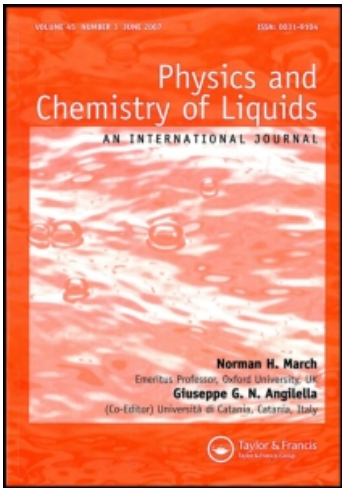

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Apparent Molar Volumes of Amino Acids in Very Dilute Aqueous Solutions at 25,00°C

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APPARENT MOLAR VOLUMES OF AMINO ACIDS IN VERY DILUTE AQUEOUS SOLUTIONS AT 25,00°C

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The apparent molar volumes of DL-α-alanine, DL-β-alanine, DL-α-aminobutyric acid, DL-α-phenylalanine, DL-serine and DL-aspartic acid in very dilute aqueous solutions at 25,00°C were determined from density measurements. From these data it is shown that the concentration dependence of the apparent molar volume of these amino acids at very low molality differs from the behavior found at concentrations higher than 0,01m. This change has been attributed to solute-water interactions which prevail at very high dilution.

Keywords: Amino acid; apparent molar volume; solute-water interactions

1. INTRODUCTION

It is well known the linear dependence of concentration that shows the apparent molar volume of amino acids in aqueous solutions [1–14]. The equation that describes this behavior can be written:

$$\phi_v = \phi_v^0 + S_v m \tag{1}$$

The experimental measurements used to establish this behavior have been done mostly at concentrations greater than 0,01m. The highest concentration is determined by the solubility of each amino acid. From the linear dependence shown in this region, it has been concluded that the dipole–dipole interactions between amino acids have a predomi-

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nant influence that shows in the whole concentration range even at infinite dilution [1, 5, 8, 13].

In this article we report the densities and apparent molar volumes of DL-α-alanine, DL-β-alanine, DL-α-aminobutyric acid, DL-α-phenylalanine, DL-serine and DL-aspartic acid in very dilute aqueous solutions at 25,00°C. The study has been done to have information about the volumetric behavior of these solutes at concentrations as low as 0,003m and to test the validity of the conclusions of other works.

2. EXPERIMENTAL

The amino acids used in this study were the following: DL-α-alanine (Merck), DL-β-alanine (Baker), DL-α-aminobutyric acid (Sigma), DL-α-phenylalanine (Merck), DL-serine (Sigma) and DL-aspartic acid (Sigma). All the amino acids were of the highest purity available and were used without further purification. They were previously dried under vacuum for 48 h.

The solutions were prepared by weight with water treated according to literature recommendations [15] (bidistilled and degassed just before use).

The density of solutions was measured using a magnetic float densimeter described elsewhere [16] at $25{,}00 \pm 0{,}002$°C. The densimeter was calibrated with aqueous KCL solutions of known density. For each amino acid solution the equilibrium voltage was measured ten times with one float and ten times with a second float. The density was determined from the calibration equations with a precision of $\pm 2{,}0 \times 10^{-6}$ g/cm^3.

The apparent molar volumes were calculated from the equation:

$$\phi_v = M/d + 1000(d_0 - d)/mdd_0 \qquad (2)$$

where M is the molecular weight of the amino acid, d and d_0 are the densities of the solution and the solvent (water density [17] at 25,00°C was taken as 0,997047 g/cm^3) and m is the molal concentration. The experimental uncertainty is less than 0,1 cm^3/mol for concentrations above 0,0100 molal and less than 0, 5 cm^3/mol for concentrations above 0,0030 molal.

