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Effect of Solvent on the Electrostrictive Contribution to the Apparent Molal Volume Using Glycine and Methyl Carbamate as Model Compounds

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Apparent molal volumes for glycine and methyl carbamate have been obtained at 298.15 and 313.15 K in methanol-water and TBA-water. The solution composition was varied up to *ca.* 40% (w/w) organic co-solvent. Values for the electrostriction contribution, ϕ_V^o (elec), are calculated and the results discussed.

INTRODUCTION

Recent publications from this laboratory dealt with volumetric studies on tris[1] and tricine[2] in mixed aqueous solvents. In continuation of this type of study, this communication deals exclusively with the electrostrictive contribution to the infinite dilution apparent molal volume (ϕ_V^o). The term electrostriction denotes the decrease in (ϕ_V^o) of an ionic solute due to the compression of solvent in the immediate neighbourhood of the charges. Thus, for ionic solutes, the observed (ϕ_V^o)may be viewed as the sum of a positive bulk contribution (ϕ_V^o)(bulk), and a negative electrostriction contribution, (ϕ_V^o)(elec). Glycine ($^+NH_3CH_2COO^-$) and methyl carbamate ($H_2NCOOCH_3$) were selected for investigation. These compounds are identical in atomic composition and are thus expected to have essentially equivalent (ϕ_V^o)(bulk) values. However, only the zwitter ionic glycine possesses an electrostrictive component. Thus the neutral methyl carbamate can serve as a probe for evaluating (ϕ_V^o)(elec) of glycine under various experimental conditions. To this end, measurements were carried out in aqueous methanol and aqueous tertiary butyl alcohol (TBA) at 298.15 and 313.15 K. The choice of organic co-solvents was made with a view of the contrasting information that each may provide. Thus whereas both methanol and TBA have been reported to 'enhance' the structure of water, methanol is said to do so largely via hydrophilic interactions[3] and TBA via the hydrophobic type[3–5]. Apart from the intrinsic value

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of elucidating the solvent influence on electrostriction, it is noteworthy that amino acids in proteins may be located in hydrophobic or hydrophilic environments. The nature of the environment is important in determining the physical properties of amino acids and hence the bulk properties of proteins. Any added understanding of the solvent role may thus assist in understanding the complex interactions that eventually determine the relationship between protein structure and function.

EXPERIMENTAL

Methanol and tertiary butyl alcohol (TBA) were of spectro quality. Glycine and methyl carbamate were reagent grade and were dried for *ca.* 48 hrs. in *vacuo* before use. The composition of the mixed solvent was varied from pure water up to *ca.* 40% (w/w) methanol or TBA. For each solvent composition, measurements were carried out on twelve solutions, containing either glycine or methyl carbamate, in the range 0.01–0.1 m, at 298.15 and 313.15 ± 0,02 K. Other measurement details have been previously described[1]. The maximum error in a given (ϕ_V^o)was estimated as ± 0.07 cm^3 mol^{-1}.

RESULTS AND DISCUSSION

The apparent molal volumes, ϕ_V, of glycine and methyl carbamate were calculated using the equation

$$\phi_V = \frac{M}{d} - \frac{1000(d - d_o)}{dd_om} \tag{1}$$

in which M is the molecular weight of the solute and m is the molality. d and d_o are the densities of the solution and solvent, respectively. In order to obtain (ϕ_V^o)the experimental ϕ_V values were least-squares fitted to the equation

$$\phi_V = \phi_V^o + bm \tag{2}$$

where b is a constant that provides a measure of solute-solute interaction. At the small solute molalities employed, the bm term for methyl carbamate was essentially zero in both solvent systems. For glycine, however, this term climbed slowly with organic solvent addition, reaching 0.20 cm^3 mol^{-1} for 0.1 m glycine in the most TBA-rich solution. Nevertheless, in order to eliminate the small contribution from solute-solute interactions, comparisons were made solely on the basis of ϕ_V^o.

