Diffusivity of aliphatic alcohols through polyurethane membrane

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Diffusivity of ten aliphatic alcohols through a polyurethane membrane has been studied by monitoring the dimensional response of polymer. It is found that the lower alcohols show higher diffusivities than the higher homologues. There appears to be no quantitative correlation of swelling coefficient or percentage increase in thickness of the membrane with diffusivity.

Presently we have assessed the hydrodynamic resistivity and dimensional response of a commercially available polyurethane membrane towards a number of aliphatic alcohols. Such membranes are finding increasing use in industry. The properties which are relevant to this approach are diffusivity, swelling parameter and the dimensional response of the polymer. Attempts have been made to analyse the swelling results in terms of the Flory-Rehner model.

Experimental

The reagent grade solvents were distilled twice before use. Polyurethane was purchased from PSI, Austin, Texas. The base polymer used was a Vibramethene-bis-(o-chloroaniline). The swelling experiments were performed on uniformly cut circular samples (diameter = 1.94 cm). The thickness of the membrane was measured at several points using a precision micrometer. The samples were then soaked at 25°C in test liquids taken in specially designed screw-tight metal-capped bottles. At periodic intervals, the membranes were removed, dried, their thicknesses measured at several points and immediately placed back into the test bottles. For each sorbent, at least two independent experiments were performed until the membranes attained maximum swelling.

Results and discussion

The percentage increase in thickness \( L_t = (\Delta L / L_0) \times 100 \) was measured from the change in thickness \( \Delta L \) from the initial thickness \( L_0 \). For many polymer-solvent systems, the diffusion coefficient \( D \) is a function of penetrant concentration and requires a solution to Fick's second law of diffusion:

\[
\frac{\partial C}{\partial t} = D(C) \frac{\partial^2 C}{\partial x^2}
\]

where \( C \) is penetrant concentration, \( t \) is the time, \( x \) is the distance along the direction of diffusion and \( D(C) \) is the concentration-dependent differential diffusion coefficient. Since sorption data do not reveal the boundary conditions, Eq. (1) cannot be solved in a straightforward manner. Other mathematical approaches must be used to evaluate \( D \), which can be considered as some average value depending upon the specific method of analysis. In this note the diffusion coefficient has been calculated from sorption data at early stages of diffusion using Eq. (2):

\[
D(\text{cm}^2/\text{s}) = \pi (h/4 L_m)^2/60
\]

where \( h \) is sample thickness (0.245 cm), \( L_m \) is the maximum increase in thickness after saturation and \( \theta \) is the slope as obtained from the initial linear portion of the plot of \( L_t \) versus square root of time \( (t^{1/2}) \). Such plots for various solvent-polyurethane systems are given in Figs 1 and 2; the computed diffusivities are given in Table 1. These results suggest an inverse dependence of solvent molar volume on diffusivity for all the sorbent except t-amylalcohol. The possible explanation for this anomalous diffusion behaviour is that t-amylalcohol may be bound strongly to the polar groups of polyurethane chains through H-bond formation. However, for the majority of the sorbents the diffusion data seem to follow the normal Fickian behaviour (Figs 1 and 2).

Realising the importance of Flory-Rehner model to analyse swelling data, attempts have been made to estimate the molar mass \( (M_c) \) between crosslinks for each polymer-sorbent pair. Details of calculations to estimate the swelling coefficient \( (\alpha) \), interaction parameter \( (x) \) and \( M_c \) are given elsewhere. These parameters are also included in Table 1. Due to the nonavailability of reliable solubility parameter data for t-butanol and t-amyl alcohol, we could not compute \( x \) and \( M_c \) for these systems. However, for solvents such as methanol, n-butanol and 2-butanol, \( x \) values are higher than the critical value of 0.5 as suggested
NOTES

Fig. 1 - Plots of percentage increase in thickness \((L_m)\) versus square root of time \((t^{1/2})\) for various polyurethane-sorbent systems

Fig. 2 - Plots of percentage increase in thickness \((L_m)\) versus square root of time \((t^{1/2})\) for various polyurethane-sorbent systems

Table 1 - Sorption data of polyurethane-alcohol systems at 25°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molar volume ((\text{cm}^2/\text{mol}))</th>
<th>(L_m(%))</th>
<th>(\alpha)</th>
<th>(D.10^8) ((\text{cm}^2/\text{s}))</th>
<th>(\chi)</th>
<th>(M_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>40.73</td>
<td>13.59</td>
<td>0.343</td>
<td>43.20</td>
<td>1.93</td>
<td>a</td>
</tr>
<tr>
<td>Ethanol</td>
<td>58.68</td>
<td>13.80</td>
<td>0.389</td>
<td>19.82</td>
<td>0.34</td>
<td>172</td>
</tr>
<tr>
<td>(n)-Propanol</td>
<td>75.14</td>
<td>20.24</td>
<td>0.668</td>
<td>10.12</td>
<td>0.42</td>
<td>484</td>
</tr>
<tr>
<td>(i)-Propanol</td>
<td>76.92</td>
<td>14.57</td>
<td>0.425</td>
<td>9.37</td>
<td>0.35</td>
<td>249</td>
</tr>
<tr>
<td>(n)-Butanol</td>
<td>91.97</td>
<td>18.27</td>
<td>0.612</td>
<td>8.93</td>
<td>2.70</td>
<td>a</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>92.35</td>
<td>19.18</td>
<td>0.599</td>
<td>7.42</td>
<td>1.65</td>
<td>a</td>
</tr>
<tr>
<td>2-Methyl-1-propanol</td>
<td>92.91</td>
<td>18.65</td>
<td>0.595</td>
<td>6.79</td>
<td>0.44</td>
<td>535</td>
</tr>
<tr>
<td>(t)-Butanol</td>
<td>94.88</td>
<td>14.82</td>
<td>0.412</td>
<td>3.03</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>(i)-Amyl alcohol</td>
<td>109.22</td>
<td>18.78</td>
<td>0.467</td>
<td>6.37</td>
<td>0.35</td>
<td>398</td>
</tr>
<tr>
<td>(t)-Amyl alcohol</td>
<td>109.50</td>
<td>17.80</td>
<td>0.551</td>
<td>11.56</td>
<td>b</td>
<td>b</td>
</tr>
</tbody>
</table>

(a) Negative values are found; (b) not determined

by Flory\(^8\) and for these, \(M_c\) values are negative. Similar observations have also been recorded earlier\(^9\). There is however, no correlation between values of \(\alpha\) and \(M_c\). For \(n\)-propanol, with the highest observed value of \(\alpha(=0.668)\), \(M_c\) is around 484, whereas 2-methyl-1-propanol with \(\alpha=0.595\) exhibits the highest \(M_c\) (= 535). For ethanol and isopropanol with \(\chi\) values around 0.35, the calculated \(M_c\) values are respectively 172 and 249. On the other hand, isoamyl alcohol with a \(\chi\) value of 0.357 yields \(M_c = 398\). However, the smallest value of swelling coefficient \((\alpha=0.343)\) for methanol resulted in negative value for \(M_c\). It may be noted here that the numerical values of \(\alpha\) and the maximum percentage increase in thickness \((L_m)\) vary in a direct manner; for instance, highest value of \(\alpha\) and \(L_m\) are exhibited by \(n\)-propanol and lowest values are seen for methanol.

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References