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Apparent Molar Volumes of Water in Methanol and Tetrahydrofuran at 298.15 K

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Synopsis. The densities of water–methanol(MeOH) and water–tetrahydrofuran(THF) mixtures have been measured at 298.15 K. The apparent molar volumes of water, $V_{\phi,\mathrm{w}}$, have been derived as a function of concentration. The values of $V_{\phi,\mathrm{w}}$ in MeOH increase monotonously with the concentration, while for THF solutions the $V_{\phi,\mathrm{w}}$ curve passes through a minimum at low mole fraction of water. These are interpreted in terms of the formation of water–organic solvent and water–water hydrogen bonding.

Previously, we have reported that the apparent molar volumes of water, $V_{\phi,\mathrm{w}}$, are almost independent of the concentration in very dilute solutions of water in benzene and in methanol.[1)] In this paper we will report the density data for water–methanol(MeOH) and water–tetrahydrofuran (THF) mixtures over a wide range of concentration, and will compare the results with those reported by Benson and his co-workers.[2–4)]

Experimental

The MeOH and THF were dried over anhydrous calcium sulfate and then fractionally distilled. The water was deionized and distilled using a quartz still. The mole fractions of water, X_w, of the mixtures in the organic solvent-rich region (*ca.* $X_\mathrm{w}<0.1$) were determined with an automatic Karl Fischer titration apparatus (Hiramuma, AQ-3). In most cases the error in the mole fraction was estimated to be less than 1×10^{-4}. The densities, ρ, of the mixtures relative to pure water at 298.15 K were determined with an oscillating tube densimeter (Paar, DMA 60/601). The density of water was taken as 0.997045 g cm^{-3}.[5)] Details of the apparatus and its operating procedure have been described previously.[1)]

Results and Discussion

The experimental results are summarized in Table 1. The apparent molar volume of water is given by:

$$V_{\phi,\mathrm{w}} = (\rho^*-\rho)/c\rho^* + M_\mathrm{w}/\rho^*, \quad (1)$$

where ρ^* is the density of pure solvent, c is molar concentration, and M_w is the molar mass of water. Since we could not obtain any sample of solvents completely free from water, the value of ρ^* was estimated by the extrapolation of the solution densities to $c=0$, as will be described below.

For dilute solutions the apparent molar volume of nonelectrolytes can be represented in terms of molarity:

$$V_\phi = V^\infty + b_\mathrm{v}c, \quad (2)$$

where V^∞ is partial molar volume at infinite dilution. From Eqs. 1 and 2, the density of the solution is given by:

$$\rho = \rho^* + (M_\mathrm{w}-\rho^*V_\mathrm{w}^\infty)c-\rho^*b_\mathrm{v}c^2. \quad (3)$$

Table 1. Densities of the MeOH and THF solutions of water at 298.15 K

X_w	ρ / g cm^{-3}	X_w	ρ / g cm^{-3}
	MeOH solutions		
0.0169	0.789234	0.0903	0.801739
0.0208	0.789857	0.0953	0.802677
0.0247	0.790546	0.1074	0.804863
0.0256	0.790677	0.1077	0.804816
0.0303	0.791498	0.1305	0.808860
0.0339	0.792131	0.1347	0.809728
0.0415	0.793381	0.1487	0.812227
0.0433	0.793734	0.1827	0.818221
0.0487	0.794575	0.2545	0.831852
0.0488	0.794555	0.3565	0.851527
0.0556	0.795801	0.5142	0.884120
0.0574	0.796085	0.5963	0.901940
0.0676	0.797883	0.6975	0.924446
0.0770	0.799434	0.7917	0.945453
0.0875	0.801317		
	THF solutions		
0.0019	0.882014	0.0343	0.883377
0.0036	0.882077	0.0426	0.883783
0.0040	0.882109	0.0930	0.886363
0.0057	0.882174	0.1363	0.888838
0.0070	0.882220	0.1426	0.889158
0.0097	0.882325	0.1753	0.891182
0.0108	0.882363	0.2363	0.895218
0.0111	0.882374	0.2606	0.896978
0.0157	0.882568	0.3077	0.900397
0.0189	0.882690	0.3467	0.903528
0.0254	0.882982	0.5623	0.924206

Table 2. Densities[a)] and partial molar volumes for the MeOH and THF solutions of water at 298.15 K

	ρ^* / g cm^{-3}	V_w^∞ / cm^3 mol^{-1}	b_v / cm^3 dm^3 mol^{-2}
MeOH[b)]	0.786427	14.42	0
THF	0.881950	17.00	−0.8

a) Values of ρ^*/g cm^{-3} from the literature are: 0.786350,[4)] 0.78660,[6)] 0.78636,[7)] 0.78686[8)] for pure MeOH; 0.88195,[2)] 0.881968,[3)] 0.88194[9)] for pure THF. b) Ref. 1.

