

Volumetric Behavior on Interactions of α -Amino Acids with Sodium Acetate, Potassium Acetate, and Calcium Acetate in Aqueous Solutions

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The apparent molar volumes (V_{Φ}) of L-lysine monohydrochloride, L-histidine, and L-arginine in water and in aqueous of sodium acetate, potassium acetate, and calcium acetate solutions have been determined at temperatures from (303.15 to 323.15) K from density measurements. The partial molar volumes at infinite dilution (V^{∞}) obtained from V_{Φ} data have been used to calculate the transfer volume (ΔV_{tr}) of amino acids in water and in the presence of the cosolutes at different temperatures. These parameters have been discussed in terms of various interactions between the α -amino acids and organic salts in these solutions. The dehydration effect of sodium, potassium, and calcium acetates has also been discussed.

Introduction

Interaction of proteins with their surrounding environment plays an important role in their conformational characteristics. These interactions are mainly those between the protein molecules and the solvent ions. Most of these interactions, such as hydrogen bonding and electrostatic interactions, have non-covalent nature. The study of these interactions provides important insight into the conformational stability and folding/unfolding behavior of globular proteins.¹ To get a better understanding of these interactions, various low molecular weight model compounds, such as amino acids and peptides, have been studied because of the complexities of proteins and infeasibility of direct thermodynamic studies.

Amino acids belong to an important family of biomolecules, which serve primarily as basic building blocks of proteins. Because proteins are large complex molecules, direct study of protein–electrolyte interactions is difficult. It is therefore useful to investigate the interaction of model compounds such as amino acids, peptides, and their derivatives that constitute part of the protein structures.^{2–5} Solution studies of amino acids with their surrounding environment play an important role in conformational characteristics of proteins.

A survey of the literature showed that many studies on physicochemical properties of amino acids have been reported,^{1–15} but these studies have focused only on the solution behavior of amino acids having nonpolar side chains. Thus, it will be of significance to examine the solution behavior of amino acids having polar side chains. Moreover, there are only a few studies of the properties of amino acids in aqueous organic salt solutions,^{16–28} probably due to the complex nature of their interactions. Partial molar volumes and expansibilities are known to be insightful to the nature of hydration, which is temperature dependent. Thus, these studies are of better help in characterizing the structure and properties of solutions, which give vital information for understanding the nature of the action of biomolecules in the body.

Kishore and Singh²⁸ have studied the effect of sodium acetate, sodium sulfate, and sodium thiocyanate on the stability of lysozyme and α -lactalbumin and suggested that sodium acetate

stabilizes these proteins. Robinson and Jencks²⁹ studied the effect of concentrated salt solutions on the activity coefficients of acetyltetraglycine ethyl ester and recommended that the acetate and trimethylacetate ions exert salting-out effects, whereas the trichloroacetate ion exerts a salting-in effect on the stability of proteins. Some other workers^{21,22,25,27} also have investigated the effect of sodium acetate and many other acetate salts on the physicochemical properties of amino acids and peptides.

In the present work, we have studied the effect of sodium acetate and other members of the acetate salt series, namely, potassium acetate and calcium acetate, on the physicochemical properties of amino acids with charged side chains. Volumetric studies of L-lysine monohydrochloride, L-arginine, and L-histidine have been carried out in aqueous solutions of sodium acetate (SA), potassium acetate (PA), and calcium acetate (CA). Apparent molar volumes of these amino acids in aqueous solutions of SA, PA, and CA at (303.15, 308.15, 313.15, 318.15, and 323.15) K have been determined from density measurements. From these data, partial molar volume and transfer volume have been calculated. These parameters are discussed in terms of various interactions going on in these solutions with particular concern on the polar and charged side chains of these amino acids.

Material and Methods

L-Lysine monohydrochloride ($\geq 99\%$), L-histidine ($\geq 99\%$), and L-arginine ($\geq 99\%$) and the salts sodium acetate ($\geq 99\%$) and potassium acetate ($\geq 99\%$) of high purity were from Sisco Research Laboratories, India, and E. Merc (India), Ltd., respectively, while calcium acetate ($\geq 99\%$) was from Qualigen India, Ltd. of GlaxoSmithKline India. These chemicals were used without further purification. However, they were dried in a vacuum desiccator over P_2O_5 for 72 h before use. The triplicate distilled water (with the specific conductivity of $1.29 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$) was used for making all the amino acids and Stock solution. The weighing was done on an electronic balance (model: GR-202R, AND Japan) with a precision of ± 0.01 mg. All the solutions were stored in special airtight bottles to avoid the exposure of solutions to air and evaporation.

