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Activity coefficients of the electrolyte and the amino acid in water + $NaNO_3$ + glycine and water + NaCl + DL-methionine systems at 298.15 K

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Abstract

The activity coefficients at 298.15 K of glycine in water + $NaNO_3$ + glycine system and DL-methionine in water + NaCl + DL-methionine system are reported. The measurements were performed in an electrochemical cell with two ion selective electrodes, a cation and an anion ion selective electrode, each versus a double junction reference electrode. The concentrations of the electrolytes and the amino acids studied covered up to 1.0 molality electrolyte, 2.4 molality glycine and 0.2 molality DL-methionine. The results of the activity coefficients of glycine are compared with the activity coefficients of glycine in water + NaCl + glycine and water + KCl + glycine systems, obtained from the previous studies. The results show that the nature of both the cation and the anion of an electrolyte have significant effects on the activity coefficient of glycine in aqueous electrolyte solutions. The results also show that there are attractive interactions between the molecules of glycine and $NaNO_3$ and repulsive interactions between the molecules of DL-methionine and NaCl. © 1997 Elsevier Science B.V.

Keywords: Amino acid; Electrolyte; Activity coefficient; Ion

1. Introduction

The interaction of amino acids with electrolytes play an important role in their behavior in mixtures. It affects both the solubility of the amino acids [1] and their partitioning in different solvents in liquid–liquid extraction processes [2]. The interactions of electrolytes with biochemical compounds have been the subject of numerous studies [1]. The study of the effect of the nature and concentration of the ions and the chemical structure of an amino acid on their interactions may have applications for the development of separation processes for amino acids and other more complex biomolecules. This is one of the reasons for the increasing interest [3] in studying the thermodynamics of amino acid solutions. A quantitative knowledge of the activity coefficients of amino acids in electrolyte solutions helps in the design of equilibrium-based separation processes without the use of empirical methods. Among the various amino acids, glycine, due to its significant biological importance and the fact that its simple structure can be

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used as a prototype for more complex amino acids and peptides, has been the subject of several theoretical [4] and experimental studies [5].

The measurement of the activity coefficients of amino acids in aqueous electrolyte solutions has been performed by either the isopiestic method [6–8] or electrochemical cells with a single ion selective electrode [9,10]. Recently we proposed a method for measuring the activity coefficients of amino acids in aqueous electrolyte solutions using an electrochemical cell with two ion selective electrodes [5]. The electrochemical cell consisted of an anion and a cation ion selective electrode, and the potential of each was measured versus a reference electrode.

In this study, the activity coefficients at 298.15 K of glycine in a water + $NaNO_3$ + glycine system and DL-methionine in a water + NaCl + DL-methionine system were measured using an electrochemical cell with two ion selective electrodes. The electrochemical potential (e.m.f.) of both the cation and the anion ion selective electrode were measured versus a double junction reference electrode (DJ). The e.m.f. values thus measured were then converted to the mean ionic activity coefficient of the electrolyte and subsequently to the activity coefficients of the amino acid at various molalities. The experimental data obtained in this work and those previously reported for the systems water + NaCl + glycine [5] and water + KCl + glycine [3] are compared and the effect of the cation and the anion of the electrolyte on the activity coefficients of glycine are discussed.

2. Theory of experiments

The difference of the potentials of a cation and an anion ion selective electrode, versus a reference electrode, measured in cells of type (1):

Cation ISE|electrolyte (m_S)|DJ

Anion ISE|electrolyte (m_S)|DJ

are related to the mean ionic activity coefficient of the electrolyte by the Nernst equation. The Nernst equation for the above mentioned cell, for the case of a 1:1 single electrolyte system at molality m_S, reads:

$$E_+ - E_- = \left(E_+^{ISE} - E_-^{ISE}\right) + \frac{2RT}{F}\ln\left(m_S\gamma_\pm^{(1)}\right) \qquad (1)$$

