Activity Coefficients from Cell Potential Measurements in the NaCl + Glycine + Water Ternary System at (298.2, 308.2, and 318.2) K

Florinela Sîrbu*[†] **and Olga Iulian**[‡]

Romanian Academy, Institute of Physical Chemistry "Ilie Murgulescu", 202 Splaiul Independenţei str.,
060021, Bucharest, Romania, and "Politehnica" University of Bucharest, Faculty of Applied Chemistry and Material Science,
1 Polizu str., 011061, Bucharest, Romania

Activity coefficient values for NaCl and glycine are determined by studying their aqueous mixtures at different electrolyte and glycine concentrations. The mean ionic activity coefficient of NaCl was calculated from cell potential measurements: Na-ISE/NaCl (m_{NaCl}); glycine (m_{Gly})/Ag/AgCl. Measurements were made over the concentration range of (0.005 to 2) $\mathrm{mol \cdot kg^{-1}}$ glycine and of (0.05 to 2) $\mathrm{mol \cdot kg^{-1}}$ NaCl at temperatures (298.2, 308.2, and 318.2) K. The experimental data were correlated with the Roberts−Kirkwood and Scatchard−Prentiss virial expansion series. The activity coefficient of glycine is related to the mean ionic activity coefficient of the electrolyte through the cross-differential relation and evaluated by the standard deviation, σ. The mean ionic activity coefficient of NaCl decreases as the molality of glycine in the solution increases. The presence of NaCl decreases the activity coefficient of glycine and consequently represents a salt-in effect for amino acid.

Introduction

The thermodynamic study of aqueous organic systems containing electrolytes is important from both theoretical and practical points view for separation and concentration processes of nonelectrolytes (amino acids, proteins, enzymes) and for investigation of salt−nonelectrolyte interactions. Biomolecules are physiologically active in aqueous solutions. Addition of salts modifies their structure by affecting properties like solubility, denaturation, and thermodynamic activity.[1] The behavior of organic components in mixtures depends on various factors such as chemical structure, pH, temperature, surface charge distribution, and type and concentration of electrolyte. There is a considerable and renewed interest in this field.[2,3] The knowledge of the activity coefficients of nonelectrolytes in aqueous salt solutions is very important to understand the interactions between organic compounds and different electrolytes.[4−7]

Continuing our research of ternary aqueous systems with electrolytes,[8−10] this work presents the obtained activity coefficients of salt and an organic compound in the NaCl−glycine−H_2O system at different molalities of NaCl and glycine, by using an electrochemical method with a single ion selective electrode. The experimental data were correlated with the Roberts−Kirkwood[11,12] and Scatchard−Prentiss[13−15] virial expansion series.

The NaCl−glycine−H_2O system was studied in the literature on various areas of temperature and NaCl and glycine concentrations. In earlier works, the system has been studied by Joseph[7] with cell potential without transference measurements and by Scatchard and Prentiss[13] with freezing point methods. Recently, Khoshkbarchi and Vera[4] have studied the system at 298.15 K for $m_{\mathrm{NaCl}} = (0.1 \text{ to } 1)\ \mathrm{mol \cdot kg^{-1}}$ and $m_{\mathrm{Gly}} = (0.1 \text{ to } 2.6)\ \mathrm{mol \cdot kg^{-1}}$. Phang and Steel[14] obtain the data for $m_{\mathrm{NaCl}} = (0.01 \text{ to } 1)\ \mathrm{mol \cdot kg^{-1}}$ and $m_{\mathrm{Gly}} = (0.5 \text{ to } 4)\ \mathrm{mol \cdot kg^{-1}}$ at temperatures between (273.15 and 323.15) K. The study of Han and Tan[16] presents the supersaturated solutions of glycine and NaCl at 298.15 K in solubility terms.

Our study extends the field of low glycine molalities (region of biochemical concentrations) and high salt molalities. The activity coefficients of glycine and NaCl in the ternary NaCl−glycine−H_2O system have been investigated from cell potential measurements at various molalities between (0.005 and 2) $\mathrm{mol \cdot kg^{-1}}$ for glycine and between (0.05 and 2) $\mathrm{mol \cdot kg^{-1}}$ for NaCl and at (298.2, 308.2, and 318.2) K.

Experimental Section

Chemicals. All chemicals used in this work were supplied by Merck and Fluka without further purification. The purity of these materials was 99.8 % for NaCl and 99 % for glycine. Glycine was dried at 340 K for 72 h before use. NaCl was also dried at 410 K for about 48 h. Both were stored and cooled in desiccators over silica gel.

