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Partial Molar Volumes in Aqueous Mixtures of Nonelectrolytes. IV. Aromatic Hydrocarbons

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The densities of binary mixtures of water with benzene, toluene, and ethylbenzene were measured for both ends of the concentration range at 5, 15, 25, 35, and 45 °C. The partial molar volumes were evaluated for both components by assuming a linear correlation of the density with the concentration. The partial molar volumes of the aromatic hydrocarbons (V_A) in a water-rich region are smaller than the molar volumes of the respective solutes, but the temperature dependences of the V_A are almost the same as the molar expansibilities of the solutes. On the other hand, the partial molar volumes of water (V_W) and their temperature dependences in a hydrocarbon-rich region are appreciably larger compared with the molar volume and molar expansibility of pure water, respectively. The results are discussed on the basis of the scaled particle theory and interpreted in terms of the difference of the compressibilities of the solvents. The volumetric behavior of the aromatic hydrocarbons in aqueous solutions does not bear out any influence of a so-called iceberg structure.

There have been extensive studies on the volumetric properties of nonionic organic solutes in water in order to obtain information about the influence of hydrophobic groups on the structure of water (so-called iceberg formation or hydrophobic hydration).[1] However, no definitive evidence of the iceberg structure has been offered up to the present time. In the previous papers of this series, we have examined the partial molar volume behavior in water-alcohol systems and showed that the results could be explained by the hydrogen-bonding interactions between alcohol and water molecules rather than by the iceberg formation.[2-4] For aqueous alcohol solutions, it appears that the structural change of water originated from the iceberg even if it should be really formed around the alkyl groups, but may be masked by the strong hydrogen-bonding interaction.

It is preferred to investigate the properties of aqueous solutions of more hydrophobic solutes than alcohols in order to obtain information on the structural contributions. Furthermore, it is necessary to investigate the properties of water in organic-rich solutions where the characteristic structure of water does not exist, so as to elucidate the interactions between monomeric water molecule and organic solvent molecules. The present paper describes the partial molar volume behavior in three aromatic hydrocarbons-water systems at both ends of the composition.

Experimental

The benzene, toluene, and ethylbenzene were dried over molecular sieve 3A and then fractionally distilled. The water was distilled using a quartz still.

The solution densities were measured with an oscillating-tube densimeter (Paar, DMA 60/601). The densities of water were taken from the table given by Kell.[5] The concentrations of water in the hydrocarbon solutions were determined with an automatic Karl-Fischer titration apparatus (Hiranuma, AQ3). Details of the experimental procedures have been described earlier.[6]

Results

In a binary solution, the apparent molar volume of solute, V_{ϕ_2} is given by

$$V_{\phi_2} = M_2/\rho_1 - (\rho - \rho_1)/\rho_1 c, \tag{1}$$

where M_2 is the molar mass of the solute, ρ_1 and ρ are the densities of the solvent and the solution, respectively, and c is the concentration of the solute. For the very dilute solutions studied here, V_{ϕ_2} can be assumed to be constant independent of the concentration; accordingly V_{ϕ_2} equals the partial molar volume of the solute, V_2, by virtue of its definition. It follows that the density of the solution varies linearly with the concentration:

$$\rho = \rho_1 + (M_2 - \rho_1 V_2)c. \tag{2}$$

In Fig. 1 are given the concentration dependences of $(\rho - \rho_W)$ for three aqueous aromatic hydrocarbon solutions at various temperatures. The partial molar

