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Effect of NaBr, KCl, KBr, and $MgCl_2$ on Viscosities of Aqueous Glycine and L-Alanine Solutions at 298.15 K

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Viscosities, η, of glycine and L-alanine are measured in aqueous solutions of NaBr, KCl, KBr, and $MgCl_2$ up to high concentrations at 298.15 K. This study suggests that 1:1 electrolytes enhance the structure-making ability of the amino acids whereas $MgCl_2$ does not. The viscosities of the above solutions are correlated using a simple model with two interaction parameters.

Introduction

Ionic species play a significant role in governing the physical, chemical, and biological behavior of biological macromolecules such as proteins, nucleic acids, and enzymes.[1] Many biomolecules are complex molecules, and their behavior in ionic solutions is governed by a combination of different types of interactions. One way to reduce the complexity in the study of ion−biomolecule interactions is to study the solutions of model compounds. Because of the lack of studies of amino acids in concentrated electrolytic solutions, we have recently embarked on a program to study interactions in aqueous amino acid + electrolyte solutions.[2−7] In the previous studies, the ion−amino acid interactions were examined by measuring densities and speeds of sound of the solutions and analyzing the apparent molar properties calculated from them. Viscosity, η, is another important property that can yield information on solute−solute interactions. There are some reports on the viscosities of dilute aqueous solutions of amino acids and electrolytes.[8−17] However, no viscosity reports are available at high concentrations of amino acid and electrolyte. In this work, the viscosities of aqueous glycine and L-alanine in solutions of NaBr, KCl, KBr, and $MgCl_2$ up to high concentrations are presented. The mixture viscosities of these solutions are accurately fitted using a simple two-parameter equation. The viscosity data were required to test a model in the developmental stage in this laboratory for calculating viscosities of concentrated mixtures of the simple amino acids in strong electrolytes.

Experimental Section

Glycine and L-alanine (biochemistry grade, mass fraction >0.997, chloride, mass fraction $<5 \times 10^{-5}$) were procured from Merck and Loba Chemicals. The amino acids were used without further treatment. NaBr (extra pure 99% pure) was procured from S. D. Fine Chemicals; KBr, KCl, and $MgCl_2$ (extra pure 99.5% pure) were procured from Merck. The electrolytes were dried at 523 K for 3 h prior to their use. Solutions were prepared on the molality basis using water with a specific conductivity of less than 0.055×10^{-6} S·cm^{-1}. The concentration of amino acids was in the range of (0 to 3) mol·kg^{-1}, whereas those of electrolytes varied from (0 to 4) mol·kg^{-1}· The solutions were prepared by weight using a digital balance. The molalities of the solutions were accurate to within 2×10^{-4} mol·kg^{-1}. Throughout the article, the molalities of amino acid and electrolyte are represented by m_A and m_J, respectively.

The viscosity of the solutions was measured using a Ubbelhodde viscometer as described elsewhere.[6] Flow times were measured using a Racer digital stopwatch having an accuracy of ±0.01 s. The viscometer was calibrated with water using accurate literature data.[18] The viscosities were uncertain to ±0.003 mPa·s. The densities required for the calculation of the viscosities of the glycine + electrolyte and L-alanine + electrolyte solutions were taken from earlier studies.[2,4]

The viscosity of the solution, η, is given by following equation:

$$\frac{\eta}{\rho} = Ct - \frac{K}{t} \tag{1}$$

where t is the flow time (s), ρ is the density of the solution, and C and K are the viscometer constants that were obtained by measuring flow times for water at (283.15, 293.15, 298.15, 303.15, 313.15, and 323.15) K. The values of C and K obtained are 6.924×10^{-6} mPa·s·m^3·kg^{-1} and 1.390×10^{-4} mPa· s^2· m^3· kg^{-1}, respectively.

Temperature was controlled to ±0.01 K with a constant-temperature bath supplied by Julabo. The experimental solutions were allowed to equilibrate for 30 min before taking the readings.

