

The mixing effect of glycine with sodium chloride from activity coefficients investigations at T = (303.15 and 313.15) K

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The mixing effect of electrolyte and amino acid on activity coefficients in NaCl+Glycine+Water mixtures, for molality of glycine and NaCl up to 2 mol kg⁻¹ was investigated. The activity coefficients at (303.15 and 313.15) K of NaCl and glycine in aqueous solutions were measured using potentiometric method. The obtained experimental data were fitted by Scatchard-Prentiss and Roberts-Kirkwood equations. The mean ionic activity coefficient of NaCl decreases as the molality of glycine in the solution increases. The presences of NaCl diminish the activity coefficient of glycine giving a salt-in effect for amino acid.

(Received March 3, 2010; accepted May 26, 2010)

Keywords: Mixing effect, Potentiometric method, NaCl, Glycine, NaCl

1. Introduction

The thermodynamic study of the activity coefficients in aqueous multicomponent systems containing electrolytes and biomolecules had a marked increase in interest for investigation of salt-non-electrolyte interactions [1-4]. Addition of salts modifies the behavior of organic component in aqueous mixtures which depends on various factors such as: chemical structure, pH, temperature, surface charge distribution and electrolyte concentration that affect the properties like solubility, denaturation and thermodynamic activity [5-7]. The interaction of neutral salts and amino acids in water depends both the nature of the salt and the length of the hydrocarbon chain of the amino acid [8, 9].

As a part of our study of aqueous ternary systems containing salt and amino acid, the activity coefficients of organic component and salt have been obtained in NaCl-Glycine-H₂O ternary system at different glycine and NaCl molalities [10-12]. This ternary system was studied in literature on a limited domain of temperatures and concentrations for NaCl and glycine [1, 13, 14].

In this purpose we resorted to the potentiometric technique, which is reported in an article of ours previous [10]. The results are determined at various concentrations between (0.005 and 2) mol·kg⁻¹ for glycine and between

(0.05 and 2) mol·kg⁻¹ for NaCl at two temperatures (303.15 and 313.15) K [15].

The obtained experimental values were fitted with Roberts-Kirkwood and Scatchard-Prentiss virial equations [13, 16-19]. A comparison between mean ionic activity coefficients calculated with Schatchard-Prentiss and Roberts-Kirkwood equations and those obtained experimentally was made. The mixing effect on solute

(amino acid existent as zwitterion form) [4] and solvent (salt-water), respectively, was discussed.

2. Experimental

2.1. Materials

All substances used in this study were products by Merck and Fluka of the highest purity commercially available: 99.8% for NaCl and 99% for glycine, without further purification.

Glycine (Gly) was dried at 340 K for 72 hour before use. NaCl was also dried at 410 K for about 48 hours. Both were stored and cooled in desiccators over silica gel. Stock aqueous solutions of NaCl (4 mol·kg⁻¹) and glycine (2.5 mol·kg⁻¹) were prepared by direct weighing.

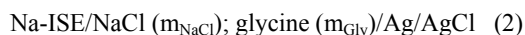
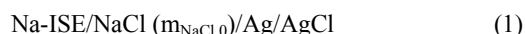
Work solutions were prepared by direct weighing from stock aqueous solutions of NaCl and glycine (Gly) respectively. Twice-distilled water until the electric conductivity of the rising water reaches a value of 5×10^{-5} S·m⁻¹ was used as solvent. The accurate in compositions of the initial solutions was within 2×10^{-4} mol·kg⁻¹.

2.2. Method

The potential difference experimental data was done by using an electrochemical cell with Na ion selective electrode of type "pHoenix Sodium Ion Combination Epoxy Electrode, Cat. No. NA71503" (Na-ISE) against a reference electrode Ag/AgCl incorporate in a jacketed glass cell containing 100 ml of solution and a stirrer. In all experiments, the conditioning procedure for electrode was followed exactly according to the manufactures instructions. For all series of measurements, the

temperature was kept constant using a thermostatic water bath and was measured with platinum wire resistive thermometer with a precision of ± 0.1 K. The potential difference was measured by employing Crison micropH 2002 electrometer with a resolution of $\pm 10^{-4}$ V. For each solution, two to four reproducible readings were repeated, thus calculating the mean measured value.

