Diffusion of Phenols & Benzyl Alcohol through Porous (G-4) Diaphragm

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Stokes’ diaphragm cell technique has been used for the determination of diffusion coefficients of aqueous solutions of phenol, resorcinol, p-cresol and benzyl alcohol. The data are interpreted in terms of relative degree of solvation and local structure-breaking effects of the solutes.

In a previous communication¹ we determined the isothermal diffusion coefficients of sodium salts of aliphatic carboxylic acids using the Stokes’ diaphragm diffusion cell². Presently we have determined the diffusion coefficients of aqueous solutions of phenol, resorcinol, p-cresol and benzyl alcohol at 30° and 40°C employing the same technique. The data have been interpreted qualitatively in terms of effects of solvation and structure-breaking influences of the solutes on the diffusional transport.

The commercially available AR grade samples of non-electrolytes were purified by distillation or recrystallisation from suitable solvents, as the case may be.

Diaphragm cell of the type close to that designed by Stokes² was used. The vertical cell (int. diam. 2.3 cm) was divided into two compartments by a pyrex G-4 sintered glass disc. The compartments above and below this diaphragm had volumes of 45.8 and 48.0 ml, respectively. The temperatures were maintained with an accuracy of ±0.05° using an air thermostat.

The solution-filled methodology was followed in the present case thereby eliminating the long pre-diffusion period for establishing the steady state in the diaphragm³.

The cell constants were determined from the calibration experiments which allowed KCl solutions (0.05 M each) to diffuse into pure water at 30° and 40°C. The experiments were repeated until four successive such experimental runs at each temperature afforded identical results within the limits of experimental error. The chloride ion concentration in each compartment was estimated by conductimetric titration.

Actual diffusion runs with the present solutes were performed following the same technique as used in the calibration experiment.

At the conclusion of the appropriate diffusion periods (~48 hr), solutions from both the compartments were withdrawn and their concentrations measured spectrophotometrically using a Carl-Zeiss Spectrophotometer. For this purpose, a calibration curve was drawn, which passed through origin.

Diffusion coefficient (D) has been calculated using simple logarithmic formula (1)⁴,

\[ D = \frac{1}{\beta I} \ln \left( \frac{C_1 - C_2}{C_3 - C_4} \right) \]

where \( D \) is the (double-average) diaphragm cell integral diffusion coefficient, \( \beta \) is the cell constant, \( t \) is the time of diffusion and \( (C_1 - C_2) \) and \( (C_3 - C_4) \) are the initial and final (i.e. after time \( t \)) concentration differences between the cell compartments.

The values of cell constants (\( \beta \)) at 30° and 40°C were calculated from Eq.(1). The required \( D_{KCl} (D_1) \) at 30° (and at 40°) was obtained from the literature value⁵ of \( D_{KCl} \) at 25°C (\( D_2 \)) using Eq.(2), assuming that the radius of the hydrated diffusing entity, i.e. KCl does not change between 25° and 40°C

\[ D_1 = \frac{\eta_2}{\eta_1} \frac{T_1}{T_2} D_2 \]

In Eq.(2) \( D_1, \eta_1 \) and \( D_2, \eta_2 \) values are at temperatures \( T_1 \) and \( T_2 \) respectively.

The diffusion data thus obtained at 30° and 40°C are given in Table 1. The maximum random errors calculated for four different experiments by considering 95% confidence limits for various Ds have been found to be about 0.5%.

A lower diffusion coefficient of resorcinol than phenol, also observed earlier⁶, is due to the formation of larger solvated species⁶,⁷ involving two weakly polarising phenolic hydroxyl groups, thereby decreasing the mobility of resorcinol.

In terms of \( pK_a \) values at 25°C the relative acidity of p-cresol (\( pK_a = 10.14 \)) is the least as compared to that of resorcinol (\( pK_a = 9.44 \)) or phenol (\( pK_a = 9.98 \)). Due to this the structure-breaking effect of the hydroxyl group⁶,⁹ is also expected to be the highest in the case of p-cresol. This in turn leads to reduced ‘local’ viscosity, and hence to a higher \( D \). The experimental diffusion coefficients of phenols follow the order: p-cresol > phenol > resorcinol.

Benzyl alcohol, isomeric with p-cresol but an alcohol, has somewhat higher \( D \) as compared to that of p-cresol. This perhaps results from a partial
Table 1—Diffusion Coefficient Data of Phenols and Benzyl Alcohol at 30° and 40°C

<table>
<thead>
<tr>
<th>Solution</th>
<th>$10^5 D_{30}$(cm²s⁻¹) at 30°C</th>
<th>$D_{30}/D_{40}$</th>
<th>$10^5 D_{40}$ (cm²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol (5.0 x 10⁻⁴ M)</td>
<td>0.71</td>
<td>0.75</td>
<td>0.87</td>
</tr>
<tr>
<td>Resorcinol (5.0 x 10⁻⁴ M)</td>
<td>0.51</td>
<td>0.85</td>
<td>0.77</td>
</tr>
<tr>
<td>p-cresol (2.5 x 10⁻⁴ M)</td>
<td>0.95</td>
<td>0.82</td>
<td>0.83</td>
</tr>
<tr>
<td>Benzyl alcohol (5.0 x 10⁻³ M)</td>
<td>1.15</td>
<td>0.79</td>
<td>1.06</td>
</tr>
</tbody>
</table>

*Diffusion data at 30°C are taken from reference 5; these values are for 0.1 M aqueous solutions and obtained using a flow-cell technique.

Overlapping of the structure-promoting and structure-breaking spheres of influence of the proximate hydrophobic methylene and hydrophilic hydroxyl groups in benzyl alcohol.

On the assumption of the validity of Einstein-Stokes equation for $D$ over the temperature range used, one would expect the ratio, $D_{30}/D_{40}$, to correspond to $\left(\frac{\eta_{30}}{\eta_{40}}\right)^{3/2}$ where for dilute solutions, as used in the present case, $\eta_{30}$ and $\eta_{40}$ may be approximated to the corresponding viscosity coefficients of pure water at 30° and 40°C, respectively. Using such values of $\eta$, the above ratio $(D_{30}/D_{40})$ turns out to be 0.79, which is indeed rather close to the experimentally observed values of $(D_1/D_2)$ for the various compounds studied (see Table 1).

It is satisfying to note that in spite of differences in the concentration ranges employed for evaluating $D$ in the present study and those reported in literature, both sets of $D$ values agree, in general, as far as the order of magnitude and the rough qualitative trends are concerned ($D$ values are reported to be insensitive to concentration changes).

References