Stock aqueous solutions of NaCl and glycine (Gly) were prepared by direct weighing. Working solutions of different NaCl and glycine molalities were prepared using double-distilled and deionized water with a specific conductivity-grade water of $5 \cdot 10^{-5}\ \mathrm{S \cdot m^{-1}}$ at 298.2 K. All the solutions were prepared based on molality, and the water was also weighed using a digital balance. The molalities of the initial solutions were prepared with an accuracy of $2 \cdot 10^{-4}\ \mathrm{mol \cdot kg^{-1}}$.

For the preparation of mixtures, the following values of solubility in water at normal presssure were taken into account: (25.02 and 30.17) g/(100 g of water)$^{-1}$ at (298.15 and 308.15) K, respectively, for glycine,[1] and (6.159, 6.179, and 6.224) $\mathrm{mol \cdot kg^{-1}}$ at (298.15, 303.15, and 313.15) K, respectively, for sodium chloride.[17]

Measurements of Activity Coefficients. The experiments were done by measuring potential difference of the Na ion-selective electrode of type "pHoenix Sodium Ion Combination Epoxy Electrode, Cat. No. NA71503" (Na-ISE) against a reference electrode Ag/AgCl, incorporated in a jacketed glass cell containing 100 mL of solution and a stirrer. In all experiments,

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* Corresponding author. E-mail: sflorinela@yahoo.com. Fax: +40.21.312.11.47.
[†] Institute of Physical Chemistry "Ilie Murgulescu".
[‡] "Politehnica" University of Bucharest.

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the conditioning procedure for the electrode was followed exactly according to the manufacturer instructions.

For each series of measurements, the temperature was kept constant using a thermostatic water bath and was measured with a platinum wire resistive thermometer with a precision of ± 0.1 K.

The potential difference of the electrochemical cells was measured by employing a Crison micropH 2002 electrometer with a resolution of ± 0.1 mV. For each solution, two to four reproducible readings were repeated, thus calculating the mean measured value. The readings of the potentiometer were made only when drift was less than 0.1 mV. Consequently, the 95 % confidence interval for the values of the ratio of the mean ionic activity coefficients of NaCl in the presence of the amino acid and in the absence of the amino acid at the same NaCl molality was calculated as ± 0.003.

We verified the electrode by measuring the potential difference of the reference cell

$$\text{Na-ISE/NaCl}(m_{\text{NaCl},0})\text{/Ag/AgCl} \tag{1}$$

The electrochemical cell used is schematically represented by

$$\text{Na-ISE/NaCl}(m_{\text{NaCl}})\text{; glycine}(m_{\text{Gly}})\text{/Ag/AgCl} \tag{2}$$

From the potential difference between two electrochemical cells (2) and (1), the ratio of the mean ionic activity coefficients of NaCl ($\gamma_{\text{NaCl}}/\gamma^0_{\text{NaCl}}$) was calculated

$$\ln\left(\frac{\gamma_{\text{NaCl}}}{\gamma^0_{\text{NaCl}}}\right) = \frac{E_2 - E_1}{S} + \ln(m_{\text{NaCl},0}/m_{\text{NaCl}}) \tag{3}$$

In the two cells, m_{NaCl} and $m_{\text{NaCl},0}$ are the NaCl molality with or without Gly, respectively; m_{Gly} represents the molality of glycine; E_1, E_2 are the cell potentials for cells (1) and (2), respectively; γ_{NaCl}, γ^0_{NaCl} are the mean ionic activity coefficients of NaCl in the mixtures with and without glycine, respectively; and S is the electrode slope, whose theoretical value is described by the Nernst equation. The Nernstian behavior of the Na-ISE electrode was checked by calibration with aqueous NaCl solutions at concentrations between (0.05 and 2) $\text{mol}\cdot\text{kg}^{-1}$ at all studied temperatures. The obtained experimental values (53.2, 55.1, and 57.1) mV were used for (298.2, 308.2, and 318.2) K, respectively. These values of S differ from the theoretical values[18] by about 3.38 %, 3.61 %, and 3.97 % at the studied temperatures.

