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Partial Molar Volumes of Transfer of Some Amino Acids from Water to Aqueous Glycerol Solutions at 25°C

Tarlok S. Banipal,[1,*] **Gagandeep Singh,**[1] **and Bhajan S. Lark**[2]

Apparent molar volumes of glycine, DL-α-alanine, L-valine, L-leucine, and L-phenylalanine in 0.5, 1.0, 2.0, 3.5, and 5.0 m_B (mol-kg^{-1}) aqueous solutions of glycerol have been obtained from solution densities at 25°C using precise vibrating-tube digital densimeter. The estimated partial molar volumes at infinite dilution V_2^o have been used to obtain the corresponding transfer volumes $\Delta_{tr}V_2^o$ from water to different glycerol–water mixtures. The transfer volumes are positive for glycine and DL-α-alanine, and both positive and negative for the other amino acids over the concentration range studied. Interaction coefficients have been obtained from McMillan–Mayer approach and the data have been interpreted in terms of solute–cosolute interactions.

KEY WORDS: Partial molar volumes; glycine; DL-α-alanine; L-valine; L-leucine; L-phenylalanine.

1. INTRODUCTION

The process of denaturation of proteins in aqueous solutions remains a subject of extensive investigations[1–6] and physicochemical studies of aqueous solutions of amino acids and peptides are of considerable importance in understanding denaturation and other complex biological processes.[7–14]

Glycerol is an important polyhydroxy compound. It has biophysical importance, because it occurs as a primary biomolecule in the intestine, as a product of hydrolysis of lipids, and also in liver, where it participates in metabolism of glucose. Very few reports are available on the behavior of amino acids in aqueous glycerol solutions. Palecz and Piekarski reported[11] enthalpies of solution of glycine in aqueous solutions of 1,2-diols and glycerol. We have undertaken the study of the interactions of various amino acids with glycerol and explore the effect

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of increasing hydrophobic side-chain length of these amino acids on these interactions through volumetric studies. Consequently, we determined apparent molar volumes V_ϕ of glycine, DL-α-alanine, L-valine, L-leucine, and L-phenylalanine in water [reported earlier in *Indian J. Chem.* **39A**, 1011(2000)] and in 0.5, 1.0, 2.0, 3.5, and 5.0 m_B (mol-kg^{-1}) aqueous solutions of glycerol from density measurements at 25°C. The data have been used to estimate partial molar volumes of transfer of amino acids from water to aqueous glycerol solutions. The McMillan–Mayer model has been used to determine molecular interaction coefficients.

2. EXPERIMENTAL

Five amino acids, namely glycine (G-7126), DL-α-alanine (A-7502), L-valine (V-0500), L-leucine (L-8000), L-phenylalanine (P-2126) of highest purity (99 + %) were obtained from Sigma Chemical Co. These, along with glycerol (AR, Glaxo Qualigens), were used as such without further purification. Solutions of amino acids were prepared in deionized double-distilled water, which was degassed before use. All the solutions were made on weight basis using a balance having an accuracy of 0.1 mg. Densities of solutions were measured with a vibrating-tube digital densimeter (Model DMA 60/602 Anton Paar, Austria). The details of its principle and working have been described elsewhere.[15] Temperature of water flowing through the densimeter cell was controlled within ±0.01 K by a temperature bath (Heto Birkerod/Denmark). The densimeter was calibrated with dry air and water and all the measurements were made relative to pure water. Its working was checked by measuring the densities of aqueous sodium chloride solutions and excellent agreement was found with literature values.[15,16] The reproducibility of density measurements was better than 3×10^{-6} g-cm^{-3}.

3. RESULTS AND DISCUSSION

Densities of amino acid solutions in aqueous glycerol solutions at 25°C as a function of molality and the corresponding the V_ϕ values, obtained using the following relation, are summarized in Table I.

$$V_\phi = M/d - [(d - d_0)1000/m_A dd_0] \tag{1}$$

where M is the molecular mass of the solute, m_A(mol-kg^{-1}) is the molality of the amino acid in solution, and d_0 and d are the densities of solvent and solution, respectively. At infinite dilution apparent molar and partial molar volumes are identical ($V_\phi = V_2^o$). In cases involving negligible concentration dependence of V_ϕ within the uncertainity limits of measurements, V_2^o were determined by taking

Table I. Densities and Apparent Molar Volumes of Some Amino Acids in Aqueous Glycerol Mixtures at 25°C

