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SHORT ARTICLE

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Densities, Partial Molar Volumes at Infinite Dilution, Side-Chain Partial Molar Volumes, and Transfer Volumes of Dipeptides in Sucrose and 2,3-Butanediol Aqueous Solutions at T = (283.15 to 333.15) K

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ABSTRACT: Apparent molar volumes and partial molar volumes at infinite dilution, $\overline{V}_2^o$, for dipeptides (glycyl glycine, glycyl valine, glycyl leucine, glycyl phenylalanine, and glycyl asparagine) in aqueous sucrose and 2,3-butanediol solutions have been calculated from the measured densities in the temperature range of T = (283.15 to 333.15) K. Side-chain partial molar volumes, $\overline{V}_{2,tr}^o$, and transfer volumes, ΔV_{tr}^o, for the dipeptides and side chains from water to aqueous additive environment have been calculated and analyzed in terms of possible solute−water, solute−cosolute, and cosolute−water interactions.

INTRODUCTION

Proteins are large complex biopolymers formed by peptide linkage between amino acid chains in a sequential manner. The knowledge of stability and conformational state of proteins in aqueous solution is of paramount importance in understanding their structure and specific enzymatic functions or activity.[1] The origin of protein stability in aqueous solutions is traced to the solute (protein amino acid side chain)−solvent (mostly water) interactions. The extent of these interactions are influenced by several structural and steric factors of the solute molecules and also by the nature of the solvent media, that is, whether it is pure water or contain electrolytic or nonelectrolytic additives. To study the stability of proteins experimentally, their native structure is disrupted by adding denaturants. The process of denaturation converts the native folded structure in to a form that is predominantly unfolded but still with some residual folded structure. Thus the studies with ideal conformational state of proteins are experimentally not feasible. A greater understanding of the properties of the proteins is only possible by studying the model systems of peptides with shortest of the possible chains. It is also often reported that the presence of cosolutes like sugars, polyhydroxyalcohols, nonelectrolytes such as urea, and surfactants decrease the denaturation ability of certain proteins.[2−5] Whether the diminished denaturation ability of protein is due to the direct binding of denaturants, for example, polyhydroxy compounds or sugars with protein molecules, or indirectly through alteration of water structure is still not known definitely. Simple amino acids and di- and tripeptides are some of the best model compounds to represent the shortened protein forms. A literature survey shows that the effects due to solute−solvent interactions in the aqueous solutions of several of the amino acids or di- or tripeptides have been monitored through the measurements of various thermophysical quantities based on volumetric, speed of sound, and transport properties. In contrast to numerous reports on the above systems, there are only few studies dealing with amino acid or short chain peptides in aqueous solutions of nonelectrolytes. For example, the integral enthalpies,[6,7] molar enthalpies,[8] heat capacities,[9,10] apparent molar volumes,[9−15] viscosities,[12,14] and speeds of sound[16] of some amino acids,[6−8,11−16] dipeptides,[9] and oligopeptides[10] in aqueous solutions and in the presence of additives such as glycerol,[11] 1,2-propanediol,[12] *t*-butanol,[6] urea,[8−10] and sugars[13−15] have been measured to calculate both partial molar properties as well as their limiting values and estimate the respective transfer functions corresponding to the change from water to aqueous additive environment. It has been suggested that the interactions between the hydrophilic−ionic groups, hydrophilic−hydrophilic groups, and hydrophilic−hydrophobic groups of the additive and amino acids predominate and contribute to the transfer functions. To know whether which one or combination of the interactions among the solute−solute, solute−solvent (water), solute−cosolute (additive), and cosolute−solvent contribute to the overall properties in such mixed complex systems, the experimental data on the thermophysical properties of simple dipeptides (with different side chains) in aqueous solutions of hydrophilic additives in identical conditions are highly useful. Since all biochemical processes occur in aqueous media, the data on thermophysical properties of dipeptides are of special interest to understand the stability of complex biological molecules.

Keeping this utility in mind and also looking into the scarcity of the data on various thermophysical properties of complex ternary systems of dipeptide−additive−water, the paper reports the new experimental data of densities for five dipeptides, namely, GlyGly, GlyVal, GlyLeu, GlyPhe, and GlyAsn in aqueous solutions containing sucrose and 2,3-butanediol at T = (283.15 to 333.15) K. The reason behind selecting these dipeptides is as follows. GlyGly has the simplest structure of the protein forms and is often taken as a reference for estimating the properties of the side chains typically present in large proteins. GlyVal and GlyLeu have aliphatic isopropyl and isobutyl side chains, while chains in GlyPhe are of aromatic type. GlyAsn has a carboxylamide moiety. Therefore, it is thought to be worthwhile to study these systems and estimate the partial molar volumes of different

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Table 1. Densities of Water, Sucrose, and 2,3-Butanediol Aqueous Solutions at Different Temperatures

T	ρ/g·cm^{-3}		ρ/g·cm^{-3}		ρ/g·cm^{-3}	
K	exp.	lit.[a].	exp.	lit.	exp.	
	Water		5 % (w/w) Sucrose		10 % (w/w) Sucrose	
283.15	0.999701	0.999699	1.020650		1.040432	
293.15	0.998203	0.998203	1.018840		1.038341	
298.15			1.017501	1.017018[b]	1.036980	1.032485[b]
303.15	0.995647	0.995645	1.016042		1.035325	
313.15	0.992214	0.992212	1.012432		1.031436	
323.15	0.988032	0.988030	1.008092		1.026662	
333.15	0.983193	0.983191	1.002961		1.020722	
	20 % (w/w) Sucrose		5 % (w/w) 2,3-Butanediol			
283.15	1.083813		1.002001			
293.15	1.080456		1.000325			
298.15	1.078769	1.061987[b]				
303.15	1.077111		0.997603			
313.15	1.073742		0.994005			
323.15	1.070410		0.989660			
333.15	1.067101		0.984675			

[a] Ref 20. [b] Interpolated values from ref 21.