3. RESULTS

The apparent molar volumes for amino acids in water at 25,00°C are reported in Table I. The dependence of the apparent molar volume on concentration is shown in Figures 1 to 6.*

All Figures show clearly the existence of two concentration regions with different and characteristic behavior. It can be seen that for concentrations higher than 0,02 m the behavior follows the linear dependence described by equation (1), that has been reported by many authors. At lower concentrations the behavior of the apparent molar volume undergoes an abrupt change which follows a defined tendency as dilution increases that seems to be beyond experimental uncertainty.

The existence of the two regions just described, each of them with a characteristic behavior can be attributed to a change of the dominant interactions amino acid – amino acid in solution as dilution increases. The occurrence of this change at such low concentrations could be explained as the result of very strong solute – solute interactions that even at low concentration are able to compensate the weaker amino acid-water interactions. Only at very high dilution the solute-solvent interactions prevail.

The behavior shown by the apparent molar volumes of amino acids in aqueous solutions is similar to the behavior followed by other mixed solutes such as alcohols. They show a transition concentration at which the behavior of properties like apparent molar volumes and heat capacities suffer deep changes.

When the data corresponding to the higher concentration region are fitted by least-squares to equation (1), the limiting apparent molar volumes obtained by extrapolation to infinite dilution ϕ_v^0 are in good agreement with those reported in literature as it is shown in Table II. However, we consider that the linear extrapolation done with the volumetric data in the region of higher concentrations does not represent the apparent molar volume at infinite dilution but the apparent molar volume that the amino acid would have if the dipole – dipole interactions prevail at infinite dilution.

*Complete set of density data is available as supplementary material.

TABLE I Apparent Molar Volume of Aqueous Solutions Amino Acids at 25,00°C

DL-α-Alanine		*DL-β-Alanine*		*DL-Aminobutyric*	
m *mol/kg*	ϕ_v cm^3/mol	*m* *mol/kg*	ϕ_v cm^3/mol	*m* *mol/kg*	ϕ_v cm^3/mol
0,12008	60,48	0,12011	58,28	0,12007	75,21
0,11000	60,40	0,11057	58,28	0,10999	75,24
0,09997	60,46	0,10362	58,39	0,10002	75,24
0,08997	60,41	0,09012	58,31	0,09002	75,28
0,08105	60,26	0,08199	58,26	0,08009	75,31
0,06927	60,30	0,07005	58,33	0,07086	75,28
0,06009	60,29	0,06218	58,35	0,06013	75,28
0,04982	60,40	0,05014	58,33	0,05006	75,31
0,04001	60,45	0,04034	58,41	0,04155	75,35
0,02980	60,38	0,03016	58,45	0,03005	75,28
0,02000	60,60	0,02008	58,56	0,02000	75,27
0,01003	60,96	0,01002	58,82	0,01013	75,20
0,00889	61,37	0,00899	58,80	0,00910	75,11
0,00793	61,06	0,00817	58,93	0,00807	74,99
0,00707	61,32	0,00720	59,45	0,00700	75,10
0,00602	60,61	0,00611	59,22	0,00600	74,58
0,00506	63,31	0,00507	59,19	0,00509	74,36
0,00408	63,71	0,00406	58,88	0,00402	73,14
		0,00306	61,08	0,00308	73,37

DL-Phenylalanine		*DL-Serine*		*DL-Aspartic Acid*	
m *mol/kg*	ϕ_v cm^3/mol	*m* *mol/kg*	ϕ_v cm^3/mol	*m* *mol/kg*	ϕ_v cm^3/mol
0,05030	121,48	0,12028	60,72	0,04044	73,77
0,04007	121,49	0,11006	60,67	0,03046	73,56
0,03011	121,59	0,10072	60,68	0,02097	73,44
0,02646	121,29	0,08999	60,55	0,01002	73,22
0,02017	121,14	0,08053	60,59	0,00904	73,15
0,02000	121,51	0,07060	60,56	0,00836	73,06
0,01500	121,21	0,06011	60,56	0,00713	72,80
0,01011	120,95	0,05037	60,61	0,00613	72,26
0,00925	120,39	0,04012	60,59	0,00502	71,56
0,00854	120,52	0,03005	60,40	0,00418	70,91
0,00819	120,32	0,02000	60,39	0,00296	70,27
0,00752	120,43	0,01001	60,06		
0,00703	120,28	0,00918	60,45		
0,00404	119,10	0,00905	60,36		
0,00303	118,19	0,00805	59,65		
		0,00702	58,67		
		0,00614	59,84		
		0,00507	58,96		
		0,00399	59,51		
		0,00319	59,36		

