APPARENT MOLAR VOLUMES OF SOME AMINO ACIDS IN METHANOL-WATER MIXTURES

J.S. Sandhu and Urmila Kashyap

Department of Chemistry, Punjabi University, Patiala - 147 002, India

For a better understanding of the state of water in the living cells, it is neoessary to carry out systematic investigations of amino acids under various conditions. Studies of molar volumes in mixed solvents have received attention of some workers [1-5]. In the present work, densities of the different solutions of glycine (GLY). α - alanine (α-ALA), β-amino-n-butyric acid (β-ABA), α - amino-i-valeric acid (VAL), α - amino-n-valeric acid (NOR) and ε-amino-n-caproic acid (ε-CAP, have been measured at 298.15, 308.15 and 318.15°K for aqueous methanol solutions. Apparent molar volumes and their limiting values have been calculated from these data.

EXPERIMENTAL

The source and preliminary preparation of amino acids have been mentioned in an earlier communication [6]. Methanol was purified [7] and stored in well stoppered bottles and distilled afresh before use.

Densities of solutions were determined with the aid of a pykrometer of about 14 ml capacity [6]. The reproducibility in density measurements was found to be $\pm 3 \times 10^{-5}$ g cm^{-3} .

RESULTS AND DISCUSSION

The densities measured at each temperature have been used to calculate the apparent molar volumes, ϕ_v, (in cc/mole) of the solutes. A linear extrapolation using the least-squares fit to the following equation:

$$\phi_v = \phi_v^\circ + S_v C \qquad (1)$$

gives ϕ_v° , the apparent molar volume at infinite dilution and S_v , the experimental slope. The values of ϕ_v° along with their standard errors, σ_v , are given in Table 1.

The apparent molar volume at infinite dilution, becomes equal to partial molar volume, [$\phi_v^\circ = \bar{V}^c$]. The limiting partial molar volumes of transfer $\Delta\bar{V}_{tr}^\circ$ (eg 2) gives a measure of the influence of methanol on partial molar volumes. The transfer functions

TABLE 1

THE VALUES OF LIMITING APPARENT MOLAR VOLUME (σ_v) STANDARD ERRORS (ϕ_v°) OF AMINO ACIDS IN METHANOL-WATER MIXTURES AT 298.15, 308.15 AND 318.15° K

MeOH (w/w)	ϕ_v° σ_v cm^3 /mol		
	298.15° K	308.15° K	318.15° K
GLY			
0	43.08 ± 0.04	43.83 ± 0.08	44.26 ± 0.08
5	42.52 ± 0.05	43.38 ± 0.11	44.09 ± 0.10
15	41.26 ± 0.14	41.51 ± 0.07	41.95 ± 0.11
25	41.89 ± 0.09	42.05 ± 0.11	42.43 ± 0.14
35	42.20 ± 0.23	42.78 ± 0.21	43.07 ± 0.20
α-ALA			
0	60.35 ± 0.12	60.91 ± 0.12	61.48 ± 0.07
5	59.19 ± 0.03	60.77 ± 0.09	61.00 ± 0.11
15	58.03 ± 0.12	58.45 ± 0.06	58.69 ± 0.12
25	57.78 ± 0.01	58.12 ± 0.03	58.31 ± 0.02
35	58.09 ± 0.28	58.43 ± 0.14	59.13 ± 0.10
β-ABA			
0	75.53 ± 0.10	76.68 ± 0.08	77.52 ± 0.14
5	75.22 ± 0.11	76.48 ± 0.08	76.86 ± 0.04
15	74.56 ± 0.07	74.75 ± 0.10	75.13 ± 0.14
25	73.11 ± 0.29	73.57 ± 0.09	73.98 ± 0.09
35	73.94 ± 0.15	74.32 ± 0.13	74.59 ± 0.06
VAL			
0	90.28 ± 0.15	90.49 ± 0.21	91.82 ± 0.22
5	87.84 ± 0.23	90.03 ± 0.23	90.70 ± 0.23
15	85.64 ± 0.15	86.49 ± 0.33	87.29 ± 0.17
NOR			
0	91.47 ± 0.23	92.06 ± 0.10	92.93 ± 0.17
5	89.01 ± 0.29	91.02 ± 0.18	91.86 ± 0.19
15	86.07 ± 0.21	87.68 ± 0.30	90.18 ± 0.10
ε-CAP			
0	104.07 ± 0.13	104.32 ± 0.12	104.85 ± 0.17
5	102.04 ± 0.14	102.82 ± 0.13	103.69 ± 0.12
15	99.28 ± 0.22	100.12 ± 0.13	101.46 ± 0.25
25	97.69 ± 0.21	98.56 ± 0.14	99.41 ± 0.13
35	98.25 ± 0.24	99.07 ± 0.26	99.87 ± 0.35

may be interpreted in terms of water structure making and breaking effects of solutes [7].

$$\Delta\bar{V}_{tr}^\circ = \phi_{v(m,s)}^\circ - \phi_{v(W)}^\circ \qquad (2)$$

where $\phi_{v\ ms}$ and $\phi_{v(W)}$ are the apparent molar volumes at infinite dilution in mixed solvent and in pure water. $\Delta\bar{V}_{tr}^\circ$ has been plotted as a function of methanol concentration (Fig. 1).