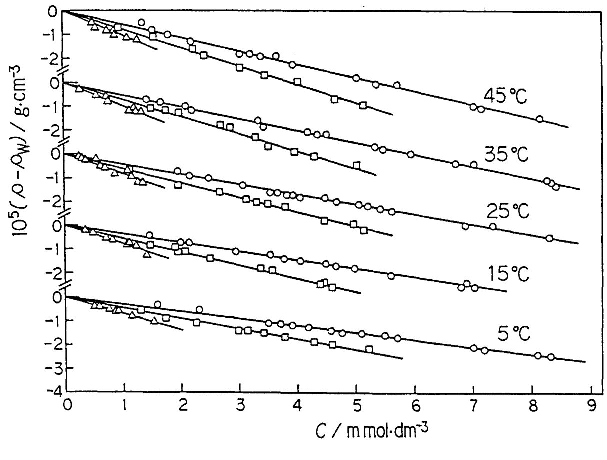

Fig. 1. The densities of aqueous solutions of the hydrocarbons as a function of concentration at various temperatures.
○: benzene, □: toluene, △: ethylbenzene.

Table 1. Partial Molar Volumes V_A and Excess Partial Molar Volumes V_A^E of Aromatic Hydrocarbons in Water at Various Temperatures

T	V_A	$-V_A^E$	V_A	$-V_A^E$	V_A	$-V_A^E$
°C	cm^3 mol^{-1}	cm^3 mol^{-1}	cm^3 mol^{-1}	cm^3 mol^{-1}	cm^3 mol^{-1}	cm^3 mol^{-1}
	Benzene		Toluene		Ethylbenzene	
5	81.11±0.04	6.18	96.57±0.07	8.1	112.9±0.2	7.8
15	81.83±0.04	6.51	97.71±0.07	8.0	113.6±0.4	8.3
25	82.60±0.03	6.81	98.55±0.06	8.3	114.5±0.5	8.6
35	83.64±0.04	6.88	99.83±0.11	8.2	116.5±0.3	7.9
45	84.53±0.06	7.13	100.90±0.09	8.3	117.6±0.4	8.1

Table 2. Partial Molar Volumes of Water V_W in the Aromatic Hydrocarbons and the Densities ρ of the Pure Hydrocarbons at Various Temperatures

T	ρ	V_W	ρ	V_W	ρ	V_W
°C	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}	g cm^{-3}	cm^3 mol^{-1}
	Benzene		Toluene		Ethylbenzene	
5	0.894879	21.61±0.10	0.880721	20.39±0.26	0.879908	20.03±0.15
15	0.884281	22.11±0.06	0.871463	20.62±0.10	0.871162	20.52±0.25
25	0.873658	22.55±0.15	0.862177	21.10±0.15	0.862385	21.00±0.18
35	0.862932	22.98±0.08	0.852825	21.42±0.14	0.853566	21.66±0.12
45	0.852182	23.51±0.10	0.843430	21.64±0.19	0.844712	22.24±0.12

volumes of the hydrocarbons in water, V_A, determined by the method of least squares, are listed in Table 1 with their standard deviations. The accuracy of the V_A values is not so good for longer alkyl chain homologues because of their very low solubilities in water; the errors in V_A were estimated to be less than 0.06, 0.1, and 0.5 cm^3 mol^{-1} for benzene, toluene, and ethylbenzene, respectively. The V_A values at 25 °C are comparable with those found in the literature: 83.2,[7] 81.27,[8] 82.55,[9] 82.95,[10] 83.5,[11] and 85.3 cm^3 mol^{-1} [12] for benzene, 97.71,[13] 97.0,[8] 97.47,[9] 96.6,[11] and 101.9 cm^3 mol^{-1} [12] for toluene, and 114.6 cm^3 mol^{-1} [12] for ethylbenzene.

The densities of pure hydrocarbons, ρ_A, and the partial molar volumes of water in the hydrocarbons, V_W, were also estimated by least squares based on Eq. 2 and summarized in Table 2, in which the data for the benzene solution have been reported in the earlier paper.[6] In Fig. 2 are shown the concentration dependences of $(\rho-\rho_A)$. The error in V_W has, in most cases, been estimated within 0.2 cm^3 mol^{-1}. The literature values of V_W for benzene solution are 22.1,[14] 21.40,[15] and 24.37 cm^3 mol^{-1} [9] at 25 °C. For toluene and ethylbenzene solutions, no V_W data are available with which the presented results could be compared.