where $\gamma_\pm^{(1)}$ is the mean ionic activity coefficient, R is the universal gas constant, T is the absolute temperature, F is the Faraday number and subscripts plus and minus denote the cation and the anion ion selective electrode, respectively. The superscript (1) refers to the electrochemical cell type (1), containing electrolyte and water only. The terms E_+^{ISE} and E_-^{ISE} in Eq. (1) include all asymmetry, internal solutions and reference potentials of the cation and the anion ion selective electrode. Eq. (1), which is only valid when the same reference electrode is used versus both the anion and the cation ion selective electrodes, can be written in a more general form as:

$$\Delta E^{(1)} = E^\circ + S\ln\left(m_S\gamma_\pm^{(1)}\right) \qquad (2)$$

where $\Delta E = E_+ - E_-$; $E^\circ = E_+^{ISE} - E_-^{ISE}$, and S is a general slope for the response of the pair of electrodes, used here instead of the Nernstian slope. The values of S and E° in Eq. (2) can be calculated from a linear fitting of the values of ΔE vs. $\ln(m_S\gamma_\pm^{(1)})$ with values of $\gamma_\pm^{(1)}$ obtained from the literature [11] at each molality m_S.

The potentials of the electrochemical cells of type (1) change when an amino acid is added to the solution in the cell. This is due to the interaction of the amino acid molecules and the ions in the solution, resulting in a change in the mean ionic activity coefficient of the electrolyte. Thus, for cells of type (2):

Cation ISE|electrolyte (m_S) + amino acid (m_A)|DJ

Anion ISE|electrolyte (m_S) + amino acid (m_A)|DJ

using the same method as discussed above, the potential differences of the cation and the anion ion selective electrode are related to the mean ionic activity coefficient of the electrolyte, $\gamma_\pm^{(2)}$, at molality m_S, in the presence of an amino acid at molality m_A, by:

$$\Delta E^{(2)} = E^\circ + S\ln\left(m_S\gamma_\pm^{(2)}\right) \qquad (3)$$

Provided that the same ion selective electrodes and reference electrode are used in both cells of type (1) and type (2), the values of S and E° are the same in both Eq. (2) and Eq. (3). Subtracting Eq. (3) from Eq. (2), and rearranging gives:

$$\ln\left(\frac{\gamma_\pm^{(2)}}{\gamma_\pm^{(1)}}\right) = \frac{\Delta E^{(2)} - \Delta E^{(1)}}{S} \qquad (4)$$

Eq. (4) relates the ratio between $\gamma_{\pm}^{(2)}$ and $\gamma_{\pm}^{(1)}$ to the potential differences measured in cells of type (2) and (1). The theoretical basis of this method is discussed in detail elsewhere [5].

3. Materials and methods

Sodium nitrate and sodium chloride of 99.9% purity and glycine and DL-methionine of 99.0% purity were obtained from A&C American Chemicals (Montreal, PQ). Glycine and DL-methionine were used as received. The salts were oven-dried prior to use. The sodium, chloride and nitrate ion selective electrodes, and the double-junction reference electrode were obtained from Orion (Boston, MA). An Orion pH/ISE meter (Boston, MA) model EA 920 with a resolution of ± 0.1 mV, was used to monitor the e.m.f. measurements.

All the solutions were prepared based on molality, and the water was also weighed. The compositions of the initial solutions were accurate within ± 0.01 wt%. In all experiments, deionized water with a conductivity of less than 0.8 μS/cm was used. Before using it to prepare samples, the distilled water was passed through ion exchange columns type Easy pure RF, Compact Ultrapure Water System, Barnstead Thermoline (Bubugue, IA). The conditioning procedure of electrodes was exactly followed according to the manufacturer's instructions.

The experiments were performed by measuring the e.m.f. of both the cation and the anion ion selective electrode, against a double junction reference electrode, in a jacketed glass beaker containing 200 ml of solution. To avoid the bias potential between different reference electrodes, in each experiment, the response of both the cation and the anion ion selective electrode were measured at the same time versus the same reference electrode. All the instruments were grounded prior to and during the experiments. In order to minimize the risk of the presence of concentration gradients in the beaker, the solutions were stirred constantly during the experiments with a magnetic stirrer, and the temperature was kept constant at 298.15 ± 0.1 K using a thermostatic bath. Fig. 1 shows the schematic of the set-up used in this study.