Table 1 lists, at 298.15 and 313.15 K, ϕ_V^o values for glycine and methyl carbamate in methanol-water and Table 2 lists the corresponding values in TBA-water. The value of 42.90 cm^3 mol^{-1} for glycine in water at 298.15 K is in agreement with published results[6,7] Table 1 reveals that ϕ_V^o for glycine varies

TABLE 1
DEPENDENCE OF (ϕ_V^o)OF GLYCINE AND METHYL CARBAMATE ON METHANOL CONTENT. (UNIT: cm^3 mol^{-1})

% Methanol (w/w)	ϕ_V^o (Glycine)		ϕ_V^o (Methyl carbamate)	
	298.15 K	313.15 K	298.15 K	313.15 K
0	42.90	44.75	59.43	61.88
9.09	44.43	46.25	63.49	64.19
16.67	45.57	47.40	65.26	65.83
23.08	43.70	45.23	64.60	65.96
28.57	43.10	46.70	64.92	66.03
33.33	42.32	46.89	65.32	67.00
37.50	45.73	48.12	65.85	68.37
41.18	47.23	50.00	68.53	70.75

TABLE 2
DEPENDENCE OF (ϕ_V^o)OF GLYCINE AND METHYL CARBAMATE ON TBA CONTENT. (UNIT: cm^3 mol^{-1})

% TBA (w/w)	ϕ_V^o (Glycine)		ϕ_V^o (Methyl carbamate)	
	298.15 K	313.15 K	298.15 K	313.15 K
0	42.90	44.75	59.43	61.88
9.09	43.70	44.80	63.81	65.20
16.67	44.90	45.98	63.58	64.46
23.08	46.92	48.05	63.30	64.91
28.57	49.47	51.03	64.78	64.73
33.33	50.05	51.23	62.74	64.59
37.50	51.65	52.33	62.11	64.34
41.18	53.15	54.56	61.33	61.80

only slightly with methanol addition, a shallow minimum of 42.32 cm^3 mol^{-1} being observed for the 33.3% solution at 298.15 K. This appears anomalous since methanol (ε^{25} = 35.7) addition decreases the dielectric constant of the solution and hence is expected to cause a reduction in the extent and compactness of solvent cages around the ions. But here it must also be noted that methanol enhances the structure of water, with the maximum effect located *ca.* 37% (w/w) methanol[5]. Thus methanol addition also causes a transfer of the zwitter ion to a more ordered medium, thereby promoting its ability to form compact solvent cages. This effect is opposed to the structure breaking tendency of the ionic portion of glycine which tends to increase ϕ_V^o. Table 1 also shows that ϕ_V^o values for methyl carbamate are, as expected from electrostriction, much larger than those for glycine. Moreover, it is apparent that ϕ_V^o for methyl carbamate is more influenced by methanol addition. For example, on going from water to 41.18%

methanol at 298.15 K, ϕ_V^o is 4.33 $cm^3 mol^{-1}$ for glycine and 9.10 $cm^3 mol^{-1}$ for methyl carbamate. It thus appears that the structure enhancing ability of methanol acts in such a way as to favour more compact cages for ions than for neutral species.

Table 2 reveals that ϕ_V^o for glycine in TBA-water increases significantly with TBA addition, the extent of this increase at 298.15 K being in general agreement with previously reported results[4,5]. By contrast, ϕ_V^o for methyl carbamate exhibits little sensitivity to TBA, even dropping somewhat in TBA-rich solutions. For example, on going from water to 41.18% TBA at 298.15 K, ϕ_V^o is 10.25 $cm^3 mol^{-1}$ for glycine and only 1.90 $cm^3 mol^{-1}$ for methyl carbamate. It has been reported[3,4] that up to *ca.* 15% (w/w), TBA enhances the structure of water. However, the largely hydrophobic nature of TBA seems to hinder the involvement of the zwitter ionic glycine in a solvent cage and to favour the neutral methyl carbamate which has itself a hydrophobic segment.

ϕ_V^o (elec) in methanol-water and TBA-water was calculated from the data in Tables 1 and 2 using the expression

$$\phi_V^o \text{ (elec)} = \phi_V^o \text{ (Methyl carbamate)} - \phi_V^o \text{ (glycine)} \qquad (3)$$