Results and Discussions

The ratio of the mean ionic activity coefficients of NaCl in the presence and in the absence of glycine ($\gamma_{\text{NaCl}}/\gamma^0_{\text{NaCl}}$) determined in this work in the ternary NaCl−Gly−H_2O system at different NaCl and glycine concentrations at (298.2, 308.2, and 318.2) K are presented in Table 1. They were calculated with eq 3 from experimental data obtained from cell potentials at different glycine and NaCl molalities. In columns 1, 3, and 4 of the table are shown in parentheses the values of the mean ionic activity coefficients of NaCl obtained for the same system and published in the literature.[4,14,19] The determined values in this work are in satisfactory agreement with the available literature values as seen in Table 1.

The obtained values for ($\gamma_{\text{NaCl}}/\gamma^0_{\text{NaCl}}$) reflect the influence of glycine and NaCl concentrations on the ratio of the mean ionic activity coefficients of NaCl in the presence and in the absence of glycine at the same NaCl molality at different temperatures.

The experimental data were fitted to a virial expansion series of Roberts−Kirkwood (eq 4) and Scatchard−Prentiss (eq 5).[14]

Equation 4 is recommended, generally, for a molality less than 0.5 $\text{mol}\cdot\text{kg}^{-1}$, both for electrolyte and nonelectrolyte compounds. Equation 5 is recommended for extended areas of salt and organic compound concentrations, offering a good representation of interactions between ions and nonelectrolyte molecules.[20,21]

$$\lg(\gamma_{\text{NaCl}}/\gamma^0_{\text{NaCl}}) = m_{\text{Gly}}(B_{10} + B_{11}m^{1/2}_{\text{NaCl}} + B_{12}m_{\text{NaCl}}) + B_{20}m^2_{\text{Gly}} \tag{4}$$

$$\lg(\gamma_{\text{NaCl}}/\gamma^0_{\text{NaCl}}) = m_{\text{Gly}}(B_{10} + B_{11}m^{1/2}_{\text{NaCl}} + B_{12}m_{\text{NaCl}} + B_{13}m^{3/2}_{\text{NaCl}}) + m^2_{\text{Gly}}(B_{20} + B_{21}m^{1/2}_{\text{NaCl}}) \tag{5}$$

Equations 4 and 5 represent the activity coefficients of salt as a power series of amino acids and electrolyte molalities. According to the author,[13,22−24] B_{ij} are the adjustable parameters expressing the contributions of the binary, ternary, and quaternary interactions in mixture; i is the number of two-halves ($2\cdot1/2$) of the solute 1 (Gly and NaCl, respectively, as ions); $i = 1$, 2; j is the number of halves of the solute 2 (1/2 of NaCl and Gly, respectively, as ions); and $j = 0$, 1, 2, 3.

For aqueous electrolyte systems with nonelectrolytes of the zwitterionic type, the B_{10} parameter is important, and its significance was investigated by different authors.[4,25−27] Thus, Vera considers that the B_{10} parameter is dominant, and it is a function of the temperature and the dielectric constant of the solvent.[4]

The obtained B_{ij} parameters can be used to calculate the values for the ratio of the activity coefficients of glycine ($\gamma_{\text{Gly}}/\gamma^0_{\text{Gly}}$) in the NaCl−Gly−$H_2O$ ternary system. The activity coefficient of amino acid is related to the mean ionic activity coefficient of the electrolyte through the cross-differential relation[1]

$$\upsilon\left(\frac{\partial \ln \gamma_{\text{NaCl}}}{\partial m_{\text{Gly}}}\right)_{m_{\text{NaCl}},T,P} = \left(\frac{\partial \ln \gamma_{\text{Gly}}}{\partial m_{\text{NaCl}}}\right)_{m_{\text{Gly}},T,P} \tag{6}$$

where υ is the number of moles of ions per mole of NaCl, and $\upsilon = \upsilon_1 + \upsilon_2 = 2$ with υ_1 and υ_2 being the number of cation and anion, respectively.

The activity coefficient of glycine can be expressed as a power series of m_{Gly} and m_{NaCl} by applying the cross-differentiation relation 6 on eq 5, resulting in eq 7

$$\lg(\gamma_{\text{Gly}}/\gamma^0_{\text{Gly}}) = m_{\text{NaCl}}(2B_{10} + (4/3)B_{11}m^{1/2}_{\text{NaCl}} + B_{12}m_{\text{NaCl}} + (4/5)B_{13}m^{3/2}_{\text{NaCl}}) + 4m_{\text{Gly}}m_{\text{NaCl}}(B_{20} + (2/3)B_{21}m^{1/2}_{\text{NaCl}}) \tag{7}$$

where γ_{Gly} and γ^0_{Gly} are the activity coefficients of glycine in the mixture with and without NaCl, respectively.