From out point of view, in the region of higher concentrations it can be shown that solutes with an important apolar surface enough to compensate the dominant charge–charge interactions have a negative

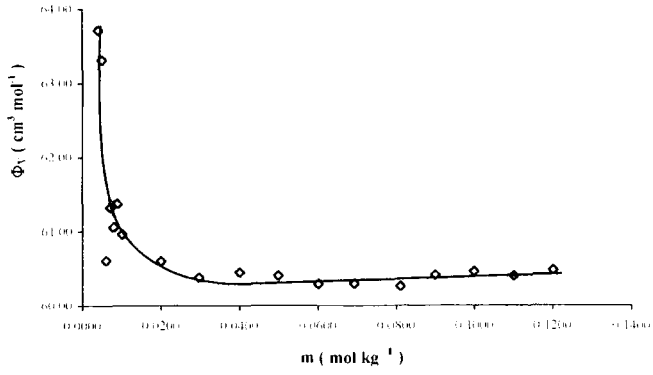

FIGURE 1 Apparent molar volumes of α-Alanine in water at 25,00°C.

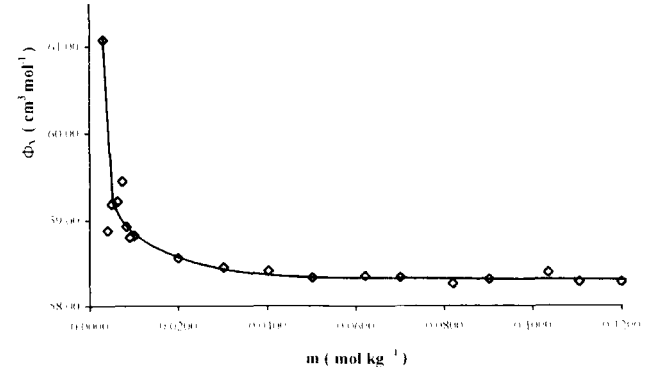

FIGURE 2 Apparent molar volumes of β-Alanine in water at 25,00°C.

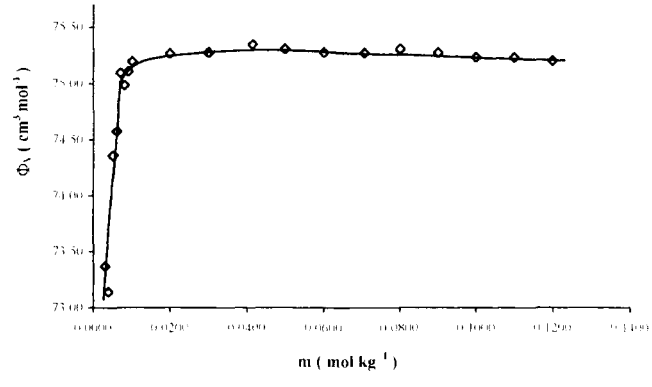

FIGURE 3 Apparent molar volumes of aminobutyric acid in water at 25,00°C.

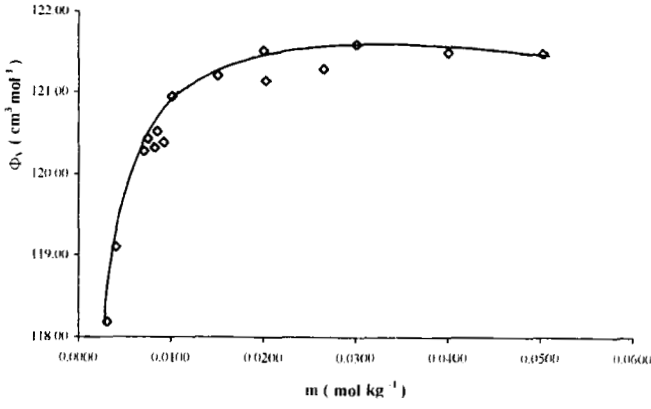

FIGURE 4 Apparent molar volumes of phenylalanine in water at 25,00°C.