Densities of the mixed solvent and amino acid solutions were measured using a single-capillary pycnometer (made of Boro-

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Table 1. Densities ($\rho/\text{g}\cdot\text{cm}^{-3}$) and Apparent Molar Volume ($V_{\Phi}/\text{cm}^3\cdot\text{mol}^{-1}$) of L-Lysine Monohydrochloride, L-Arginine, and L-Histidine in Water and in Aqueous Solution of SA, PA, and CA Salts as a Function of Concentration ($\text{mol}\cdot\text{kg}^{-1}$) at $T = (303.15 \text{ to } 323.15) \text{ K}$

m $\text{mol}\cdot\text{kg}^{-1}$	$T/K = 303.15$		$T/K = 308.15$		$T/K = 313.15$		$T/K = 318.15$		$T/K = 323.15$	
	ρ $\text{g}\cdot\text{cm}^{-3}$	V_{Φ} $\text{cm}^3\cdot\text{mol}^{-1}$	ρ $\text{g}\cdot\text{cm}^{-3}$	V_{Φ} $\text{cm}^3\cdot\text{mol}^{-1}$	ρ $\text{g}\cdot\text{cm}^{-3}$	V_{Φ} $\text{cm}^3\cdot\text{mol}^{-1}$	ρ $\text{g}\cdot\text{cm}^{-3}$	V_{Φ} $\text{cm}^3\cdot\text{mol}^{-1}$	ρ $\text{g}\cdot\text{cm}^{-3}$	V_{Φ} $\text{cm}^3\cdot\text{mol}^{-1}$
L-Lysine Monohydrochloride in Aqueous Solution										
0.0000	0.9956	—	0.9940	—	0.9922	—	0.9902	—	0.9880	—
0.0302	0.9973	126.377	0.9957	126.487	0.9939	126.614	0.9919	126.735	0.9897	126.905
0.0606	0.9990	126.422	0.9974	126.534	0.9956	126.660	0.9936	126.800	0.9914	126.954
0.0913	1.0007	126.454	0.9991	126.566	0.9973	126.693	0.9953	126.855	0.9931	126.988
0.1224	1.0024	126.545	1.0008	126.657	0.9990	126.754	0.9970	126.925	0.9948	127.080
0.1536	1.0041	126.582	1.0025	126.920	1.0007	126.787	0.9987	126.974	0.9964	127.135
L-Lysine Monohydrochloride in $1 \text{ mol}\cdot\text{kg}^{-1}$ Aqueous $\text{Na}(\text{CH}_3\text{COO})$										
0.0000	1.0329	—	1.0318	—	1.0293	—	1.0275	—	1.0254	—
0.0291	1.0344	128.100	1.0333	128.240	1.0308	128.609	1.0289	128.847	1.0269	129.150
0.0584	1.0358	128.370	1.0347	128.555	1.0322	128.751	1.0304	129.022	1.0283	129.380
0.0880	1.0373	128.557	1.0362	128.857	1.0337	128.946	1.0319	129.130	1.0298	129.700
0.1181	1.0388	128.787	1.0377	129.034	1.0352	129.069	1.0344	129.252	1.0313	129.865
0.1480	1.0402	129.170	1.0391	129.420	1.0367	129.327	1.0349	129.420	1.0327	130.070
L-Lysine Monohydrochloride in $1 \text{ mol}\cdot\text{kg}^{-1}$ Aqueous $\text{K}(\text{CH}_3\text{COO})$										
0.0000	1.0397	—	1.0381	—	1.0361	—	1.0335	—	1.0320	—
0.0289	1.0411	130.470	1.0395	130.600	1.0375	130.983	1.0349	131.240	1.0334	131.500
0.0580	1.0424	130.824	1.0408	131.118	1.0388	131.284	1.0362	131.750	1.0347	131.760
0.0879	1.0428	131.006	1.0422	131.460	1.0402	131.521	1.0376	132.000	1.0361	131.973
0.1173	1.0452	131.205	1.0436	131.738	1.0416	131.908	1.0390	132.128	1.0375	132.170
0.1470	1.0465	131.635	1.0449	132.150	1.0429	132.005	1.0403	132.549	1.0388	132.500
L-Lysine Monohydrochloride in $1 \text{ mol}\cdot\text{kg}^{-1}$ Aqueous $\text{Ca}(\text{CH}_3\text{COO})_2$										
0.0000	1.0751	—	1.0732	—	1.0716	—	1.0693	—	1.0671	—
0.0281	1.0760	141.880	1.0741	141.950	1.0725	142.435	1.0702	142.760	1.0680	142.910
0.0564	1.0768	142.196	1.0749	142.370	1.0733	142.569	1.0710	142.816	1.0688	143.209
0.0850	1.0777	142.361	1.0758	142.564	1.0742	142.736	1.0719	142.983	1.0697	143.325
0.1141	1.0786	142.656	1.0767	142.706	1.0751	142.878	1.0728	143.204	1.0706	143.520
0.1429	1.0794	142.791	1.0776	143.000	1.0760	143.045	1.0736	143.300	1.0714	143.640