$m_A{}^a$	d^b	$V_\phi{}^c$	$m_A{}^a$	d^b	$V_\phi{}^c$
Glycine in aqueous glycerol solutions			L-Leucine in aqueous glycerol solutions		
0.5 $m_B{}^d$			0.5 m_B		
0.22067	1.014214	43.64	0.01723	1.007555	106.29
0.26887	1.015681	43.69	0.04780	1.008285	106.58
0.33218	1.017555	43.85	0.05440	1.008432	106.64
0.40611	1.019734	43.97	0.06351	1.008643	106.71
0.45657	1.021208	44.04	0.07031	1.008798	106.78
0.52069	1.023066	44.12	0.08851	1.009210	106.94
1.0 m_B			1.0 m_B		
0.06878	1.019258	43.58	0.02014	1.017347	107.07
0.16735	1.022298	43.64	0.04049	1.017790	107.40
0.27804	1.025658	43.73	0.05009	1.018003	107.44
0.32120	1.026959	43.76	0.05996	1.018207	107.65
0.41999	1.029893	43.84	0.07057	1.018434	107.71
0.55254	1.033732	44.02	0.10159	1.019079	107.95
2.0 m_B			2.0 m_B		
0.12046	1.037351	44.42	0.04865	1.035298	107.32
0.24120	1.040900	44.54	0.06844	1.035700	107.40
0.28613	1.042207	44.57	0.07689	1.035870	107.43
0.34137	1.043789	44.64	0.08944	1.036120	107.49
0.42295	1.046080	44.77	0.10153	1.036365	107.49
0.48100	1.047736	44.79	0.12870	1.036901	107.58
0.61187	1.051340	44.94			
3.5 m_B			3.5 m_B		
0.11489	1.060034	44.79	0.02026	1.056380	108.03
0.21472	1.062881	44.93	0.02883	1.056533	108.06
0.28130	1.064737	45.06	0.03311	1.056606	108.15
0.29595	1.065135	45.11	0.04691	1.056846	108.25
0.36327	1.066966	45.25	0.05285	1.056949	108.29
0.44544	1.069174	45.39	0.06831	1.057218	108.37
5.0 m_B			5.0 m_B		
0.12128	1.073702	45.27	0.02873	1.075591	108.78
0.29652	1.078513	45.51	0.03698	1.075713	108.85
0.36195	1.080233	45.69	0.04947	1.075895	108.96
0.43305	1.082119	45.75	0.06015	1.076045	109.09
0.46863	1.083043	45.79	0.07772	1.076291	109.23
0.61813	1.086802	46.08	0.09599	1.076536	109.40

Table I. Continued

$m_A{}^a$	d^b	$V_\phi{}^c$	$m_A{}^a$	d^b	$V_\phi{}^c$
DL-α-Alanine in aqueous glycerol solutions			L-Phenylalanine in aqueous glycerol solutions		
	0.5 m_B			0.5 m_B	
0.12581	1.010656	60.59	0.01128	1.007840	120.42
0.18990	1.012426	60.63	0.02102	1.008259	120.88
0.23110	1.013562	60.62	0.02493	1.008426	121.01
0.37321	1.017389	60.73	0.02772	1.008542	121.18
0.39949	1.018084	60.76	0.03216	1.008747	121.30
0.59439	1.023156	60.90	0.03557	1.008869	121.50
	1.0 m_B			1.0 m_B	
0.11130	1.020106	60.74	0.01620	1.017547	121.06
0.14937	1.021142	60.77	0.02226	1.017800	121.28
0.19944	1.022490	60.83	0.02702	1.018000	121.33
0.25279	1.023904	60.92	0.03235	1.018217	121.56
0.29160	1.024912	61.01	0.04242	1.018627	121.84
0.34997	1.026421	61.11	0.05465	1.019117	122.15
0.50736	1.030406	61.31			
	2.0 m_B			2.0 m_B	
0.15249	1.038220	61.80	0.01598	1.035363	122.05
0.19024	1.039277	61.32	0.01939	1.035498	122.13
0.26253	1.041169	61.23	0.02226	1.035607	122.28
0.32649	1.042773	61.34	0.02606	1.035758	122.36
0.37580	1.043972	61.47	0.03786	1.036215	122.69
0.51104	1.047395	61.38			
0.63829	1.050469	61.47			
	3.5 m_B			3.5 m_B	
0.13268	1.060003	61.71	0.00893	1.057013	123.29
0.20228	1.061711	61.76	0.01151	1.057109	123.21
0.24544	1.062756	61.80	0.01320	1.057171	123.23
0.34793	1.065287	61.67	0.01892	1.057382	123.21
0.35828	1.065506	61.74	0.02246	1.057511	123.26
0.43924	1.067431	61.77			
0.66805	1.072803	61.76			
	5.0 m_B			5.0 m_B	
0.12392	1.077922	62.53	0.01089	1.074991	124.57
0.14956	1.078636	62.51	0.01189	1.075024	124.61
0.23930	1.080562	62.56	0.01682	1.075184	124.88
0.30506	1.082064	62.46	0.01878	1.075247	124.97
0.36836	1.083522	62.44	0.02488	1.075440	125.26
0.47631	1.085956	62.39			
0.61997	1.089005	62.56			

