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Bahram Ghalami-Choobar<sup>a</sup>; Majid Arvand<sup>a</sup>; Majid Moghimi<sup>a</sup>; Mohammad A. Bagherinia<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, University of Guilan, Rasht, Iran

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## Thermodynamic study of the ternary aqueous mixed electrolyte system [(1 - y)MgCl<sub>2</sub> + yKCl] by electromotive force measurements

Bahram Ghalami-Chooabar, Majid Arvand\*, Majid Moghimi and  
Mohammad A. Bagherinia

*Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box 1914, Rasht, Iran*

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The activity coefficients for magnesium chloride in the MgCl<sub>2</sub> + KCl + H<sub>2</sub>O ternary system were determined from electromotive force measurements as a function of total ionic strength and composition of the mixture. In this work, emf measurements were performed on the galvanic cell without liquid junction of the type: Ag|AgCl|MgCl<sub>2</sub> (*m*<sub>1</sub>), KCl (*m*<sub>2</sub>), H<sub>2</sub>O|Mg-ISE, at the temperature 298 K and over total ionic-strengths from 0.015 to 6 mol kg<sup>-1</sup> for different series of salt molal ratios. The sol-gel-based magnesium ion selective electrode (SG-ISE) and Ag/AgCl electrode used in this work were prepared in our laboratory. The Pitzer model was used for the experimental results correlation of activity coefficients. The unknown Pitzer mixing interaction parameters were evaluated ( $\theta_{\text{MgK}} = 0.1249$ ,  $\psi_{\text{MgKCl}} = -0.0572$ ). Then, these parameters were used to predict the thermodynamic properties for the systems under investigation as a function of total ionic strength.

**Keywords:** activity coefficients; Pitzer model; emf; sol-gel electrode; MgCl<sub>2</sub>; KCl

### 1. Introduction

In recent years, there has been an increasing amount of work concerning the investigation of the thermodynamic properties of mixed aqueous electrolyte solutions, particularly at high total ionic strengths. This is because many fields, such as chemistry, chemical engineering, biology, geology, atmospheric science, and food processing are involved with the thermodynamic properties of mixed aqueous electrolytes [1–3]. These properties also constitute important information for the design and operation of several chemical processes. In order to facilitate the use of mixed electrolytes in these processes, it is desirable to know accurately the thermodynamic properties of aqueous multi-component systems. To measure the thermodynamic properties in mixed electrolyte solutions, the most common methods are the isopiestic vapour pressure, hygrometry, and potentiometric techniques. The emf method presents advantages such as rapidity and relative simplicity to generate experimental data, in comparison with the other foregoing techniques [4–6].

In this article, the thermodynamic properties for the mixed aqueous electrolyte system of magnesium chloride and potassium chloride have been investigated by using the potentiometric technique at 298 K. The emf method was employed to determine the mean

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\*Corresponding author. Email: arvand@guilan.ac.ir

ionic activity coefficient of magnesium chloride in 0.015 to 6 mol kg<sup>-1</sup> total ionic strength range for each ionic strength fraction ( $y$ ) of KCl, with  $y = I_{\text{KCl}}/(I_{\text{MgCl}_2} + I_{\text{KCl}}) = 0.063, 0.117, \text{ and } 0.250$ . In previous work, the solvent polymeric membrane electrodes for the determination of activity coefficients have been used [7–11]. In the present work, we report for the first time the results relating to the application of a new type of the sol–gel-based selective electrode for measuring the activity coefficients of the mixed aqueous electrolyte solutions. The sol–gel-based magnesium ion selective electrode was prepared by the sol–gel procedure in our laboratory. In addition, the ternary system of the present study,  $\text{MgCl}_2 + \text{KCl} + \text{H}_2\text{O}$ , is one of the systems with limited thermodynamic data in the literature [12]. The Pitzer ion-interaction model was used for the experimental results correlation and calculation of activity coefficients [13,14]. The activity coefficients in the mixture, osmotic coefficients, and excess Gibbs free energy of mixing were calculated as a function of total ionic strength.