L-Arginine in Aqueous Solution										
0.0000	0.9956	—	0.9940	—	0.9922	—	0.9902	—	0.9880	—
0.0302	0.9971	123.980	0.9955	124.110	0.9937	124.490	0.9917	124.600	0.9895	124.720
0.0607	0.9986	124.732	0.9970	124.800	0.9952	124.980	0.9932	125.138	0.9910	124.304
0.0914	1.0001	124.735	0.9985	125.000	0.9967	125.290	0.9947	125.440	0.9925	125.620
0.1220	1.0015	125.560	0.9999	125.560	0.9981	125.698	0.9961	125.851	0.9939	126.020
0.1533	1.0030	126.005	1.0014	126.129	0.9996	126.269	0.9976	126.425	0.9954	126.597
L-Arginine in $1 \text{ mol}\cdot\text{kg}^{-1}$ Aqueous $\text{Na}(\text{CH}_3\text{COO})$										
0.0000	1.0329	—	1.0318	—	1.0293	—	1.0275	—	1.0254	—
0.0291	1.0342	125.973	1.0331	126.500	1.0306	126.914	1.0288	127.062	1.0267	127.235
0.0585	1.0355	126.352	1.0344	126.710	1.0319	126.970	1.0301	127.118	1.0279	127.455
0.0882	1.0368	126.513	1.0357	126.817	1.0332	127.023	1.0314	127.172	1.0292	127.563
0.1179	1.0381	126.673	1.0369	126.924	1.0344	127.131	1.0326	127.280	1.0305	127.699
0.1478	1.0393	126.954	1.0382	127.045	1.0357	127.252	1.0339	127.402	1.0318	127.903
L-Arginine in $1 \text{ mol}\cdot\text{kg}^{-1}$ Aqueous $\text{K}(\text{CH}_3\text{COO})$										
0.0000	1.0397	—	1.0381	—	1.0361	—	1.0335	—	1.0320	—
0.0289	1.0409	128.987	1.0393	129.120	1.0373	129.310	1.0347	129.550	1.0331	129.800
0.0581	1.0420	129.357	1.0404	129.497	1.0384	129.673	1.0358	129.741	1.0343	129.873
0.0874	1.0432	129.530	1.0415	129.777	1.0396	129.848	1.0370	130.079	1.0355	130.212
0.1171	1.0444	129.831	1.0428	129.973	1.0408	130.151	1.0382	130.383	1.0367	130.517
0.1471	1.0454	130.026	1.0438	130.489	1.0419	130.669	1.0393	130.710	1.0385	130.680
L-Arginine in $1 \text{ mol}\cdot\text{kg}^{-1}$ Aqueous $\text{Ca}(\text{CH}_3\text{COO})_2$										
0.0000	1.0751	—	1.0732	—	1.0716	—	1.0693	—	1.0671	—
0.0281	1.0760	134.209	1.0741	134.209	1.0725	134.556	1.0702	134.785	1.0680	135.052
0.0565	1.0768	134.551	1.0749	134.640	1.0733	134.901	1.0710	135.132	1.0688	135.353
0.0852	1.0777	134.789	1.0758	134.082	1.0742	135.347	1.0719	135.579	1.0697	135.803
0.1139	1.0786	135.290	1.0766	135.352	1.0750	135.746	1.0727	135.980	1.0705	136.205
0.1428	1.0793	136.050	1.0775	136.600	1.0758	135.900	1.0735	136.360	1.0713	136.878
L-Histidine in Aqueous Solution										
0.0000	0.9956	—	0.9940	—	0.9922	—	0.9902	—	0.9880	—
0.0303	0.9973	99.073	0.9957	99.142	0.9939	99.218	0.9919	99.303	0.9897	99.390
0.0606	0.9989	99.630	0.9973	99.760	0.9955	99.800	0.9935	99.840	0.9913	99.980
0.0913	1.0006	100.093	0.9990	100.165	0.9972	100.245	0.9952	100.335	0.9930	100.433
0.1221	1.0022	100.645	1.0006	100.719	0.9988	100.802	0.9968	100.893	0.9946	100.994
0.1526	1.0038	100.804	1.0022	100.878	1.0004	100.961	0.9984	101.054	0.9962	101.156
L-Histidine in $1 \text{ mol}\cdot\text{kg}^{-1}$ Aqueous $\text{Na}(\text{CH}_3\text{COO})$										
0.0000	1.0329	—	1.0318	—	1.0293	—	1.0275	—	1.0254	—
0.0291	1.0343	103.488	1.0333	104.500	1.0307	105.190	1.0289	105.800	1.0267	106.640
0.0585	1.0357	103.640	1.0346	104.950	1.0321	105.279	1.0302	105.897	1.0281	106.735
0.0879	1.0372	103.829	1.0359	105.150	1.0334	105.537	1.0316	106.002	1.0294	106.850
0.1176	1.0386	103.972	1.0373	105.410	1.0348	105.790	1.0330	106.060	1.0308	106.982
0.1474	1.0400	104.054	1.0387	105.740	1.0361	105.920	1.0343	106.180	1.0321	107.080