Table I. Continued

$m_A{}^a$	d^b	$V_\phi{}^c$	$m_A{}^a$	d^b	$V_\phi{}^c$
L-Valine in aqueous glycerol solutions			L-Valine in aqueous glycerol solutions		
0.5 m_B			2.0 m_B		
0.01827	1.007771	89.67	0.03243	1.035266	91.43
0.02668	1.007993	89.81	0.04648	1.035585	91.55
0.03646	1.008244	90.08	0.05237	1.035728	91.41
0.04723	1.008519	90.27	0.07477	1.036236	91.51
0.05389	1.008626	90.39	0.08245	1.036416	91.46
0.06597	1.008987	90.58	0.10609	1.036955	91.47
0.07140	1.009118	90.70			
			3.5 m_B		
1.0 m_B			0.02192	1.056779	92.21
0.01700	1.017337	90.65	0.02895	1.056919	92.38
0.03952	1.017892	90.96	0.05071	1.057365	92.37
0.05093	1.018166	91.13	0.06329	1.057623	92.35
0.06483	1.018500	91.25	0.07589	1.057894	92.18
0.08588	1.018986	91.56	0.08398	1.058048	92.31
			0.10535	1.058508	92.08
			5.0 m_B		
			0.02091	1.075584	92.64
			0.05374	1.076204	92.51
			0.07476	1.076591	92.59
			0.07802	1.076651	92.59
			0.08987	1.076867	92.63
			0.11138	1.077271	92.58

^{a} Amino acid molality, mol-kg^{-1}.
^{b} Density, g-cm^{-3}.
^{c} Units, cm^3- mol^{-1}.
^{d} Glycerol molality, mol-kg^{-1}.

the average of all the data points. However, where finite concentration dependence was observed V_2^o was determined by least-squares fitting of the equation

$$V_\phi = V_2^o + S_v m_A \tag{2}$$

where S_v is the slope.[17] V_2^o values in water reported earlier[18] and presently determined in aqueous glycerol solutions for various amino acids are summarized in Table II. The partial molar volume of transfer of a particular amino acid from water to aqueous glycerol solution at infinite dilution ($\Delta_{tr}V_2^o$) is defined by

$$\Delta_{tr}V_2^o = V_2^o(\text{in aqueous glycerol solution}) - V_2^o(\text{in water}) \tag{3}$$

Table II. Partial Molar Volume of Some Amino Acids in Water and Aqueous Glycerol Solutions at 25°C[a]

Compound	V_2^{ob}					
	Water	0.5 m_B	1.0 m_B	2.0 m_B	3.5 m_B	5.0 m_B
Gycine	43.15[c] ± 0.03[d] (2.03)[e]	43.27 ± 0.02[d] (1.67)[e]	43.49 ± 0.03[d] (0.89)[e]	44.28 ± 0.02[d] (1.08)[e]	44.55 ± 0.02[d] (1.87)[e]	45.06 ± 0.03[d] (1.62)[e]
DL-α-Alanine	60.36[c] ± 0.02[d] (1.33)[e]	60.49 ± 0.02[d] (0.67)[e]	60.55 ± 0.02[d] (1.15)[e]	61.43 ± 0.06[d]	61.43 ± 0.03[d]	62.49 ± 0.05[d]
L-Valine	90.70[c] ± 0.3[d]	89.33 ± 0.03[d] (19.35)[e]	90.44 ± 0.02[d] (12.99)[e]	91.47 ± 0.04[d]	92.27 ± 0.06[d]	92.59 ± 0.03[d]
L-Leucine	107.74[c] ± 0.01[d] (4.20)[e]	106.14 ± 0.01[d] (9.09)[e]	106.92 ± 0.05[d] (10.65)[e]	107.18 ± 0.02[d] (3.15)[e]	107.88 ± 0.02[d] (7.48)[e]	108.51 ± 0.02[d] (9.29)[e]
L-Phenylalanine	121.49[c] ± 0.04[d] (40.70)[e]	119.94 ± 0.03[d] (43.75)[e]	120.61 ± 0.04[d] (28.41)[e]	121.59 ± 0.03[d] (29.30)[e]	123.24 ± 0.03[d]	124.03 ± 0.01[d] (49.83)[e]

[a] The uncertainity associated with each partial molar volume is its standard deviation. The entries in parenthesis are the slopes S_v of Eq. (2).
[b] $cm^3\text{-}mol^{-1}$.
[c] Ref. 18.
[d] Standard deviation in V_2^o.
[e] Slope.