Table 2. Densities (ρ) for Dipeptides Aqueous Solutions as a Function of Molality, m, in mol·kg^{-1} at Different Temperatures

m	ρ/g·cm^{-3}						m	ρ/g·cm^{-3}					
T/K	283.15	293.15	303.15	313.15	323.15	333.15		283.15	293.15	303.15	313.15	323.15	333.15
	GlyGly							GlyVal					
0.0100	1.000274	0.998763	0.996198	0.992760	0.988569	0.983723	0.0099	1.000277	0.998772	0.996206	0.992763	0.988562	0.983712
0.0500	1.002557	1.000992	0.998390	0.994932	0.990704	0.985829	0.0250	1.001153	0.999636	0.997055	0.993598	0.989368	0.984501
0.1501	1.008189	1.006482	1.003784	1.000274	0.995963	0.991013	0.0400	1.002019	1.000490	0.997894	0.994424	0.990165	0.985282
0.2502	1.013708	1.011848	1.009051	1.005483	1.001105	0.996072	0.0749	1.004020	1.002461	0.999832	0.996332	0.992006	0.987086
0.5003	1.027030	1.024728	1.021672	1.017940	1.013449	1.008195	0.0999	1.005441	1.003859	1.001208	0.997686	0.993313	0.988368
0.9994	1.051688	1.048299	1.044661	1.040518	1.036046	1.030266	0.1199	1.006572	1.004969	1.002301	0.998764	0.994353	0.989387
	GlyLeu							GlyPhe					
0.0100			0.996133	0.992686	0.988502	0.983654	0.0100	1.000400	0.998880	0.996315	0.992869	0.988688	0.983842
0.0199			0.996611	0.993151	0.988965	0.984109	0.0200	1.001096	0.999555	0.996980	0.993521	0.989340	0.984489
0.0399			0.997569	0.994086	0.989892	0.985021	0.0401	1.002488	1.000905	0.998308	0.994825	0.990641	0.985780
0.0599			0.998518	0.995013	0.990808	0.985924	0.0601	1.003862	1.002239	0.999617	0.996112	0.991923	0.987053
0.0799			0.999456	0.995932	0.991713	0.986818	0.0801	1.005227	1.003565	1.000915	0.997390	0.993191	0.988315
0.0998			1.000378	0.996839	0.992604	0.987699	0.1001	1.006580	1.004881	1.002203	0.998659	0.994447	0.989567
	GlyAsn												
0.0100			0.996431	0.992988	0.988799	0.983949							
0.0250			0.997602	0.994145	0.989944	0.985078							
0.0400			0.998769	0.995296	0.991084	0.986202							
0.0750			1.001471	0.997962	0.993721	0.988801							
0.1000			1.003384	0.999849	0.995587	0.990640							
0.1300			1.005662	1.002094	0.997805	0.992826							

side chains and calculate the volumes of transfer due to change in solvent environment, that is, from aqueous to additive solutions. The sign and magnitude of transfer volumes would indicate the effect of the given side chain on the nature of solute−solvent interactions. A wide range of temperature for the measurements is selected to explore how volumetric properties are affected by the possible change in conformational equilibrium within dipeptide molecules[17] in dilute aqueous solutions. Moreover, the hydrophobic hydration effects especially caused by alkyl side chains are also sensitive to temperatures,[18,19] and therefore, temperature-dependent side chain volumes and their transfer functions are also of great utility.

The partial molar volumes at infinite dilution and at different temperatures were calculated from the experimental density data.

Table 3. Densities (ρ) for Dipeptides in Sucrose and 2,3-Butanediol Aqueous Solutions as a Function of Molality, m, in mol·kg^{-1} at Different Temperatures

m	ρ/g·cm^{-3}						m	ρ/g·cm^{-3}					
T/K	283.15	293.15	303.15	313.15	323.15	333.15		283.15	293.15	303.15	313.15	323.15	333.15
5 % (w/w) Sucrose													
GlyGly								GlyVal					
0.0101	1.021218	1.019399	1.016591	1.012973	1.008627	1.003488	0.0100	1.021217	1.019402	1.016593	1.012971	1.008614	1.003468
0.0503	1.023466	1.021610	1.018763	1.015124	1.010746	1.005573	0.0250	1.022063	1.020242	1.017417	1.013775	1.009393	1.004227
0.1509	1.029001	1.027052	1.024113	1.020423	1.015964	1.010713	0.0399	1.022899	1.021071	1.018230	1.014571	1.010162	1.004976
0.2516	1.034411	1.032375	1.029345	1.025607	1.021070	1.015749	0.0749	1.024844	1.023000	1.020123	1.016426	1.011954	1.006723
0.5032	1.047381	1.045135	1.041892	1.038053	1.033335	1.027865	0.0998	1.026210	1.024358	1.021456	1.017732	1.013214	1.007955
1.0063	1.071060	1.068458	1.064875	1.060904	1.055844	1.050217	0.1298	1.027840	1.025975	1.023045	1.019293	1.014717	1.009426
GlyLeu								GlyPhe					
0.0100			1.016518	1.012901	1.008558	1.003417	0.0100	1.021366	1.019535	1.016719	1.013084	1.008741	1.003609
0.0200			1.016993	1.013367	1.009022	1.003872	0.0200	1.022080	1.020226	1.017394	1.013734	1.009388	1.004255
0.0400			1.017936	1.014296	1.009943	1.004776	0.0400	1.023498	1.021601	1.018735	1.015027	1.010672	1.005539
0.0600			1.018871	1.015217	1.010857	1.005673	0.0601	1.024911	1.022970	1.020072	1.016316	1.011952	1.006819
0.0800			1.019798	1.016131	1.011762	1.006562	0.0801	1.026305	1.024321	1.021392	1.017589	1.013214	1.008082
0.1000			1.020718	1.017038	1.012660	1.007445	0.1001	1.027688	1.025659	1.022701	1.018852	1.014466	1.009336
GlyAsn													
0.0100			1.016793	1.013174	1.008829	1.003687							
0.0250			1.017914	1.014281	1.009928	1.004770							
0.0400			1.019030	1.015384	1.011022	1.005847							
0.0750			1.021610	1.017933	1.013549	1.008338							
0.1000			1.023434	1.019735	1.015333	1.010096							
0.1300			1.025602	1.021877	1.017451	1.012183							
10 % (w/w) Sucrose													
GlyGly								GlyVal					
0.0103	1.041003	1.038903	1.035871	1.031972	1.027194	1.021243	0.0101	1.040984	1.038882	1.035855	1.031958	1.027166	1.021232
0.0515	1.043273	1.041142	1.038063	1.034125	1.029317	1.023324	0.0253	1.041812	1.039692	1.036650	1.032742	1.027924	1.021948
0.1545	1.048851	1.046647	1.043453	1.039422	1.034538	1.028441	0.0405	1.042636	1.040498	1.037440	1.033521	1.028678	1.022681
0.2575	1.054294	1.052018	1.048716	1.044594	1.039639	1.033439	0.0759	1.044542	1.042360	1.039265	1.035323	1.030420	1.024373
0.5149	1.067327	1.064888	1.061326	1.056997	1.051868	1.045417	0.1012	1.045892	1.043676	1.040557	1.036599	1.031653	1.025570
1.0298	1.091054	1.088352	1.084364	1.079665	1.074246	1.067330	0.1315	1.047493	1.045240	1.042089	1.038115	1.033116	1.026997
GlyLeu								GlyPhe					
0.0100			1.035774	1.031881	1.027103	1.021156	0.0100	1.041117	1.038997	1.035956	1.032060	1.027278	1.021342
0.0200			1.036220	1.032324	1.027542	1.021587	0.0200	1.041799	1.039651	1.036585	1.032680	1.027891	1.021960
0.0400			1.037109	1.033205	1.028415	1.022444	0.0400	1.043155	1.040950	1.037834	1.033914	1.029110	1.023188
0.0600			1.037989	1.034076	1.029278	1.023292	0.0599	1.044493	1.042231	1.039066	1.035130	1.030311	1.024398
0.0800			1.038861	1.034940	1.030134	1.024133	0.0799	1.045827	1.043509	1.040294	1.036342	1.031508	1.025604
0.1000			1.039726	1.035794	1.030981	1.024965	0.0999	1.047150	1.044776	1.041512	1.037544	1.032695	1.026800
GlyAsn													
0.0100			1.036060	1.032164	1.027383	1.021432							
0.0250			1.037158	1.033250	1.028460	1.022493							
0.0400			1.038250	1.034330	1.029530	1.023547							
0.0749			1.040770	1.036822	1.031993	1.025975							
0.0999			1.042557	1.038587	1.033734	1.027695							
0.1299			1.044680	1.040684	1.035801	1.029734							
20 % (w/w) Sucrose													
GlyGly								GlyVal					
0.0098	1.084338	1.080971	1.077620	1.074232	1.070896	1.067572	0.0104	1.084345	1.080988	1.077629	1.074234	1.070884	1.067552
0.0491	1.086443	1.083050	1.079649	1.076197	1.072833	1.069452	0.0260	1.085139	1.081782	1.078403	1.074970	1.071591	1.068226

