Densities of Solutions of *p*-Dioxan in H_2O and D_2O

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Summary Density–composition curves for *p*-dioxan–H_2O and *p*-dioxan–D_2O solutions indicate a different extent of interaction of *p*-dioxan with H_2O than with D_2O; i.r. results for the same systems confirm this.

The densities of *p*-dioxan–H_2O and *p*-dioxan–D_2O solutions were measured with a modified Weld pycnometer in a water bath maintained at 25·00 ± 0·01 °C. The data for *p*-dioxan–H_2O are in good agreement with measurements reported by Havorka *et al.*[1] and Griffiths.[2]

The marked contrast in the density–composition curves of the two systems indicates that *p*-dioxan interacts with H_2O to a different extent than with D_2O. The dominant intermolecular interaction in these solutions is hydrogen (deuterium) bonding and the density curves suggest that differences in the strengths of the bonds formed between *p*-dioxan and H_2O and *p*-dioxan and D_2O might lead to the formation of different structures in the two systems.

The deuterium bonds in D_2O are stronger than the hydrogen bonds in H_2O. However, according to Arnett and McKelvey the transfer of nonelectrolytes from H_2O to D_2O is exothermic.[3] Accepting these findings, since nonelectrolytes which are appreciably soluble in water dissolve because they form hydrogen bonds with the water, the exothermicity associated with the transfer of nonelectrolytes from H_2O to D_2O means, for the present case, that in a general sense the *p*-dioxan–deuterium bonds in

D_2O solution are stronger than the *p*-dioxan-hydrogen bonds in H_2O solution.

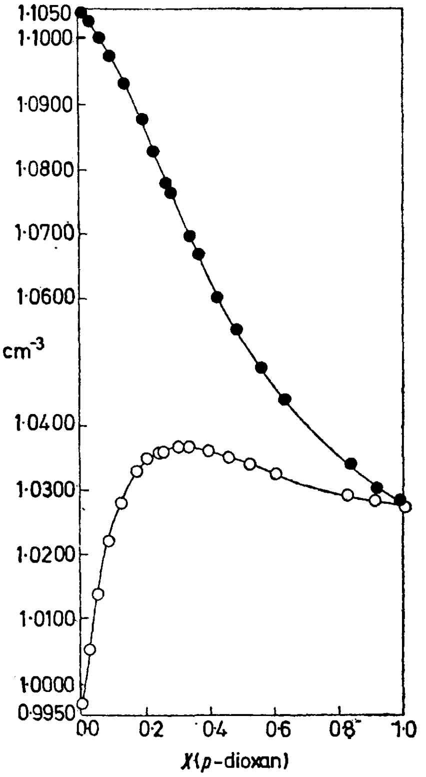

FIGURE 1. Densities *vs.* mole fractions (*X*) of solutions of: ○, *p*-dioxan–H_2O; ●, *p*-dioxan–D_2O, at 25·00 °C.

When ice melts hydrogen bonds are cleaved and an increase in density is observed. Applying this model to the *p*-dioxan–H_2O system, it is reasonable to assume that at high H_2O concentrations all the *p*-dioxan molecules in the solution are hydrated to a maximum and that the H_2O–H_2O hydrogen bonds which are ruptured should lead to an increase in density, whereas the hydrogen bonds formed between *p*-dioxan and H_2O should lead to a decrease in density. Experimentally, the densities of the H_2O solutions increase significantly when small quantities of *p*-dioxan are added to H_2O. This implies that the increase in the density due to the breaking of H_2O–H_2O hydrogen bonds outweighs the decrease in the density due to *p*-dioxan–H_2O complex formation. Alternatively, it may be that any complex formed in this concentration region exhibits a greater density than the sum of the densities of each pure component and if the ice-melting model applies to the H_2O this augments the density change accompanying the cleavage of H_2O–H_2O hydrogen bonds. If the ice-melting model does not apply a greater density of the complex as compared with the pure components can account for the density increase in this region. The composition at the density maximum is near a molar ratio of H_2O:*p*-dioxan of 2:1. The nearly linear density decrease above a *p*-dioxan mole fraction of 0·33 suggests that a simple density additivity rule applies between the complexes in solution at the composition of maximum density and pure *p*-dioxan.