## 2. Experimental

### 2.1. Reagents and solutions

Potassium chloride (analytical grade and >99 mass % purity), magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , analytical grade and >98 mass % purity), sodium tetraphenyl borate (NaTPB), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), tetraethoxysilane (TEOS), diethoxydimethylsilane (DEDMS), *N*-phenylaza-15-crown-5 and all other reagents were obtained from Merck and Fluka chemical companies. Potassium chloride was heated at  $T = 393.15 \text{ K}$  in an oven for 5 h, and afterwards stored over silica gel in a desiccator before use. The aqueous stock solution of magnesium chloride was prepared from  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and doubly distilled water, whose specific conductance was  $< 2.0 \times 10^{-4} \text{ S m}^{-1}$ . The concentration of magnesium chloride (aq) was determined by potentiometric titration method with a standard solution of silver nitrate. Working solutions were prepared by adding weighted amounts of solid potassium chloride using an analytical balance (Sartorius GMBH 2842) with an accuracy 0.1 mg to the corresponding prepared solution from stock solution and doubly distilled water to give the different desired fractional ionic strengths.

### 2.2. Apparatus and procedure

The cell vessel was a double-walled glass bottle held at a constant temperature of  $298.0 \pm 0.1 \text{ K}$  by circulating water from a Model GFL circulation. The solutions were continuously stirred using a magnetic stirrer at a slow, constant rate to avoid concentration gradients in the test solutions. The emf measurements were carried out on the following galvanic cells, without liquid junction, containing Mg-ISE and Ag/AgCl electrodes by using a digital multimeter (Eutech 2100), whose resolution was 0.1 mV.

The sol–gel membrane (Mg-ISE) was prepared according to the previously reported method [15]. TEOS (90  $\mu\text{L}$ ), DEDMS (250  $\mu\text{L}$ ), ethanol (280  $\mu\text{L}$ ), 0.1 mol dm<sup>-3</sup> HCl aqueous solution (80  $\mu\text{L}$ ), additive NaTPB (2 mg), and *N*-phenylaza-15-crown-5 as ionophore (3 mg) were mixed in a sample tube, and the mixture was then allowed to stand at 80°C for 1 h to give a viscous sol–gel solution. The clean graphite electrode was then coated by viscous sol–gel solution and allowed to dry for 48 h at room temperature. The electrodes were then rinsed with water and conditioned in  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$  magnesium chloride solution. The Ag/AgCl electrode was prepared according to the electrolysis method [16].

The activity coefficients for  $\text{MgCl}_2$  in the ternary system ( $\text{MgCl}_2/\text{KCl}/\text{H}_2\text{O}$ ) were determined from the emf measurements using the following galvanic cells:



where  $m_A$  and  $m_B$  are molalities of  $\text{MgCl}_2$  and  $\text{KCl}$  as single salts in water, respectively.  $m_1$  and  $m_2$  are the molalities of  $\text{MgCl}_2$  and  $\text{KCl}$  in the mixture, respectively.

The emf measurements of the galvanic cell (B) were made by using a standard addition procedure. For this purpose, the concentrated mixed electrolyte solutions were added into the cell (B) containing a proportional volume of doubly distilled water. The standard addition steps were carried out using a proper burette and suitable Hamilton syringes (CH-7402 Bonaduz). In each series and for each standard addition step, data collection was performed for a period of 30 min for dilute solutions and 20 min for concentrated solutions, as in each step the emf arrived to a stable equilibrium value with a fluctuation of  $\pm 0.1$  mV.

