A calorimetric study of various alcohols in a poly(dimethylsiloxane) membrane‡

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The state of various alcohols with carbon numbers from one to eight in a poly(dimethylsiloxane) (PDMS) membrane was investigated by d.s.c. Methanol, ethanol, 2-propanol, 1-butanol and 1-pentanol were present in the PDMS membrane in the bound state as well as in the bulk state, while 1-octanol was comprised only of free 1-octanol. The amount of bound alcohol increased with increase in the carbon number up to four and then decreased with further increase in the carbon number. We concluded that the interaction between the methyl group in the PDMS membrane and the alkyl moiety in the alcohol was a specific interaction to form bound alcohol in the PDMS membrane.

(Keywords: differential scanning calorimetry; bound state; bulk (free) state; melting point suppression; poly(dimethylsiloxane); alcohol)

Introduction

Interaction between macromolecules and low molecular weight compounds, in gas (or vapour)[1–8] as well as liquid phases[9–15], has attracted scientific interest for many years. In particular, studies on the effect of low molecular weight compounds on polymer properties are required for the development of polymer materials for separation, packaging, coating and engineering plastics.

Attention has also been paid to the state of permeants in polymeric membranes, in other words, to the interaction between polymeric membranes and permeants, in connection with membrane separation research[16–21]. In our studies, we first reported that organic liquids such as methanol[18], ethanol[19], 2-propanol[20] and cyclohexane[21] were present in a poly(dimethylsiloxane) (PDMS) membrane in the bound state as well as in the bulk state. In other words, melting points of these alcohols were suppressed in the membrane. Furthermore, we also observed an increase in saturation vapour pressure of alcohols in the membrane in pervaporation studies[18–20].

The present paper is an extension of previous research, where organic permeants such as methanol[18], ethanol[19], 2-propanol[20] and cyclohexane[21] showed anomalous physico-chemical properties in a PDMS membrane. In particular, our attention is focused on the melting point suppression of the organic permeant in a PDMS membrane. The melting behaviour of alcohols with carbon numbers from one to eight is investigated.

Experimental

Alcohols including 1-butanol, 1-pentanol and 1-octanol were purified in the usual manner[22] PDMS membranes (7.62×10^{-5} m thick), supplied by General Electric Co., were used for membrane samples.

The state of alcohols in the membrane was studied by a SEIKO DSC 200 coupled to a SSC 5000. After the membrane was dried *in vacuo* at 56°C for 2 days, the dried membrane sample was immersed in the alcohols at 25°C for at least 4 days. After equilibrium was attained, membrane to be studied by d.s.c. was blotted with a filter paper to remove excess liquid and transferred to an aluminium pan which was hermetically sealed. The sample was cooled to -160°C and then heated at a rate of 10°C min^{-1} to 20°C. Nitrogen at a flow rate of 40 $\mathrm{cm}^3\ \mathrm{min}^{-1}$ was used throughout the d.s.c. measurements.

Results and discussion

Figures 1–3 show the relationships between the change in enthalpy (ΔH) and the alcohol content in the membrane. The plots for each alcohol are linear with a slope of 125.4 J g^{-1} for 1-butanol (*Figure 1*), 119.0 J g^{-1} for 1-pentanol (*Figure 2*) and 176.7 J g^{-1} for 1-octanol (*Figure 3*) by the method of least squares. The slopes of 1-butanol and 1-pentanol are approximately equal to the literature values[22] of 126.4 and 119.1 J g^{-1}, respectively. The heat of melting for 1-octanol was also determined from pure 1-octanol when the amount of 1-octanol was in the range 0.89–3.26 mg. In the literature[22,23], the heat of fusion for 1-octanol was reported to be 324.4 J g^{-1} by theoretical calculation using the heat of sublimation and that of vaporization.

The straight lines of the 1-butanol/PDMS and 1-pentanol/PDMS systems do not pass through the origin, while that of 1-octanol/PDMS system does pass through the origin. The intercepts of the straight lines for 1-butanol and 1-pentanol at $\Delta H = 0$ should coincide with the amount of bound alcohol. The amounts of bound 1-butanol and 1-pentanol are, respectively, 1.02 and 0.14 g g^{-1} membrane according to *Figures 1* and *2*.