Table III.   Partial Molar Volume of Transfer of Some Amino Acids from Water to Aqueous Glycerol Solutions at 25°C[a]

Compound	$\Delta_{tr} V_2^{0b}$				
	0.5 m_B	1.0 m_B	2.0 m_B	3.5 m_B	5.0 m_B
Glycine	0.12	0.34	1.13	1.40	1.91
DL-α-Alanine	0.13	0.19	1.07	1.38	2.13
L-Valine	−1.37	−0.26	0.77	1.57	1.89
L-Leucine	−1.60	−0.82	−0.56	0.14	0.41
L-Phenylalanine	−1.55	−0.88	0.10	1.75	2.54

[a]Standard deviation in $\Delta_{tr} V_2^o$ varies from 0.01 to 0.06 cm^3-mol^{-1}.
[b]cm^3-mol^{-1}.

$\Delta_{tr} V_2^o$ values are summarized in Table III and illustrated in Fig. 1. It may be seen that $\Delta_{tr} V_2^o$ values are positive for glycine and DL-α-alanine throughout the concentration range of glycerol studied. The magnitude is slightly more in the case of glycine except after $m_B \geq 4.0$ and, for remaining amino acids, both positive and
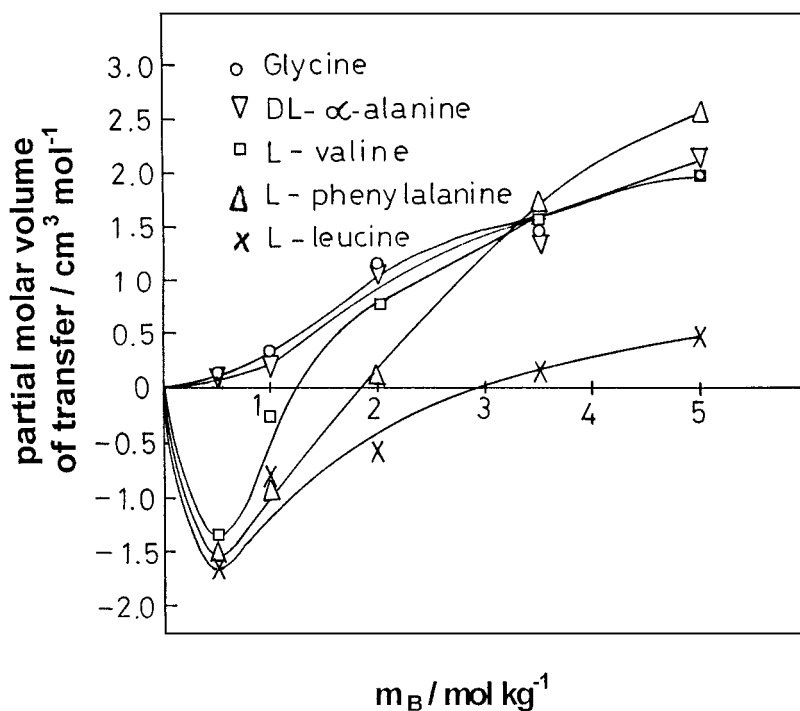
Fig. 1. Partial molar volume of transfer of amino acids from water to aqueous glycerol solutions.