### 3. Method

#### 3.1. Pitzer model

The Pitzer ion interaction model was used for the experimental data correlation and calculation of thermodynamic properties for mixed electrolyte solutions. According to the Pitzer model, the mean molal activity coefficient for  $\text{MgCl}_2$  in the aqueous mixed electrolyte solution,  $(1 - y)\text{MgCl}_2 + y\text{KCl}$ , is written as:

$$\begin{aligned} \ln \gamma_{\pm \text{MgCl}_2} = & \ln \gamma_{\pm \text{MgCl}_2}^0 + \frac{1}{3}yI \left[ \left( 4B_{\text{KCl}} - \frac{2}{3}B_{\text{MgCl}_2} \right) + I \left( 4B'_{\text{KCl}} - \frac{2}{3}B'_{\text{MgCl}_2} + \frac{8}{3}C_{\text{KCl}}^\varphi \right) \right] \\ & + \frac{1}{3}y^2I^2 \left( 2B'_{\text{KCl}} - \frac{2}{3}B'_{\text{MgCl}_2} + \frac{4}{3}C_{\text{KCl}}^\varphi - \frac{\sqrt{2}}{6}C_{\text{MgCl}_2}^\varphi \right) + \frac{2}{3}yI \left[ \theta + \frac{1}{3} \left( 2 - \frac{y}{2} \right) I\psi \right], \end{aligned} \tag{1}$$

where

$$\ln \gamma_{\pm \text{MgCl}_2}^0 = 2f^\gamma + \frac{4}{9}B'_{\text{MgCl}_2}I + \frac{2\sqrt{2}}{9}C_{\text{MgCl}_2}^\varphi I^2, \tag{2}$$

$$f^\gamma = -A_\varphi \left[ \frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right], \tag{3}$$

$$B_{\text{MX}} = \beta_{\text{MX}}^{(0)} + \frac{2\beta_{\text{MX}}^{(1)}}{\alpha^2 I} \left[ 1 - (1 + \alpha\sqrt{I}) e^{-\alpha\sqrt{I}} \right], \tag{4}$$

$$B'_{\text{MX}} = 2\beta_{\text{MX}}^{(0)} + \frac{2\beta_{\text{MX}}^{(1)}}{\alpha^2 I} \left[ 1 - \left( 1 + \alpha\sqrt{I} - \frac{\alpha^2}{2} I \right) e^{-\alpha\sqrt{I}} \right], \tag{5}$$

$$B''_{\text{MX}} = \frac{2\beta_{\text{MX}}^{(1)}}{\alpha^2 I^2} \left[ -1 + \left( 1 + \alpha\sqrt{I} + \frac{\alpha^2}{2} I \right) e^{-\alpha\sqrt{I}} \right]. \tag{6}$$

Table 1. Pitzer parameter values  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^\phi$  for single electrolytes of  $\text{MgCl}_2$  and  $\text{KCl}$  together with the constant values of  $\alpha$  and  $b$ .

Electrolyte	$\beta^{(0)}$ ( $\text{kg mol}^{-1}$ )	$\beta^{(1)}$ ( $\text{kg mol}^{-1}$ )	$C^\phi$ ( $\text{kg}^2 \text{mol}^{-2}$ )	$m_{\text{max}}$ ( $\text{mol kg}^{-1}$ )	$\sigma$	Reference
$\text{MgCl}_2$	0.35093	1.6508	0.006507	4	0.003	[4]
$\text{KCl}$	0.04835	0.2122	-0.00084	4.8	0.0005	[4]

Note:  $\alpha = 2$  ( $\text{kg mol}^{-1}$ )<sup>1/2</sup>;  $b = 1.2$  ( $\text{kg mol}^{-1}$ )<sup>1/2</sup>.

In these equations,  $A_\phi$  denotes the Debye–Huckel parameter for the osmotic function, which has a value of  $0.3915 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  for an aqueous solution at 298 K.  $I$  and  $y$  are the total ionic strength on a molality scale and ionic strength fraction, respectively.  $\text{MX}$  stands for  $\text{MgCl}_2$  and  $\text{KCl}$  in mixture solutions.  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^\phi$  symbolise the parameters of the Pitzer equation for a single salt electrolyte solution, were taken from the literature [13] and are presented in Table 1.  $\theta$  and  $\psi$  indicate the unknown mixing interaction parameters, which should be determined. The other constants have their usual meaning.