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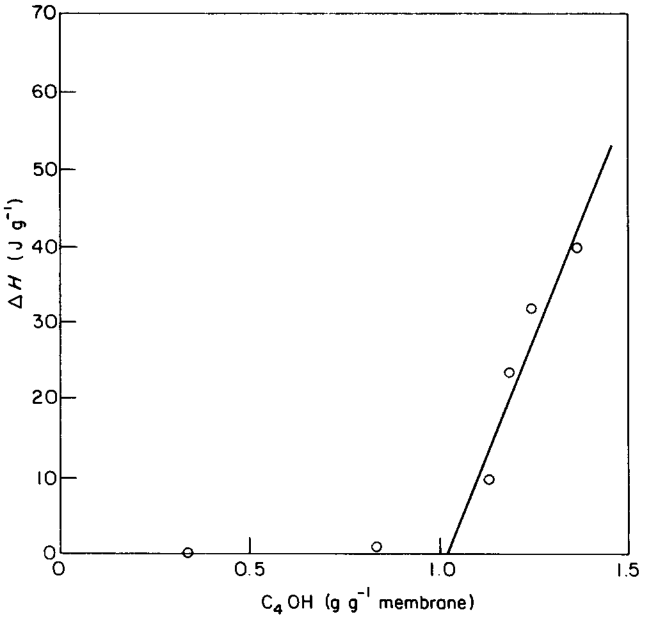

Figure 1 Relationship between change in enthalpy for 1-butanol in a PDMS membrane and total 1-butanol content in the membrane

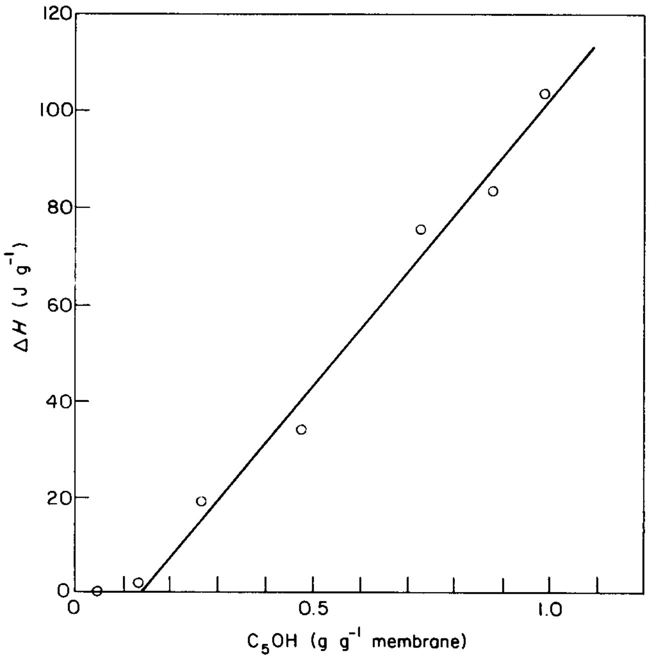

Figure 2 Relationship between change in enthalpy for 1-pentanol in a PDMS membrane and total 1-pentanol content in the membrane

Table 1 Bound permeant in the PDMS membrane

	Amount of bound permeant		
	(g g^{-1} membrane)	(mmol g^{-1} membrane)	Surface area ratio^a (A_{R-}/A_{-OH})
Water	0^b	0^b	0
Methanol	0.10^c	3.1^c	1.5^c
2-Propanol	0.47^b	7.8^b	3.3^c
1-Butanol	1.02	13.8	4.2
1-Pentanol	0.14	1.6	5.2
1-Octanol	0	0	7.9

^{a}Calculated from data provided in ref. 24
^{b}From ref. 20
^{c}From ref. 18

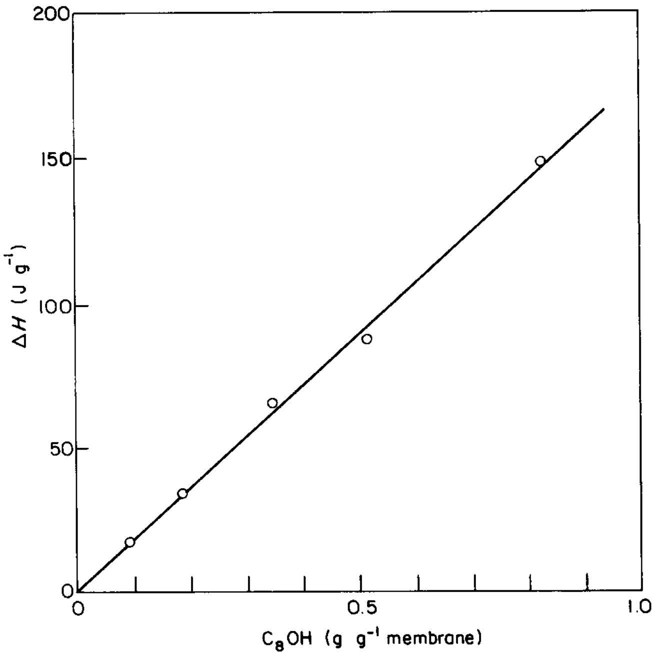

Figure 3 Relationship between change in enthalpy for 1-octanol in a PDMS membrane and total 1-octanol content in the membrane