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Table 3. Continued

m			ρ/g·cm^{-3}				m			ρ/g·cm^{-3}			
0.1473	1.091624	1.088166	1.084645	1.081033	1.077605	1.074082	0.0416	1.085928	1.082571	1.079172	1.075702	1.072294	1.068896
0.2455	1.096691	1.093173	1.089535	1.085768	1.082277	1.078615	0.0780	1.087755	1.084399	1.080952	1.077397	1.073923	1.070449
0.4910	1.108876	1.105234	1.101315	1.097177	1.093531	1.089531	0.1040	1.089046	1.085691	1.082210	1.078597	1.075075	1.071547
0.9820	1.131293	1.127477	1.123073	1.118271	1.114350	1.109695	0.1352	1.090579	1.087227	1.083704	1.080023	1.076443	1.072854
			GlyLeu							GlyPhe			
0.0101			1.077513	1.074139	1.070799	1.067476	0.0095	1.084390	1.081015	1.077652	1.074275	1.070932	1.067621
0.0201			1.077909	1.074530	1.071182	1.067844	0.0189	1.084959	1.081566	1.078184	1.074799	1.071446	1.068133
0.0402			1.078699	1.075309	1.071945	1.068578	0.0379	1.086100	1.082671	1.079249	1.075850	1.072476	1.069158
0.0602			1.079478	1.076075	1.072697	1.069300	0.0568	1.087226	1.083760	1.080297	1.076885	1.073490	1.070166
0.0803			1.080253	1.076837	1.073444	1.070017	0.0758	1.088347	1.084844	1.081338	1.077914	1.074498	1.071168
0.1004			1.081019	1.077589	1.074183	1.070725	0.0947	1.089452	1.085912	1.082359	1.078927	1.075490	1.072153
			GlyAsn										
0.0100			1.077812	1.074429	1.071090	1.067774							
0.0250			1.078858	1.075454	1.072105	1.068777							
0.0400			1.079898	1.076474	1.073113	1.069774							
0.0750			1.082299	1.078830	1.075441	1.072075							
0.1000			1.083995	1.080495	1.077083	1.073698							
0.1300			1.086007	1.082471	1.079032	1.075621							
							5 % (w/w) 2,3-Butanediol						
			GlyGly							GlyVal			
0.0098	1.002553	1.000870	0.998137	0.994534	0.990175	0.985180	0.0100	1.002563	1.000896	0.998163	0.994555	0.990185	0.985184
0.0490	1.004751	1.003037	1.000264	0.996640	0.992223	0.987191	0.0250	1.003404	1.001749	0.999001	0.995377	0.990969	0.985946
0.1469	1.010158	1.008370	1.005498	1.001824	0.997268	0.992140	0.0401	1.004247	1.002604	0.999840	0.996200	0.991755	0.986709
0.2448	1.015449	1.013591	1.010622	1.006901	1.002208	0.996987	0.0752	1.006192	1.004577	1.001775	0.998099	0.993567	0.988472
0.4896	1.028189	1.026168	1.022976	1.019141	1.014121	1.008670	0.1003	1.007571	1.005976	1.003146	0.999443	0.994852	0.989722
0.9791	1.051649	1.049365	1.045782	1.041762	1.036165	1.030274	0.1304	1.009213	1.007639	1.004777	1.001041	0.996379	0.991210
			GlyLeu							GlyPhe			
0.0100			0.998104	0.994493	0.990146	0.985153	0.0100	1.002760	1.001064	0.998323	0.994707	0.990352	0.985363
0.0200			0.998603	0.994979	0.990629	0.985629	0.0199	1.003508	1.001793	0.999034	0.995399	0.991033	0.986041
0.0400			0.999596	0.995946	0.991591	0.986576	0.0398	1.005005	1.003250	1.000455	0.996783	0.992396	0.987396
0.0599			1.000577	0.996900	0.992540	0.987510	0.0597	1.006492	1.004697	1.001865	0.998156	0.993749	0.988740
0.0799			1.001555	0.997851	0.993486	0.988441	0.0796	1.00796	1.006133	1.003266	0.999519	0.995091	0.990073
0.0999			1.002526	0.998794	0.994425	0.989364	0.0995	1.009433	1.007559	1.004655	1.000871	0.996422	0.991395
			GlyAsn										
0.0100			0.998384	0.994775	0.990424	0.985430							
0.0249			0.999543	0.995918	0.991557	0.986550							
0.0399			1.000704	0.997062	0.992691	0.987672							
0.0748			1.003383	0.999702	0.995309	0.990258							
0.0998			1.005284	1.001574	0.997166	0.992092							
0.1297			1.007536	1.003793	0.999366	0.994264							

The partial molar volumes for the side chains and their transfer volumes at different temperatures have been calculated from the corresponding data of amino acids and dipeptide aqueous solutions respectively to compare and discuss the differences.