negative $\Delta_{tr}V_2^o$ values have been observed. The $\Delta_{tr}V_2^o$ values are negative up to about 1.2, 3.1, and 1.8 m_B aqueous glycerol solutions for L-valine, L-leucine, and L-phenylalanine, respectively. It is interesting to note that in these three cases $\Delta_{tr}V_2^o$ vs m_B plots show minima and in all the cases these lie around $m_B \approx 0.5$. This may be attributed to the increased hydrophobic effect due to the increase in size of nonpolar side chains of amino acids from L-valine to L-phenylalanine. The magnitude of $\Delta_{tr}V_2^o$, after passing the minimum, increases with glycerol concentration very gradually for L-leucine and quite sharply for L-phenylalanine. In the case of glycine and DL-alanine, the shape of the curves, in spite of the overall positive $\Delta_{tr}V_2^o$ values, show that there is some small negative contribution too which flattens the plot for concentration of glycerol ≤ 1.0 m_B. It is interesting to note that $\Delta_{tr}V_2^o$ plots of all the amino acids, except L-leucine, cross at around 3.2 m_B, with $\Delta_{tr}V_2^o \approx 1.5$ cm³-mol⁻¹. Mishra and Ahluwalia reported[19] enthalpies, heat capacities, and apparent molar volumes of transfer of some amino acids from water to aqueous t-butanol solutions. The behavior of the apparent molar volume of transfer at 0.1 mol-kg⁻¹ of amino acids in aqueous solutions of t-butanol is similar to that observed in aqueous glycerol solutions. All the amino acids, except glycine, show a minimum around 0.03 mole fraction of t-butanol and the negative value of $\Delta_{tr}V_2^o$ around this mole fraction increases with increasing side-chain length of amino acids. However, after passing through minima, the $\Delta_{tr}V_2^o$ values increase and becomes highly positive with increasing mole fraction of t-butanol. In the present case, the mole fraction of glycerol in water around the 0.5 m_B becomes $0.0089 \approx 0.01$, thus suggesting that glycerol acts more strongly for this negative contribution; the logical reason is the increasing hydrophilic behavior of glycerol. They have suggested that the combined effects of various hydrophobic and hydrophilic interactions are operating in these solutions. The present behavior is just in consonance.

Franks et $al.$[20] showed that the partial molar volume of a nonelectrolyte is a combination of the intrinsic volume V_{int} of the nonelectrolyte and volume V_s due to its interactions with the solvent. The intrinsic volume is considered to be made up of two types of contributions.

$$V_{int} = V_{vw} + V_{void}$$

Shahidi et $al.$[21] modified this equation to include the contribution of interactions of a nonelectrolyte solute with the solvent.

$$V_2^o = V_{vw} + V_{void} - n\sigma_s$$

where σ_s is the shrinkage in volume produced by the interactions of hydrogen bonding groups present in the solute with water molecules and n is the potential number of hydrogen bonding sites in the molecule. For electrolytes and zwitterionic

solutes, the shrinkage is caused by electrostriction; finally, V_2^o can be evaluated as

$$V_2^o = V_{vw} + V_{void} - V_{shrinkage}$$

It has been reported[22] that V_{vw} and V_{void} have the same magnitude in water and in mixed solvents for the same class of compounds. Therefore, the observed positive $\Delta_{tr}V_2^o$ values can be attributed to the decrease in volume of shrinkage, whereas negative $\Delta_{tr}V_2^o$ values are attributed to an increase in volume of shrinkage in the presence of glycerol. For glycine and DL-α-alanine, having positive $\Delta_{tr}V_2^o$ values, shrinkage will be very small, however; and for L-valine, L-leucine, and L-phenylalanine, where both positive and negative $\Delta_{tr}V_2^o$ values have been observed, $V_{shrinkage}$ will be large in the lower concentration range and very small in at higher concentration of glycerol.

The cosphere overlap model, developed by Gurney[23] and Frank and Evans[24] can also be utilized to rationalize $\Delta_{tr}V_2^o$ values in terms of solute and cosolute interactions. According to this model, properties of water molecules in the hydration cosphere depend on the nature of solute molecules. When two solute particles come close enough so that their cospheres overlap, some of the cosphere material is displaced and this is accompanied by changes in thermodynamic parameters. The following types of interactions are possible: (1) ion–dipolar interactions occurring between zwitterionic centers of amino acid and -OH groups of glycerol; (2) hydrophobic–hydrophilic interactions between nonpolar parts of amino acid and -OH groups of glycerol; (3) hydrophobic–hydrophobic interactions between nonpolar parts of amino acid and of glycerol.

