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DENSITY, VISCOSITY AND REFRACTIVE INDEX OF L-ALANINE AND L-HISTIDINE IN AQUEOUS NACL SOLUTIONS AT 298.15 K

Amalia ŞTEFANIU*, Olga IULIAN and Oana CIOCIRLAN

Dept. of Applied Physical Chemistry and Electrochemistry, University Politehnica of Bucharest, 1 Polizu, 011061, Bucharest, Roumania

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New experimental data for the density, viscosity and refractive index for L-alanine and L-histidine in NaCl aqueous solutions at different salt and amino acid concentrations and at temperature of 298.15 K are reported. The apparent molar volumes of L-alanine and L-histidine in solution with NaCl have been calculated from the measured data and correlated with a linear equation. From the data fitting the infinite dilution apparent molar volumes and the transfer volumes of amino acid in aqueous electrolyte solutions were calculated. The results generally indicate positive transfer volumes to solvent with higher NaCl molality. The viscosity data, correlated with Jones-Dole equation, show kosmotropic behavior of solutes in mixtures.

INTRODUCTION

Mixtures of amino acids with electrolytes are model systems of physiological media containing complex molecules such as polypeptides and proteins. For this reason it is important to dispose of experimental data of reliable thermodynamic properties and to obtain a good correlation between mathematical models and experimental values, in order to evaluate the behavior of the organic compound in the electrolyte aqueous solutions.

A variety of physicochemical properties such as density, viscosity, refractive index and adiabatic compressibility have been determined for aqueous solutions of various amino acids.[1-3] But the biological media are not simple solvents, so the investigations of systems containing amino acids in aqueous electrolyte solvents are necessary. The electrolyte has significant influence on the structure and properties of peptides and proteins (solubility, denaturation, dissociation, biological activity).

As a continuation of our physicochemical property studies on mixed solvents,[4] this work present the density, viscosity and refractive indices of two systems with L-alanine or L-histidine in NaCl aqueous solutions. The amino acid behavior in electrolyte aqueous solutions was investigated at different salt concentrations and different amino acid concentrations at temperature of 298.15 K. From the density experimental data, the apparent molar volumes and the transfer volumes for both amino acids in aqueous electrolyte solutions were calculated and correlated with specific equations. The viscosity data were correlated with Jones-Dole equation. By our knowledge, these systems are partially studied in literature.[2,5,6]

EXPERIMENTAL

Chemicals. Sodium chloride was purchased from Merck and its purity was higher than 99.8 mass %. Before use, NaCl was dried in vacuum desiccator for 24 h, at room temperature. L-alanine and L-histidine, both from Merck with purity higher than 99 mass%, were dried in a vacuum desiccator over $CaCl_2$ for 24 h and used without further purification.

Apparatus and procedure. The mixtures of the desired composition were prepared by weighting on a HR-120 (A&D Japan) electronic balance with a precision of ±0.0001 g. All mixed solvents were prepared by molality. In order to prepare the investigated solutions, aqueous solutions of NaCl (stock

* Corresponding author: astefaniu@gmail.com

solutions) of different concentrations were first prepared. Then different amounts of amino acid were added to stock solutions and stirred until a homogeneous solution was obtained. All the solutions were stored in special airtight bottles, to avoid the exposure to air or evaporation. The used water was bi-distillated.

The densities, ρ, of the solution were measured with a digital density meter (DMA 4500) supplied by Anton Paar, with an accuracy of ±0.05 kg m^{-3}.

Dynamic viscosities, η, were measured using an Anton-Paar AMVn falling ball viscometer. Temperature was controlled by means of a built-in Peltier thermostat within ±0.01 K. Measurements were made using a capillary with the diameter d=1.6 mm. The repeatability in the measurement of the viscosity is ± 0.1 %, and its reproducibility is ± 0.35%.

Refractive indices, n, of the mixtures at the sodium D-line were measured with a thermostated Abbe refractometer. The precision of the measurements was ±0.0001. An average of triplicate measurements was considered for each sample.

RESULTS AND DISCUSSION

The experimental data for density, viscosity and refractive index of water + NaCl + L-alanine and water +NaCl + L-histidine ternary systems at temperature of 298.15 K are presented in Table 1.