EXPERIMENTAL SECTION

Materials. The dipeptide glycylglycine (GlyGly) (CAS number 61499-00-1) was of Lancaster, U. K. make with a mole purity of 98 %. Glycylalanine (glyala) (CAS number 53483-93-9), glycylvaline (GlyVal) (CAS number 89458-24-2), glycylleucine (GlyLeu) (CAS number 869-19-2), glycylphenylalanine (GlyPhe) (CAS number 21438-66-4), and glycylasparagine (GlyAsn) (CAS number 2058-58-4) were of Sigma make with purities of 99 % on mole basis. These substances were used as received. However the samples were dried in vacuum over P_2O_5 in a desiccator for 72 h at room temperature. Sucrose of extra pure grade was purchased from HIGHMEDIA, India. 2,3-Butanediol of analytical reagent grade quality was locally purchased. The additive substances were also kept and dried over P_2O_5 in vacuum desiccator to avoid any moisture contamination.

Methods. The solutions of different molalities were prepared in fresh, degassed, and four times distilled water by mass measurements of the solute samples, accurate to ± 0.01 mg. A single pan analytical balance, (Dhona 100 DS, India) was used. The solutions were prepared fresh, and the measurements were

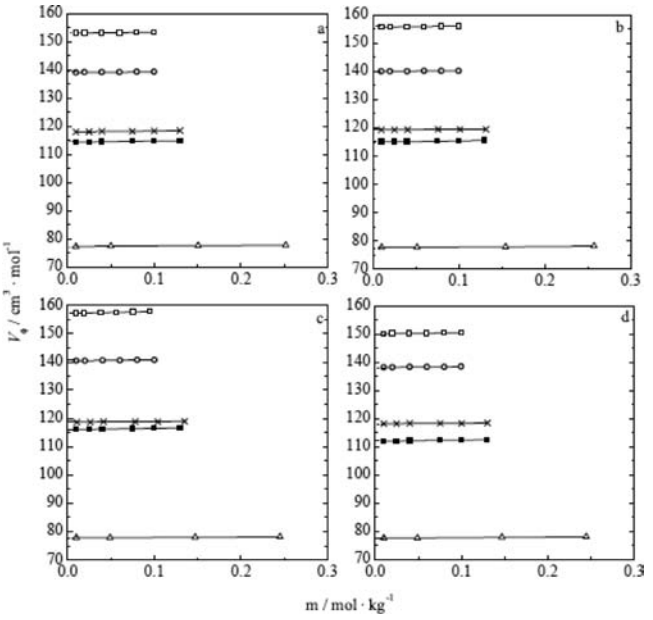

Figure 1. Apparent molar volume versus molality plots for dipeptides in additive aqueous solutions at T = 303.15 K: (a) 5 % (w/w) sucrose; (b) 10 % (w/w) sucrose; (c) 20 % (w/w) sucrose; (d) 5 % (w/w) 2,3-butanediol: △, GlyGly; ×, GlyVal; ○, GlyLeu; □, GlyPhe; ■, GlyAsn.

completed on the same day. The dipeptides are considered as solutes and the additives as cosolute. Densities of the solutions were measured using a high-precision vibrating tube digital densimeter (model DMA 5000), Anton Paar, Austria. The densimeter was calibrated with air and four times distilled and freshly degassed water at each measuring temperature through a special adjustment procedure driven by in-built software. The repeatability of the temperature has been found to be ± 0.003 K. The uncertainty in the temperature during the measurements, however, is ± 0.01 K because Pt100 measuring sensors were used. The repeatability of densities for successive measurements was ± $1.2 \cdot 10^{-6}$ g·cm^{-3}. The experimental densities of water and additive aqueous solutions along with the literature values[20,21] at different temperatures are listed in Table 1. The absolute mean deviations between the experimental and the literature values was $2.8 \cdot 10^{-6}$. Therefore, the precision and accuracy of reported densities for water are ± $1.2 \cdot 10^{-6}$ g·cm^{-3} and ± $2.8 \cdot 10^{-6}$ g·cm^{-3}, respectively.

■ RESULTS AND DISCUSSION

The experimental densities of the five dipeptides, namely, GlyGly, GlyVal, GlyLeu, GlyPhe, and GlyAsn, in water as well as in aqueous solutions of sucrose [(5 to 20) % (w/w)] and 2,3-butanediol, 5 % (w/w), at different temperatures are given in Tables 2 and 3. The apparent molar volumes, V_ϕ were calculated from the relation,

$$V_\phi = M/\rho - (1000(\rho - \rho_o)/m\rho\rho_o) \quad (1)$$

where M is molar mass of the solute, m is the molality of the solute, and ρ and ρ_o are the densities of the solutions and solvent, respectively. The standard partial molar volume, also known as partial molar volume at infinite dilution, $\overline{V}_2^o$, was then obtained by least-squares fitting to the linear equation:

$$V_\phi = \overline{V}_2^o + S_v m \quad (2)$$

in which S_v is the experimental slope.

The representative linear plots of V_ϕ versus m for dipeptide aqueous solutions at T = 303.15 K are shown in Figure 1. The summary of values of $\overline{V}_2^o$ and S_v together with standard deviations of the fit for the eq 2 at different temperatures is given in Table 4. $\overline{V}_2^o$ values varied linearly with the temperature (please see Figure 2). A perusal of the data revealed that the slope, S_v, values in general are positive, indicating strong solute−solvent interactions in these systems.