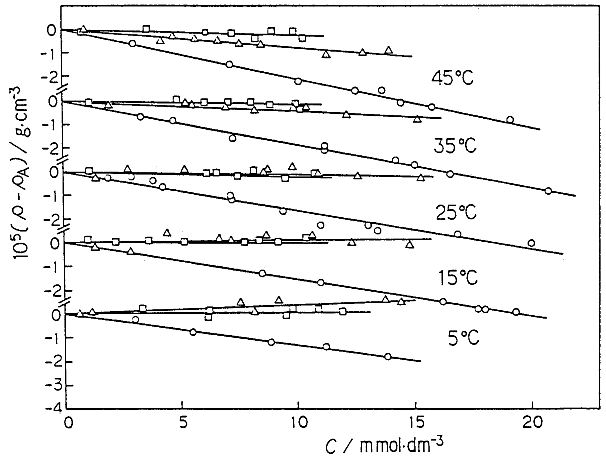

Fig. 2. The densities of the hydrocarbon solutions of water as a function of concentration at various temperatures.
○: benzene, □: toluene, △: ethylbenzene.

Discussion

It is well known that the transfer of nonelectrolytes from a nonpolar solvent to water is accompanied by a large reduction in volume, i.e., the excess partial molar volume, V_A^E $(=V_A-V_A^*$, where V_A^* is the molar volume of pure solute), is negative.[16] This is also the case for the present study as is shown in Table 1. In general such a volume contraction becomes progressively greater with the size of the nonpolar residue. Therefore it has been interpreted by many authors in terms of an iceberg structure formed in the vicinity of nonpolar groups in water. In aqueous alcohol solutions, however, the negative volume change can be explained simply by the difference in size of the solute and solvent molecules and by the strong alcohol-water hydrogen bonding.[2–4]

For nonpolar solutes such as hydrocarbons, Lee[17] has explained the volume contraction by purely geometrical factors, i.e., the size of the solvent molecules and the packing density of the pure solvent. By the application of the scaled particle theory, French and Criss[18] have reported that the contribution from cavity formation accounts for nearly all of the partial molar volumes of nonpolar solutes in water. They have come to the same conclusion that the volumetric behavior of aqueous non-electrolytes is governed mainly by the mixing of hard spheres of different size and structural considerations are not necessary, although the iceberg could be formed as indicated by some of the other physical properties.[18]

The scaled particle theory (SPT)[19] can be successfully applied to the thermodynamic study of aqueous solutions provided the parameters of solute and solvent are adequately selected.[20] The SPT expression for the partial molar volume V_2 is

$$V_2 = V_c + V_i + \kappa_T RT, \qquad (3)$$

where V_c is the volume associated with cavity formation, V_i is the contribution from solute-solvent interaction, and $\kappa_T RT$ arises from the change in the standard state between gas and solution. The cavity contribution V_c is given by

$$V_c = \kappa_T RT\left\{\frac{y}{1-y} + \frac{3yz(1+z)}{(1-y)^2} + \frac{9y^2z^2}{(1-y)^3}\right\} + \frac{\pi\sigma_2^3 N}{6} \qquad (4)$$

$$y = \pi\sigma_1^3 N/6V_1 \qquad (5)$$

$$z = \sigma_2/\sigma_1 \qquad (6)$$

where κ_T and V_1 are the isothermal compressibility and molar volume of the solvent, σ_1 and σ_2 are hard sphere diameters of solvent and solute, and R, T, and N are the gas constant, absolute temperature, and Avogadro constant, respectively.