Each set of experiments was performed at a fixed

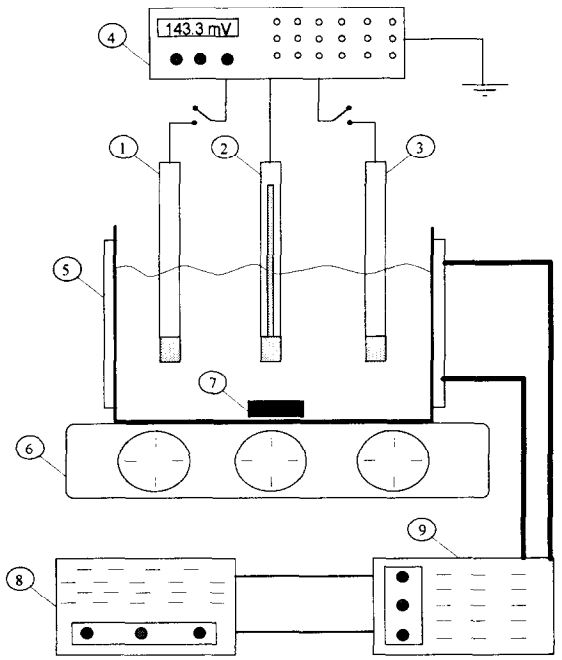

Fig. 1. Schematic design of the measurement set up. (1) Cation ISE; (2) reference electrode; (3) anion ISE; (4) millivoltmeter; (5) cell; (6) magnetic stirrer; (7) magnet; (8) bath cooler; (9) thermostatic bath.

electrolyte concentration, and the concentration of the amino acid was increased by addition of solid amino acid. The readings of the potentiometer were made only when the drift of the response was less than 0.1 mV. For each set of experiments the electrodes were calibrated by measuring the e.m.f. of the cell of type (1), without the presence of other solute, and the slope S of the electrodes was determined. The typical value obtained for the slope of the electrodes was 51.22 mV, with a correlation coefficient of 99.98%, while the theoretical value at 298.15 K is 51.38 mV, according to the Nernst equation.

Most of the experiments were replicated three times, and the data reported are the average of the replicas. Sample variances were obtained from the replicas for each point and a pooled standard deviation was calculated using these values. The calculated pooled standard deviations for a 95% confidence interval for the values of the ratio of the mean ionic activity coefficients of the electrolyte in the presence of the amino acid and in the absence of the amino acid, at the same electrolyte molality, for the

systems water + $NaNO_3$ + glycine and water + NaCl + DL-methionine, were ±0.0035 and ±0.0004, respectively.

4. Results and discussion

The potentials of a sodium and a nitrate ion selective electrode, each versus a double junction reference electrode, for the system water + $NaNO_3$ + glycine, and the potentials of a sodium and a chloride ion selective electrode, versus a double junction reference electrode, for the system water + NaCl + DL-methionine, were measured at 298.15 K for electrolyte concentrations up to 1.0 m, glycine concentrations up to 2.4 m and DL-methionine concentrations up to 0.2 m. The electrochemical potential values thus obtained, were converted, using the method described in the previous section, to the ratio of the mean ionic activity coefficients of the electrolyte, in the presence of the amino acid, to that without the presence of the amino acid, at the same electrolyte molality. These values were collected for different electrolyte and amino acid concentrations and fitted to the following virial expansion series:

$$\nu \ln\frac{\gamma_{\pm}^{(2)}}{\gamma_{\pm}^{(1)}} = C_1 m_A + C_2 m_S m_A + C_3 m_A^2 + C_4 m_A m_S^2 + C_5 m_A^3 + C_6 m_S m_A^2 \quad (5)$$

The experimental data measured are presented in Tables 1 and 2. The activity coefficient of the amino acid is related to the mean ionic activity coefficient of the electrolyte through the cross differential relation:

$$\nu\left(\frac{\partial \ln\gamma_{\pm}}{\partial m_A}\right)_{m_S,T,P} = \left(\frac{\partial \ln\gamma_A}{\partial m_S}\right)_{m_A,T,P} \quad (6)$$