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It is evident from Table 1 that the values of acids at all the three temperature decrease with the addition of methanol which results in negative $\Delta\bar{V}^{\circ}_{tr}$ (Fig. 1). The negative values are becoming more negative with the addition of methanol till it reaches a minimum value. For GLY minimum is around 15% (w/w) of methanol, while for α-ALA, β-ABA, ε-CAP, it is around 25% (w/w) of methanol. The exact position of minimum in $\Delta\bar{V}^{\circ}_{tr}$ cannot of course, be deduced from the present measurements, but it is worth noting that a maximum in the degree of short-range three dimensional order in methanol-water system occurs somewhere in this region of solvent composition. The minimum may also depend to some extent on the solute as seen in the minimum in glycine solutions at lower methanol concentration. The minima in $\Delta\bar{V}^{\circ}_{tr}$ values for VAL and NOR are not obtained since these/amino acids could not be dissolved to required strength in higher percentages of methanol.

The partial molar volume can be considered as a sum of the volume occupied by a solute molecule, $\bar{V}^{\circ}_{int}$ (intrinsic volume) and the

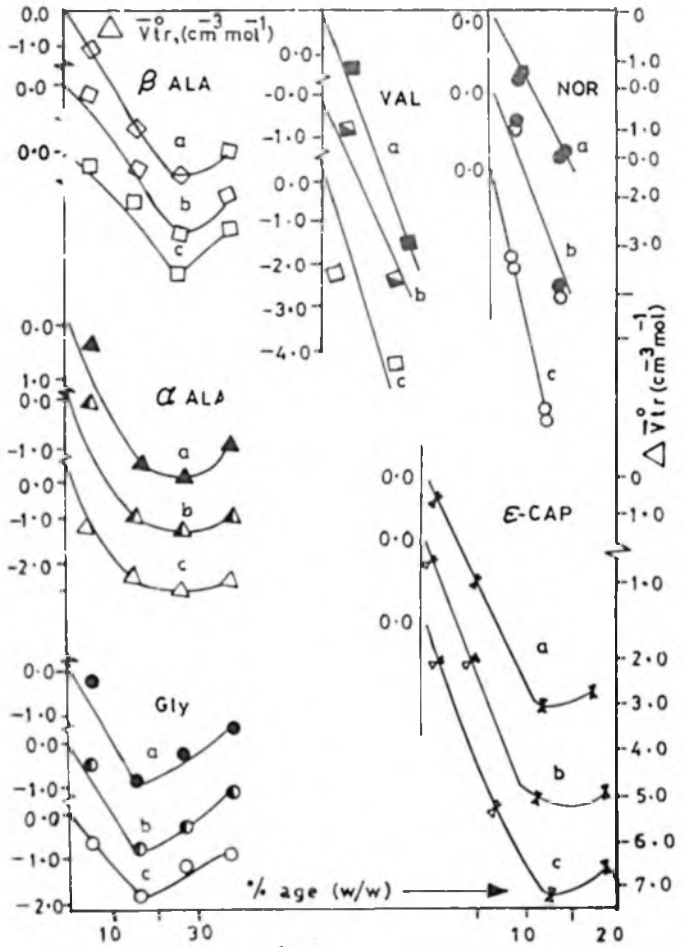


Fig. 1 Plots of $\Delta\bar{V}^{\circ}_{tr}$ vs percentageof Methanol a) 298.15 K; b) 308.15 K; c) 318.15 K

volume contribution owing to the structural modification caused by interactions with water, $\bar{V}^{\circ}_{elect.}$ The intrinsic volume is the volume of solute assuming no solute-solvent interactions:

$$\bar{V}^{\circ} = \bar{V}^{\circ}_{int.} + \bar{V}^{\circ}_{elect.} \qquad (4)$$

Prasad and Ahluwalia [8] assumed that $\bar{V}^{\circ}_{int}$ has the same magnitude in waer and in mixed solvents. The nagative values of $\Delta\bar{V}^{\circ}_{tr}$ in the prsence of cosolvent, thus arise from increase in $\bar{V}^{\circ}_{elect.}$.

It has been shown [9-10] that the ϕ°_{v} values of the zwitterionic amino acids are in general, lower than those of their respective uncharged isomers in aqueous solutions. This has been associated with the electrostriction effect caused by the zwitterionic portion of the molecules. Thus the electrostriction effect which brings about the diminution in the volume of the solvent caused by the electric fields of the dipolar solutes is increased in the mixed solvents as compared with that in pure water. Since electrostriction reflects the solute-solvent interactions, it can be inferred that the minima in $\Delta\bar{V}^{\circ}_{tr}$ values correspond to the regions where solute-solvent interactions are maximum.

REFERENCES

1. S. Phang, *Aust. J. Chem.*, **30** (1977) 1605.

2. G. Dipaola and B. Belleau, *Can. J. Chem.*, **56** (1978) 1827.

3. N.C. Dey, B.K. Saikia and I. Haque, *Can. J. Chem.*, **58** (1980) 1512.

4. A.K. Mishra and J.C. Ahluwalia, *J. Chem. Soc. Faraday Trans. I*, **77** (1981) 1469.

5. T. Ogawa, M. Yasuda and K. Mizutani, *Bull. Chem. Soc. Japan.* **57** (1984) 662, 2064.

6. J.S. Sandhu and Urmila Kashyap, *J. Electrochem. Soc. India.*, **35(2)** (1986) 103.

7. H.S. Frank and M.W. Evans, *J. Chem. Phys.*, **13** (1945) 507.

8. K.P. Prasad & J.C. Ahluwalia, *Biopolymers*, **19** (1980) 273.

9. E.J. Cohn, *Ann. rev. Biochem.*, **4** (1933) 93.

10. F.T. Gucker, Jr. W.L. Ford and C.E. Maser, *J. Phys. Chem.* **43** (1939) 153.