Table 1. Continued

m mol·kg ⁻¹	$T/K = 303.15$		$T/K = 308.15$		$T/K = 313.15$		$T/K = 318.15$		$T/K = 323.15$	
	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹	ρ g·cm ⁻³	V_Φ cm ³ ·mol ⁻¹
L-Histidine in 1 mol·kg ⁻¹ Aqueous K(CH ₃ COO)										
0.0000	1.0397	—	1.0381	—	1.0361	—	1.0335	—	1.0320	—
0.0289	1.0410	106.300	1.0394	107.170	1.0374	107.716	1.0348	108.333	1.0332	109.210
0.0580	1.0423	107.100	1.0407	107.500	1.0386	108.047	1.0360	108.490	1.0345	109.432
0.0875	1.0435	107.560	1.0419	107.914	1.0399	108.363	1.0373	108.590	1.0358	109.682
0.1168	1.0448	108.071	1.0432	108.254	1.0412	108.544	1.0386	108.682	1.0371	109.795
0.1463	1.0460	108.470	1.0444	108.525	1.0424	108.720	1.0398	108.760	1.0383	109.925
L-Histidine in 1 mol·kg ⁻¹ Aqueous Ca(CH ₃ COO) ₂										
0.0000	1.0751	—	1.0732	—	1.0716	—	1.0693	—	1.0671	—
0.0280	1.0758	121.700	1.0739	122.550	1.0723	123.340	1.0699	123.942	1.0678	124.789
0.0563	1.0765	122.420	1.0746	122.826	1.0730	123.600	1.0706	124.054	1.0685	124.840
0.0850	1.0772	122.706	1.0753	122.885	1.0737	123.720	1.0713	124.148	1.0691	124.930
0.1132	1.0778	122.989	1.0759	123.013	1.0743	123.970	1.0719	124.189	1.0698	125.000
0.1415	1.0785	123.320	1.0766	123.324	1.0750	124.230	1.0726	124.298	1.0705	125.101

Table 2. Partial Molar Volume (V_2^0 /cm³·mol⁻¹) and Standard Transfer Molar Volume (ΔV_{tr} /cm³·mol⁻¹) of L-Lysine Monohydrochloride, L-Arginine, and L-Histidine in Water and in Aqueous Solution of SA, PA, and CA Salts As a Function of Concentration (mol·kg⁻¹) at $T = (303.15 \text{ to } 323.15) \text{ K}$

