# Partial Molar Volumes of Cyclic Ethers in Dilute Aqueous Solution at 25°

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THE volumetric behaviour of dilute aqueous solutions can provide information about solute–water interactions and the influence of solutes on the intermolecular structure of liquid water.[1] Of particular interest are the relative effects of non-polar groups on the one hand and groups capable of participating in hydrogen-bond formation, on the other. The negative concentration dependence of the partial molar volumes ($\bar{V}_2$) of alcohols is well documented,[1] and it is also known that the introduction of further –OH groups into the solute molecule reduces the extent of this anomalous behaviour.[2]

We have measured the densities at 25° of aqueous solutions of tetrahydrofuran (THF), tetrahydropyran (THP), and 1,4-dioxan in the concentration range $1 < 10^4 x_2 < 20$, where $x_2$ is the solute mole fraction. A magnetic float technique[3] was employed which is capable of providing density data with a precision of better than 1 part in $10^6$, this being imperative for the evaluation of $\bar{V}_2$ at low concentrations.[3]

$\bar{V}_2$ was obtained from the apparent mol volume, $\phi_V$, given by

$$\phi_V = \frac{M}{\rho} - \frac{1000\,(\rho - \rho_0)}{\rho\rho_0 m}$$

$$\text{and} \quad \bar{V}_2 = \phi_V + m\,\frac{d\phi_V}{dm}$$

where $\rho_0$ and $\rho$ are the solvent and solution density respectively. Within the limit of the experimental error $d\phi_V/dm$ was found to be constant, characteristic for a given solute. Densities of the pure liquid solutes were taken from the literature, so that the excess partial molar volumes, $\bar{V}_2^E$, could be evaluated. These are plotted in the Figure, while the Table lists the molar volumes of the solutes and their partial molar volumes at infinite dilution, $\overline{V}_2^0$. The value of $-4{\cdot}7$ cm.$^3$ mole$^{-1}$, obtained for dioxan, agrees well with the data of Tommila and Koivisto,[4] although their extrapolations were performed from results at rather higher concentrations. The value for $\overline{V}_2^{0E}$ of $-3{\cdot}9$ cm.$^3$ mole$^{-1}$, quoted by Schott,[5] was obtained from the application of the intercept method for calculating $\overline{V}_2$ to experimental densities which were subject to errors of at least 1 part in $10^5$. The extrapolation to infinite dilution was carried out from concentrations which were higher by an order of magnitude than those used here. At higher concentrations, too, the results of Schott do not show satisfactory agreement with those of Tommila and Koivisto.

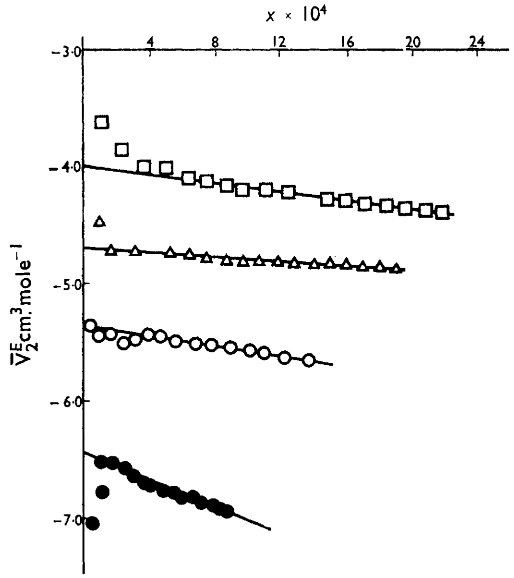

FIGURE. *Plots of* $\overline{V}_2^E(x_2)$ *for* □ = *tetrahydrofuran,* △ = *dioxan,* ○ = *butanol, and* ● = *tetrahydropyran, at* 25°.

TABLE

*Molar volumes and limiting partial molar volumes of organic solutes at* 25°

| | Molar volume (cm.$^3$ mole$^{-1}$) | $\overline{V}_0^2$ (cm.$^3$ mole$^{-1}$) |
|---|---|---|
| Dioxan .. .. .. | 85·75 | 81·1 |
| Tetrahydropyran (THP) .. | 98·20 | 91·8 |
| Tetrahydrofuran (THF) .. | 80·92 | 76·9 |
| Butanol .. .. .. | 92·02 | 86·6 |

Apparently for aqueous solutions $\overline{V}_2^{0E}$ is always negative, thus reflecting the open structure of water which allows solute molecules to occupy some of its void volume. The magnitude of $-\overline{V}_0^{2E}$ provides some indication of the ease with which solute molecules can accommodate themselves to the intermolecular structure of water. This, in turn, appears to depend not so much on the size of the solute molecule as on the balance between polar and nonpolar groups within the molecule. Thus, for hydrogen peroxide, $\overline{V}_2^{0E} \simeq -1{\cdot}5$ cm.$^3$ mole$^{-1}$, showing that this molecule does not greatly perturb the hydrogen bonding in water. (This is also indicated by the thermodynamic functions of mixing.[6])

The results in the Figure show that the enlargement of the THF ring by a $CH_2$ group produces a larger volume contraction than does the insertion of an ether oxygen, although THP and dioxan are isoelectronic and have similar molecular conformations. The difference between the $\overline{V}_2^0$ values for THP and THF, 14·9 cm.$^3$, can be regarded as the partial molar volume of the methylene group. This is in good agreement with 15 cm.$^3$ obtained from density studies on homologous alcohols in aqueous solution.[7,8]

The concentration dependence of $\overline{V}_2^E$ is also worthy of note, as it provides some indication of solute–solute interactions. Solutes for which $\partial\overline{V}_2^E/\partial x_2$ is negative also lower the compressibility,[1] and raise the temperature of maximum density of water.[9] They therefore act so as to stabilise the structural integrity of water, and the magnitude of the effect increases to a maximum at a concentration which is characteristic for a given solute. In view of the low concentrations ($< 0{\cdot}1$M) at which these effects can be observed, they must be ascribed to long-range interactions between solute molecules. The magnitudes of the slopes of the $\overline{V}_2^E(x_2)$ isotherms are proportional to the magnitudes of the interactions, and reference to the Figure shows that, here again, these are functions of the nonpolar/polar group ratios. Thus for THF and Bu$^n$OH,[9] each possessing a four-carbon chain and one oxygen atom, the $\overline{V}\,{}_2^E(x_2)$ slopes are identical. On the other hand, enlarging the nonpolar portion of the molecule (THP) produces an increase in $-(\partial\overline{V}_2^E/\partial x_2)$, whereas an increase in the number of polar sites (dioxan) leads to a reduction in $-(\partial\overline{V}_2^E/\partial x_2)$. It is of interest to note that the $\overline{V}_2^E(x_2)$ slopes for both hydrogen peroxide[6] and dimethyl sulphoxide[10] are equal to zero, thus confirming the absence of marked solute–solute interactions.

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