For all electrolytes considered here, $\nu = 2$. Combining Eq. (5) and Eq. (6), the ratio of the activity coefficient of the amino acid in the presence of an electrolyte, $\gamma_A^{(2)}$, to that in the absence of an electrolyte, $\gamma_A^{(1)}$, at the same amino acid molality can be calculated as:

$$\ln\frac{\gamma_A^{(2)}}{\gamma_A^{(1)}} = C_1 m_S + \frac{1}{2}C_2 m_S^2 + 2C_3 m_A m_S + \frac{1}{3}C_4 m_S^3 + 3C_5 m_A^2 m_S + C_6 m_S^2 m_A \quad (7)$$

Table 1
Experimental data for the ratio of the mean ionic activity coefficients of $NaNO_3$, in the presence of glycine to that in the absence of glycine, at different molalities of $NaNO_3$ and glycine

Glycine (m)	$NaNO_3$ (m)				
	0.1	0.3	0.5	0.7	1.0
	$\gamma_{\pm}^{(2)}/\gamma_{\pm}^{(1)}$				
0.1	1.0118	1.0049	1.0005	1.0000	0.9980
0.3	1.0010	0.9941	0.9865	0.9878	0.9863
0.6	0.9636	0.9644	0.9614	0.9654	0.9680
1.0	0.9105	0.9229	0.9265	0.9301	0.9389
1.3	0.8748	0.8927	0.9016	0.9076	0.9170
1.6	0.8446	0.8651	0.8760	0.8852	0.8964
2.0	0.7955	0.8335	0.8455	0.8554	0.8703
2.3	0.7811	0.8110	0.8255	0.8359	0.8533
2.6	0.7589	0.7891	0.8057	0.8185	0.8350

A least squares method was employed to calculate the values of the parameters of Eq. (5). The results of the evaluation of parameters using Eq. (5), together with the root mean square deviations for both water + $NaNO_3$ + glycine and water + NaCl + DL-methionine systems, are presented in Table 3. As can be seen from Table 3, the values of the C_1, the coefficient of the leading terms in Eq. (5) and Eq. (7), which represents the pairwise interactions between amino acid molecules and electrolyte molecules (considered to be undissociated), is negative for water + $NaNO_3$ + glycine system and positive for water + NaCl + DL-methionine system. This indicates the presence of an attractive force between glycine and $NaNO_3$ and a repulsive force between DL-methionine and NaCl.

Table 2
Experimental data for the ratio of the mean ionic activity coefficients of NaCl, in the presence of DL–methionine to that in the absence of DL–methionine, at different molalities of NaCl and DL–methionine

DL-methionine (m)	NaCl (m)				
	0.1	0.3	0.5	0.7	1.0
	$\gamma_{\pm}^{(2)}/\gamma_{\pm}^{(1)}$				
0.025	1.0015	1.0020	1.0025	1.0031	1.0029
0.050	1.0024	1.0039	1.0049	1.0054	1.0068
0.100	1.0024	1.0049	1.0063	1.0081	1.0097
0.150	1.0010	1.0049	1.0063	1.0101	1.0126
0.200	1.0010	1.0060	1.0092	1.0120	1.0155

Table 3
Values of the parameters of Eq. (5)

Coefficients of Eq. (5)	DL-methionine + KCl	Glycine + $NaNO_3$
C_1	0.15883	−0.10493
C_2	0.24817	0.11990
C_3	−1.83288	−0.11307
C_4	−0.08235	−0.06431
C_5	4.92509	0.02559
C_6	0.00309	0.01391
R.m.s.d.[a]	0.0005	0.0051

[a] R.m.s.d. = root mean square deviation.

Fig. 2 shows the ratio of the mean ionic activity coefficients of $NaNO_3$ in the presence of glycine and in the absence of glycine, at the same $NaNO_3$ molality, as a function of the glycine molality. The solid lines are those obtained by the curve fitting of the experimental data using Eq. (5) with the coefficients presented in Table 3. Fig. 2 shows that the mean ionic activity coefficient of $NaNO_3$, for a fixed $NaNO_3$ molality, decreases as the molality of glycine increases. The decrease in the mean ionic activity coefficient of $NaNO_3$, with an increase in the glycine molality, is less at higher $NaNO_3$ concentrations. These effects remain the same over the entire range of the molalities of glycine and $NaNO_3$ studied.