Table 1. Experimental Values for ($\gamma_{\mathrm{NaCl}}/\gamma^0_{\mathrm{NaCl}}$) in the NaCl−Gly−$H_2O$ Ternary System for Various NaCl and Glycine Molalities at (298.2, 308.2, and 318.2) K

m_{Gly}	$\gamma_{\mathrm{NaCl}}/\gamma^0_{\mathrm{NaCl}}$					
	m_{NaCl}/mol·kg^{-1}					
mol·kg^{-1}	0.050	0.250	0.500	1.000	1.500	2.000
T/K = 298.2						
0.005	0.9991	0.9991	0.9991	0.9991	0.9991	0.9991
0.007	0.9981	0.99812	0.9981	0.9981	0.9991	0.9991
0.009	0.9972	0.99718	0.9972	0.9981	0.9981	0.9981
0.011	0.9963	0.99625	0.9963	0.9972	0.9972	0.9981
0.050	0.9925	0.99438	0.9944	0.9972	0.9963	0.9972
0.080	0.9879	0.99158	0.9934	0.9953	0.9953	0.9963
0.500	0.9293	0.95051	0.9622	0.9740	0.9832	0.9916
0.500	(0.9324)[a]		(0.96339)[a]	(0.97477)[a]		
0.500	(0.94471)[b]		(0.96294)[b]	(0.97163)[b]		
0.500			(0.9658)[c]	(0.9763)[c]		
1.000	0.8751	0.91201	0.93106	0.9523	0.9676	0.9814
1.000	(0.87862)[a]		(0.93261)[a]	(0.9517)[a]		
1.000	(0.90053)[b]		(0.93304)[b]	(0.94842)[b]		
1.000			(0.9364)[c]	(0.9559)[c]		
1.250	0.8523	0.89587	0.9189	0.9434	0.9595	0.9759
2.000	0.8033	0.86119	0.8908	0.9198	0.9425	0.9577
2.000	(0.80556)[a]		(0.88777)[a]	(0.9118)[a]		
2.000	(0.83792)[b]		(0.88879)[b]	(0.91306)[b]		
2.000			(0.8965)[c]	(0.9297)[c]		
T/K = 308.2						
0.005	0.9991	0.9991	0.9991	0.9991	0.9991	0.9991
0.007	0.9991	0.9982	0.9982	0.9991	0.9991	0.9991
0.009	0.9982	0.9973	0.9973	0.9982	0.9982	0.9991
0.011	0.9973	0.9955	0.9964	0.9973	0.9982	0.9982
0.050	0.9928	0.9946	0.9955	0.9964	0.9973	0.9982
0.080	0.9883	0.9919	0.9937	0.9955	0.9964	0.9973
0.500	0.9334	0.9530	0.9626	0.9749	0.9829	0.9910
1.000	0.8807	0.9141	0.9325	0.9522	0.9670	0.9811
1.250	0.8578	0.8976	0.9191	0.9419	0.9591	0.9767
2.000	0.8058	0.8602	0.8879	0.9166	0.9368	0.9591
T/K = 318.2						
0.005	0.9991	0.9991	0.9991	0.9991	0.9991	0.9991
0.007	0.9983	0.9983	0.9983	0.9991	0.9991	0.9991
0.009	0.9974	0.9974	0.9974	0.9983	0.9983	0.9991
0.011	0.9965	0.9965	0.9956	0.9983	0.9983	0.9983
0.050	0.9930	0.9948	0.9965	0.9974	0.9983	0.9983
0.080	0.9896	0.9922	0.9939	0.9956	0.9878	0.9974
0.500	0.9381	0.9547	0.9639	0.9749	0.9826	0.9913
1.000	0.8862	0.9170	0.9332	0.9522	0.9664	0.9818
1.250	0.8632	0.9003	0.9194	0.9414	0.9588	0.9766
2.000	0.8083	0.8587	0.8846	0.9127	0.9414	0.9614

[a] From ref 14. [b] From ref 19. [c] From ref 4.