In Table 3 are summarized the solvent parameters used for the V_c calculation. The results are given in Tables 4 and 5, which include the results for some alcohols, methyl alcohol (MeOH), ethyl alcohol (EtOH) and *t*-butyl alcohol (*t*-BuOH), for comparison. Table 4 clearly shows that, as has been described by French and Criss,[18] the partial molar volumes of the hydrocarbons or alcohols studied here can be virtually accounted for by the cavity formation term alone. The small positive or negative V_i values tell us nothing about solute-solvent interaction since the calculation of V_c is sensitive to the selection of both σ_1 and σ_2 values; e.g., in the calculation of the V_c value for benzene in water the variation of only ±0.01 nm for σ_1 and σ_2 values results in the variation of ±1.3 $cm^3\,mol^{-1}$.

Table 3. Some Physical Properties of Solvents at 25 °C

Solvent	V_1	κ_T	σ
	$cm^3\,mol^{-1}$	GPa^{-1}	nm
Water	18.07	0.452[a]	0.275[d]
Benzene	89.41	0.973[b]	0.526[e]
Toluene	106.87	0.916[b]	0.564[e]
MeOH	40.74	1.240[c]	0.369[e]
EtOH	58.69	1.157[c]	0.434[e]
t-BuOH	94.98	1.206[c]	0.539[f]

a) Ref .5. b) Ref. 21. c) Ref. 22. d) Ref. 23. e) Ref. 24. f) Ref. 25.

Table 4. The SPT Cavity and Interaction Contributions to the Partial Molar Volumes of Various Solutes in Water at 25 °C

	Benzene	Toluene	MeOH	EtOH	*t*-BuOH
$V_A/cm^3\,mol^{-1}$	82.5	98.6	38.2[a]	55.1[a]	87.8[b]
$V_c/cm^3\,mol^{-1}$	82.1	97.9	35.2	51.5	87.2
$V_i/cm^3\,mol^{-1}$	−0.7	−0.2	1.9	2.5	−0.5

a) Ref. 26. b) Ref. 2.

Table 5. The SPT Cavity and Interaction Contributions to the Partial Molar Volumes of Water in Various Solvents at 25 °C

	Benzene	Toluene	MeOH	EtOH	*t*-BuOH
$V_W/cm^3\,mol^{-1}$	22.5	21.1	14.5[a]	13.8[a]	17.1[b]
$V_c/cm^3\,mol^{-1}$	35.1	34.0	31.4	32.5	42.5
$V_i/cm^3\,mol^{-1}$	−15.0	−15.2	−20.0	−21.5	−28.4

a) Ref. 27. b) Ref. 2.

On the other hand, as is shown in Table 5, large negative V_i values characterize the SPT calculation for water as a solute. French and Criss have found large negative V_i values not only for water, but also for alkanes or alcohols as solutes in various organic solvents.[18] They have clearly shown that the solvent effect on the V_i term is attributable to the difference in solvent compressibilities. That is to say, similarly to the positive V_c contribution indicated by Eq. 4, the negative V_i contribution can be considered to increase in magnitude with the compressibility of the solvent. The exceptionally small compressibility coefficient of solvent water results in small V_i values in Table 4. The distinct difference in the V_i values between hydrocarbons and alcohols shown in Table 5 is interpreted in the same way.

It should be kept in mind that, strictly speaking, the application of the scaled particle theory is restricted to the mixing of hard and spherical molecules that is more or less impractical in real liquid. Although some uncertainty in the results may therefore be unavoidable, the present results confirm that the solvent compressibility is one of the decisive factors in determining the volumetric behavior in solution. Our previous papers[2–4] show that the partial molar volumes in alcohol-water systems are governed by hydrogen-bonding between solute and solvent molecules. However, no definitive evidence of such interactions could be presented in Table 4 and 5. This is probably due, at least in part, to the restriction of the theory which is applicable to a system containing no strong solute-solvent interaction. No detailed discussion on the nature of solute-solvent interactions can be given on the basis of the scaled particle theory.