Fig. 3 shows the ratio of the activity coefficients of glycine in the presence of $NaNO_3$ and in the absence of $NaNO_3$, at the same glycine molality, as a function of $NaNO_3$ molality, as obtained from Eq. (7). As is shown in Fig. 3, the presence of $NaNO_3$, for a fixed glycine molality, decreases the activity coefficient of glycine until it reaches a minimum value at approximately 1.27 m glycine, it then increases with an increase in the glycine molality. This effect remains the same over the entire range $NaNO_3$ concentrations studied.

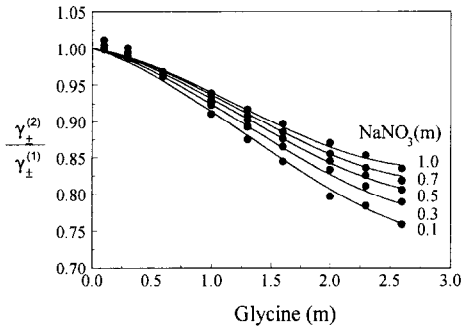

Fig. 2. Effect of glycine and $NaNO_3$ concentrations on the ratio of the mean ionic activity coefficients of $NaNO_3$, in the presence of glycine and in the absence of glycine, at the same $NaNO_3$ molality. ● = Experimental data; ———— = results of Eq. (5).

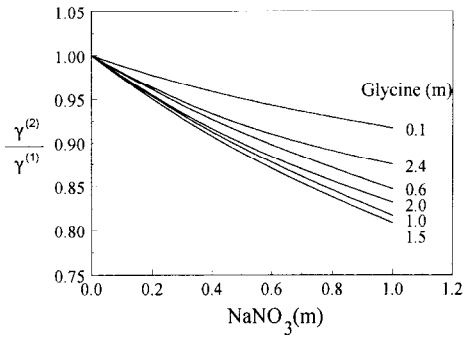

Fig. 3. Effect of $NaNO_3$ concentration with the glycine molality as the parameter on the ratio of the activity coefficients of glycine, in the presence of $NaNO_3$ and in the absence of $NaNO_3$, at the same glycine molality.

Fig. 4 shows more clearly the effect of the glycine molality on its activity coefficient in the presence of $NaNO_3$, using the molality of $NaNO_3$ as a parameter. The ratio of the activity coefficients of glycine in the presence of $NaNO_3$ and in the absence of $NaNO_3$, at the same glycine molality, was obtained from Eq. (7). From Fig. 4 it can be seen that, for a fixed $NaNO_3$ molality, the activity coefficient of glycine presents a minimum at around 1.3 m glycine. This minimum is more pronounced at higher $NaNO_3$ molality.

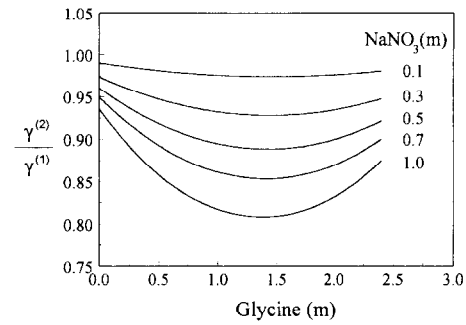

Fig. 4. Effect of glycine concentration with the $NaNO_3$ molality as the parameter on the ratio of the activity coefficients of glycine, in the presence of $NaNO_3$ and in the absence of $NaNO_3$, at the same glycine molality.

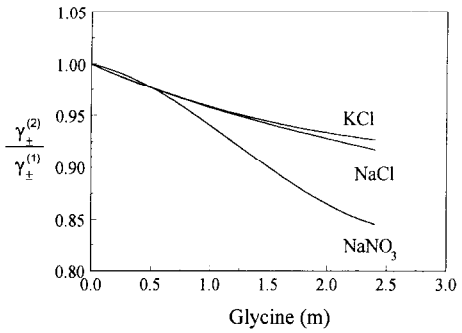

Fig. 5. Comparison of the effect of the anion and the cation of the electrolyte on the ratio of the mean ionic activity coefficients of electrolyte, in the presence of glycine and in the absence of glycine, at an electrolyte concentration of 1 m.