The unknown Pitzer mixing interaction parameters ( $\theta_{\text{MgK}}$ ,  $\psi_{\text{MgKCl}}$ ) were evaluated by the graphical procedure recommended by Pitzer (without higher order effect). The value of the higher order mixing terms ( ${}^E\theta$  and  ${}^E\theta'$ ) are often omitted for activity coefficient calculations [17,18]. This procedure defines the quantity of  $\Delta \ln \gamma$  as the difference between the measured mean activity coefficients for the mixture ( $\ln \gamma_{\text{exp}}$ ) and that calculated ( $\ln \gamma_{\text{calc}}$ ) on the basis of  $\theta = \psi = 0$  from Equation (1). Then Equation (1) is simplified and rearranged to yield:

$$\frac{3}{2m_k} \Delta \ln \gamma = \theta + \left( m_{\text{Mg}} + \frac{1}{2} m_{\text{Cl}} \right) \psi. \quad (7)$$

So a plot of the left side of Equation (7) versus  $(m_{\text{Mg}} + 0.5m_{\text{Cl}})$  should give  $\theta$  as the intercept and  $\psi$  as the slope. Firstly, from the measurements on ternary solutions, the mixing ionic parameters were determined; then, these parameters were used to calculate the thermodynamic properties, such as osmotic coefficients, activity coefficients in the mixture, and excess Gibbs free energy for systems under investigation as a function of total ionic strength.

### 3.2. Potentiometric measurements

The values of the experimental mean activity coefficients for  $\text{MgCl}_2$  in the mixture were obtained from the emf measurements using the galvanic cells (A, B) at the temperature 298 K. At first, the electromotive force of cell (A) was measured in order to calibrate the electrode pair composing the cell (A) and also to obtain its apparent standard potentials ( $E^0$ ) and slope ( $s$ ), in accordance to the Nernst equation:

$$E_A = E^0 + s \log(\gamma_{\pm, \text{MgCl}_2} I). \quad (8)$$

Then, the emf measurements of the galvanic cell (B) were obtained by using a standard addition procedure to give the experimental mean activity coefficients of  $\text{MgCl}_2$  at

different ionic strengths in mixed electrolyte solutions. The experimental mean activity coefficients of  $\text{MgCl}_2$  in a mixture can be calculated from the following equation [19]:

$$E_B = E'_B + s' \log \left[ \gamma_{\pm, \text{MgCl}_2}^3 m_1 (2m_1 + m_2)^2 + K_{\text{MgK}} \gamma_{\pm, \text{KCl}}^4 m_2^2 (2m_1 + m_2)^2 \right]. \quad (9)$$

In the above equation,  $K_{\text{MgK}}$  denotes the selectivity coefficient of Mg-ISE for  $\text{K}^+$ , which illustrates the interfering effect of  $\text{K}^+$  ions on the response of Mg-ISE.

Finally, the emf measurements of the galvanic cell (C) were performed to get the selectivity coefficient ( $K_{\text{MgK}}$ ). Due to this cause, the emf response Mg-ISE was measured by varying concentration of KCl from  $1.0 \times 10^{-4}$  to  $1.0 \text{ mol kg}^{-1}$ . The selectivity coefficient ( $K_{\text{MgK}}$ ) can be calculated from the following Equation (10):

$$E_C = E'_C + s' \log [K_{\text{MgK}} \gamma_{\pm, \text{KCl}}^4 m_B^4]. \quad (10)$$

The value of  $K_{\text{MgK}}$  was found to be  $< 1.2 \times 10^{-4}$ . Therefore, the selectivity coefficient is so small that the second term on the right of Equation (9) can be neglected. Consequently, we will get the simplified form of Equation (9):

$$E_B = E'_B + s' \log \left[ \gamma_{\pm, \text{MgCl}_2}^3 m_1 (2m_1 + m_2)^2 \right]. \quad (11)$$

Accordingly, the mean activity coefficients of  $\text{MgCl}_2$  in the aqueous mixture can be determined in relation to Equation (11).