According to the cosphere overlap model, the first type of interaction results in positive volumes of transfer, while the second and third type in negative volumes of transfer. Therefore, the positive $\Delta_{tr}V_2^o$ obtained here for glycine and DL-α-alanine, over the entire concentration range, indicate that the ion–hydrophilic interactions are dominating over the second and third type of interaction and the contribution increases with the concentration of glycerol. The negative $\Delta_{tr}V_2^o$ for L-valine, L-leucine, and L-phenylalanine in the low concentration range indicate the dominance of second and third, type of interactions over the first type. Minima observed at about 0.5 m_B glycerol indicate that the contribution from these interactions becomes a maximum at that concentration. The positive $\Delta_{tr}V_2^o$ values again suggest that the first type of interaction are dominant over the other types at higher concentrations. These observations indicate the dominant role of the charged end groups $-NH_3^+$ and $>COO^-$, in case of glycine and DL-α-alanine. The hydration spheres of glycine and DL-α-alanine are mainly composed of charge-dipole forces and an overlap of cospheres of these amino acids and glycerol would squeeze out water, resulting in positive $\Delta_{tr}V_2^o$ values. However, in the case of L-valine, L-leucine, and L-phenylalanine, the negative $\Delta_{tr}V_2^o$ values in the lower concentration region may be assigned to the dominating effect of large nonpolar side chains, which reduce the electrostriction effect of charged ends in the amino acids. Destruction

of the hydration shell of nonpolar side chain, due to its overlap with the hydration spheres of glycerol, have a negative contribution. This effect is predominant in the lower concentration region and starts diminishing after passing through the minima, which suggests that the contribution from the overlap of charged end groups of amino acids and hydroxyl groups starts building up and thus have positive $\Delta_{\text{tr}} V_2^{\text{o}}$ values at higher concentration of glycerol. These observations indicate that the hydrophobic effect dominates in the lower concentration region and the hydrophilic effect dominates in the higher concentration region. This is in line with earlier observations made on the basis of $V_{\text{shrinkage}}$.

Kozak *et al.* have proposed[25] a theory based on the McMillan–Mayer theory of solutions that permit the formal separation of effects due to interactions between pairs of solute molecules and those due to interactions involving three or more solute molecules. This approach has further been discussed by Friedman and Krishnan,[26] and Franks and Evans[24] in order to include the solute–cosolute interactions in the solvation sphere and used by various workers[9,18,22,27] to study the interactions of the amino acids and cosolutes in aqueous medium. According to this treatment, a thermodynamic transfer function at infinite dilution, e.g., $\Delta_{\text{tr}} V_2^{\text{o}}$ can be expressed as

$$\Delta_{\text{tr}} V_2^{\text{o}} = 2V_{\text{AB}}m_{\text{B}} + 3V_{\text{ABB}}m_{\text{B}}^2 + 4V_{\text{ABBB}}m_{\text{B}}^3 + \cdots \tag{4}$$

where V_{AB}, V_{ABB}, and V_{ABBB} are, respectively, the pair, triplet, and quartet interaction coefficients corresponding to a particular thermodynamic property and m_{B} is the molality of the cosolute. $\Delta_{\text{tr}} V_2^{\text{o}}$ data have been fitted into the above equation to obtain V_{AB}, V_{ABB}, and V_{ABBB} interaction coefficients, which are given in Table IV. V_{AB} is positive for glycine and DL-α-alanine and is negative for the remaining amino acids. V_{AB} is maximum for glycine, but decreases continuously from glycine to DL-α-alanine to L-valine to L-leucine to L-phenylalanine, which again strengthens the view that hydrophobic–hydrophobic and hydrophobic–hydrophilic interactions are dominating in the lower concentration ranges and their contribution increases with increasing side chains of the amino acids. Unlike V_{AB}, V_{ABB} is positive for all the amino acid studied and its magnitude increases with increase in the side chain of amino acids. The triplet interaction coefficient V_{ABB} is difficult to interpret, as these also include pairwise interaction terms. The relative weight of the various coefficients may be judged from their contribution to $\Delta_{\text{tr}} V_2^{\text{o}}$ at various molalities of glycerol and, accordingly, these contributions have been illustrated in Figs. 2–6. In case of glycine (Fig. 2), V_{AB} interactions are the most prominent and V_{ABB} and V_{ABBB} are zero up to $m_{\text{B}} \geq 2.5$. However, the DL-α-alanine V_{AB} contribution (Fig. 3) is smaller in comparision to glycine, but V_{ABB} and V_{ABBB} are a little more prominent and become more so with increasing m_{B} of glycerol. In both cases, V_{AB} varies linearly with concentration of glycerol. Figures 4–6 show that the contribution of V_{AB} for L-valine, L-leucine, and L-phenylalanine are negative

Table IV. Interaction Coefficients for Various Amino Acids in Aqueous Glycerol Solutions