The utilized electrochemical cells for measuring of potential differences are:



The experimental values for ratio of the mean ionic activity coefficients of NaCl, $(\gamma_{\text{NaCl}} / \gamma_{\text{NaCl}}^0)$, was calculated from the variation of the potential between two electrochemical cells (2) and (1), by (Eq. 3):

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

In the presented electrochemical cells, m_{NaCl} and $m_{\text{NaCl},0}$ are the NaCl molality in the presence and absence of glycine, respectively; m_{Gly} represent the molality of glycine; E_1 , E_2 are the cell potentials for cells (1) and (2), respectively, γ_{NaCl} , γ_{NaCl}^0 are the mean ionic activity coefficients of NaCl in mixture in the presence and absence of glycine, respectively; 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) mol·kg⁻¹ at studied temperatures.

The obtained experimental values (54.4 and 56.2) $\times 10^{-3}$ V was used for (303.15 and 313.15) K temperatures. These values of S differ from the theoretical values [20] by about 3.97% and 3.99%.

3. Results and discussion

The experimental values for ratio of the mean ionic activity coefficients of NaCl in aqueous mixture NaCl-Glycine-H₂O obtained from cell potentials measurements are listed in Table 1 at different molalities of glycine and NaCl at (303.15 and 313.15) K. They present the influence of glycine and NaCl concentrations on the ratio of the mean ionic activity coefficients of NaCl in the presence and absence of glycine, respectively, $(\gamma_{\text{NaCl}} / \gamma_{\text{NaCl}}^0)$, at the same NaCl molality and temperature. The concentrations of glycine is between (0.005 and 2) mol·kg⁻¹ and of NaCl, between (0.05 and 2) mol·kg⁻¹.

The experimental data were correlated with the Scatchard-Prentiss and Roberts-Kirkwood virial equations with four and six specific parameters (B_{ij}), respectively [18, 21].

Roberts-Kirkwood equation can be expressed as:

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

Also, the Scatchard-Prentiss equation we can write:

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

B_{ij} are the equations parameters: B_{10} in equations (5) and (6), represents the interactions between the amino acids molecules and the electrolyte molecules, B_{20} and B_{21} represent the interactions between ions at high concentrations.

The equation (4) is recommended, generally, for molalities less than 0.5 mol·kg⁻¹, both for electrolyte and non-electrolyte compounds [19, 21]. The equation (5) is recommended for extended areas of salt and organic compound concentrations, she offering a good representation of interactions between ions and non-electrolyte molecules [22-24].

The values of the activity coefficients of glycine $(\gamma_{\text{Gly}} / \gamma_{\text{Gly}}^0)$ in studied system can be calculated with the B_{ij} parameters obtained with Eq. 5.

The activity coefficient of amino acid is related to the mean ionic activity coefficient of the electrolyte through the cross-differential relation [1, 7]:

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

where v is stoichiometric number of NaCl ($v=2$).

Combining equations (5) with (6) it results the expression for calculating the activity coefficient of amino acid (glycine):

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

where γ_{Gly} , γ_{Gly}^0 are the activity coefficients of glycine in aqueous mixture in the presence and absence of NaCl, respectively.

The experimental data were fitting with a least-squares algorithm, along with the standard deviation, σ defined as follows:

$$\sigma = \left(\frac{\sum (\lg \gamma_i^{\text{exp}} - \lg \gamma_i^{\text{calc}})^2}{N - p} \right)^{0.5} \quad (8)$$

where γ_i^{exp} , γ_i^{calc} represent the activity coefficients, experimental and calculated, respectively; N being the number of experimental data points and p , the number of adjustable parameters (B_{ij}) at studied temperatures.

Table 1. Results for $(\gamma_{\text{NaCl}} / \gamma_{\text{NaCl}}^0)$ in NaCl-Gly- H_2O ternary system at various NaCl and glycine concentrations at two different temperatures