Fig. 1 shows the effect of co-solvent addition on ϕ_V^o (elec) at 298.15 K and

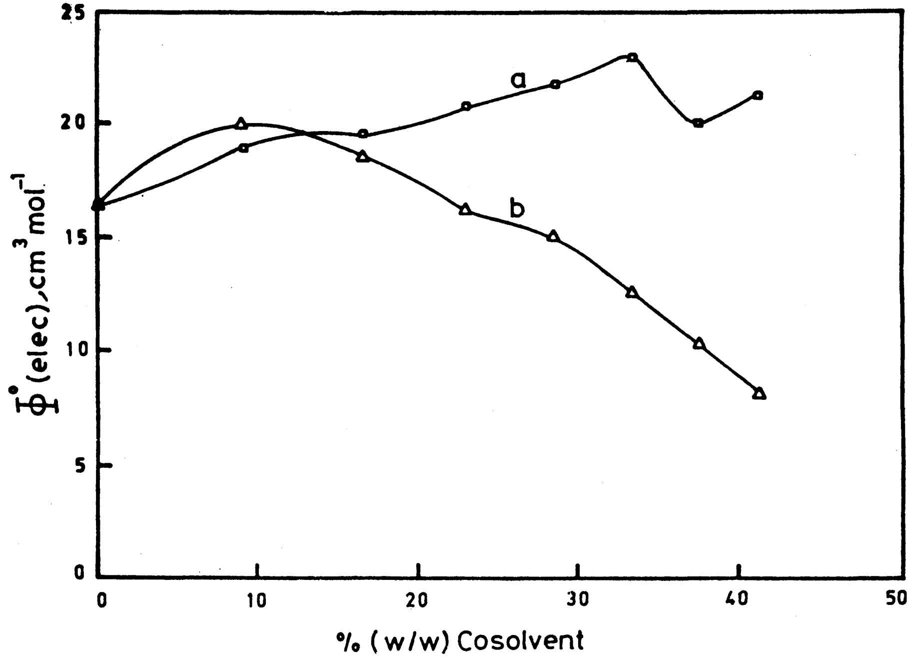

Fig. 1 Dependence of ϕ_V^o (elec) on (a) methanol and (b) TBA content at 298.15 K

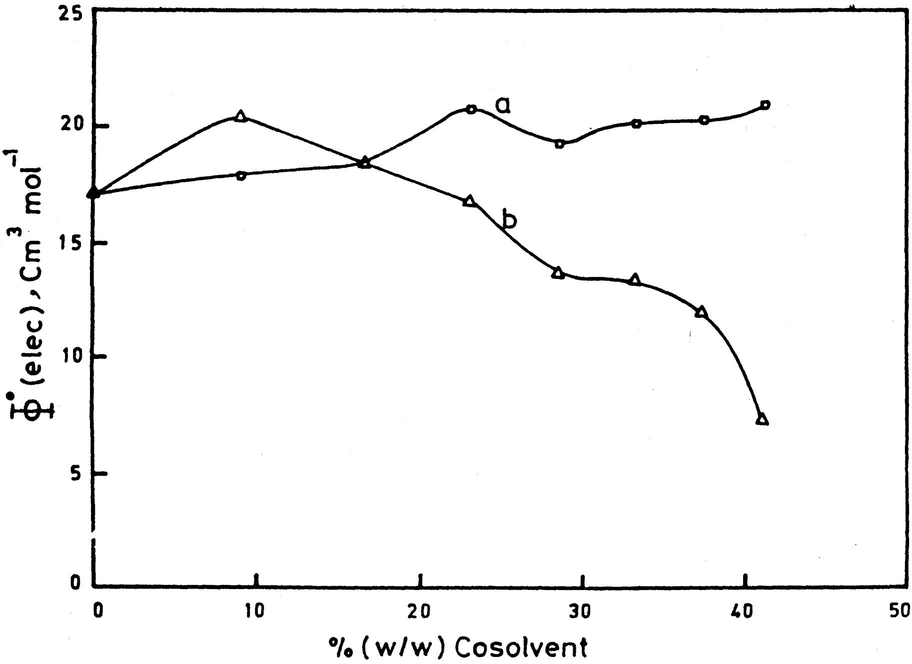

Fig. 2 Dependence of ϕ_V^o (elec) on (a) methanol and (b) TBA content at 313.15 K

Fig. 2 shows this effect at 313.15 K. For methanol-water at 298.15 K, ϕ_V^o rises from 16.53 $cm^3\ mol^{-1}$ in water to a maximum of 23.00 $cm^3 mol^{-1}$ in 33.3% methanol, with this maximum being located in the region of high enhancement of the water structure. It is interesting to note that, at 313.15 K, the maximum disappearance and a steady but slower rise in ϕ_V^o (elec.) is observed. This suggests that at the higher temperature the enhanced structure is at least partially broken down and that the electrostrictive effect is substantially reduced. In TBA-water, maxima are observed at both temperatures in the vicinity of 10% TBA, not too far away from the 15% composition corresponding to maximum enhancement (see above). The steep decline in ϕ_V^o (elec.) with continued TBA addition indicates that a high hydrophobic environment weakens electrostriction. This effect may be brought about via a process in which the compact hydrophobic hydration sphere is broken down by the zwitter ion, resulting in the release of TBA molecules to the solution.

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