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SHORT COMMUNICATION

Ultrasonic Studies of Amino Acids in Aqueous Sucrose Solution at Different Temperatures

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Abstract: *The density (ρ), viscosity (η) and ultrasonic velocity (U) were measured for L-histidine, L-arginine and L-lysine in aqueous sucrose (0.5 M) solution at 298, 303 and 308 K. Using the experimental values, the adiabatic compressibility (β), hydration number (n_H), apparent molal compressibility (φ_K), apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0), the associated constants (S_K, S_V) and the viscosity B coefficient of the Jones-Dole equation were calculated. These parameters were used to study the ion-solvent interaction present in each solution.*

Keywords: ultrasonic velocity, adiabatic compressibility, apparent molal compressibility, hydration number, apparent molal volume

1. INTRODUCTION

During the last two decades, studies of ultrasonic velocity have been carried out to investigate the hydration of proteins using volume and ultrasonic measurements because these properties are sensitive to the degree and nature of hydration.[1,2] Amino acids and peptides are the fundamental structural units of proteins. Mixed aqueous solvents are used extensively in chemistry and other fields to control factors such as the stability and reactivity of systems. Poly hydroxy compounds are well-known stabilising agents for the native state of proteins/enzymes. Due to the complex nature of proteins, direct study is somewhat difficult. Therefore, to understand the nature of interactions between saccharides and proteins in aqueous solutions, it is necessary to study low-molecular-weight model compounds such as amino acids.

There have been extensive volumetric and thermo-chemical property studies of amino acids in aqueous solutions,[3] but very few have been conducted in aqueous saccharide solutions.[4] Volumetric, compressibility and viscosity

studies of amino acids in aqueous sucrose solutions are lacking. Hence, we attempted to understand the physicochemical behaviour of L-histidine, L-arginine and L-lysine in aqueous sucrose solutions (0.5 M) at different temperatures through ultrasonic velocity measurements. However, the ultrasound velocity data do not provide significant information about the native and relative strengths of various types of intermolecular or inter-ionic interactions between the components. Hence, parameters such as adiabatic compressibility (β), apparent molal volume (φ_V), apparent molal compressibility (φ_K), limiting apparent molal volume (φ_V^0), limiting apparent molal compressibility (φ_K^0), the associated constants (S_K, S_V), hydration number (n_H) and the values of the A and B coefficients of the Jones-Dole equation were obtained to shed more light on such interactions.

2. EXPERIMENTAL

Analytical reagent (AR) grade and spectroscopic reagent (SR) grade (minimum assay of 99.9%) L-histidine, L-arginine, L-lysine and sucrose were obtained from E-Merck, Germany, and SdFine Chemicals, India; these reagents were used without further purification. The water used in the experiment was deionised, distilled and degassed prior to making the solutions. Aqueous solutions of sucrose (0.5 mol.dm^{-3}) were prepared by volume and were used on the day they were prepared. Solutions of amino acids in the concentration range of 0.02–0.1 mol·dm^{-3} were made by volume on the molality concentration scale with a precision of ± 1 × 10^{-4} g on an electronic digital balance (Model: Shimadzu AX-200). The density was determined using a specific gravity bottle using the relative measurement method with an accuracy of ± 0.01 kgm^{-3}. An Ostwald's viscometer (10 ml) was used for the viscosity measurements. Efflux time was determined using a digital chronometer to within ±0.01 s. An ultrasonic interferometer having a frequency of 3 MHz (Mittal Enterprises, New Delhi, Model: F-81) with an overall accuracy of ± 0.1% was used for velocity measurements. A digital electronically operated constant temperature bath (Raaga Industries) was used to circulate water through the double-walled measuring cell made of steel containing the experimental solution at the desired temperature. The accuracy of the temperature measurement was ± 0.1 K.

3. THEORY

Various acoustic and thermodynamic parameters[5] were calculated from the measured data. These parameters included adiabatic compressibility, molal hydration number, apparent molal compressibility, apparent molal volume,

limiting apparent molal compressibility, limiting apparent molal volume, the associated constants S_K and S_V, and the viscosity A and B coefficients.

4. RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) for different molal concentrations of L-histidine, L-arginine and L-lysine in aqueous sucrose (0.5 M) solution at 298, 303 and 308 K are shown in Table 1. The values of the adiabatic compressibility (β), hydration number (n_H), apparent molal compressibility (φ_K), apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0), the associated constants (S_K, S_V) and the viscosity A and B coefficients of the Jones-Dole equation are shown in Tables 2 and Table 3.

As shown in Table 1, the ultrasonic velocity increased with increases in the concentrations of L-histidine, L-arginine and L-lysine and with increases in temperature. The existence of molecular interactions between solute and solvent molecules is responsible for the observed increase in the ultrasonic velocity of these mixtures. The increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about by ionic hydration.[6]

The adiabatic compressibility (Table 2) decreased with increases in the concentrations of amino acids in aqueous sucrose (0.5 M) solution and with increases in temperature. The decreasing adiabatic compressibility observed for amino acids in aqueous sucrose solution at all temperatures generally confirms the conclusion drawn from the velocity data. The increasing electrostrictive compression of water around the molecules results in a large decrease in the compressibility of solutions. The decrease in the compressibility implies that there are enhanced molecular associations in these systems with increases in the solute content, as the new entities (formed due to molecular association) become compact and less compressible.[7] The compressibility appeared to decrease with increasing hydrogen bond strength between the solute and solvent molecules.

The interaction between a solute and water molecules in an aqueous solution is termed as hydration. The positive hydration number (n_H) values indicate an appreciable solvation of solutes.[8] This result provides added support for the structure-promoting nature of the solute and for the presence of appreciable dipole-dipole interactions between solute and water molecules. The positive hydration number (n_H) values also suggest that the compressibility of the solution will be less than that of the pure solvent. As a result, solutes will gain mobility and have a greater probability of contacting solvent molecules. This

greater probability may enhance the interaction between solute and solvent molecules. As shown in Table 2, the hydration number decreased non-linearly with solutes, indicating an increase in solute-solvent interactions between the components of the mixture. These results demonstrate that sucrose has a dehydration effect on the amino acids.[9]

The following observations were made for the φ_K and φ_V (Figure 1 and 2) of L-histidine, L-arginine and L-lysine in aqueous sucrose (0.5 M) solution at 298, 303 and 308 K:

i. The values of φ_K and φ_V were all negative over the entire range of solute molality.

ii. The values of φ_K decreased with increasing concentrations of L-histidine but increased with increasing concentrations of L-arginine and L-lysine and with increasing temperature.

iii. The values of φ_V decreased with increasing molality of L-histidine and L-arginine but increased with increasing molality of L-lysine.

iv. The magnitude of φ_V was in the order L-histidine > L-arginine > L-lysine.

All of the above observations clearly suggest that the negative values of φ_K and φ_V are indicative of ionic and hydrophilic interactions in these systems. The decreasing values of φ_K with increasing molality of L-histidine reveal less strengthening of the ion-solvent interactions, and the increasing values of φ_K with increasing molality of L-arginine and L-lysine shows that a strong ion-solvent interaction exists in the mixture. Further, the decrease in φ_V was due to strong ion-solute interactions and vice-versa. The negative values of φ_V indicate electrostrictive solvation of ions.[10] From the magnitude of φ_V, it can be concluded that stronger molecular associations were present in the L-lysine system than in the other two amino acid systems. Hence, L-lysine is a more effective structure maker than the other two amino acids.

Table 1: Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of some amino acids in aqueous sucrose solutions (0.5 M) at 298, 303 and 308K.