$m_{\text{Gly}}/\text{mol}\cdot\text{kg}^{-1}$	$(\gamma_{\text{NaCl}} / \gamma_{\text{NaCl}}^0)^{\text{exp}}$					
	$m_{\text{NaCl}}/(\text{mol}\cdot\text{kg}^{-1})$					
	0.05	0.25	0.5	1	1.5	2
303.15K						
0.005	0.99908	0.99908	1.00092	1.00092	1.00092	0.99908
0.007	0.99816	0.99816	0.99816	1.00092	1.00092	0.99816
0.009	0.99725	0.99725	0.99816	0.99816	0.99816	0.99816
0.011	0.99633	0.99633	0.99725	0.99816	0.99816	0.99725
0.050	0.99267	0.99450	0.99633	0.99725	0.99816	0.99725
0.080	0.98812	0.99176	0.99359	0.99541	0.99541	0.99633
0.500	0.93167	0.95158	0.96213	0.97459	0.98269	0.99085
1.000	0.87764	0.91302	0.93167	0.95245	0.96745	0.98088
1.250	0.85535	0.89722	0.91892	0.94287	0.95948	0.97549
2.000	0.80426	0.86087	0.88983	0.91807	0.93425	0.95860
313.15K						
0.005	0.99911	0.99911	0.99911	0.99911	0.99911	0.99911
0.007	0.99911	0.99911	0.99822	0.99911	0.99911	0.99911
0.009	0.99822	0.99822	0.99733	0.99822	0.99822	0.99822
0.011	0.99733	0.99733	0.99733	0.99822	0.99733	0.99822
0.050	0.99291	0.99468	0.99645	0.99733	0.99822	0.99733
0.080	0.98850	0.99202	0.99379	0.99556	0.99645	0.99733
0.500	0.93545	0.95394	0.96332	0.97453	0.98324	0.99114
1.000	0.88289	0.91569	0.93296	0.95225	0.96676	0.98149
1.250	0.86040	0.89714	0.91895	0.94213	0.95905	0.97626
2.000	0.80702	0.85887	0.88683	0.91406	0.94130	0.96076

The result of experimental data fitting with Roberts-Kirkwood and Scatchard-Prentiss models (Eqs. 4 and 5) are summarized in Table 2: B_{ij} parameters and standard deviation, σ .

The relevant values of the parameter B_{10} , indispensable for the calculation of ratio of the mean activity coefficients of NaCl/glycine with and without glycine/NaCl, at the same NaCl/glycine molality, were determined from equations (4) and (5). They reflect the pairwise interactions between glycine molecules and salt molecules [1]. The negative values obtained of the B_{10} parameter indicate that these forces are attractive and that the presence of NaCl decreases the activity coefficient of

zwitterion and consequently NaCl gives a salt-in effect for glycine.

The results for the B_{10} parameters showed that the obtained values, $-0.08799 \text{ kg}\cdot\text{mol}^{-1}$ at 303.15 K, correspond well with literature data: $B_{10} = -0.08822 \text{ kg}\cdot\text{mol}^{-1}$ at 298.15 K [19]. For the studied solutions, the parameter B_{10} presents negative values; it 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 [25]. The results are interpreted as indicating not only the electrostatic attraction forces between the ions and zwitterions, but also the repulsive forces which are relatively higher in amino acids with larger alkyl radical [4].

Table 2. Parameters (B_{ij}) of the Scatchard-Prentiss and Roberts-Kirkwood equations in the aqueous mixed NaCl-Gly- H_2O at two different temperatures.

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
Equation 5							
303.15	-0.08799	0.01131	0.11219	-0.07011	0.02187	-0.00857	0.00040
313.15	-0.08128	0.00897	0.10209	-0.06633	0.02201	-0.00685	0.00032
Equation 4							
303.15	-0.07720	0.00566	0.07464	-0.02367	-	-	0.00198
313.15	-0.07249	0.00449	0.06713	-0.01963	-	-	0.00175

The standard deviation values in Table 2 show that both equations represent well the experimental data. A comparison between standard deviations obtained with Eq. (4) and (5) for activity coefficients of NaCl and glycine, shows that Scatchard-Prentiss equation gives better results than Roberts-Kirkwood equation at two studied temperatures. This is probably due to additional term of Scatchard-Prentiss equation.

The figures 1-4 summarize the activity coefficients behavior of NaCl and glycine in studied mixtures.

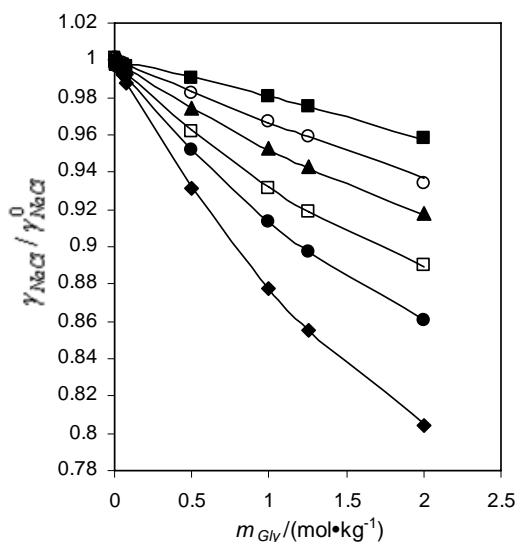


Fig. 1. Effect of glycine on $(\gamma_{NaCl} / \gamma_{NaCl}^0)$ at 303.15 K and various NaCl molalities: \blacklozenge , 0.05; \bullet , 0.25; \square , 0.5; \blacktriangle , 1; \circ , 1.5; \blacksquare , 2 $\text{kg} \cdot \text{mol}^{-1}$; —, correlation with Scatchard-Prentiss eq.