Transfer Volumes. The transfer volumes for each of the dipeptides, ΔV^o, from water to aqueous additive solutions were calculated by the relation,

$$\Delta V^o = \overline{V}_2^o(\text{in aqueous additive solutions}) - \overline{V}_2^o(\text{water}) \quad (3)$$

The results of ΔV^o are summarized in Table 5. The temperature dependence of ΔV^o values for dipeptides is depicted in Figure 3. No definite general trends could be noted in ΔV^o variations with temperature. However, it can be seen from the data presented in the Table that ΔV^o values are positive for GlyGly, GlyVal, and GlyAsn and increased continuously with the mass percent of the sucrose. This means that the GlyGly, GlyVal, and GlyAsn when added to sucrose solutions induce in general structure breaking among the cosolute molecules; at higher sucrose content, the cyclic structure of sucrose may be maximally broken, and the electrostriction effect is decreased in mixed additive/water system as compared to that in pure water. The latter effect contributes to the increase in volume of the solvent, that is, leads to more positive ΔV^o values. Similarly the addition of these three dipeptides to 5 % 2,3-butanediol aqueous solutions has also been found have a structure-breaking effect, but the extent of the effect varied from dipeptide to dipeptide.

The ΔV^o values for the solutions of GlyLeu and GlyPhe in 5 % and 10 % sucrose aqueous media were negative. The ΔV^o values for the same dipeptides in 20 % sucrose solutions were however positive. This clearly indicates that the interactions between GlyLeu and GlyPhe−sucrose are not strong in the low mass percent of sucrose [(5 to 10) %] due to the presence of highly hydrophobic isobutyl and methylphenyl side chains. However, when the sucrose mass percent is increased to 20, considerable interactions between the −OH group of sucrose and zwitterionic centers of GlyLeu and GlyPhe can occur, leading to the breaking of cyclic sucrose structures. The ΔV^o values for GlyLeu and GlyPhe are largely negative in 5 % 2,3-butanediol aqueous solutions. The negative ΔV^o values result due to the electrostriction of water. 2,3-Butanediol as such has two terminal methyl groups which would push water−water interactions and contribute to strong electrostriction and at the same time interact with the solute species through hydrophobic−ion group interactions.

Side-Chain Partial Molar Volumes, $\overline{V}_{2,tr}^o$. The side-chain partial molar volumes, $\overline{V}_{2,tr}^o$ {($\overline{V}_2^o$ of dipeptides/additive/water) − ($\overline{V}_2^o$ GlyGly/additive/water)}, and their transfer volumes ΔV^o_{tr} {($\overline{V}_{2,tr}^o$ (dipeptides/additive/water − GlyGly/additive/water)) − ($\overline{V}_{2,tr}^o$ (dipeptides/water − GlyGly/water))}, for the three side chains, namely, isopropyl, isobutyl, and methylphenyl, were estimated.

Table 6 gives a comparison of the side-chain volumes as obtained from the volumetric data on corresponding amino acids and as well as dipeptide solutes. Clear and very significant differences in the partial molar volumes for the same side chain were noted depending upon the $\overline{V}_2^o$ of the base solutes, that is, amino acids or dipeptides. The partial molar volumes of a given side chain as

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Table 4. Partial Molar Volume at Infinite Dilution ($\overline{V}_2^o$ in $cm^3 \cdot mol^{-1}$) and Slope (S_v in $cm^3 \cdot kg \cdot mol^{-2}$) for Dipeptide Aqueous Solutions at Different Temperatures

T/K	$\overline{V}_2^o$	S_v	$\overline{V}_2^o$	S_v	$\overline{V}_2^o$	S_v	$\overline{V}_2^o$	S_v
				% (w/w) Sucrose				
	0		5		10		20	
				GlyGly				
283.15	74.73	1.42	75.38	2.13	75.72	2.01	75.99	1.38
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
293.15	76.06	2.07	76.32	2.03	76.47	1.88	76.68	1.20
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
303.15	77.04	2.28	77.33	1.88	77.62	1.75	77.87	1.10
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
313.15	77.60	2.56	77.97	1.70	78.60	1.66	79.42	0.98
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
323.15	78.67	1.92	78.85	1.68	79.45	1.59	80.12	0.95
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
333.15	79.52	2.22	79.83	1.37	80.62	1.57	81.51	0.94
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
				GlyVal				
283.15	115.95	1.36	116.13	4.18	116.84	1.41	117.13	1.92
	(±0.01)	(±0.01)	(±0.01)	(±0.03)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
293.15	116.75	2.82	116.69	3.91	118.04	2.23	117.37	1.58
	(±0.01)	(±0.02)	(±0.01)	(±0.03)	(±0.01)	(±0.01)	(±0.01)	(±0.02)
303.15	117.95	2.0	117.93	3.34	119.22	2.08	118.71	1.92
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
313.15	119.13	1.36	119.43	1.89	120.20	1.21	121.11	0.88
	(±0.01)	(±0.01)	(±0.01)	(±0.02)	(±0.01)	(±0.02)	(±0.01)	(±0.02)
323.15	121.37	1.36	121.36	3.23	122.17	1.32	122.94	1.18
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
333.15	122.86	0.82	123.16	1.68	122.12	1.63	125.11	0.63
	(±0.01)	(±0.02)	(±0.01)	(±0.02)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
				GlyLeu				
303.15	139.91	6.42	139.01	3.00	139.85	2.86	140.47	1.99
	(±0.01)	(±0.05)	(±0.01)	(±0.01)	(±0.01)	(±0.03)	(±0.01)	(±0.01)
313.15	141.66	3.00	140.10	2.33	140.53	3.87	141.09	4.59
	(±0.01)	(±0.01)	(±0.01)	(±0.03)	(±0.01)	(±0.03)	(±0.01)	(±0.04)
323.15	142.20	7.13	140.76	3.53	141.37	3.86	142.13	4.11
	(±0.01)	(±0.04)	(±0.01)	(±0.02)	(±0.01)	(±0.03)	(±0.01)	(±0.03)
333.15	143.59	4.79	142.20	2.46	142.67	4.14	143.72	4.78
	(±0.01)	(±0.04)	(±0.01)	(±0.02)	(±0.01)	(±0.03)	(±0.01)	(±0.04)
				GlyPhe				
283.15	152.24	2.46	148.82	3.99	150.21	3.00	153.21	3.66
	(±0.01)	(±0.02)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.02)
293.15	154.55	0.99	151.05	4.38	153.04	3.00	155.13	4.45
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.04)
303.15	155.69	4.33	152.99	2.99	155.65	3.00	157.12	7.03
	(±0.01)	(±0.03)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.04)
313.15	157.36	1.99	155.75	1.99	156.72	3.47	158.21	5.42
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.02)	(±0.01)	(±0.03)
323.15	157.59	6.73	156.44	1.66	157.91	3.34	159.54	5.27
	(±0.01)	(±0.05)	(±0.01)	(±0.04)	(±0.01)	(±0.03)	(±0.01)	(±0.01)
333.15	158.71	4.32	157.02	2.46	158.04	3.54	160.06	6.33
	(±0.01)	(±0.04)	(±0.01)	(±0.02)	(±0.01)	(±0.02)	(±0.01)	(±0.01)