Both equations were applied using a least-squares algorithm along with the standard deviation

$$\sigma = \left(\frac{\sum |(\lg \gamma_i^{\mathrm{exp}} - \lg \gamma_i^{\mathrm{calc}})|_2}{N - p}\right)^{0.5} \tag{8}$$

where γ_i^{exp} and γ_i^{calc} represent the mean ionic activity coefficients, experimental and calculated, respectively; N is the number of experimental data; and p is the number of parameters. The result of experimental data fitting with the Roberts−Kirkwood and Scatchard−Prentiss models (eqs 4 and 5) are presented in Table 2: B_{ij} parameters and standard deviation, σ. The standard deviations show that both equations represent well the experimental data. The Scatchard−Prentiss equation, with more parameters, gives better results than the Roberts−Kirkwood equation, probably, due to the additional terms which are characteristic for short-range interactions.

The most important parameter after Khoshkbarchi and Vera,[4] the parameter B_{10}, in eqs 4, 5, and 7, respectively, represents the pairwise interactions between molecules of glycine and NaCl. It is negative for glycine which indicates attractive interactions between NaCl and glycine, respectively. The negative values of the B_{10} coefficient also indicate that the presence of NaCl decreases the activity coefficient of the amino acid and consequently represents a salt-in effect for glycine. The obtained values for the B_{ij} parameters at 298.2 K correspond well with the literature.[14] Negative values for parameter B_{10} decrease in absolute value as the temperature increases. This shows that with increasing temperature interactions between molecules of amino acid and salt are more pronounced.[4]

Figures 1 to 6 present the activity coefficients of NaCl and glycine at all studied temperatures. Figures 1 to 3 show the ratio of the mean ionic activity coefficients of NaCl in the presence of glycine and in the absence of glycine, at the same NaCl molality, as a function of glycine molality. Figure 1 shows in detail the correlation between our experimental and calculated with eq 5 values obtained for the ratio ($\gamma_{\mathrm{NaCl}}/\gamma^0_{\mathrm{NaCl}}$) at low glycine concentrations. The points are the experimental values, and the curves are the Scatchard−Prentiss fitting of experimental data

Table 2. Scatchard−Prentiss and Roberts−Kirkwood Parameters in the Ternary System NaCl−Gly−H_2O at (298.2, 308.2, and 318.2) K

T/K	B_{10}/$\text{kg}\cdot\text{mol}^{-1}$	B_{20}/$\text{kg}^2\cdot\text{mol}^{-2}$	B_{11}/$\text{kg}^{3/2}\cdot\text{mol}^{-3/2}$	B_{12}/$\text{kg}^2\cdot\text{mol}^{-2}$	B_{13}/$\text{kg}^{5/2}\cdot\text{mol}^{-5/2}$	B_{21}/$\text{kg}^{5/2}\cdot\text{mol}^{-5/2}$	σ
			Scatchard−Prentiss eq				
298.2	−0.09134	0.01261	0.11612	−0.07017	0.02116	−0.00945	0.00050
298.15	−0.08822[a]	0.01151[a]	0.11732[a]	−0.07499[a]	0.02291[a]	−0.01006[a]	
308.2	−0.08471	0.01024	0.10768	−0.06894	0.02228	−0.00786	0.00039
318.2	−0.07733	0.00748	0.09512	−0.06238	0.02100	−0.00531	0.00065
			Roberts−Kirkwood eq				
298.2	−0.07949	0.00622	0.07786	−0.02526	-	-	0.00223
308.2	−0.07381	0.00454	0.07050	−0.02191	-	-	0.00199
318.2	−0.06953	0.00364	0.06350	−0.01805	-	-	0.00170

[a] From ref 14.

between (0.05 and 2) mol·kg^{-1} NaCl, at the same NaCl molality. The mean ionic activity coefficient of NaCl decreases as the molality of glycine in the solution increases, and the variation is greater at lower salt concentrations and decreases at higher NaCl molalities. This suggests that higher electrolyte concentrations screen more electrostatic ion−dipole interactions and also increase the importance of the short-range interactions, resulting in a smaller effect of the amino acid on the mean ionic activity coefficient of NaCl.[4] This behavior is found at all studied temperatures.