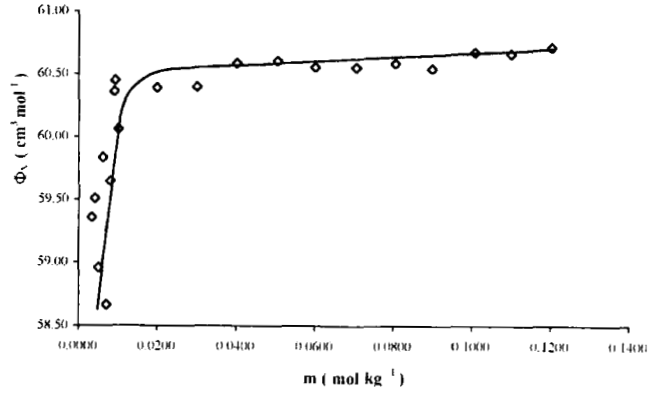

FIGURE 5 Apparent molar volumes of serine in water at 25,00°C.

slope (DL-α-aminobutyric acid and DL-α-phenylalanine), while small amino acids such as α-alanine and β-alanine which have a smaller apolar surface exposed to the solvent have a positive slope.

Also, in this region, those solutes with polar groups (DL-serine and DL-aspartic acid) show a negative slope. In this case it is due to their ability to form hydrogen bonds with water.

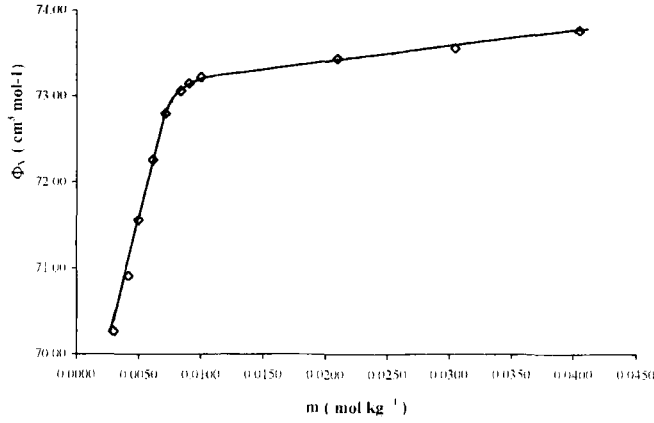

FIGURE 6 Apparent molar volumes of aspartic acid in water at 25,00°C.

TABLE II Apparent Molar Volumes of Amino Acids in Water at Infinite Dilution at 25,00°C

Amino acid	Φ_v^{0*}	S_v^*	Φ_v^0 *(Lit.)*	S_v*(Lit.)*	*Ref.*[a]
α-Ala	60,35	0,87	60,47	0,63	9
			60,45	0,70	18
			60,50	0,618	5
β-Ala	58,26	0,42	58,24	0,94	9
dl-Ser	60,55	0,62	60,62	1,3	8
			60,62	1,27	18
			60,23	0,70	10
dl-Asp	73,05	17,59	73,83	9,588	5
			71,79	1,0	6
dl-Phe	121,74	−5,43	121,48	11,731	5
			122,2	−8	8
			121,92	−0,4	6
α-dl−Abut	75,38	−1,29	75,50	0,67	8
			75,54	0,53	9

[a] ϕ_v in cm^3/mol and S_v in cm^3/mol^2kg. Other results are presented in references (1, 2, 7, 11–14, 19).

In the very dilute region the experimental uncertainty is of course high. Nonetheless, the tendency shown by all amino acids studied is quite striking. New measurements with more sensible instruments are being made to confirm this finding.

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