M/(mol·dm^{-3})	ρ/(kg.m^{-3})			η/(×10^{-3} Nsm^{-2})			U/(ms^{-1})		
	298 K	303 K	308 K	298 K	303 K	308 K	298 K	303 K	308 K
System – I L-histidine + Water + sucrose									
0.00	1030.9	1027.5	1026.7	1.5719	1.3197	1.2639	1552.2	1564.3	1568.4
0.02	1031.8	1028.3	1027.7	1.5798	1.3772	1.2890	1553.4	1565.2	1569.2
0.04	1032.6	1030.9	1028.8	1.5867	1.4118	1.3430	1555.2	1567.4	1571.2
0.06	1035.9	1032.8	1030.4	1.5905	1.4356	1.3530	1557.6	1568.8	1573.2
0.08	1038.2	1036.5	1034.5	1.6020	1.4562	1.3732	1558.6	1570.2	1574.3
0.10	1041.9	1041.3	1037.7	1.6690	1.4860	1.3942	1560.2	1571.3	1576.3
System – II L-arginine + Water + sucrose									
0.00	1030.9	1027.5	1026.7	1.5719	1.3197	1.2639	1552.2	1564.3	1568.4
0.02	1033.2	1030.6	1027.3	1.5792	1.3662	1.2781	1556.3	1571.4	1572.0
0.04	1035.9	1033.6	1031.5	1.5901	1.3999	1.2824	1558.2	1573.2	1576.7
0.06	1038.1	1036.6	1034.3	1.6102	1.4218	1.3580	1560.8	1576.3	1579.0
0.08	1041.0	1039.0	1036.8	1.6336	1.4398	1.3851	1562.9	1578.3	1581.2
0.10	1045.6	1042.2	1038.2	1.6592	1.4716	1.3990	1565.3	1579.3	1582.3
System – III L-lysine + Water + sucrose									
0.00	1030.9	1027.5	1026.7	1.5719	1.3197	1.2639	1552.2	1564.3	1568.4
0.02	1036.9	1035.7	1032.6	1.5781	1.3556	1.2733	1566.2	1573.2	1576.2
0.04	1039.4	1035.9	1033.7	1.5980	1.3870	1.2390	1569.1	1575.3	1578.1
0.06	1043.9	1043.3	1041.6	1.6021	1.4656	1.3090	1572.3	1578.4	1579.2
0.08	1046.9	1046.5	1045.5	1.6128	1.4670	1.3182	1574.2	1579.6	1581.3
0.10	1049.0	1047.4	1049.1	1.6510	1.5330	1.3800	1577.4	1581.6	1583.2

Table 2: Values of adiabatic compressibility (β) and hydration number (n_H), apparent molal compressibility (φ_K) and apparent molal volume (φ_V) of some amino acids in aqueous sucrose solutions (0.5 M) at 298, 303 and 308K.

M/(mol·dm^{-3})	β/(×10^{-10} m^2 N^{-1})			η_H			$-\varphi_K$ /(×10^{-7} m^2 N^{-1})			$-\varphi_V$ /(10^{-3} m^3 mol^{-1})		
	298 K	303 K	308 K	298 K	303 K	308 K	298 K	303 K	308 K	298 K	303 K	308 K
System – I L-histidine + Water + sucrose												
0.00	4.027	3.989	3.959	–	–	–	–	–	–	–	–	–
0.02	4.016	3.969	3.951	0.7808	0.1420	0.0585	7.18	10.62	6.10	40.7	38.6	47.2
0.04	4.004	3.948	3.937	0.0806	0.1390	0.0778	7.42	13.59	7.55	48.5	81.2	50.2
0.06	3.978	3.934	3.921	0.1133	0.1283	0.0892	11.42	12.62	8.75	78.1	83.8	59.1
0.08	3.965	3.913	3.900	0.1069	0.1326	0.1041	11.22	13.88	11.15	85.3	105.9	91.9
0.10	3.942	3.893	3.877	0.1170	0.1334	0.1156	12.75	14.57	12.05	102.8	120.1	103.5
System – II L-arginine + Water + sucrose												
0.00	4.026	3.977	3.959	–	–	–	–	–	–	–	–	–
0.02	3.996	3.929	3.938	0.2094	0.3379	0.1508	19.53	27.59	11.70	108.2	101.3	31.5
0.04	3.975	3.909	3.899	0.1774	0.2221	0.2123	18.04	21.67	19.65	117.3	144.3	113.8
0.06	3.954	3.882	3.877	0.1663	0.2109	0.1933	17.65	20.92	18.56	112.2	142.5	119.3
0.08	3.932	3.867	3.857	0.1634	0.1851	0.1802	16.69	18.72	17.62	117.6	134.6	118.7
0.10	3.903	3.847	3.842	0.1701	0.1751	0.1573	16.50	18.22	15.64	135.9	137.0	107.9
System – III L-lysine + Water + sucrose												
0.00	4.026	3.977	3.957	–	–	–	–	–	–	–	–	–
0.02	3.931	3.901	3.898	0.6577	0.3372	0.4319	58.26	53.94	41.93	285.1	387.4	279.4
0.04	3.907	3.890	3.884	0.4130	0.3056	0.2651	38.06	29.89	25.55	198.5	197.5	165.4
0.06	3.874	3.847	3.849	0.3498	0.2961	0.2572	33.79	28.51	27.92	201.4	246.2	232.5
0.08	3.854	3.829	3.826	0.2924	0.2578	0.2322	29.29	25.21	25.73	185.2	220.7	213.3
0.10	3.831	3.816	3.803	0.2699	0.2254	0.2198	26.57	21.76	24.21	167.7	185.1	213.2