The activity coefficients of glycine calculated with eq 7 are presented in Figures 4 to 6. The figures present the ratio of the

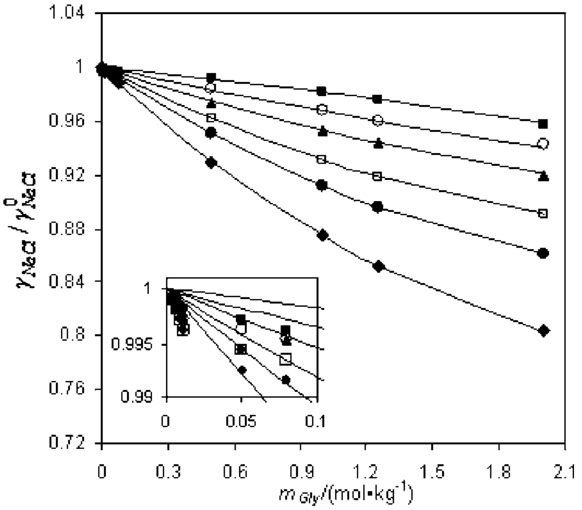

Figure 1. Effect of glycine on the ratio of the mean ionic activity coefficients of NaCl in the presence or absence of Gly, respectively, at 298.2 K and various NaCl molalities: ♦, 0.05; ●, 0.25; □, 0.5; ▲, 1; ○, 1.5; ■, 2; —, correlation with the Scatchard−Prentiss equation.

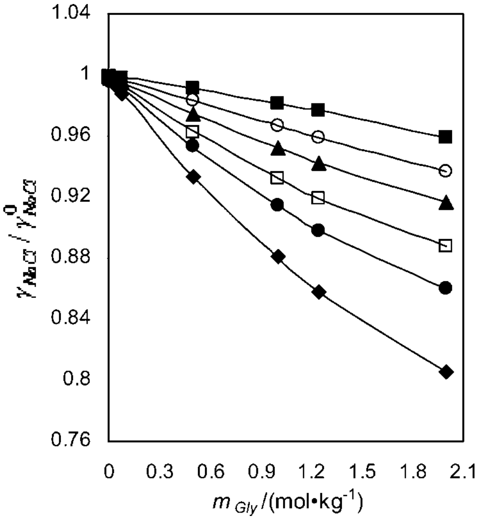

Figure 2. Effect of glycine on the ratio of the mean ionic activity coefficients of NaCl in the presence or absence of Gly, respectively, at 308.2 K and various NaCl molalities: ♦, 0.05; ●, 0.25; □, 0.5; ▲, 1; ○, 1.5; ■, 2; —, correlation with the Scatchard−Prentiss equation.

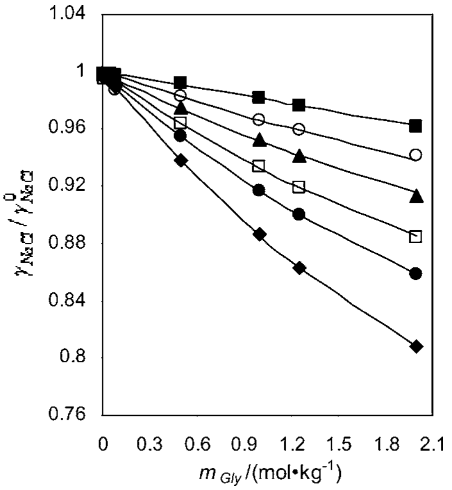

Figure 3. Effect of glycine on the ratio of the mean ionic activity coefficients of NaCl in the presence or absence of Gly, respectively, at 318.2 K and various NaCl molalities: ♦, 0.05; ●, 0.25; □, 0.5; ▲, 1; ○, 1.5; ■, 2; —, correlation with the Scatchard−Prentiss equation.

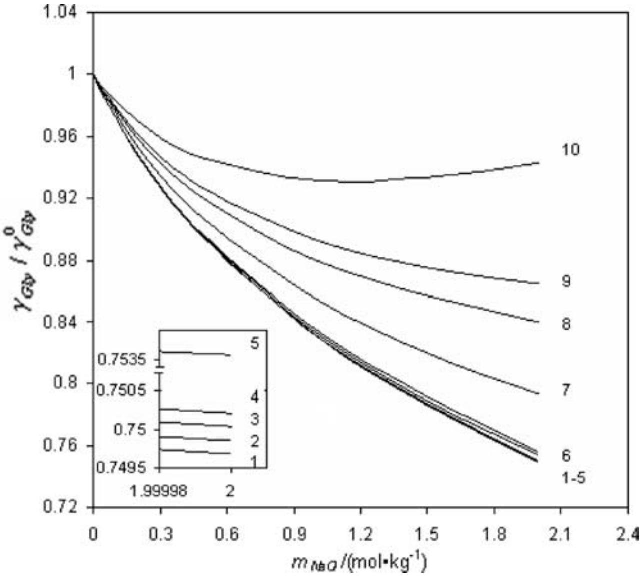

Figure 4. Effect of NaCl on the ratio of the activity coefficients of glycine (eq 7) in the presence or absence of NaCl, respectively, at 298.2 K and different glycine molalities: 1, 0.005; 2, 0.007; 3, 0.009; 4, 0.011; 5, 0.05; 6, 0.08; 7, 0.5; 8, 1; 9, 1.25; 10, 2.