## 4. Results and discussion

### 4.1. Calibration of Mg-ISE and Ag/AgCl electrode pairs

In order to calibrate the electrodes of a system before performing each series of experiments, the emf of cell (A) was measured at electrolyte concentrations ranging from  $1.0 \times 10^{-4}$  to  $1.0 \text{ mol kg}^{-1}$ . Since the activity coefficients of the  $\text{MgCl}_2$  as a single salt in water are well known [13], the plot of  $E$  versus  $\log a_{\text{MgCl}_2}$  ( $a_{\text{MgCl}_2}$  indicates the activity of the  $\text{MgCl}_2$ ) allow carrying out a calibration of the electrode system using Equation (8). A very good linear relationship was obtained when  $E$  versus  $\log a_{\text{MgCl}_2}$  was plotted. The value obtained by applying the least-squares regression analysis is  $s = 35.7 \pm 0.1 \text{ mV}$ , with a correlation coefficient equal to 0.9999 and the fit standard deviation of  $0.2 \text{ mV}$  (Figure 1). It is evident that the used electrode pair has a satisfactory response and that it is suitable for our measurements. The preliminary steps were performed due to measurements of the apparent standard potentials ( $E^0$ ) and slope ( $s$ ), according to the Nernst Equation (8). The obtained results of the corresponding values of apparent standard potentials ( $E^0$ ) and slope ( $s$ ) for each series of experiments are listed in Table 2.

### 4.2. Determination of the mean activity coefficients

The emf measurements of galvanic cell (B) were performed for determination of the experimental mean activity coefficients of  $\text{MgCl}_2$  in the mixed electrolyte solutions. Experimental mean activity coefficients of  $\text{MgCl}_2$  were determined for various series of salt molal ratios by using the Nernst equation. The values for the mean ionic activity coefficient of  $\text{MgCl}_2$  in the mixture over total ionic strengths from  $0.015$  to  $6 \text{ mol kg}^{-1}$  for different series of salt molal ratios ( $r = m_{\text{MgCl}_2}/m_{\text{KCl}}$ ) with  $r = 1, 2.5,$  and  $5$  are illustrated

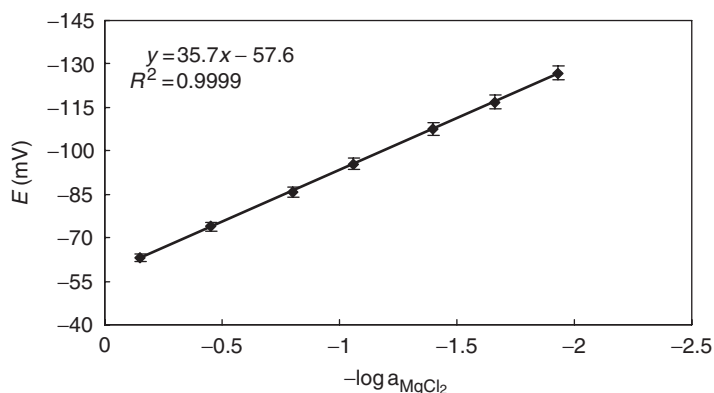


Figure 1. The emf vs.  $\log a_{\text{MgCl}_2}$  for the calibration of the Mg-ISE and Ag|AgCl electrode pair at 298 K.

Table 2. Values of the slope and apparent standard potentials for each series of the mixed electrolyte systems defined by its molal salt ratio ( $r = m\text{MgCl}_2/m\text{KCl}$ ) at 298 K.

$r$	1	2.5	5
$E^\circ \pm \text{SD}$	$-55.0 \pm 0.2$	$-58.2 \pm 0.2$	$-56.7 \pm 0.2$
$S \pm \text{SD}$	$36.2 \pm 0.1$	$35.3 \pm 0.1$	$33.4 \pm 0.1$

in Table 3. Further, Figure 2 shows the natural logarithm of the correlated activity coefficients of  $\text{MgCl}_2$  based on Pitzer's model against the square root of the total ionic strength for various series of salt molal ratios.