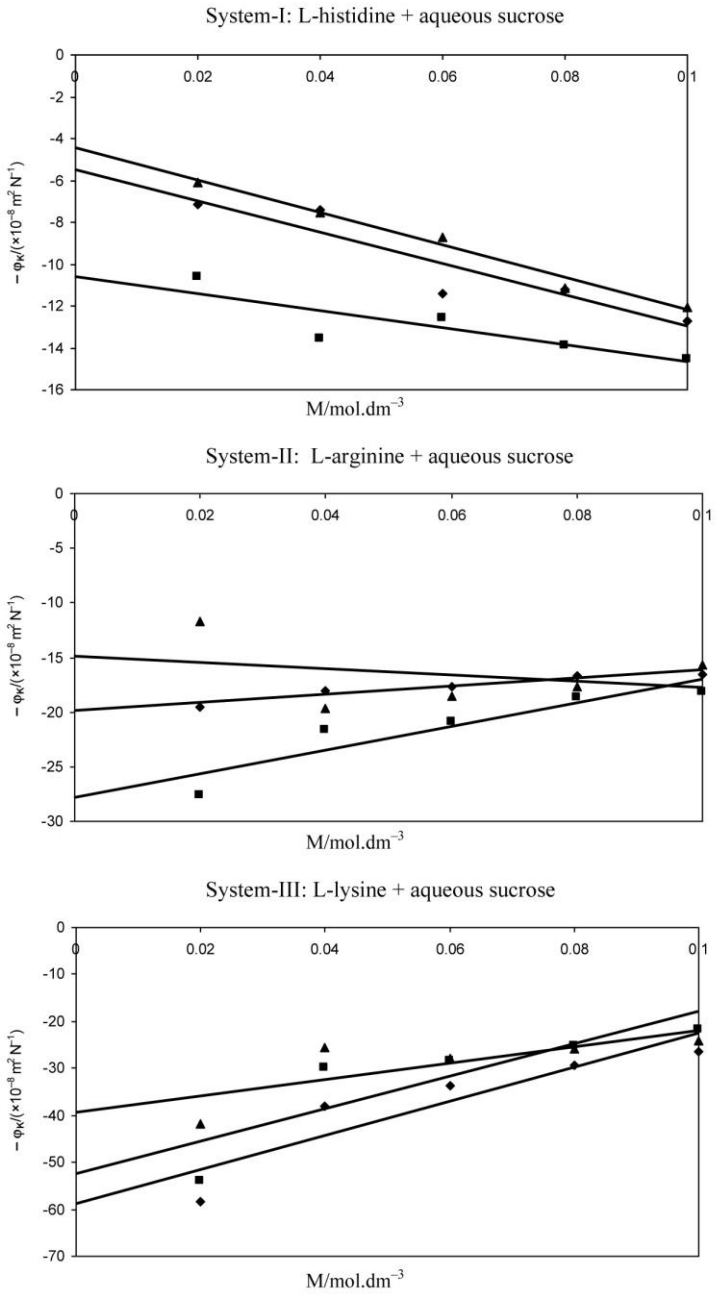

Figure 1: Variation of apparent molal compressibility (φ_K) with molality of some amino acids in aqueous sucrose (0.5 M) solution at 298, 303 and 308 K.