Previously we have found that the densities of MeOH solutions of water increase linearly with the molarity in the concentration range less than about 0.7 mol dm^{-3} ($X_\mathrm{w}<0.027$), that is, $b_\mathrm{v}\simeq0$.[1)] On the other hand, no linearity was found for the THF solutions. In Table 2 are given the values of ρ^*, V_w^∞, and b_v determined by the method of least squares in the concentration range less than about 0.5 mol dm^{-3}

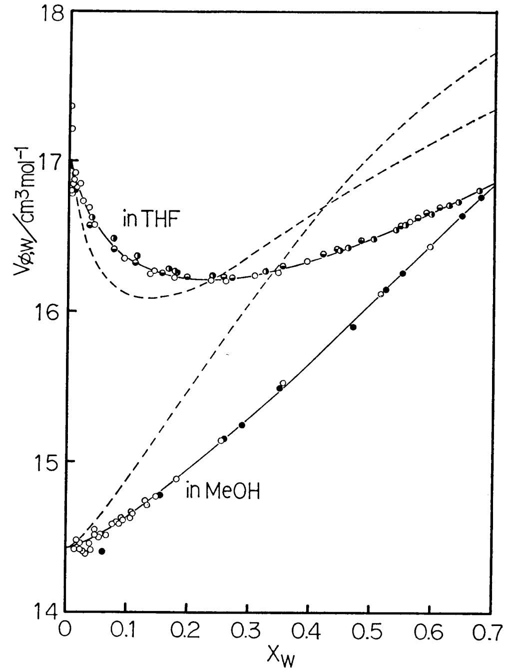

Fig. 1. Concentration dependence of the apparent (solid lines) and partial(dotted lines) molar volumes of water in MeOH and THF solutions at 298.15 K. ○: This work, ◑: Ref. 2, ◒: Ref. 3, ●: Ref. 4.

(X_w<0.04), along with the values for the MeOH solutions.$^{1)}$

The V_w^∞ values in both the solvents, as well as in other polar solvents,$^{10-12)}$ are less than the molar volume of pure water (18.07 cm^3 mol^{-1}). This decrease in volume may be related to the loss of the open structure of bulk water and to the formation of hydrogen bonds between water molecules and the solvent molecules. The smaller V_w^∞ value in MeOH can be attributed mainly to the strong hydrogen bond formation between water and MeOH molecules.

Using the ρ^* values obtained, we can estimate the $V_{\phi,w}$ at finite concentrations. The results are shown in Fig. 1. The closed and half-closed circles represent the values calculated from excess volumes reported by Benson and his co-workers.$^{2-4)}$ These are in fair agreement with our results. The dotted lines are the partial molar volumes of water estimated by the relation:

$$V_w = V_{\phi,w} + X_w(1-X_w)\partial V_{\phi,w}/\partial X_w. \quad (4)$$

The values of $V_{\phi,w}$ (or V_w) in MeOH increase monotonously with the increase in X_w, while for THF solutions the $V_{\phi,w}$ *vs.* X_w curve passes through a broad minimum at near 0.25 mole fraction of water ($X_w \simeq$ 0.13 for minimum V_w).

It is well known that the partial molar volumes of various nonelectrolytes and organic electrolytes in water have a characteristic minimum in the water-rich region. The occurrence of this minimum has been ascribed to a balance between the enhancement of water structure by the solutes and the breaking of the structure with further increase in the concentration.$^{13)}$ The minimum in the $V_{\phi,w}$ curve shown in Fig. 1, on the other hand, could not be attributed to such a structural influence because the open structure of water no longer exists in the THF-rich region. At present the molecular significance of the minimum is not clear but it may be related to the fact that THF–water hydrogen bonding is weaker than water–water hydrogen bonding.$^{2)}$ The addition of water to THF will result in the formation of stronger hydrogen bonds between water molecules that would bring about volume contraction. Further increase in X_w may result in the formation of the well-known, three-dimensional open structure of water and the $V_{\phi,w}$ (or V_w) would increase to 18 cm^3 mol^{-1} in pure water.

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References

1) M. Sakurai and T. Nakagawa, *J. Chem. Thermodyn.*, **14**, 269 (1982).
2) O. Kiyohara and G. C. Benson, *Can. J. Chem.*, **55**, 1354 (1977).
3) O. Kiyohara, P. J. D'Arcy, and G. C. Benson, *Can. J. Chem.*, **56**, 2803 (1978).
4) G. C. Benson and O. Kiyohara, *J. Solution Chem.*, **9**, 791 (1980).
5) G. S. Kell, *J. Chem. Eng. Data*, **20**, 97 (1975).
6) D. Hamilton and R. H. Stokes, *J. Solution Chem.*, **1**, 213 (1972).
7) J. L. Hales and J. H. Ellender, *J. Chem. Thermodyn.*, **8**, 1177 (1976).
8) M. Diaz Pena and G. Tardajos, *J. Chem. Thermodyn.*, **11**, 441 (1979).
9) W. Hayduk, H. Laudie, and O. H. Smith, *J. Chem. Eng. Data*, **18**, 373 (1973).
10) C. de Visser, W. J. M. Heuvelsland, L. A. Dunn, and G. Somsen, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1159 (1978).
11) A. D'Aprano, I. D. Donato, E. Caponetti, and V. Agrigento, *Gazz. Chim. Ital.*, **108**, 601 (1978).
12) Y. Baratoux and J. Juillard, *Talanta*, **27**, 427 (1980).
13) F. Franks and D. S. Reid, "Water, A Comprehensive Treatise," ed by F. Franks, Plenum Press, New York (1973), Vol. 2, Chap. 5.