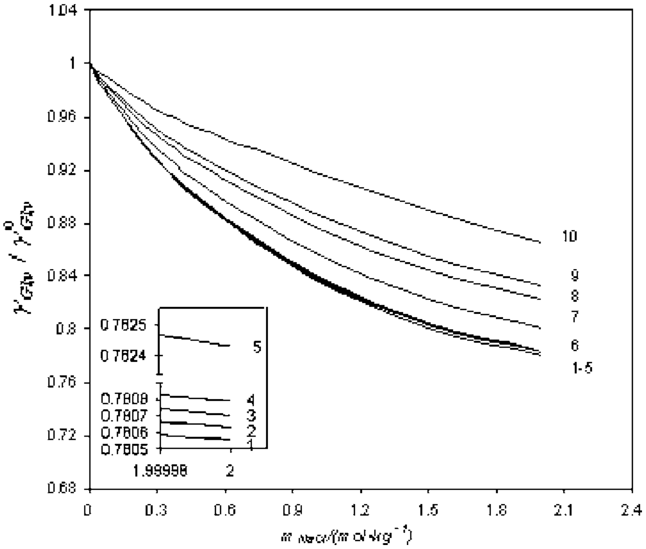

Figure 5. Effect of NaCl on the ratio of the activity coefficients of glycine (eq 7) in the presence or absence of NaCl, respectively, at 308.2 K and different glycine molalities: 1, 0.005; 2, 0.007; 3, 0.009; 4, 0.011; 5, 0.05; 6, 0.08; 7, 0.5; 8, 1; 9, 1.25; 10, 2.

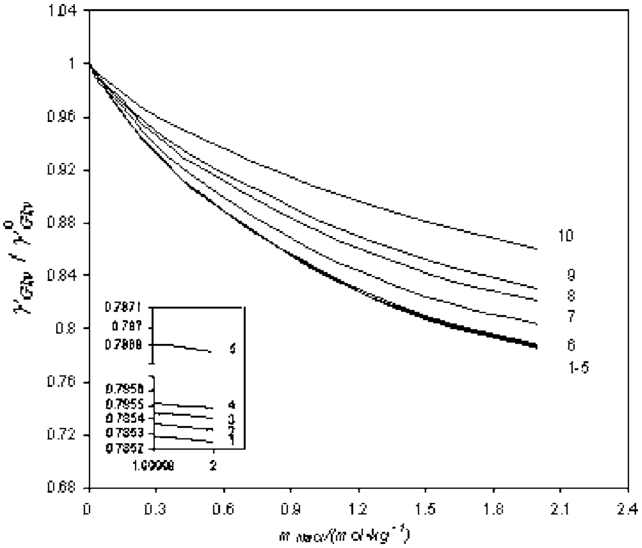

Figure 6. Effect of NaCl on the ratio of the activity coefficients of glycine (eq 7) in the presence or absence of NaCl, respectively, at 318.2 K and different glycine molalities: 1, 0.005; 2, 0.007; 3, 0.009; 4, 0.011; 5, 0.05; 6, 0.08; 7, 0.5; 8, 1; 9, 1.25; 10, 2.