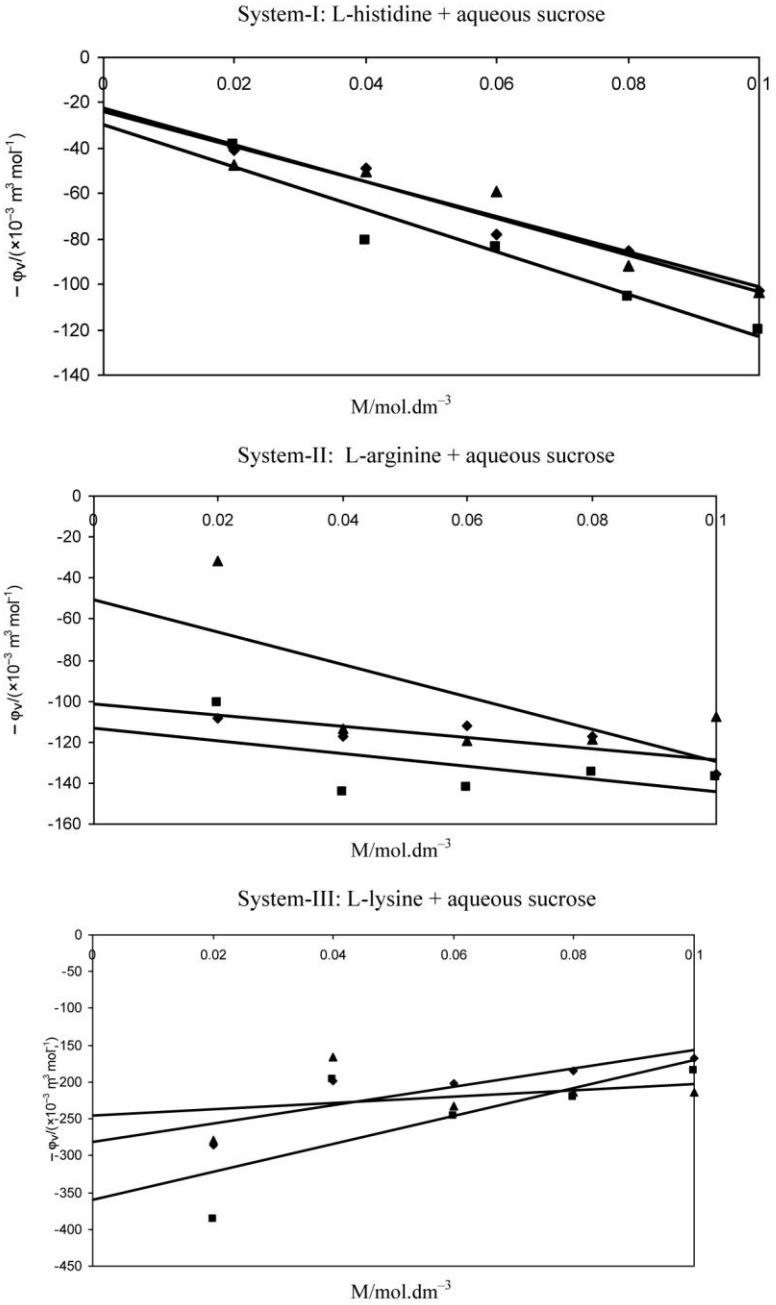

Figure 2: Variation of apparent molal volume (φ_V) with molality of some amino acids in aqueous sucrose (0.5 M) solution at 298, 303 and 308 K.