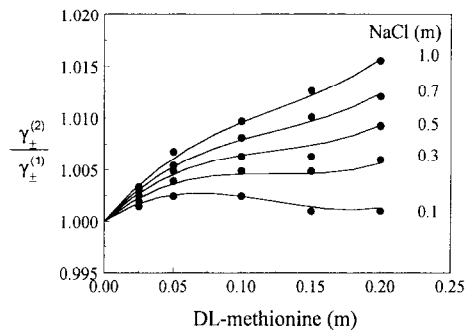

Fig. 6. Effect of DL-methionine and NaCl concentrations on the ratio of the mean ionic activity coefficients of NaCl, in the presence of DL-methionine and in the absence of DL-methionine, at the same NaCl molality. ● = Experimental data; ———— = results of Eq. (5).

Fig. 5 compares, at an electrolyte concentration of 1 m, the ratio of the mean ionic activity coefficients of an electrolyte in the presence of glycine, to that without the presence of glycine, as a function of glycine molality. The electrolytes compared are NaCl, KCl and $NaNO_3$. Experimental data for the systems water + NaCl + glycine and water + KCl + glycine are those reported by Khoshkbarchi and Vera [5] and by Bower and Robinson [6], respectively. As is shown in Fig. 5, at low glycine concentrations, the effect of the presence of glycine on the mean ionic activity coefficient of an electrolyte is approximately the same for all three electrolytes studied. At high glycine concentrations, however, the effect of the presence of glycine on the mean ionic activity coefficient of an electrolyte is approximately the same for both NaCl and KCl as the electrolyte and is different from $NaNO_3$. This difference can be explained by the fact that the nitrate ion, in contrast to the chloride ion, consists of four atoms. At glycine molalities higher than 0.5, the ratios $\gamma_{\pm}^{(2)}/\gamma_{\pm}^{(1)}$ for NaCl or KCl are larger than the ratio $\gamma_{\pm}^{(2)}/\gamma_{\pm}^{(1)}$ for $NaNO_3$, as the electrolyte present in the solution. It should be noted that NaCl has the same anion as KCl and the same cation as $NaNO_3$. These results show the importance of the nature of the anion of an electrolyte on its interactions with glycine.

Fig. 6 shows the ratio of the mean ionic activity coefficients of NaCl in the presence of DL-methionine and in the absence of DL-methionine, at the same NaCl molality, as a function of the DL-methionine molality. The solid lines are those obtained by the curve fitting of the experimental data using Eq. (5). Fig. 6 shows that for water + NaCl + DL-methionine system the mean ionic activity coefficient of NaCl, for a fixed NaCl molality, increases as the molality of DL-methionine increases. The increase in the mean ionic activity coefficient of the NaCl, with an increase in the DL-methionine molality, is higher at higher NaCl molalities. At 0.1 m NaCl, the mean ionic activity coefficient of NaCl showed a maximum for a molality of DL-methionine of around 0.05.

Fig. 7 shows the ratio of the activity coefficients of DL-methionine in the presence of NaCl and in the absence of the NaCl, at the same DL-methionine molality, as a function of NaCl molality. The solid lines are those obtained from Eq. (7) with parameters presented in Table 3. From Fig. 7 it can be seen that,

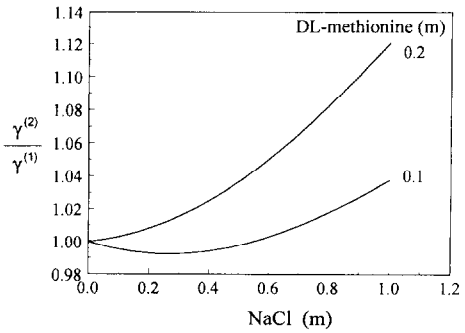

Fig. 7. Effect of NaCl concentration with the DL-methionine molality as the parameter on the ratio of the activity coefficients of DL-methionine, in the presence of NaCl and in the absence of NaCl, at the same DL-methionine molality.