Results and Discussions

The viscosities of aqueous glycine and L-alanine in NaBr, KCl, KBr, and $MgCl_2$ solutions are listed in Table 1. Ogawa et al. measured the viscosities of several amino acids in aqueous LiCl, NaCl, and KCl solutions with their concentrations ranging up to 2 mol·kg^{-1} water.[8] These authors have not reported any direct viscosity data but have listed the viscosity B and D coefficients. If the viscosities of glycine and L-alanine in aqueous KCl are calculated using these coefficients and their equation, then the resultant viscosities agree to within 0.009 mPa·s. It may be noted that the agreement between our viscosity data and the calculated data from the work of Ogawa et al.[8] was obtained up to 2 mol·kg^{-1} aqueous KCl using our molalities. Again, the number of data points has not been mentioned

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Table 1. Experimental Viscosity, η, of Aqueous Glycine and L-Alanine in NaBr, KBr, KCl, and $MgCl_2$ Solutions at 298.15 K

m_J/mol·kg^{-1}	η/mPa·s	m_J/mol·kg^{-1}	η/mPa·s	m_J/mol·kg^{-1}	η/mPa·s	m_J/mol·kg^{-1}	η/mPa·s
(Glycine + NaBr)							
m_A = 0.4994 mol·kg^{-1}		m_A = 0.9999 mol·kg^{-1}		m_A = 1.9989 mol·kg^{-1}		m_A = 2.9998 mol·kg^{-1}	
0.4994	0.999	0.4974	1.074	0.4994	1.232	0.5003	1.445
0.9988	1.032	0.9999	1.115	0.9999	1.285	0.9979	1.503
2.0007	1.114	2.0009	1.222	1.9998	1.427	2.0001	1.670
2.9997	1.238	2.9987	1.328	3.0001	1.565	3.0016	1.847
3.9972	1.365	3.9984	1.481	4.0001	1.743	3.9992	2.038
(Glycine + KCl)							
m_A = 0.4991 mol·kg^{-1}		m_A = 1.0004 mol·kg^{-1}		m_A = 1.9993 mol·kg^{-1}		m_A = 2.9999 mol·kg^{-1}	
0	0.956	0	1.189	0	1.189	0	1.374
0.5003	0.967	0.5002	1.040	0.5002	1.201	0.1001	1.375
1.0006	0.972	0.9994	1.041	0.9979	1.211	0.4999	1.396
1.9999	0.979	1.9999	1.055	1.9993	1.220	1.0002	1.390
3.0006	0.997	3.0006	1.083	3.0009	1.252	2.0004	1.415
3.9981	1.023	3.9985	1.099	3.9995	1.290	3.0001	1.467
(Glycine + KBr)							
m_A = 0.4995 mol·kg^{-1}		m_A = 0.9990 mol·kg^{-1}		m_A = 1.9996 mol·kg^{-1}		m_A = 2.9998 mol·kg^{-1}	
0.4999	0.952	0.4999	1.017	0.5001	1.190	0.4995	1.372
1.0001	0.962	0.9998	1.013	0.9996	1.203	1.0001	1.365
1.9992	0.947	2.0001	1.012	1.9998	1.178	2.0001	1.386
2.9988	0.970	2.9992	1.023	2.9997	1.189	3.0002	1.391
4.0005	0.976	3.9993	1.044	4.0001	1.225	3.9997	1.422
(Glycine + $MgCl_2$)							
m_A = 0.4999 mol·kg^{-1}		m_A = 0.9998 mol·kg^{-1}		m_A = 1.9990 mol·kg^{-1}		m_A = 3.0002 mol·kg^{-1}	
0.0987	0.991	0.0998	1.060	0.0998	1.230	0.0998	1.424
0.5010	1.086	0.5001	1.180	0.4999	1.334	0.4989	1.539
1.0001	1.196	0.9988	1.292	0.9987	1.466	0.9999	1.696
1.5001	1.333	1.5007	1.418	1.4976	1.621	1.4989	1.881
(L-Alanine + KCl)							
m_A = 0.1003 mol·kg^{-1}		m_A = 0.4995 mol·kg^{-1}		m_A = 0.7497 mol·kg^{-1}		m_A = 1.0002 mol·kg^{-1}	
0	0.918	0	1.017	0	1.079	0	1.152
0.5003	0.924	0.5003	1.016	0.5002	1.091	0.5003	1.154
0.9992	0.916	0.9992	1.012	1.0005	1.082	1.0006	1.155
1.9984	0.933	1.9995	1.025	1.9995	1.108	2.0001	1.164
2.9999	0.947	2.9989	1.044	2.9995	1.118	3.0002	1.188
3.9999	0.943	4.0016	1.077	3.9999	1.149	3.9999	1.217
(L-Alanine + $MgCl_2$)							
m_A = 0.1003 mol·kg^{-1}		m_A = 0.4995 mol·kg^{-1}		m_A = 0.7498 mol·kg^{-1}		m_A = 1.0002 mol·kg^{-1}	
0.0494	0.942	0.0504	1.035	0.0515	1.104	0.0504	1.171
0.5010	1.043	0.4999	1.154	0.4999	1.224	0.5001	1.300
0.9999	1.161	1.0009	1.287	0.9999	1.361	0.9989	1.453
1.4990	1.290	1.4999	1.419	1.5001	1.512	1.4998	1.626