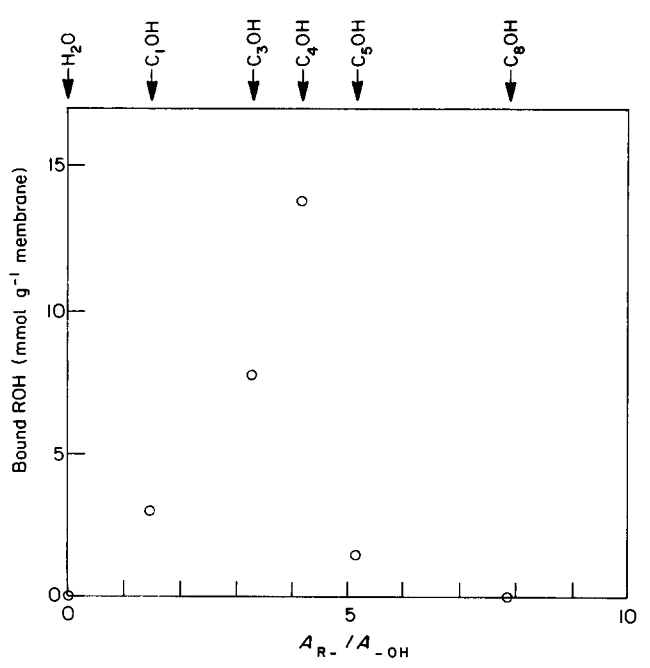

Figure 4 Relationship between amount of bound permeant in a PDMS membrane and the surface area ratio (A_{R-}/A_{-OH}) of the permeant

These results suggest that there are specific interactions between the membrane and alcohols such as 1-butanol and 1-pentanol. On the other hand, it can be concluded that all the 1-octanol in the PDMS membrane is assigned to free (bulk) 1-octanol. This indicates that there is no observable interaction between the membrane and 1-octanol.

In order to compare various alcohol/PDMS systems, the amount of bound alcohol and the ratio of the surface area of the alkyl moiety to that of the hydroxyl group in the alcohol[24] are summarized in *Table 1* together with the values for water. These values are shown diagrammatically in *Figure 4*. Based on previous results[18–20], it was expected that both 1-butanol and

1-pentanol, which were present in the bound as well as in the bulk state in the membrane, would show an increase in the saturation vapour pressure in the PDMS membrane by the pervaporation technique. However, saturation vapour pressures of bulk 1-butanol and 1-pentanol at 25°C were only 824 Pa (6.18 mmHg)[22] and 313 Pa (2.35 mmHg)[22], respectively. These values were too low to allow the authors to obtain any meaningful results concerning the saturation vapour pressure increase in pervaporation.

It can be seen from *Figure 4* that the amount of bound alcohol increases with an increase in the ratio of surface area of the alkyl moiety to that of the hydroxyl group up to a carbon number of four and then decreases with a further increase in the surface area ratio. As a result, 1-octanol is comprised only of free 1-octanol in the PDMS membrane like water molecules[20]. The increase in the surface area ratio parallels the increase in carbon number and represents the increase in hydrophobicity of the alcohol. The following two factors are considered effective in the formation of bound alcohol in the membrane: (1) the interaction between hydrophobic moieties in the membrane and alcohol becomes stronger as the carbon number of permeant alcohol increases; (2) an increase in the carbon number of the permeant alcohol hinders the formation of bound alcohol because of the fluctuation of the long alkyl chain. Apparently the above two effects were superimposed when the carbon number of the permeant was increased and led to the relationship shown in *Table 1* and *Figure 4*. The interaction between the methyl group in the PDMS membrane and alkyl moiety in the alcohol seems to be a specific interaction to form bound alcohol in the PDMS membrane. The apparent saturation vapour pressure of permeant alcohol in the membrane, which was evaluated by pervaporation experiments, can also support the above conclusion. The saturation vapour pressures of methanol[18], ethanol[19] and 2-propanol[20] were higher than those of bulk alcohols by the pervaporation technique, while the change in the saturation vapour pressure of cyclohexane was not observable in the cyclohexane/PDMS system[21]. If the dominant interaction to form bound alcohol was a hydrogen-bonding interaction between the hydroxyl group in the alcohol and the oxygen atom in the repeat unit of PDMS, an increase in saturation vapour pressure in the membrane would not occur because the hydrogen-bonding interaction is much stronger than the interaction between hydrophobic moieties.

Through the present work and previous studies[18–21] on the state of permeant in the PDMS membrane, we conclude that the formation of bound permeant in the PDMS membrane was caused by the interaction between hydrophobic moieties of the permeant and those of the membrane.

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