m mol·kg ⁻¹	$T/K = 303.15$		$T/K = 308.15$		$T/K = 313.15$		$T/K = 318.15$		$T/K = 323.15$	
	V_2^0 cm ³ ·mol ⁻¹	ΔV_{tr} cm ³ ·mol ⁻¹	V_2^0 cm ³ ·mol ⁻¹	ΔV_{tr} cm ³ ·mol ⁻¹	V_2^0 cm ³ ·mol ⁻¹	ΔV_{tr} cm ³ ·mol ⁻¹	V_2^0 cm ³ ·mol ⁻¹	ΔV_{tr} cm ³ ·mol ⁻¹	V_2^0 cm ³ ·mol ⁻¹	ΔV_{tr} cm ³ ·mol ⁻¹
L-Lysine Monohydrochloride										
Aqs	125.53	—	125.61	—	126.04	—	126.31	—	126.52	—
SA	127.84	2.31	127.97	2.36	128.42	2.38	128.70	2.39	128.94	2.42
PA	130.22	4.69	130.31	4.70	130.75	4.71	131.03	4.72	131.25	4.73
CA	141.70	16.17	141.81	16.21	142.28	16.24	142.58	16.27	142.80	16.28
L-Arginine										
Aqs	123.82	—	124.05	—	14.16	—	124.25	—	124.33	—
SA	125.74	1.92	125.98	1.93	126.29	2.13	126.44	2.19	126.65	2.32
PA	128.47	4.65	128.74	4.69	129.11	4.95	129.31	5.06	129.65	5.32
CA	133.66	9.84	133.92	9.87	134.24	10.08	134.38	10.13	134.52	10.21
L-Histidine										
Aqs	98.78	—	99.67	—	100.35	—	101.06	—	101.86	—
SA	103.36	4.58	104.27	4.60	104.96	4.61	105.71	4.65	106.52	4.66
PA	105.92	7.14	106.84	7.17	107.53	7.18	108.26	7.20	109.07	7.21
CA	121.49	22.71	122.40	22.73	123.13	22.78	123.87	22.81	124.70	22.83

silicate glass) having a bulb capacity $\sim 9 \text{ cm}^3$. The capillary, with graduated marks, had a uniform bore and was closed by a well-fitted glass cap. The marks on the capillary were calibrated by using triply distilled water at different temperatures. The thermostated paraffin bath (JULABO, model-MD Germany) used for measurements of densities was maintained at a desired temperature ($\pm 0.02 \text{ K}$) for about 30 min prior to recording of readings at each temperature of study.

The uncertainty in measurement of density values was ascertained by comparing the experimental values with corresponding literature values at different temperatures for water. The experimental values of the density of water were found to be (0.9972, 0.9941, 0.9903, and 0.9879) g·cm⁻³ at (298.15, 308.15, 318.15, and 323.15) K, respectively, whereas the corresponding literature values³⁰ are (0.997045, 0.994032, 0.990213, and 0.988036) g·cm⁻³. The uncertainties in the density and molal concentration values have been found to be within $0.02 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$ and $1.0 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$, respectively.

Results and Discussion

The density (ρ) of amino acids in water and in aqueous solutions of sodium acetate (SA), potassium acetate (PA), and calcium acetate (CA) at (303.15, 308.15, 313.15, 318.15, and 323.15) K (given in Table 1) are used to calculate apparent molar volume (V_Φ), apparent molar volume at infinite dilution (V_2^0) (which has the same meaning as the standard partial molar

volume), and transfer volume (ΔV_{tr}) with the help of the following equations, respectively

$$V_\Phi = (M/\rho) - [10^3(\rho - \rho_0)/(m\rho\rho_0)] \quad (1)$$

$$V_\Phi = V_2^0 + S_v m \quad (2)$$

$$\Delta V_{tr} = V_2^0 (\text{in solutions}) - V_2^0 (\text{in water}) \quad (3)$$

where M and m are the molar mass of solute and molality (mol·kg⁻¹) of the amino acids, respectively; ρ and ρ_0 are the densities of solution (amino acids + solvent) and the solvent (water + sodium acetate or potassium acetate or calcium acetate or water), respectively; V_2^0 is the apparent molar volume at infinite dilution; and S_v is the experimental slope. The values of apparent molar volume are mentioned in Table 1, while the standard partial molar volume and standard transfer volume values are summarized in Table 2.

The V_2^0 values of L-lysine monohydrochloride in aqueous solution at 318.15 K have been found to be 126.43 (± 0.03) m³·mol⁻¹ (shown in Table 2), with a literature value³¹ of 126.35 (± 0.01) m³·mol⁻¹. The V_2^0 values of L-arginine in aqueous solution at 298.15 K have been found to be 123.92 (± 0.02) m³·mol⁻¹, and literature values^{17,32,33} are 123.72 (± 0.10), 123.70 (± 0.10), and 127.34 (± 0.12) m³·mol⁻¹. In L-histidine, V_2^0 values of aqueous solution at 308.15 K have been found to be 99.67 (± 0.04) m³·mol⁻¹, and reported values in the

literature³¹ are $100.07 (\pm 0.03) \text{ m}^3 \cdot \text{mol}^{-1}$. To the best of our knowledge, this is the first report on volumetric data for these amino acids in aqueous organic salt solutions.