in their report. A direct comparison of our viscosity data of glycine and L-alanine in aqueous KCl solution is, however, possible with the recent data of Banipal et al.[17] An average agreement of 0.007 mPa·s was obtained for both amino acids in aqueous KCl solutions. Such a comparison, however, is not be possible with the data of Rodriguez et al., who measured the viscosity of DL-alanine in NaCl solutions but not in other electrolytes of interest to us.[12] The effect of electrolytes on the viscosities of amino acid + electrolyte mixtures is shown in Figure 1a and b. The viscosities of glycine and L-alanine in the electrolyte solutions increase with increasing concentration of amino acid as well as electrolyte. An examination of Figure 1a and b signifies a higher effect of $MgCl_2$ on the viscosity of the amino acid−electrolyte mixture as compared to 1:1 electrolytes. For example, the $\partial\eta/\partial m_A$ value at 1 mol·kg^{-1} glycine in water is 0.156 mPa·s·kg·mol^{-1}, which increases to 0.181, 0.168, and 0.172 mPa·s·kg·mol^{-1} on addition of 1:1 electrolytes NaBr, KCl, and KBr, respectively. The maximum value of $\partial\eta/\partial m_A$ of 0.198 mPa·s·kg·mol^{-1} for glycine solutions is observed because of the addition of $MgCl_2$. In the case of 1 mol·kg^{-1} L-alanine, the $\partial\eta/\partial m_A$ value changes from 0.258 mPa·s·kg·mol^{-1} in water to 0.272 mPa·s·kg·mol^{-1} in 1 mol·kg^{-1} KCl and 0.310 mPa·s·kg·mol^{-1} in 1 mol·kg^{-1} $MgCl_2$. The $\partial\eta/\partial m_A$ values of aqueous amino acid + electrolyte mixtures do not show very large increases with these added electrolytes, in contrast to those seen on addition of tetra-*n*-alkylammonium bromide.[5]

The structure-making or -breaking ability of solutes can be rationalized in terms of the Jones−Dole viscosity *B* coefficient. The *B* coefficient of amino acids in 1 mol·kg^{-1} electrolyte is obtained using the following equation:

$$\frac{\eta}{\eta^0} = 1 + Bc + Dc^2 \tag{2}$$

where η^0 is the viscosity of the solvent (electrolyte + water). The molar concentration, *c*, is calculated from the molality using the density of solution published in our recent reports.[2−4] The *B* coefficients of aqueous glycine and L-alanine observed in this work are 0.136 dm^3·mol^{-1} and 0.271 dm^3·mol^{-1}, respectively. The *B* coefficient values are in close agreement with the literature values (0.135 dm^3·mol^{-1} and 0.247 dm^3·mol^{-1} for aqueous glycine and alanine, respectively).[2−4] The viscosity *B* coefficients for glycine and L-alanine on addition of 1 mol·kg^{-1} electrolytes are listed in Table 2. The *B* coefficients of glycine and L-alanine also increase on addition of NaBr, KCl, and KBr but do not change on addition of $MgCl_2$. This again confirms that the 1:1 electrolytes promote the structure-making ability of the amino acid solution, whereas $MgCl_2$ has no influence.