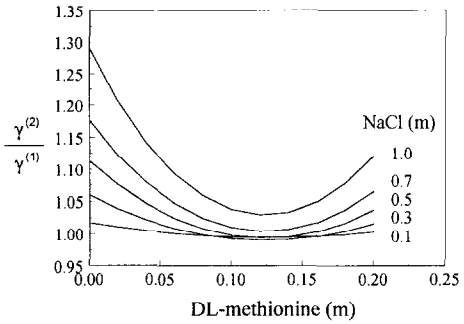

Fig. 8. Effect of DL-methionine concentration with the NaCl molality as the parameter on the ratio of the activity coefficients of DL-methionine, in the presence of NaCl and in the absence of NaCl, at the same DL-methionine molality.

at 0.2 m DL-methionine, the activity coefficient of DL-methionine increases with an increase in NaCl molality, and this increase is higher at higher NaCl molalities. At 0.1 m DL-methionine, the activity coefficient of DL-methionine decreases at low NaCl molality and increases for NaCl molalities higher than 0.3.

Fig. 8 shows better the effect of the DL-methionine molality on the ratio of the activity coefficients of DL-methionine in the presence of NaCl and in the absence of NaCl, at the same DL-methionine molality, obtained from Eq. (7). From Fig. 8 it can be seen that, for a fixed NaCl molality, the activity coefficient of DL-methionine first decreases with an increase in the DL-methionine molality until it reaches a minimum value then it increases. Note that the minimum value occurs at a DL-methionine molality around 0.125. As shown in Fig. 8, the change in the activity coefficient of DL-methionine with an increase in its molality is higher at higher NaCl molalities.

The above mentioned effects are most probably due to the ion–dipole and dipole–dipole interactions. Amino acids, due to the presence of a carboxyl and an amino groups in their chemical structures, have large dipole moments [12] which give rise to important dipole–dipole interactions between the molecules of amino acids with each other and with other dipolar molecules such as water. The presence of the charged amino and carboxyl groups also produces an electrostatic field around the amino acid molecule which is the reason for the ion–dipole interactions between the molecules of the amino acid and charged ions in the solution. In addition, the presence of ions affects the structure of the molecules of water and this may also affect the dipole–dipole interactions between the molecules of water and amino acid. The mutual effect of an amino acid and an electrolyte on their activity coefficients can be partly attributed to the formation of physically bonded ion-pair complexes between the molecules of the amino acid and ions in the solution which become intensified at high electrolyte concentrations. The formation of these complexes, due to the neutralization of the amino acid charges, reduces the dipole–dipole interactions between the amino acid molecules and ion–dipole interactions between the ions amino acid molecules. It should be noted that the formation of ion-pair complexes, similar to the ion condensation phenomenon in polyelectrolytes, is due to the formation of weak physical bonds, and not chemical bonds, between the charged carboxyl and amino groups of the amino acid molecules and the ions. The reduction of the electrostatic forces between the charged ions and amino acid molecules, due to the neutralization of the charges of the carboxyl and the amino groups of the amino acid, also renders the importance of the short range interactions more pronounced. These short range interactions are mainly between the ions, molecules of water and the nonpolar hydrocarbon backbone of the amino acid. This may also be a reason for the difference in the activity coefficient of an amino acid at higher electrolyte and amino acid concentrations. It should be emphasized that the structure of the nonpolar hydrocarbon backbone of an amino acid has significant effect on its interactions with ions. For example, it has been shown [13] that although DL-alanine and glycine only differ by one $-CH_2$ group, their solubility behavior in aqueous electrolyte solutions is different. The effect of larger nonpolar hydrocarbon backbones can also reduce the importance of ion–dipole interactions as is evident from the different solubility behavior of glycine and L-leucine in NaCl solution, although their dipole moments are almost equal. The effect of glycine on the mean ionic activity coefficient of an electrolyte can be attributed to the different physicochemical behavior of the ion-pair complexes formed between amino acids and electrolytes. Other factors can be the effect of ions on the dielectric constant of the

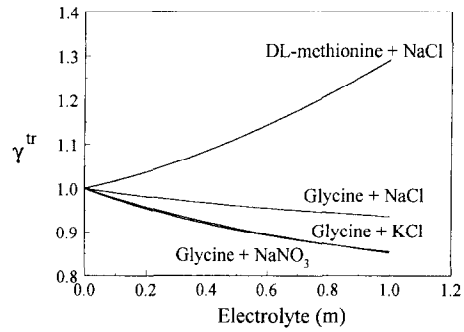

Fig. 9. Trace activity coefficients of DL-methionine in the presence of NaCl and glycine in the presence of KCl, NaCl or $NaNO_3$.

solution and their interaction with charge resonance in the carboxyl group of the amino acid, affecting the pK value of the carboxyl group and its ionization.