The experimental densities data were used to calculate the apparent molar volumes, V_Φ, of L-alanine and L-histidine, respectively, in NaCl solutions of different salt concentrations, according to the following equation:

$$V_\Phi = \frac{M}{\rho} - \frac{\rho - \rho_0}{m\rho\rho_0} \qquad (1)$$

where M represents the molar mass of the amino acid, m is the molality of the amino acid solution, ρ and ρ_0 are the densities of the solution and the solvent, respectively. For both investigated systems, the mixture of water + NaCl is considered as the solvent. The calculated values of V_Φ are also gathered in Table 1.

The apparent molar volumes were found to be linear functions of molality over the studied concentrations range; consequently, equation (2) was used in order to correlate the experimental values of apparent molar volumes:

$$V_\Phi = V_\Phi^0 + S_V m \qquad (2)$$

where V_Φ^0 and S_V are the fitting coefficients. S_V is the experimental slope and V_Φ^0 is the infinite dilution apparent molar volume or the standard partial molar volume of amino acid in aqueous NaCl solutions. This property is important because, at infinite dilution, the interactions between amino acid molecules are negligible and V_Φ^0 reflects the interactions between the amino acid molecules and the mixed solvent.

Table 1

Experimental properties and apparent molar volumes of amino acids in NaCl aqueous solutions at 298.15 K

Amino acid molality, mol kg^{-1}	ρ, kg m^{-3}	$10^6 V_\Phi$, m^3 mol^{-1}	η, mPa s	n
L-Alanine		**NaCl molality**		
		0.0 mol kg^{-1}		
0.0000	997.04	-	0.8910	1.3325
0.1028	999.96	60.66	0.8904	1.3346
0.2918	1005.14	60.96	0.9344	1.3370
0.6908	1015.73	61.00	1.0341	1.3428
0.9967	1023.53	61.01	1.1133	1.3471
		0.5027 mol kg^{-1}		
0.0000	1016.85	-	0.9115	1.3375
0.1002	1019.68	60.12	0.9489	1.3391
0.3921	1027.28	61.26	1.0173	1.3435
1.0043	1042.19	61.67	1.1866	1.3530
1.2972	1048.84	61.82	1.2788	1.3552
		1.0000 mol kg^{-1}		
0.0000	1036.0	-	0.9570	1.3420
0.1013	1038.52	62.67	0.9843	1.3439
0.4027	1045.84	62.62	1.0673	1.3485
0.6964	1052.73	62.60	1.1815	1.3520
0.9959	1059.50	62.59	1.2735	1.3569
1.2910	1065.92	62.60	1.3792	1.3600
1.4784	1069.86	62.61	1.4443	1.3621

Table 1 (continued)

		1.4960 mol kg^{-1}		
0.0000	1054.60	-	1.0078	1.3464
0.0911	1056.49	65.69	1.1458	1.3479
0.6277	1068.87	63.18	1.2455	1.3558
0.9135	1074.86	63.32	1.3323	1.3601
1.1874	1080.99	62.92	1.4667	1.3622
L-Histidine				
		0.0 mol kg^{-1}		
0.0000	997.04	-	0.8910	1.3325
0.0511	999.93	98.74	0.8855	1.3348
0.1003	1002.61	99.29	0.8996	1.3361
0.1985	1007.88	99.63	0.9394	1.3389
0.3021	1013.31	99.83	0.9802	1.3420
		0.4998 mol kg^{-1}		
0.0000	1016.74	-	0.9112	1.3375
0.0504	1019.67	96.10	0.9271	1.3390
0.0969	1022.12	98.39	0.9529	1.3401
0.1962	1027.30	99.50	0.9961	1.3433
0.2869	1031.98	99.72	1.0359	1.3458
		0.9993 mol kg^{-1}		
0.0000	1035.97	-	0.9569	1.3419
0.0519	1038.71	100.29	0.9872	1.3439
0.0935	1040.86	100.58	1.0028	1.3460
0.1869	1045.59	100.85	1.0461	1.3480
0.2803	1050.21	101.04	1.0861	1.3509
		1.4972 mol kg^{-1}		
0.0000	1054.64	-	1.0079	1.3464
0.0509	1056.57	112.80	1.0276	1.3482
0.0881	1058.42	108.11	1.0439	1.3495
0.1793	1062.88	104.98	1.0873	1.3525
0.2723	1067.29	104.09	1.1335	1.3559

The transfer volume ΔV_{Φ}^{0} is defined by the following equation:

$$\Delta V_{\Phi}^{0} = V_{\Phi}^{0}(in\ NaCl - water\ mixture) - V_{\Phi}^{0}(in\ pure\ water) \quad (3)$$

$V_{\Phi}^{0}(in\ NaCl - water\ mixture)$ is the infinite dilution apparent molar volume of amino acid in water + NaCl + amino acid ternary system and $V_{\Phi}^{0}(in\ pure\ water)$ is the infinite dilution apparent molar volume in water + amino acid binary system.