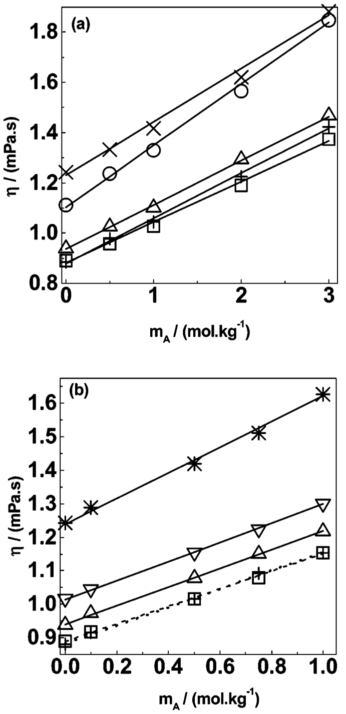

Figure 1. Effect of electrolytes on η of the mixture of aqueous amino acids + electrolytes: (a) aqueous glycine (□), glycine + 4 mol·kg^{-1} KCl (△), + 3 mol·kg^{-1} NaBr (○), 4 mol·kg^{-1} KBr (+), + 1.5 mol·kg^{-1} $MgCl_2$ (×); (b) aqueous L-alanine (□), L-alanine + 0.5 mol·kg^{-1} KCl (+), + 4 mol·kg^{-1} KCl (△), + 0.5 mol·kg^{-1} $MgCl_2$ (▽), 1.5 mol·kg^{-1} $MgCl_2$ (*).

Table 2. Viscosity *B* Coefficients for Aqueous Glycine and L-Alanine on Addition of 1 mol·kg^{-1} Electrolytes at 298.15 K

electrolyte	B/dm^3·mol^{-1}	electrolyte	B/dm^3·mol^{-1}
glycine		L-alanine	
NaBr	0.161	KCl	0.325
KCl	0.177	$MgCl_2$	0.279
KBr	0.210		
$MgCl_2$	0.121		

The viscosity of these mixtures can be analyzed by a simple equation. If an amino acid is added to water making a concentrated aqueous amino acid solution having molality m_A, then the viscosity of aqueous amino acid solutions, η_{AW}, can be given by

$$\eta_{AW} = \eta^0_W + q_{A1}m_A + q_{A2}m_A^2 \tag{3a}$$

where η^0_W is the viscosity of water (0.8903 mPa·s at 298.15 K) and q_{A1} and q_{A2} are the empirical parameters required to account for the concentration dependence of the viscosity of aqueous amino acid. Similarly, the viscosity of a concentrated aqueous electrolyte solution can be correlated by eq 3b:

$$\eta_{JW} = \eta^0_W + q_{J1}m_J + q_{J2}m_J^2 \tag{3b}$$

One can write the modified viscosity of an aqueous amino acid, η'_{AJW}. Let the viscosity of amino acid in the mixture be given as

$$\eta'_{AJW} = \eta_{AW} + \delta^0_{AJW}m_Am_J + \delta^1_{AJW}m_A^2m_J^2 \tag{4a}$$

and that of electrolyte as

$$\eta'_{JAW} = \eta_{JW} + \delta^0_{JAW}\, m_Am_J + \delta^1_{JAW}m_A^2m_J^2 \tag{4b}$$

Table 3. Amino Acid + Electrolyte Interaction Parameters, δ^0_{AJW} and δ^1_{AJW}, for Aqueous Glycine and L-Alanine in the Presence of Different Electrolytes at 298.15 K[a]

	δ^0_{AJW}	δ^1_{AJW}	rmsd
system	mPa·s·kg^2·mol^{-2}	mPa·s·kg^4·mol^{-4}	mPa·s
glycine + NaBr	0.0881 (0.0034)	−0.0023 (0.0004)	0.02
glycine + KCl	0.0554 (0.0041)	−0.0025 (0.0006)	0.02
glycine + KBr	0.0498 (0.0035)	−0.0020 (0.0004)	0.02
glycine + $MgCl_2$	0.1956 (0.0137)	−0.0177 (0.0040)	0.03
L-alanine + KCl	0.1266 (0.0113)	−0.0186 (0.0038)	0.03
L-alanine + $MgCl_2$	0.4352 (0.0244)	−0.1128 (0.0212)	0.02

[a] Values given in parentheses are the standard errors of the parameters.

