

Free Volumes of Aqueous Nonelectrolytes

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Free volumes (V_f) have been evaluated for aqueous solutions of *p*-dioxane, pyridine, *N*-methylformamide (NMF) and *N,N*-dimethylformamide (DMF) as a function of concentration using ultrasonic velocity, density and heat capacity data at 298.15 K. V_f is found to be minimum at $X_2 \approx 0.16, 0.23, 0.25$ and 0.25 for *p*-dioxane, pyridine, NMF and DMF respectively. These results indicate the formation of 5:1 water-dioxane and 3:1 water-pyridine, water-NMF and water-DMF complexes.

Earlier papers from our laboratory¹⁻³ reported on such properties of aqueous nonelectrolytes as heat capacities etc., and the data were utilised to understand solute-solvent interactions. *p*-Dioxane, pyridine, *N*-methylformamide (NMF) and *N,N*-dimethylformamide (DMF) are known to destabilize the hydrogen bonded structure of water leading to the formation of complexes of varying compositions³⁻¹¹. To examine how far this aspect is characterized by free volumes, we have evaluated the free volumes of aqueous mixtures of *p*-dioxane, pyridine, NMF and

DMF using ultrasonic velocity, density and heat capacity data and the results are reported in this note.

According to Kincaid and Eyring¹² the sound velocity in a liquid (u_l) is related to the free volume (V_f) by the relation (1)

$$V_f = V \left(\frac{u_g}{u_l} \right)^3 \quad \dots (1)$$

where V and u_g represent the molar volume and sound velocity in the vapour respectively. The sound velocity in the vapour can be calculated using the relation (2)

$$u_g = \left(\frac{\gamma RT}{\bar{M}} \right)^{1/2} \quad \dots (2)$$

where γ , R , T and $\bar{M}$ represent the ratio of specific heats, gas constant, temperature of the liquid in absolute scale and effective molecular weight.

The free volumes of aqueous mixtures of *p*-dioxane, pyridine, NMF and DMF at different concentrations have been evaluated making use of necessary experimental data obtained earlier^{3,7,8} and Eqs (1) and (2). The variation of V_f with X_2 , the mol fraction of the organic component in the mixture for all the systems is shown graphically in Fig. 1.

An examination of the data presented in Fig. 1 indicates that V_f becomes minimum in the water-rich region for all the systems. The value of X_2 at which V_f becomes minimum is $\approx 0.16, 0.23, 0.25$ and 0.25 respectively for *p*-dioxane, pyridine, NMF and DMF. These concentrations correspond to the formation of

Table 1—Thermodynamic Property Versus Extremum Concentration, $(X_2)_{extr}$ for Aqueous Mixtures of *p*-Dioxane, Pyridine, NMF and DMF at 298.15 K

Water + <i>p</i> -Dioxane		Water + Pyridine		Water + NMF		Water + DMF	
Property	$(X_2)_{extr}$	Property	$(X_2)_{extr}$	Property	$(X_2)_{extr}$	Property	$(X_2)_{extr}$
C_p^E	0.18	β^E	0.27	β^E	0.23	β^E	0.25
C_p^E	0.18	K^E	0.27	K^E	0.23	K^E	0.25
V_f^E	0.16	C_p^E	0.40	C_p^E	0.35	C_p^E	0.33
V_f^E	0.16*	C_r^E	0.27	C_r^E	0.27	C_r^E	0.27
		π^E	0.32	π^E	0.23	π^E	0.23
		H^E	0.21	H^E	0.33	H^E	0.23
		TS^E	0.27	TS^E	0.22	TS^E	0.22
		G^E	0.21	G^E	0.33	G^E	0.21
		V_f^E	0.23	V_f^E	0.25	V_f^E	0.25
		V_f^E	0.22*	V_f^E	0.23*	V_f^E	0.23*

$\beta^E, K^E, C_p^E, C_r^E, \pi^E, H^E, TS^E, G^E$ and V_f^E represent the excess adiabatic compressibility, isothermal compressibility, molar heat capacity at constant pressure, molar heat capacity at constant volume, internal pressure, enthalpy, entropy Gibbs' free energy and free volume respectively.

* The extremum concentration has been evaluated from V_f^E versus X_2 data for all the systems using V_f versus X_2 data of the present work. V_f^E is obtained using the relation $V_f^E = V_{f,exp} - (X_1 V_{f1} + X_2 V_{f2})$ where V_{f1} and V_{f2} represent free volumes of pure water and the organic solute respectively.

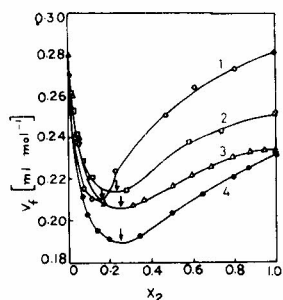


Fig. 1—Variation of free volume (V_f) with mol fraction (X_2) of nonelectrolytes [1, *p*-dioxane; 2, pyridine; 3, NMF; 4, DMF]

complexes of the type 5:1 water-dioxane and 3:1 water-pyridine, water-NMF and water-DMF complexes. Beyond the optimum concentration, further addition of nonelectrolyte breaks the structure of water as well as the polymeric clusters and aqueous solution behaves as a normal liquid and that is why we observe the value of V_f tending towards the value corresponding to the pure nonelectrolyte. Extrema in many thermodynamic functions as a function of concentration for these systems^{3,7,8} as detailed in Table I occur at or around the same X_2 observed in the variation of V_f with X_2 in the present study.

The results of the present study confirm the applicability of free volume parameter as a potential probe to investigate the solute-solvent interactions in aqueous nonelectrolytes.

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