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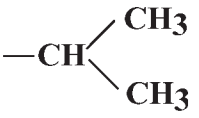
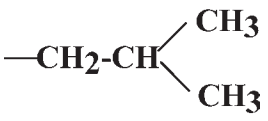
Table 4. Continued

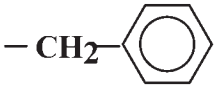
T/K	$\overline{V}_2^o$	S_v	$\overline{V}_2^o$	S_v	$\overline{V}_2^o$	S_v	$\overline{V}_2^o$	S_v
				GlyAsn				
303.15	111.80	2.66	114.29	4.18	114.99	3.43	116.02	4.48
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.03)
313.15	112.90	3.33	115.34	4.00	115.85	4.21	117.42	3.68
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.3)	(±0.01)	(±0.01)
323.15	113.79	4.09	116.00	5.44	116.63	6.18	118.18	4.88
	(±0.01)	(±0.03)	(±0.01)	(±0.04)	(±0.01)	(±0.03)	(±0.01)	(±0.02)
333.15	115.09	4.09	117.32	5.01	117.98	5.23	119.01	5.23
	(±0.01)	(±0.03)	(±0.01)	(±0.02)	(±0.01)	(±0.01)	(±0.01)	(±0.01)
				5 % (w/w) 2,3-Butanediol				
	GlyGly		GlyVal		GlyLeu		GlyPhe	
283.15	75.66	1.89	117.76	1.23			146.07	2.43
	(±0.01)	(±0.01)	(±0.01)	(±0.01)			(±0.01)	(±0.04)
293.15	76.47	1.75	117.01	1.68			148.19	2.55
	(±0.01)	(±0.01)	(±0.01)	(±0.02)			(±0.01)	(±0.02)
303.15	77.58	1.61	118.23	1.99	138.22	2.47	150.24	2.48
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.02)	(±0.01)	(±0.02)
313.15	78.20	1.55	119.49	2.24	139.85	3.08	152.39	3.01
	(±0.01)	(±0.01)	(±0.01)	(±0.03)	(±0.01)	(±0.04)	(±0.01)	(±0.01)
323.15	79.81	1.41	112.37	1.64	140.49	3.13	153.82	3.02
	(±0.01)	(±0.01)	(±0.01)	(±0.02)	(±0.01)	(±0.03)	(±0.01)	(±0.01)
333.15	80.94	1.42	124.31	0.66	141.73	3.34	154.63	3.55
	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.01)	(±0.03)	(±0.01)	(±0.02)
	GlyAsn							
303.15	112.02	4.01						
	(±0.01)	(±0.01)						
313.15	113.24	4.40						
	(±0.01)	(±0.02)						
323.15	114.05	4.36						
	(±0.01)	(±0.01)						
333.15	115.12	4.78						
	(±0.01)	(±0.01)						



Isopropyl



Isobutyl



Methylphenyl

calculated using $\overline{V}_2^o$ of dipeptides were smaller as compared to the values derived from $\overline{V}_2^o$ of amino acids. These observed differences can be explained by taking into the consideration of the fact that the charged $-NH_3^+$ and $-COO^-$ groups are positioned differently in amino acids and dipeptides structures. The two charged functional groups are adjacent to the side chains in amino acids and while the side chains in dipeptides are adjacent only to $-COO^-$ groups. Moreover, the electrostriction of $-NH_3^+$ and $-COO^-$ groups and the contribution to $\overline{V}_2^o$ for a side chain will be more positive in amino acids than for glycyl dipeptides due to the shielding of the side chains in amino acids. The partial molar volumes for the carboxylamide ($-CH_2CONH_2$) side chain as calculated from $\overline{V}_2^o$ results of dipeptides however were higher. Hence it can be concluded that the carboxylamide side chain hardly undergoes any shielding effect. ΔV^o_{tr} are small and negative for the isopropyl side chain, and the same becomes more negative for the isobutyl and methylphenyl side chains irrespective of the contributions derived either from amino acid or dipeptides solutes. The ΔV^o_{tr} was more positive for the carboxylamide side chain when dipeptides were used as base solutes in (5 to 20) % aqueous sucrose

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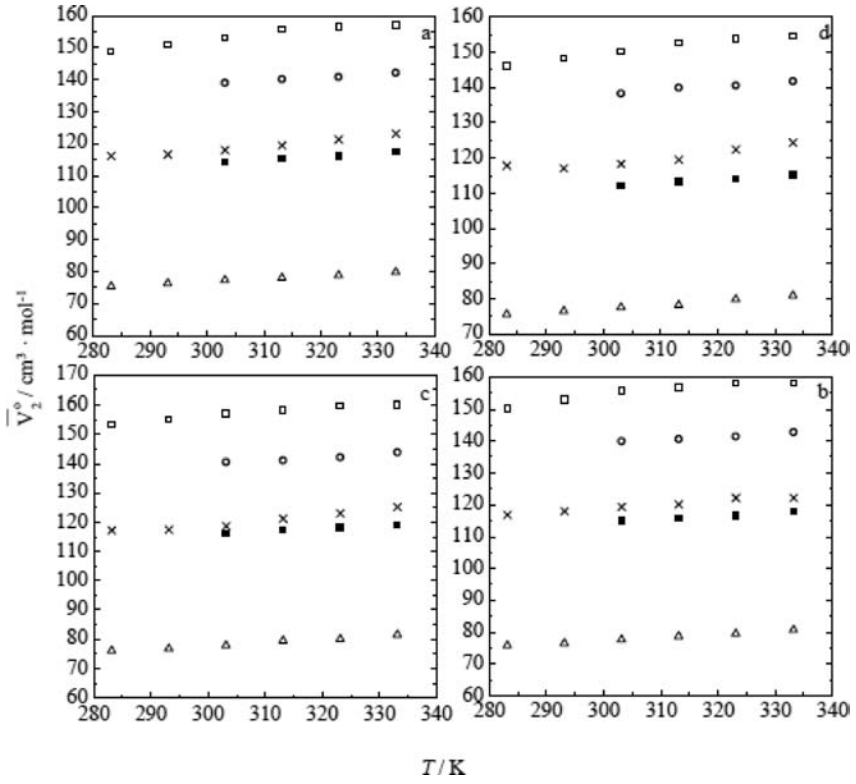

Figure 2. Temperature dependence of partial molar volumes at infinite dilution, $\overline{V}_2^\circ$ of dipeptides in aqueous additive solutions: (a) 5 % (w/w) sucrose; (b) 10 % (w/w) sucrose; (c) 20 % (w/w) sucrose; (d) 5 % (w/w) 2,3-butanediol: △, GlyGly; ×, GlyVal; ○, GlyLeu; □, GlyPhe; ■, GlyAsn.