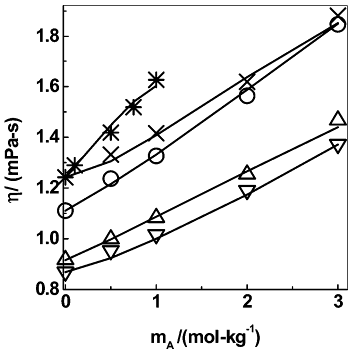

Figure 2. Experimental and fitted viscosities (points, experimental; lines, fitted by eq 6): glycine + 3 mol·kg^{-1} KCl (△), glycine + 0.5 mol·kg^{-1} KBr (▽), glycine + 3 mol·kg^{-1} NaBr (○), glycine + 1.5 mol·kg^{-1} $MgCl_2$ (×), L-alanine + 1.5 mol·kg^{-1} $MgCl_2$ (*).

The mixing parameters (symmetric in nature $\delta^0_{AJW} = \delta^0_{JAW}$ and $\delta^1_{AJW} = \delta^1_{JAW}$) are called the amino acid−electrolyte viscous flow interaction parameters.

The bulk viscosity, η, of such a mixture is given by

$$\eta = \frac{m_A\eta'_{AJW} + m_J\eta'_{JAW}}{m_A + m_J} \tag{5}$$

Substituting eqs 4a and 4b into eq 5 and simplifying gives

$$\eta = \eta_{ideal} + m_Am_J[\delta^0_{JAW} + \delta^1_{JAW}m_Am_J\ ] \tag{6}$$

where η_{ideal} is given by

$$\eta_{ideal} = \frac{m_A\eta_{AW} + m_J\eta_{JW}}{m_A + m_J} \tag{7}$$

The parameters δ^0_{AJW} and δ^1_{AJW} are obtained by the regression of the viscosity data listed in Table 1. The δ^0_{AJW} and δ^1_{AJW} parameters obtained for glycine and L-alanine in different electrolytes are listed in Table 3. These parameters depend on the nature of the amino acid and electrolyte and are independent of the concentration of electrolytes. The correlation power of eq 6 is shown in Figure 2, where the points show the experimental data and the lines are the fitted values. The Figure depicts the close agreement between the experimental and fitted viscosities of glycine and L-alanine in different electrolytes. The viscosities of aqueous glycine in the solutions of 1:1 electrolytes studied here can be estimated using parameters listed in Table 3 with an average rmsd (rmsd = $[(\sum(\eta_{exptl} - \eta_{fitted})^2/N)]^{0.5}$, where N = number of data points) of 0.020 mPa·s, whereas in a solution of $MgCl_2$ the rmsd is

0.04 mPa·s. In the case of L-alanine in the above electrolytes, an average rmsd of 0.03 mPa·s is obtained.

The δ^0_{AJW} and δ^1_{AJW} parameters signify the interactions between the amino acid and electrolyte in their solutions. The δ^0_{AJW} parameter decreases with an increase in ionic size for a given amino acid. This observation is supported by a volumetric study, where $MgCl_2$ shows maximum interactions with the charged centers of amino acids giving higher transfer volumes as compared to those of larger cations such as K^+ or Na^+.

Conclusions

We have investigated the viscosities of aqueous amino acid in electrolyte solutions. The effect of $MgCl_2$ (2:1 electrolyte) on the viscosity of the solutions is higher as compared to that of 1:1 electrolytes. It is possible to fit the viscosities of solution containing amino acid and electrolytes with the help of two parameters.

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