It is important to mention here that sodium acetate, potassium acetate, and calcium acetate are salts of weak acids and strong bases and undergo hydrolysis to give basic solutions. The density values of aqueous solution of $1 \text{ mol} \cdot \text{kg}^{-1}$ SA were found to be $(1.03449, 1.03186, \text{ and } 1.02752) \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$, while literature^{34,35} values are $(1.03475, 1.03156, \text{ and } 1.02723) \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$. For PA densities at $1 \text{ mol} \cdot \text{kg}^{-1}$, $(1.04099, 1.03815, \text{ and } 1.0335) \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ were found, while literature³⁶ values are $(1.04151, 1.03802, \text{ and } 1.03389) \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ at $(298.15, 308.15, \text{ and } 318.15) \text{ K}$, respectively. The V_0^2 values for the studied amino acids increase with increase in cosolute concentrations and temperature (plots as Supporting Information). From a comparison of the V_0^2 values for the studied amino acids in sodium acetate, potassium acetate, and calcium acetate solutions, it is found that these values increase in the order of $\text{SA} < \text{PA} < \text{CA}$ for all the amino acids studied. Presently observed V_0^2 values are also higher with various cosolutes in comparison to its values in water. It is interesting that the increases in V_0^2 values of L-lysine monohydrochloride and L-arginine in the presence of SA and PA are very small as compared with CA. The V_0^2 value increases are almost linear with concentration.

The cosphere overlap model³⁷ can be utilized to rationalize the ΔV_{tr} values in terms of solute–cosolute interactions. The overlap of cosolute ions and amino acids comes into play because of interactions between: (i) the $(-\text{NH}_3^+, \text{COO}^-)$ charged ends of amino acids and ions of the cosolute (SA, PA, or CA); (ii) the hydrophobic parts of the amino acids and cosolute ions and the charged ends/hydrophilic parts of amino acids and the hydrophobic parts of the cosolutes; and (iii) the hydrophobic parts of the amino acids and hydrophobic parts of ions of cosolutes.

Ion–ion interactions result in positive ΔV_{tr} values, whereas ion–hydrophobic and hydrophobic–hydrophobic group interactions result in negative ΔV_{tr} values according to the cosphere model.³⁷ The present study observed higher V_0^2 values for amino acids in various cosolutes as compared with their values in water, which suggests that ion–ion interactions dominate the ion–hydrophobic and hydrophobic–hydrophobic interactions. A similar kind of result has also been observed by several workers^{21–25} with the other salts. The large increase in V_0^2 values observed for basic amino acids, as compared to amino acids with a nonpolar side chain in the presence of cosolutes, can be attributed to the combined effect of the $(-\text{NH}_3^+, -\text{COO}^-)$ groups of amino acids, and the polar side chains are present in basic amino acids. The overall results observed in this work can be thought of as predominant interaction contributions of types (i) and (ii) relative to (iii). This conclusion supports our results of the standard partial molar volumes. The transfer parameter, ΔV_{tr} , for the amino acids studied here showed that the dehydration effect of Ca^{2+} is more than Na^+ and K^+ ions. The stabilization effect of cations on the proteins also appears in the same order as in the Hofmeister series reported earlier.³⁸

Conclusions

In the present work, the partial molar volumes, apparent molar volume, and transfer volume of some acidic amino acids in aqueous solutions of sodium acetate, potassium acetate, and calcium acetate were obtained by density measurements at $(303.15, 308.15, 313.15, 318.15, \text{ and } 323.15) \text{ K}$. Higher V_0^2 values observed for amino acids in the studied cosolutes suggest

that ion charged group interactions dominate over ion–nonpolar group interactions in all of the cosolutes. L-Lysine monohydrate interacts more strongly in these cosolute solutions as compared to L-histidine and L-arginine. The reported value shows that the dehydration effect of Ca^{2+} is more than that of Na^+ and K^+ on these amino acids.

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Supporting Information Available:

The plots of apparent molar volume as a function concentration at $T = (303.15 \text{ to } 323.15) \text{ K}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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