Fig. 9 compares the trace activity coefficients of glycine and DL-methionine, γ^{tr}, as a function of electrolyte molality. The trace activity coefficient of an amino acid in the aqueous solution of an electrolyte is the value of its activity coefficient when its molality approaches zero. To calculate the trace activity coefficient, all amino acid molality terms in Eq. (7) were set equal to zero. For comparison, Fig. 9 also indicates the values of the trace activity coefficients of glycine in the presence of NaCl obtained from the literature [5,6]. From Fig. 9 it can be seen that the trace activity coefficients of glycine decreases as the molality of $NaNO_3$ increases, whereas the trace activity coefficients of DL-methionine increases as the molality of NaCl increases. A reason for this phenomenon can be the attractive nature of the interactions between glycine and $NaNO_3$ molecules and the repulsive nature of the interactions between DL-methionine and NaCl, as indicated by the sign of the C_1 parameter, the coefficient of the leading term in Eq. (5). From Fig. 9 it can also be seen that for all three electrolytes studied, the trace activity coefficients of glycine decreases as the concentration of electrolyte increases. Fig. 9 shows that at infinite dilution of glycine the nature of the cation and the anion of the electrolyte does not have a significant effect on the trace activity coefficient of glycine. This means that at low glycine concentrations, the electrostatic forces between the charged amino and carboxyl groups of glycine and ions in the solution are the dominant forces. At high concentrations, however, the short range interactions between the hydrocarbon backbone of glycine and ions become important.

5. Conclusions

Activity coefficients data for the systems water + $NaNO_3$ + glycine and water + NaCl + DL-methionine were obtained using an electrochemical cell. The cell consisted of a cation and an anion ion selective electrode, each measured versus a double junction reference electrode. The results obtained in this study, and those measured for the water + NaCl + glycine reported by Khoshkbarchi and Vera [5] and water + KCl + glycine reported by Bower and Robinson [6], showed that the nature of the anion of the electrolyte significantly affects the interactions between the electrolyte and the amino acid and as a result, the activity coefficient of the amino acid in aqueous electrolyte solutions. The results show that there are attractive interactions between the molecules of glycine and $NaNO_3$, and repulsive interactions between the molecules of DL-methionine and NaCl.

The difference in the effects of different electrolytes on the activity coefficient of an amino acid can be attributed to the formation of ion-pair complexes between the ions in the solution and the charged amino and carboxyl groups of the amino acid. The formation of the ion-pair complexes also affects the dipole–dipole interactions and reduces the electrostatic interactions through the neutralization of the charges of the amino acid.

6. Notation

C_i = adjustable parameters

E_+ = potential of the cation ion selective electrode

E_- = potential of the anion ion selective electrode

E_+^{ISE} = internal potential of the cation ion selective electrode

E_-^{ISE} = internal potential of the anion ion selective electrode

E° = difference between the internal potentials of the cation and the anion ion selective electrode

$\Delta E^{(1)}$ = potential difference in electrochemical cell with electrolyte but without the presence of solutes
$\Delta E^{(2)}$ = potential difference in electrochemical cell with both electrolyte and other solutes
F = Faraday number
ISE = ion selective electrode
m_A = molality of amino acid
m_S = molality of electrolyte
S = slope of electrode potential
T = absolute temperature
P = pressure
R = universal gas constant

7. Greek letters

γ_A = activity coefficient of the amino acid
$\gamma_{\pm}^{(1)}$ = mean ionic activity coefficient of the electrolyte in electrochemical cell without the presence of other solutes
$\gamma_{\pm}^{(2)}$ = mean ionic activity coefficient of electrolyte in electrochemical cell with other solutes

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