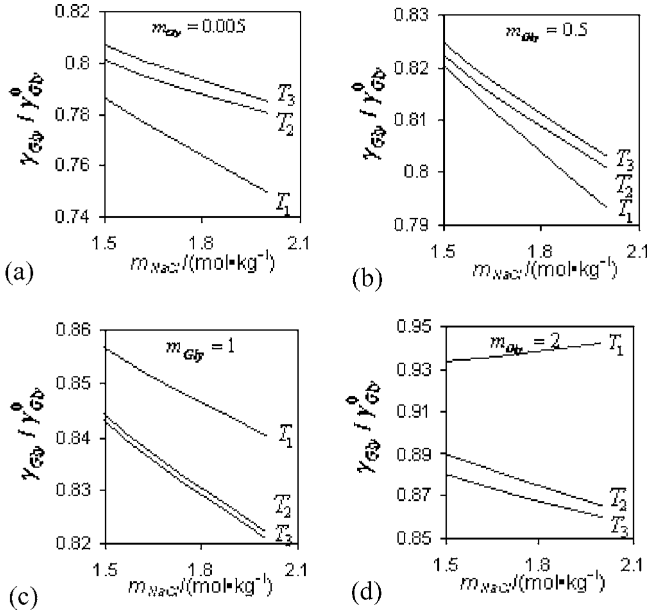

Figure 7. (a) to (d) Influence of temperature on the ratio of the activity coefficients of glycine in the presence or absence of NaCl, respectively, for m_{Gly} = (0.005, 0.5, 1, and 2) mol·kg^{-1} and different NaCl molalities: T_1 = 298.2 K; T_2 = 308.2 K; and T_3 = 318.2 K.

activity coefficients of glycine in the presence and in the absence of NaCl, at the same glycine molality, as a function of NaCl molality. Figure 4 shows the differences between curves 1 to 5, obtained for low concentrations of glycine, equal to (0.005, 0.007, 0.009, 0.011, and 0.05) mol·kg^{-1}. It can be observed that at the same glycine molality the activity coefficient of glycine decreases as the molality of NaCl in solution increases. This decrease in the activity coefficient of glycine with an increase in NaCl concentration is smaller at higher molalities of glycine and NaCl. This behavior is due to the formation of ion−dipole pairs at the higher electrolyte and amino acid concentrations and suggests a salt-in effect for glycine in the presence of NaCl. The results obtained agree well with those found in the literature.[4]

A similar behavior is found in the following systems: L-α-alanine−NaCl−water, diglycine−NaCl−water, triglycine−NaCl−water. For the last system, NaCl ($m_{NaCl} \leq 0.05$ mol·kg^{-1}) gives a salt-in effect at low amino acid concentrations and a salt-out effect at higher amino acid concentrations. In the series of glycine, diglycine, and triglycine, it was observed that the salt-in effect diminishes with the increase of hydrocarbon radical.[28] Also, other salts show a salt-in effect: $CaCl_2$ or sodium glutamate for glycine in Gly−$CaCl_2$−water[26] and Gly−sodium glutamate−water[29] systems, respectively.

It is of interest to consider the transition from a salt-in to salt-out effect for glycine by NaCl at m_{Gly} = 2 mol·kg^{-1} and 298.2 K. This trend may reflect the replacement of ion−dipole interactions in solutions with interactions between ions and zwitterions[6,7] formed by dipole−dipole attractions or hydrogen bonds. The temperature increase from (308.2 to 318.2) K enhances the salt-in effect of NaCl on amino acid.

The influence of temperature on the NaCl mean ionic activity coefficients at constant concentration of glycine is not significant. However, the glycine activity coefficients at the same glycine molality vary with increasing temperature in the aqueous mixtures studied. Considering this factor, it is advantageous to compare the dependence of the temperature and m_{NaCl} of ($\gamma_{Gly}/\gamma^0_{Gly}$), at m_{NaCl} >1.5 mol·kg^{-1} and four constant glycine concentrations: m_{Gly} = (0.005, 0.5, 1, and 2) mol·kg^{-1} in Figures 7(a) to (d).

The influence of temperature on the ratio ($\gamma_{Gly}/\gamma^0_{Gly}$) presents different behavior: when m_{Gly} = (0.005 to 0.5) mol·kg^{-1}, the ratio increases with a temperature increase, and when m_{Gly} > 0.5 mol·kg^{-1}, ($\gamma_{Gly}/\gamma^0_{Gly}$) decreases with a temperature increase. For a better understanding, more thermodynamic data for aqueous mixtures containing electrolytes and nonelectrolytes at various temperatures are needed.

Conclusions

The mean ionic activity coefficient data for NaCl in the ternary system NaCl−Gly−H_2O at different molalities of glycine and NaCl using the electrochemical method have been obtained. The mean ionic activity coefficient of NaCl decreases as the molality of glycine in the solution increases. The decreases are smaller at higher NaCl molalities. A reason for this behavior is the importance of short-range interactions at higher electrolyte concentrations. The activity coefficient of glycine, at the same glycine molality, decreases as the NaCl molality in solution increases. This decrease is smaller at higher molalities of glycine and NaCl. NaCl presents a salt-in effect for glycine.

Two correlative models for activity coefficients of NaCl and glycine have been presented and tested with the obtained experimental data. The Roberts−Kirkwood and Scatchard−Prentiss equations represent well the experimental data and allow calculation of the glycine activity coefficients in the ternary system studied.

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