It is profitable to examine the temperature dependence of the partial molar volume (i.e., partial molar expansibility) in order to clarify the solute-solvent interactions. The values of V_A are plotted as a func-

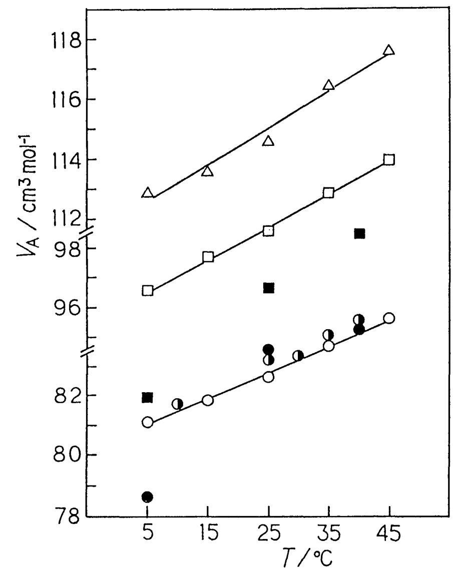

Fig. 3. The temperature dependences of the partial molar volumes of the hydrocarbons in water.
○: benzene, □: toluene, Δ: ethylbenzene. half closed: Ref. 7, closed: Ref. 11.

tion of temperature in Fig. 3, where some literature values are included. It is evident that the V_A values increase linearly with the temperature within the experimental error. Furthermore, Table 1 shows that the V_A^E values are almost independent of the temperature especially for toluene and ethylbenzene. In other words, the partial molar expansibilities of these hydrocarbons in water are almost the same as the molar expansibilities of the pure hydrocarbons. These facts are in contrast to the partial molar expansibitity behavior of alcohols in aqueous solution where the V_2-T curves are always concave upward and the negative V_2^E values become greater as the temperature is raised.[2,27] For aqueous alcohol solutions, it appears doubtful to interpret these characteristics in terms of the water-structural concept,[2–4] but, in any event, the structural change of water is undoubtedly sensitive to temperature. The present results therefore suggest that the expansibility behavior of the aqueous benzene derivatives studied here is irrelevant to the iceberg structure. Even if such a structure could be formed, it has little influence on the volumetric behavior.

The temperature dependences of the partial molar volumes of water in the three hydrocarbons are shown in Fig. 4. These exhibit linear relationships with approximately the same positive slope. It is evident that the partial molar volumes and the partial molar expansibilities of water in the hydrocarbons are large compared to the molar volume and expansibility of pure water, respectively. For various alcohol solutions the partial molar expansibility of water varies significantly with the chain length and branching of the alkyl groups; the partial molar expansibility of water is low (negative in some cases) for lower or branched-chain alcohols and becomes larger as the chain length increases.[2–4,27] The slope in Fig. 4 is almost the same as those observed for hexanol or octanol solutions, in which the water-alcohol hydrogen-bonding make relatively small contributions to over-all solution properties. It appears that Fig. 4 characterizes the volumetric behavior of water dissolved in nonpolar solvents without strong interactions such as hydrogen bond.

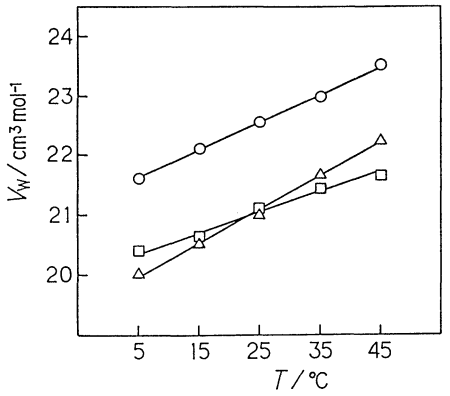

Fig. 4. The temperature dependences of the partial molar volumes of water in the hydrocarbons.
○: benzene, □: toluene, Δ: ethylbenzene.

In conclusion, the present results can be interpreted on the basis of a hard-sphere mixing model without assuming any special interactions such as hydrogen bond or iceberg formation. The difference of the solvent compressibility determines essentially the partial molar volume behavior of the aromatic hydrocarbons in water and water in the hydrocarbons.

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