Compound	V_{AB}	V_{ABB}	V_{ABBB}
Glycine	0.226	0.005	0.002
DL-α-Alanine	0.171	0.015	0.002
L-Valine	-0.647	0.324	-0.032
L-Leucine	-1.013	0.349	-0.031
L-Phenylalanine	-1.144	0.473	-0.043
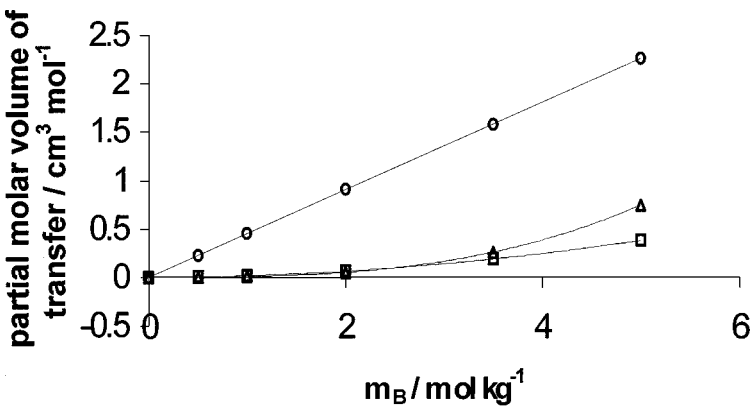
Fig. 2. Contribution of interaction coefficents to partial molar volume of transfer of glycine at various molalities of glycerol. ○, V_{AB}; □, V_{ABB}; ▲, V_{ABBB}.
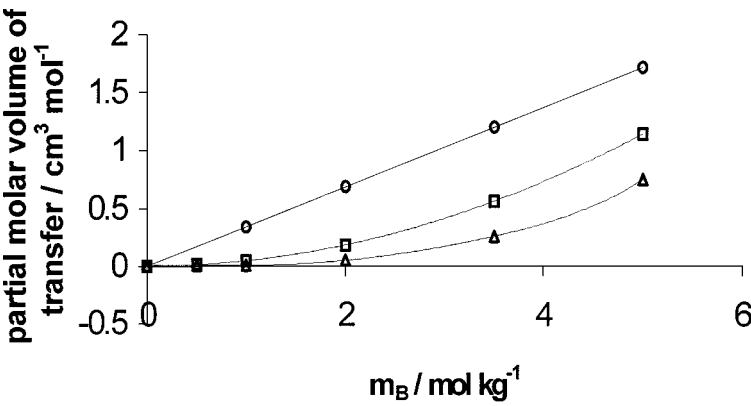
Fig. 3. Contribution of interaction coefficients to partial molar volume of transfer of DL-alanine at various molalities of glycerol. ○, V_{AB}; □, V_{ABB}; ▲, V_{ABBB}.
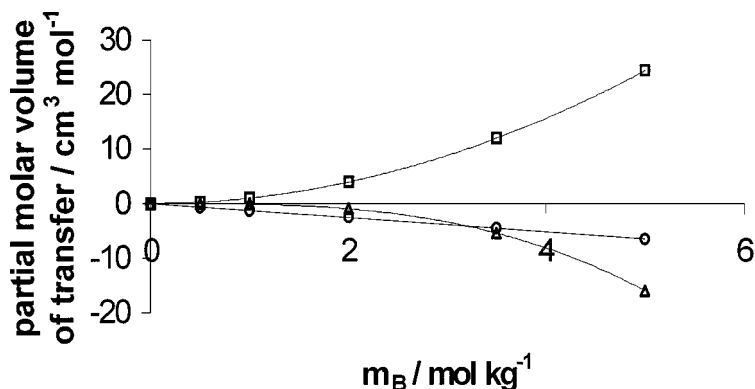
Fig. 4. Contribution of interaction coefficients to partial molar volume of transfer of L-valine at various molalities of glycerol. $\bigcirc$, V_{AB}; $\square$, V_{ABB}; $\triangle$, V_{ABBB}.

and linear. V_{ABB} is positive and highly dependent on m_B. V_{ABBB} is also negative and the magnitude increases rapidly for m_B greater than 2.