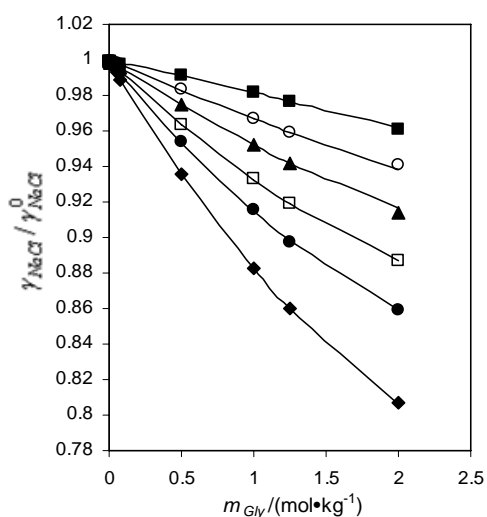


Fig. 2. Effect of glycine on $(\gamma_{NaCl} / \gamma_{NaCl}^0)$ at 313.15 K and various NaCl molalities: \blacklozenge , 0.05; \bullet , 0.25; \square , 0.5; \blacktriangle , 1; \circ , 1.5; \blacksquare , 2 $\text{kg} \cdot \text{mol}^{-1}$; —, correlation with Scatchard-Prentiss eq.

The ratio of the mean ionic activity coefficients of NaCl in the presence of glycine and in the absence of glycine *versus* glycine molality at various NaCl molalities is represented graphically at 303.15 K in Fig. 1 and at 313.15 K in Fig. 2. The experimental values for mean ionic activity coefficient of NaCl are represented with points and the results of correlation with Scatchard-Prentiss equation with solid lines.

These curves indicate that the mean ionic activity coefficient of NaCl decreases with the glycine molality increase. At lower NaCl molalities the variation is greater and decreases at higher salt concentrations.

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 [1]. It can be seen that the same behavior is found at both temperatures. The influence of temperature on mean ionic activity coefficients values of NaCl is not significant.

The glycine activity coefficient behavior is observed in Figs. 3 and 4, which present the ratio of the activity coefficients of glycine in the presence and in the absence of NaCl *versus* NaCl molality, at various glycine molalities. It is evident that at the same glycine molality, the activity coefficient of glycine diminishes with the increase of NaCl molality. This decrease is smaller at higher molalities of glycine and NaCl.

The global variation of the glycine activity coefficient reveals a salt-in effect for glycine in the presence of NaCl. Also, it indicates the presence of ion-dipole interactions at higher salt and amino acid molalities.

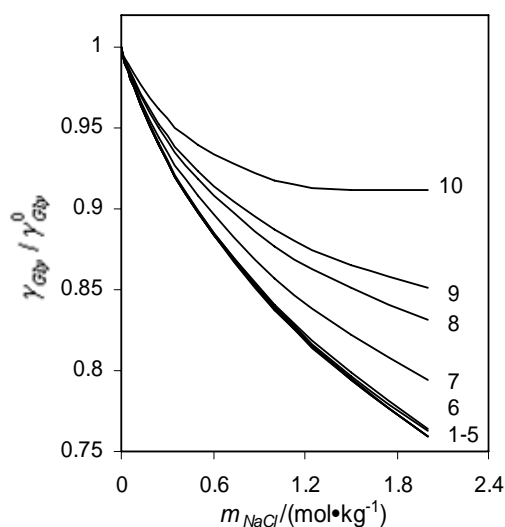


Fig. 3. Effect of NaCl on $(\gamma_{Gly} / \gamma_{Gly}^0)$ at 303.15 K and different glycine molalities: (1), 0.005; (2), 0.007; (3), 0.009; (4), 0.011; (5), 0.05; (6), 0.08; (7), 0.5; (8), 1; (9), 1.25; (10), 2 $\text{mol} \cdot \text{kg}^{-1}$