Viscosity is one of the key transport properties of solutions. Accurate viscosity data give useful information regarding ion-solvent interactions (long-range electrostatic interactions), which are the controlling forces in dilute solutions where ion-ion interactions are absent. Precise viscosity data are necessary to accurately calculate the physical parameters of Jones-Dole equation, which was used to analyze the experimental data.[7,8]

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad (4)$$

A and *B* are adjustable parameters, η_r is the relative viscosity, η is the viscosity of the water + NaCl + amino acid ternary system and η_0 is the viscosity of the solvent (water + NaCl). *A* is the Falkenhagen coefficient and represents the solute-solute interactions coupled with the size and the shape effects of the solute and to some extent, solute-solvent interactions. Due to the lack of appropriate theoretical knowledge, its significance is not fully understood. *B*, the Jones-Dole coefficient, reflects the effect of solute-solvent interactions on the mixture viscosity.

The correlations were made using standard deviation defined as:

$$\sigma = \left[\frac{\sum_{i=1}^{n} (Y_i^{\exp} - Y_i^{calc})^2}{N_{\exp}} \right]^{0.5} \quad (5)$$

where $Y_i^{\exp}$ is the experimental property (apparent molar volume or relative viscosity), Y_i^{calc}, the calculated property, N_{exp}, the number of experimental data.

The fitting parameters resulted from volumetric and viscometric analysis, together with the standard deviations, *σ,* are gathered in Table 2. For comparison, V_Φ^0 literature values for the two amino acids in water are also listed.[2,5] The results of the present study are in good agreement with the literature values, within the experimental uncertainties. The transfer volumes, calculated from the V_Φ^0 data for both solutions, are listed in Table 2.

From Table 1 the density values indicate that the increase of amino acid concentration at a fixed NaCl molality, generally, has little influence on V_Φ values for both amino acids. The presence of NaCl affects the behavior of amino acids in aqueous solutions. For a fixed amino acid concentration the increase of NaCl molality increases V_Φ values on the studied range of salt concentrations, as can be observed in Table 1. This indicates positive transfer volumes to solvent at higher NaCl concentrations. This behavior can be attributed to the zwitter – ion structure of L-alanine and L – histidine in aqueous solutions (Fig.1) and to the predominance of electrostatic interactions between the charged groups of the amino acids and the counter ions.

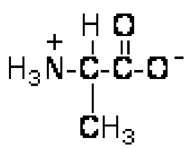
In the ternary systems of amino acid, salt and water the following types of interactions can occur: ion-ion interactions, between Na^+ ions and COO^- groups and between the anions of the salt and the NH^+ groups, ion-non polar group interactions and ion-amino acid group interactions. The positive values for transfer volume indicate that the ionic groups of amino acids have a more dominant effect on the interactions between the molecules in solution than the non-polar groups.[6]

Table 2 presents the infinite dilution apparent molar volume for amino acids in electrolyte aqueous solution. Generally, V_Φ^0 increases with the molar mass and size of amino acid. Due to its positively charged imidazole functional group, L-histidine has a larger size than L-alanine and consequently V_Φ^0 values of L-histidine are larger than that of L-alanine. Since the non polar interactions between amino acid molecules can be ignored at infinite dilution, V_Φ^0 reflects the interactions between amino acids molecules and solvent. The values of V_Φ^0 increase with the increase of salt molality, presenting a similar trend like V_Φ, as it can be observed in Fig. 2, which generally indicate a positive transfer volume to solvent with higher salt molality.

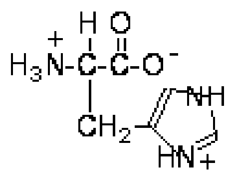
Table 2

Parameters of Eqs. (2) and (4) for amino acids in NaCl aqueous solutions at 298.15 K