φ_K^0 provides information regarding solute-solvent interactions, and S_K provides information regarding solute-solute interactions in the mixtures. As shown in Table 3, the φ_K^0 values were negative and varied non-linearly with increasing temperature. The appreciable negative values of φ_K^0 for all of the systems reinforce our earlier view about the existence of ion-solvent interactions. The magnitude of φ_K^0 was in the order L-lysine > L-arginine > L-histidine. The limiting apparent molal volumes at infinite dilution, φ_V^0, reflect the effects of solute-solute interactions.[11] The values of φ_V^0 (Table 3) in all the three systems were negative and decreased non-linearly with increasing temperature. The decrease in φ_V^0 may be attributed to the increased hydrophilicity/polar character of the side chains of the amino acids. The magnitude of φ_V^0 was in the order L-histidine > L-arginine > L-lysine. Further, it is evident from Table 3 that the S_K and S_V values were positive for L-histidine and L-arginine and were negative for L-lysine. The negative value indicates a strong ion-solute interaction and less complex ion formation.

Viscosity is another important parameter that contributes to understanding the structure and molecular interactions occurring in the solutions. Viscosity variations are attributed to structural changes. The structural changes influence the viscosity to a greater extent than they affect density and compressibility. As shown in Table 1, the viscosity increased with increasing solute concentration and decreased with increasing temperature. This increasing trend indicates the existence of molecular interactions in these mixtures. To further investigate the role of viscosity, the B coefficient was also obtained.

As shown in Table 3, the values of A were negative, and the values of B were positive for all systems studied. A is a measure of ionic interactions,[12] and the negative values of A demonstrate the existence of ion-solute interactions in the amino acid solutions studied. The B coefficient is also known as a measure of solute-solvent interactions and of the relative size of the solute and solvent molecules. The behaviour of the B coefficient in all the three systems suggests the existence of strong ion-solvent interactions between the -OH group of sucrose and the Zwitterionic centre of the amino acid. The magnitude of the B values was in the order L-histidine < L-arginine < L-lysine. This result is in excellent agreement with the φ_v^0 data, and the larger values of B indicate the structure-making capacity of the solute.

Table 3: Values of limiting apparent molal compressibility (φ_k^0), constant (S_K), limiting apparent molal volume (φ_v^0), constant (S_V) and A and B coefficients of Jones-Dole equation of some amino acids in aqueous sucrose solutions (0.5 M) at 298, 303 and 308K.

System	$-\varphi_K^0$ /(×10^{-7} m^2N^{-1})			S_k/(×10^{-7} $N^{-1}m^{-1}.mol^{-1}$)			φ_V^0 /(×10^{-3} $m^3.mol^{-1}$)		
	298 K	303 K	308 K	298 K	303 K	308 K	298 K	303 K	308 K
L-histidine + Water + sucrose	1.89	8.71	7.89	34.20	17.84	351.5	15.56	14.50	63.77
L-arginine + Water + sucrose	20.27	33.70	11.73	10.77	51.80	20.21	90.10	94.30	292.00
L-lysine + Water + sucrose	78.07	102.90	40.61	–172.4	–291.4	–866.9	311.3	378.6	275.9

System	S_v/(× $m^3lt^{½}.mol^{-3/2}$)			–A / ×10^{-2} $dm^{3/2}$ $mol^{-1/2}$			B /×10^{-2} dm^3 mol^{-1})		
	298 K	303 K	308 K	298 K	303 K	308 K	298 K	303 K	308 K
L-histidine + Water + sucrose	365.4	423.8	2987.2	9.42	25.13	21.87	7.27	43.86	20.80
L-arginine + Water + sucrose	118.3	158.3	402.4	9.50	17.52	19.74	82.63	57.19	17.89
L-lysine + Water + sucrose	–437.8	–553.6	–232.8	3.22	6.07	25.83	506.80	177.53	154.64

5. CONCLUSION

In the study, we determined the experimental values for the density, viscosity and ultrasonic velocity of L-histidine, L-arginine and L-lysine in aqueous sucrose solutions at different temperatures. From these data, some acoustic parameters were calculated to explain the intermolecular interactions of ionic hydrogen bonding and hydrophilic interactions that occur between the Zwitterionic centre of the amino acids and the –OH group of sucrose. From the magnitude of φ_V, φ_V^0 and the B coefficient, it can be concluded that the existence of molecular interactions was greater in L-lysine solutions than in solutions of the other two amino acids.

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