Table 5. Transfer Volumes (ΔV° in cm$^3 \cdot$mol^{-1}) for Dipeptides in Sucrose and 2,3-Butanediol Aqueous Solutions at Different Temperatures

T/K	283.15	293.15	303.15	313.15	323.15	333.15	283.15	293.15	303.15	313.15	323.15	333.15
sucrose in % (w/v)												
			GlyGly						GlyVal			
5	0.65	0.26	0.29	0.37	0.18	0.31	0.18	−0.06	−0.02	0.3	−0.01	0.30
10	0.99	0.41	0.58	1.00	0.78	1.10	0.89	1.29	1.27	1.07	0.80	−0.74
20	1.26	0.62	0.83	1.82	1.45	1.99	1.18	0.62	0.76	1.98	1.57	2.25
5 % 2,3-butanediol												
	0.93	0.41	0.54	0.6	1.14	1.42	1.81	0.26	0.28	0.36	0.99	1.45
sucrose in % (w/v)												
			GlyLeu						GlyPhe			
5			−0.90	−1.56	−1.44	−1.39	−3.42	−3.50	−2.70	−1.61	−1.15	−1.69
10			−0.06	−1.13	−0.83	−0.92	−2.03	−1.51	−0.04	−0.64	0.32	−0.67
20			0.56	−0.57	−0.07	0.13	−3.42	−3.50	−2.70	−1.61	−1.15	−1.69
5 % 2,3-butanediol												
			−1.69	−1.81	−1.71	−1.86	−2.03	−1.51	−0.04	−0.64	0.32	−0.67
sucrose in % (w/v)												
			GlyAsn									
5			2.49	2.44	2.21	2.23						
10			3.19	2.95	2.84	2.89						
20			4.22	4.52	4.39	3.92						
5 % 2,3-butanediol												
			0.22	0.34	0.26	0.03						

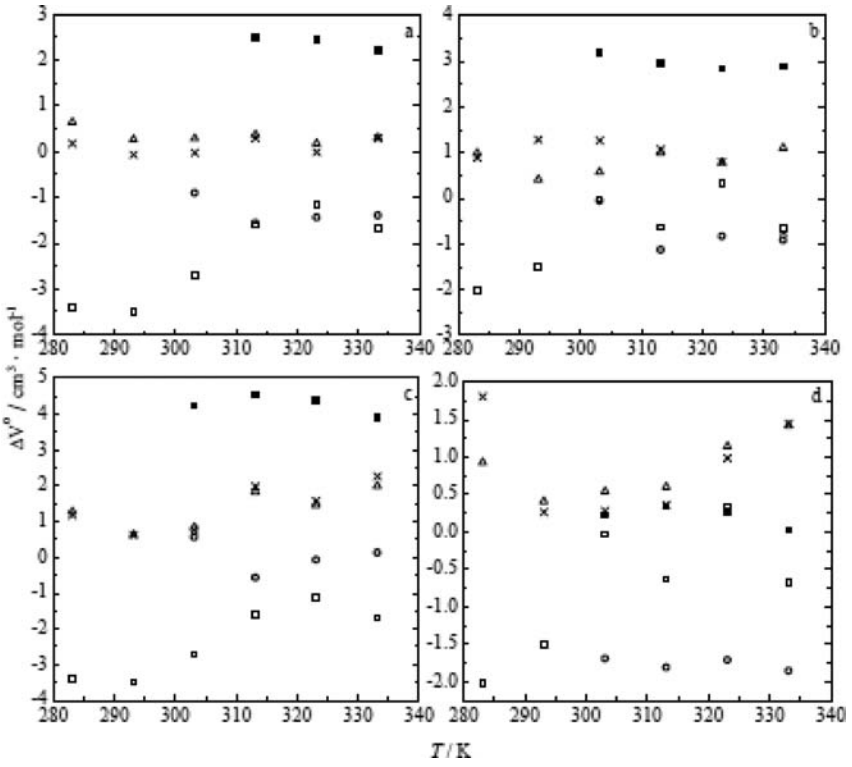

Figure 3. Temperature dependence of transfer volumes, ΔV^o (eq 3) for dipeptides: (a) 5 % (w/w) sucrose; (b) 10 % (w/w) sucrose; (c) 20 % (w/w) sucrose; (d) 5 % (w/w) 2,3-butanediol: △, GlyGly; ×, GlyVal; ○, GlyLeu; □, GlyPhe; ■, GlyAsn.

Table 6. Comparison of Side Chain Partial Molar Volumes ($\overline{V}_2^o$ in cm$^3 \cdot$mol^{-1}), and Transfer Volumes ($\Delta V^o_{tr,water \rightarrow additives}$ in cm$^3 \cdot$mol^{-1}) for Dipeptides and Amino Acids[a] in Sucrose and 2,3-Butanediol Aqueous Solutions at Different Temperatures

