage there exists a possibility that both the components pass through the membrane freely which results in high flux and poor selectivity.

5. Conclusions

D.s.c. spectra of water/EC, hydrazine/EC and hydrazine hydrate/EC systems have been obtained. Below the equilibrium sorption concentrations, water does not give any free transitional peak whereas hydrazine gives a well-defined peak of the same type. This is due to hydrazine's lower diffusion coefficient than that of water. The peak sharply increases with solvent concentration. The transitional peak due to the observed interactions of water and hydrazine with functional groups in EC is only slightly influenced by the concentrations of solvents and in this state the binding capacity of hydrazine is far greater than water which prevents free diffusion of the water molecules. Hence the membrane has a good overall selectivity to water. At very high concentrations of solvents, peaks corresponding to free, bound, and interacted/adsorbed solvent merge together resulting in a single peak. Under these conditions the membrane also has a larger quantity of bulk solvent (unassociated) along with free, bound and interacting states. Hence, its melt transitions will be almost equal to that of the pure solvent.

A new exothermic transitional peak has been observed with pure water and pure hydrazine in EC membrane which is attributed to the heat of dilution or mixing as the saturation of the polymer takes place with the solvent.

Acknowledgements

The authors are grateful to the VSSC-ISRO, India, for funding the present work under their Respond Program, and gratefully acknowledge the help from their colleagues in the experimental work using d.s.c. One of the authors (R. R.) is grateful to the Council of Scientific and Industrial Research (CSIR), India, for the award of Senior Research Fellowship.

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