The gradual decrease in the densities of the *p*-dioxan–D_2O solutions with increasing *p*-dioxan content means that if the ice-melting model were applicable here then the tendency towards a greater density when D_2O–D_2O deuterium bonds are broken is outweighed by the tendency towards a lower density owing to the formation of deuterium bonds between *p*-dioxan and D_2O. Alternatively, it could be that complexes of increasing density form as D_2O is added, increasingly, to *p*-dioxan.

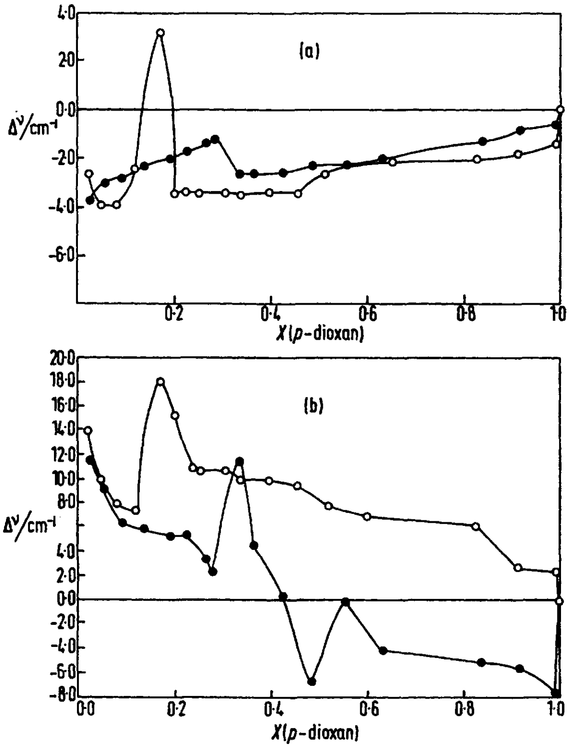

FIGURE 2. (a) Fundamental i.r. frequency shifts, Δν, of the 1081·4 cm⁻¹ CO stretching band of *p*-dioxan *vs.* mole fraction (*X*) of *p*-dioxan in: ○, H_2O; ●, D_2O solutions. (b) Fundamental i.r. frequency shifts, Δν, of the 2856·6 cm⁻¹ CH_2 stretching band of *p*-dioxan *vs.* mole fraction (*X*) of *p*-dioxan in: ○, H_2O; ●, D_2O solutions.

The i.r. spectra of pure *p*-dioxan and solutions of *p*-dioxan in H_2O and D_2O were determined in a Perkin Elmer Model 621 spectrophotometer using a sealed-liquid cell with CaF_2 windows. Each chart paper was calibrated with a 0·05 mm polystyrene film. Frequency shifts, Δν, were calculated by subtracting the frequency at maximum intensity of a given absorption band in pure *p*-dioxan from that of the same band measured with a solution in the instrument.

The frequency-shift data are included here in order to illustrate that the intermolecular interactions are quite different in the two systems. The frequency-shift curves for a CO stretching band of *p*-dioxan in both H_2O and D_2O (Figure 2a) show that, with a single exception, the shifts are bathochromic, with most of the data points in the *p*-dioxan–H_2O system being more bathochromic than their counterparts in the *p*-dioxan–D_2O system.

The frequency-shift curve for one of the CH_2 stretching bands of *p*-dioxan in H_2O (Figure 2b) shows that the shifts are hypsochromic, increasing generally as more H_2O is added to the solution. In D_2O solutions of high *p*-dioxan content the shifts of the same CH_2 stretching band of *p*-dioxan are initially bathochromic. As more D_2O is added to the solution there are discontinuities in the shift curve and above a mole fraction of *ca.* 0·58 in *p*-dioxan the shifts are hypsochromic. In this instance, with a single exception, the data points in the *p*-dioxan–H_2O system are more hypsochromic than their counterparts in the *p*-dioxan–D_2O system.

The variations in the frequency-shifts of the *p*-dioxan vibration bands in the two systems as the composition of each solution is changed show that there are significant differences in the extents of the intermolecular interactions in each system. This, in turn, implies that there are structural differences in the systems and that these structural differences, whatever their nature, account for the observed density–composition curves of Figure 1.

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[1] F. Havorka, R. A. Schaffer, and D. Dreisbach, *J. Amer. Chem. Soc.*, **1936**, **58**, 2264.

[2] V. S. Griffiths, *J. Chem. Soc.*, 1952, 1326.

[3] E. M. Arnett and D. R. McKelvey, 'Solute–Solvent Interactions', Marcel Dekker, New York, 1969, pp. 343—398.