T / K	$\overline{V}_2^o{}_{tr}$								$\Delta V^o{}_{tr,water \rightarrow additives}$							
	5 % sucrose		10 % sucrose		20 % sucrose		5 % 2,3-butanediol		5 % sucrose		10 % sucrose		20 % sucrose		5 % 2,3-butanediol	
												Side chain —CH(CH$_3$)$_2$				
	Di-peptide	Amino Acid	Di-peptide	Amino Acid	Di-peptide	Amino Acid	Di-peptide	Amino Acid	Di-peptide	Amino Acid	Di-peptide	Amino Acid	Di-peptide	Amino Acid	Di-peptide	Amino Acid
283.15	40.75	46.71	41.12	46.58	41.14	46.00	42.10	46.51	-0.47	-0.39	-0.1	-0.52	-0.08	-1.10	0.88	-0.59
293.15	40.37	46.40	41.57	46.51	40.69	46.43	40.54	46.76	-0.32	-0.87	0.88	-0.76	0.00	-0.84	-0.15	-0.51
303.15	40.60	47.11	41.60	46.83	40.84	46.81	40.65	46.25	-0.31	-0.19	0.69	-0.47	-0.07	-0.49	-0.26	-1.05
313.15	41.46	47.60	41.60	47.28	41.69	47.05	41.29	46.55	-0.07	-0.39	0.07	-0.71	0.16	-0.94	-0.24	-1.44
323.15	42.51	47.92	42.72	47.34	42.82	47.51	42.55	47.18	-0.19	-0.01	0.02	-0.59	0.12	-0.42	-0.15	-0.75
333.15	43.33	48.04	41.50	48.38	43.60	48.14	43.37	48.18	-0.01	-0.56	-1.84	-0.22	0.26	-0.46	0.03	-0.42
													Side chain —CH$_2$-CH(CH$_3$)$_2$			
303.15	61.69	61.66	62.23	62.65	62.60	62.59	60.64	62.92	-1.18	-2.61	-0.64	-1.62	-0.27	-1.68	-2.23	-1.35
313.15	62.13	62.34	61.93	62.83	61.67	62.46	61.65	62.67	-1.93	-2.73	-2.13	-2.24	-2.39	-2.61	-2.41	-2.40
323.15	61.91	62.47	61.92	63.64	62.01	62.73	60.68	63.31	-1.62	-2.63	-1.61	-1.46	-1.52	-2.37	-2.85	-1.79
333.15	62.37	62.24	62.05	63.95	62.21	62.73	60.79	63.72	-1.7	-3.09	-2.02	-1.38	-1.86	-2.60	-3.28	-1.60
												Side chain		—CH$_2$—		
303.15	75.66	75.74	77.98	75.38	79.25	76.05	72.66	76.10	-2.99	-2.51	-0.65	-2.87	0.60	-2.20	-5.99	-2.15
313.15	77.78	76.06	78.12	76.30	78.79	76.01	74.19	76.56	-1.98	-2.71	-1.64	-2.47	-0.97	-2.76	-5.57	-2.21
323.15	77.59	76.00	78.46	76.99	79.42	76.69	74.01	77.29	-1.33	-3.20	-0.46	-2.21	0.50	-2.51	-4.91	-1.91
333.15	77.19	77.65	77.42	78.06	78.55	76.99	73.69	78.11	-2.00	-2.07	-1.77	-1.66	-0.65	-2.73	-5.50	-1.61
												Side chain		-CH$_2$CONH$_2$		
303.15	36.96	35.77	37.37	36.13	38.15	36.97	34.44	37.19	2.20	0.51	2.61	0.87	3.39	1.71	-0.32	1.93
313.15	37.37	35.80	37.25	36.44	38.00	36.71	35.04	37.78	2.07	0.78	1.95	1.42	2.70	1.69	-0.26	2.76
323.15	37.15	36.43	37.18	37.36	38.06	37.13	34.24	37.85	2.03	1.22	2.06	2.15	2.94	1.92	-0.88	2.64
333.15	37.49	37.52	37.36	37.83	37.50	37.12	34.18	37.98	1.92	1.37	1.79	1.68	1.93	0.97	-1.39	1.83

* Unpublished data

[a] Unpublished data.

solutions. The temperature dependence of the ΔV^o_{tr} for different side chain groups is depicted in Figure 4. It can be seen that the variations with the temperature are complex, and hence no generalizations could be made. The increase in temperature may cause several effects such as volume expansion due to thermal motion, enhancement of structure-breaking effects, and also even

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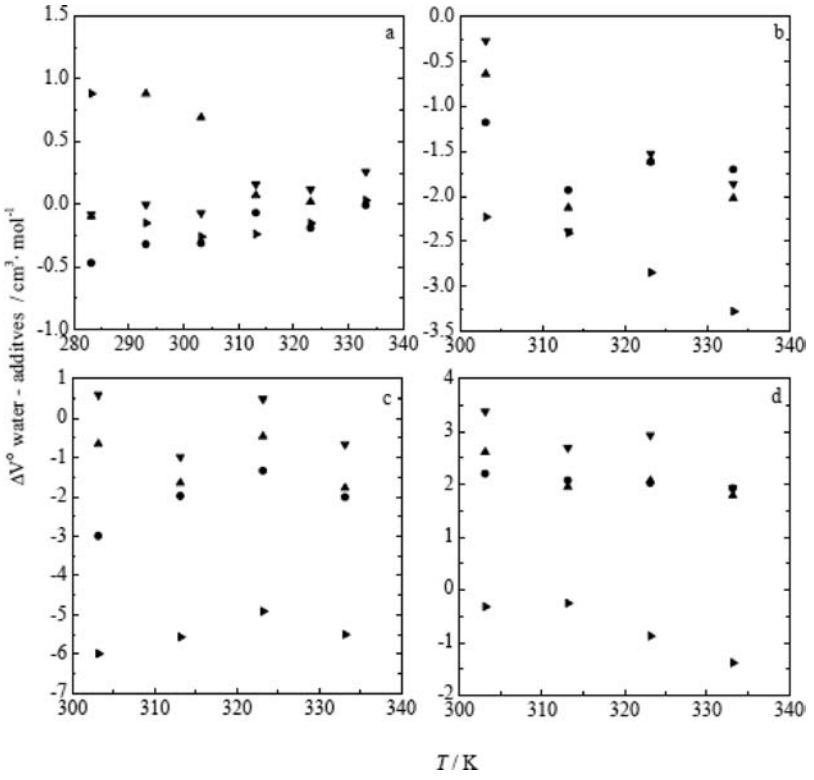

Figure 4. Temperature dependence of transfer volumes ($\Delta V^{\circ}_{\text{water}\rightarrow\text{additives}}$) for different side chains: (a) isopropyl, (b) isobutyl, (c) methylphenyl, and (d) CH_2CONH_2 in additive aqueous solutions: sucrose: ●, 5 % (w/w); ▲, 10 % (w/w); ▼ 20 % (w/w); and 2,3-butanediol: right-pointing triangle, 5 % (w/w).

contribute to structure-making effects. The balance of these effects, however, depends upon the nature and energetics of multiple interactions within the complex ternary systems. Which of these factors is predominant is difficult to predict and beyond the scope of the present investigation. Otherwise, the negative ΔV°_{tr} values indicate the dominance of overall structure-breaking type interactions as far as GlyVal, GlyLeu, and GlyPhe/additive/water ternary systems are concerned. On the other hand the positive ΔV°_{tr} values can be attributed to the structure-making type interactions in GlyAsn/additive/water systems.

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