m_{NaCl}, mol kg^{-1}	$10^6 V_\Phi^0$, m^3 mol^{-1}	ΔV_Φ^0, m^3 mol^{-1}	$10^6 S_V$, kg m^3 mol^{-2}	10^6 σ (Eq.2), m^3 mol^{-1}	*B*, kg mol^{-1}	10^3 σ (Eq.5)
			L –Alanine			
0.0000	60.14 60.19[5]	-	1.241	0.35	0.3590	2.14
0.5027	61.14	1.00	1.122	2.05	0.3031	6.83
1.0000	57.52	- 2.62	3.92	2.65	0.3841	5.31
1.4960	69.43	9.29	-7.014	2.02	0.1302	39.6
			L –Histidine			
0.0000	99.34 98.81[2]	-	-6.220	1.45	0.6468	1.37
0.4998	97.29	- 2.05	2.596	1.43	0.5308	2.23
0.9993	101.28	1.94	-8.873	1.31	0.4094	1.07
1.4972	113.64	14.3	-45.467	1.79	0.5201	0.40



a)



b)

Fig. 1 – Zwitter – ion structure of L-alanine (a) and L-histidine (b).

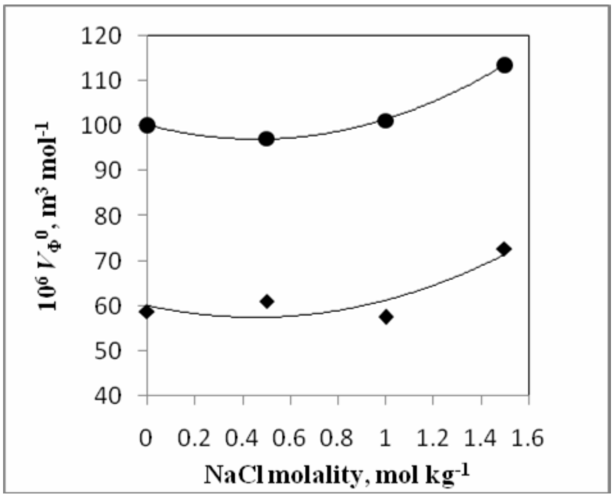


Fig. 2 – Standard partial molar volume of amino acids *versus* NaCl molality at 298.15 K in ternary systems: ♦, L-alanine; •, L-histidine.

The positive ΔV_{Φ}^{0} values show that the salt interacts directly with the solute through electrostatic interactions with the charged centers of these compounds, leading to a reduction in their electrostriction and, to positive transfer volumes. Water structure-breaking tendencies of the salt are largely overcome by these strong interactions between the salt ions and the amino acids molecules. The ion-ion interactions and ion-hydrophilic group interactions are stronger then ion-non polar group interactions.[6] The transfer volumes for both amino acids have comparable values.

The viscosity data have been analyzed using the Jones-Dole equation. It can be observed that the viscosity of the ternary systems is greater than that of the binary mixtures (Table 1). The values of Jones-Dole coefficient, *B*, for all studied systems are positive (Table 2). The sign of *B* coefficient depends on the degree of solvent structuring effect introduced by the ions. A positive value of the *B* coefficient is associated with structure-making (ordering) ions, while a negative value of the *B* coefficient is associated with structure-breaking (disordering) ions. The structure-making ions are called kosmotropes, while the structure-breaking ions, chaotropes, according to their relative abilities to induce the structuring of water. The degree of water structuring is determined mainly by the increase or decrease of solution viscosity due to added salt.[9] The positive values of *B* coefficient for all studied systems show the kosmotropic behavior (maker structure) of solutes in mixtures, indicating an alignment of zwitterions with ions/water dipols.[10] From literature data it has been found that NaCl have a kosmotrope behavior in water.[11] Amino acid addition does not affect this behavior; probably because of the zwitterionic structure of L-alanine in aqueous solution. The viscometric analyze is consistent with the results of the apparent molar volumes.

The experimental refractive index shows an increasing trend with increasing NaCl and amino acids concentrations (Table 1). This behavior is in accordance with the effect of amino acids and NaCl on the apparent molar volumes, indicating that the refractive index is also related to the interactions in mixtures.

CONCLUSIONS

The experimental data of density, viscosity and refractive index of L-alanine and L-histidine in aqueous NaCl solutions have been reported at 298.15 K. From the density data, the apparent molar volumes for both amino acids were calculated and correlated with a linear equation.

In the studied range of composition the apparent molar volumes values increase with increasing of NaCl molality for both amino acids. The transfer volumes values of the amino acids from water to NaCl solution were found to be, generally, positive. The viscosity data accurately calculated with the Jones-Dole equation indicate positive values for B coefficient. The solutes act as structure maker for pure water and for water-electrolyte solutions as well. These effects are attributed to the double charged nature of amino acids in solutions.

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