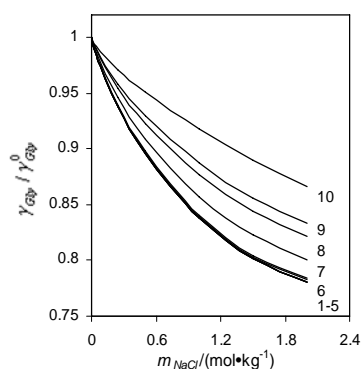


Fig. 4. Effect of NaCl on $(\gamma_{Gly} / \gamma_{Gly}^0)$ at 313.15 K and different glycine molalities: (1), 0.005; (2), 0.007; (3), 0.009; (4), 0.011; (5), 0.05; (6), 0.08; (7), 0.5; (8), 1; (9), 1.25; (10), 2 mol·kg⁻¹

The influence of temperature on $(\gamma_{Gly} / \gamma_{Gly}^0)$ ratio versus salt concentrations at different glycine molalities is presented in Fig. 5a)-d), to illustrate better the differences between values at the same glycine molality: (0.005, 0.5, 1 and 2) mol·kg⁻¹ at the two studied temperatures. It can be observed that at m_{Gly} between (0.005 and 1) mol·kg⁻¹ (Figs. 5a)-c)), the activity coefficient ratio increase with temperature, and at $m_{Gly}=2$ mol·kg⁻¹, decrease with temperature for the studied temperatures (Fig. 5d)). Also, it can be observed that at m_{Gly} between (0.005 and 1) mol·kg⁻¹, a salting-in effect of NaCl (the activity coefficient of glycine decrease with the increase of NaCl concentration) is predominant. At $m_{Gly}=2$ mol·kg⁻¹ appears a transition trend from salt-in to salt-out effect (the activity coefficient of glycine increases with the increase of NaCl concentration).

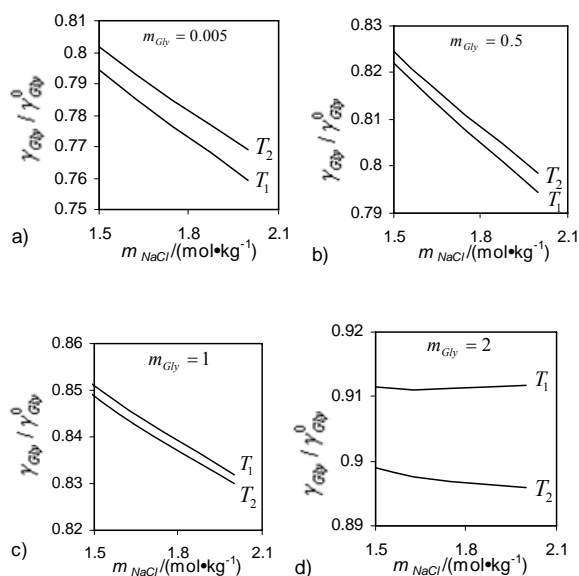


Fig. 5 a)-d). Influence of temperature on $(\gamma_{Gly} / \gamma_{Gly}^0)$ versus NaCl molality at $m_{Gly}=(0.005, 0.5, 1$ and $2)$ mol·kg⁻¹; $T_1=303.15$ and $T_2=313.15$ K

This transition from salt-out to salt-in effect of glycine at raised temperature in the presence NaCl can be the results of replacement of ion-dipole interactions with dipole-dipole interactions between the ions and zwitterions [3, 4].

4. Conclusions

The mixing effect of electrolyte and aminoacid on activity coefficients in NaCl+Glycine+Water system was investigated. The mean ionic activity coefficients for NaCl in aqueous mixed system at various glycine and NaCl molalities were experimentally determined at (303.15 and 313.15) K.

The mean ionic activity coefficient of NaCl decreases with the increase of glycine molality. The decreases are smaller at higher NaCl molalities. A reason for this behavior is the importance of short-range interactions at higher electrolyte concentrations. This behavior is found at both studied temperatures. The Roberts-Kirkwood and Scatchard-Prentiss equations were used for fitting the experimental data and obtaining the activity coefficients of glycine. Scatchard-Prentiss's equation represents better the experimental data.

The activity coefficient of glycine, at the same glycine molality, decreases as the NaCl molality in solution increases.

The presence of NaCl diminishes the activity coefficient of glycine giving a salt-in effect for amino acid. Activity coefficients of glycine and NaCl are mutually influenced by their presence in solution. The influence of temperature is more important for glycine activity coefficients than for NaCl mean ionic activity coefficients.

Acknowledgments

The work benefited from the support of the CNCSIS-Romania program (project no. 88/2006-2008).

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