Similar trends of interaction coefficients for amino acids in aqueous t-butanol have been reported by Mishra and Ahluwalia.[19] The decrease of V_{AB} with increasing side chain of the amino acid has been attributed to a reduction in volume as association commences. At lower concentration, the zwitter ionic portion of the amino acids partially breaks down the hydrogen bonded network of water molecule in the solvation sphere of t-butanol, which results in a negative $\Delta_{tr} V_2^o$ for the amino acids. The values of V_{ABB} are positive and the magnitude increases with increasing side chain of the amino acids indicate that the tendency for cooperative aggregation increases with increasing length of the amino acid side chain. Extensive collapse
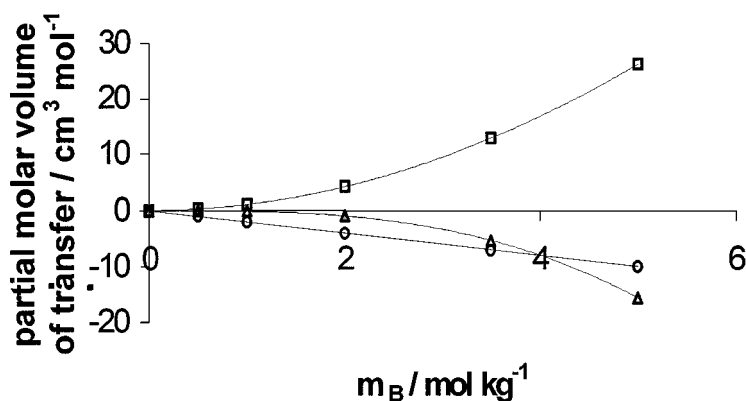

Fig. 5. Contribution of interaction coefficients to partial molar volume of transfer of L-leucine at various molalities of glycerol. $\bigcirc$, V_{AB}; $\square$, V_{ABB}; $\triangle$, V_{ABBB}.
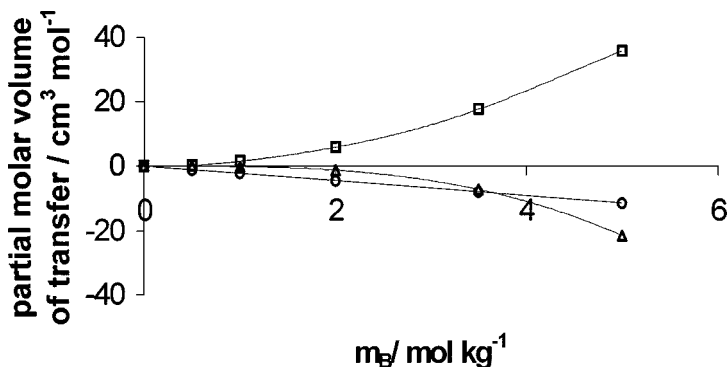
Fig. 6. Contribution of interaction coefficients to partial molar volume of transfer of
L-phenylalanine at various molalities of glycerol. ○, V_{AB}; □, V_{ABB}; ▲, V_{ABBB}.

of the long-range order of water structure does not permit any hydrophobic effect
to dominate at higher concentration.

The comparison of the volume of transfer of the amino acids, studied presently
in glycerol and reported already in 1,4-dioxane from these laboratories, is well in
place. Glycerol is highly polar ($\mu = 2.56$, $D = 42.5$), while 1,4-dioxane is a
nonpolar molecule with much smaller dielectric constant (2.2), but with a large
hydrophobic portion. Positive $\Delta_{tr}V_2^o$ for glycine and DL-α-alanine (except at 2.5%
aqueous 1,4-dioxane) were observed through out the concentration range of 1,4-
dioxane studied, as in the case of glycerol, which indicate that the ion–dipolar
interactions are dominating in both the cases for these amino acids. The magni-
tude of $\Delta_{tr}V_2^o$ for these amino acids are greater in aqueous glycerol solutions, which
may be because of hydrophilic nature of glycerol. In case of L-valine, L-leucine,
and L-phenylalanine at lower concentration in aqueous solutions of 1,4-dioxane,
where positive $\Delta_{tr}V_2^o$ values were observed, the hydrophobic hydration along
with ion–dipolar interactions dominate while at higher concentration range, the
hydrophobic–hydrophobic interactions between hydrophobic cosolvent and hy-
drophobic part of the amino acid are dominating. In aqueous solutions of glycerol,
at lower concentration, hydrophobic–hydrophobic interactions are dominating for
these amino acids, while at higher concentration, hydrophilic interactions between
charged ends of amino acids and hydrophilic cosolvent are dominating, which re-
sults in positive $\Delta_{tr}V_2^o$ values.

In conclusion, the behavior of $\Delta_{tr}V_2^o$ for amino acids in aqueous solutions of
t-butanol and glycerol is similar. In both the cases, after passing through the min-
ima, the $\Delta_{tr}V_2^o$ increases with increasing concentration of cosolvent. In both the
cases, hydrophobic interactions are dominating at lower concentration, while coop-
erative aggregation is favored at higher concentration of t-butanol and hydrophilic
interactions are dominating in aqueous glycerol. In 1,4-dioxane, the ion–dipolar

and hydrophobic hydration are dominating at lower concentration, while at higher concentration, the hydrophobic interactions are dominating.

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