#### 4.3. Determination of mixing interaction parameters ( $\theta_{\text{MgK}}$ , $\psi_{\text{MgK}}$ )

The Pitzer ion interaction model was used for the experimental data correlation of activity coefficients. According to Pitzer's model, thermodynamic properties of multi-component electrolytes can be determined using the known parameters for single electrolyte solutions together with the two parameters  $\theta_{\text{MgK}}$  and  $\psi_{\text{MgKCl}}$ . These parameters account for the short-range interactions between two cations and two cations plus an anion, which are important only at high ionic strengths. In the Pitzer treatment, the unknown Pitzer mixing interaction parameters ( $\theta_{\text{MgK}}$ ,  $\psi_{\text{MgKCl}}$ ) were evaluated by a graphical procedure, using Equation (7). All of these parameters may be temperature dependent. Table 4 shows that the obtained results are consistent with the graphical procedure at 298 K. As seen from the above results, these parameters are very small.

#### 4.4. Calculation of thermodynamic properties

These obtained parameters were used for predicting the thermodynamic properties of system under investigation by Pitzer's model. The osmotic coefficients ( $\varphi$ ), the mean activity coefficients of KCl ( $\gamma_{\text{KCl}}$ ), and the excess Gibbs free energy can be calculated for

Table 3. Total ionic strengths, electrolyte molalities, experimental MgCl<sub>2</sub> mean activity coefficients, and emf data for all of the investigated mixed electrolyte systems at 298 K.

$I$ (mol kg <sup>-1</sup> )	$m_{\text{MgCl}_2}$ (mol kg <sup>-1</sup> )	$m_{\text{KCl}}$ (mol kg <sup>-1</sup> )	$E$ (mV)	$\gamma_{\pm}$
$r = 1$				
0.0150	0.0038	0.0038	-124.9	0.7726
0.0300	0.0075	0.0075	-115.3	0.7151
0.0600	0.0150	0.0150	-105.9	0.6534
0.1500	0.0375	0.0375	-93.2	0.5902
0.3000	0.0750	0.0750	-84.1	0.5290
0.7500	0.1875	0.1875	-71.5	0.4748
1.5000	0.3750	0.3750	-60.5	0.4807
3.0000	0.7500	0.7500	-46.0	0.6091
4.5000	1.1250	1.1250	-35.8	0.7812
6.0000	1.5000	1.5000	-26.2	1.0845
$r = 2.5$				
0.0150	0.0044	0.0018	-126.9	0.7407
0.0300	0.0088	0.0035	-116.8	0.7197
0.0600	0.0176	0.0071	-107.4	0.6679
0.1500	0.0441	0.0176	-95.4	0.5883
0.3000	0.0882	0.0353	-85.9	0.5496
0.7500	0.2206	0.0882	-73.8	0.4873
1.5000	0.4412	0.1765	-63.1	0.4926
3.0000	0.8824	0.3529	-50.7	0.5568
4.5000	1.3235	0.5294	-39.8	0.7605
6.0000	1.7647	0.7059	-30.2	1.0726
$r = 5$				
0.0150	0.0047	0.0009	-123.0	0.6903
0.0300	0.0094	0.0019	-112.9	0.6984
0.0600	0.0188	0.0038	-103.2	0.6871
0.1500	0.0469	0.0094	-91.7	0.6131
0.3000	0.0938	0.0188	-82.0	0.6032
0.7500	0.2344	0.0469	-70.0	0.5574
1.5000	0.4688	0.0938	-61.5	0.5043
3.0000	0.9375	0.1875	-50.1	0.5586
4.5000	1.4063	0.2813	-39.8	0.7641
6.0000	1.8750	0.3750	-30.9	1.0664

all of the series under investigation, with common-anion [(1 - y)MgCl<sub>2</sub> + yKCl]<sub>(aq)</sub>, as the following equations:

$$\phi - 1 = \frac{2}{(1 + y)I} \left\{ \begin{aligned} & If^\phi + \frac{1}{9}(1 - y)(y + 2)I^2 \left[ B_{\text{MgCl}_2}^\phi + \frac{\sqrt{2}}{6}I(2 + y)C_{\text{MgCl}_2}^\phi \right] \\ & + \frac{1}{3}yI^2(y + 2) \left[ B_{\text{KCl}}^\phi + \frac{1}{3}I(2 + y)C_{\text{KCl}}^\phi \right] \\ & + \frac{1}{3}y(1 - y)I^2 \left[ \theta + \frac{1}{3}I(2 + y)\psi \right] \end{aligned} \right\}, \quad (12)$$

$$B_{\text{MX}}^\phi = \beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)}e^{-\alpha\sqrt{I}}, \quad (13)$$



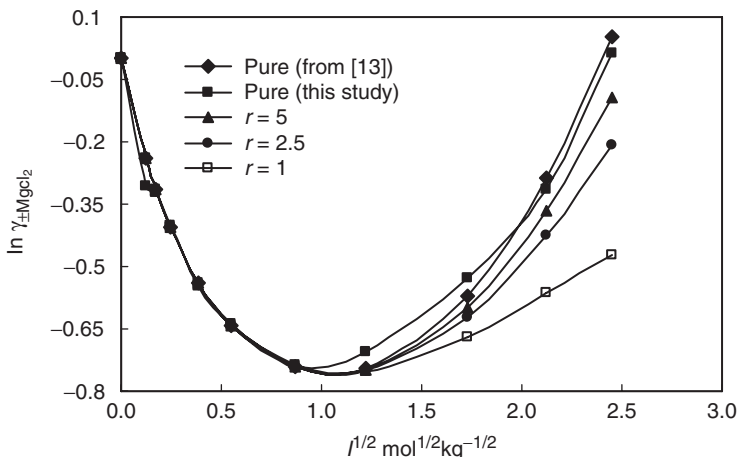


Figure 2. The mean activity coefficients for  $\text{MgCl}_2$  vs. the square root of the total ionic strength at different molal ratios ( $r = m_{\text{MgCl}_2}/m_{\text{KCl}}$ ) at 298 K.

Table 4. Pitzer mixing interaction parameters for the  $\text{MgCl}_2 + \text{KCl} + \text{H}_2\text{O}$  ternary system.

$r$	$\theta$ ( $\text{kg mol}^{-1}$ )	$\Psi$ ( $\text{kg}^2 \text{mol}^{-2}$ )	$I$ ( $\text{mol kg}^{-1}$ )	$\sigma$	Reference
–	0.0371	0	–	–	[20]
–	0.0838	–0.0139	–	–	[4]
1	0.0505	–0.0159	0.75–6	0.06	This work
2.5	0.1892	–0.0716	0.75–6	0.10	This work
5	0.1351	–0.0842	0.75–6	0.11	This work
Mean $\pm$ SD	$0.1249 \pm 0.0691$	$-0.0572 \pm 0.0362$	0.75–6	–	This work

$$\begin{aligned}
 \ln \gamma_{\text{KCl}} = & f' + \frac{1}{3}I(2B_{\text{KCl}} + B_{\text{MgCl}_2}) + \frac{2}{9}I^2 \left( C_{\text{KCl}}^\varphi + \frac{\sqrt{2}}{2}C_{\text{MgCl}_2}^\varphi + B'_{\text{MgCl}_2} \right) \\
 & + \frac{1}{3}yI(4B_{\text{KCl}} - B_{\text{MgCl}_2}) + \frac{1}{3}yI^2 \left( \frac{8}{3}C_{\text{KCl}}^\varphi - \frac{\sqrt{2}}{6}C_{\text{MgCl}_2}^\varphi + 2B'_{\text{KCl}} - \frac{1}{3}B'_{\text{MgCl}_2} \right) \\
 & + \frac{1}{3}y^2I^2 \left( \frac{7}{6}C_{\text{KCl}}^\varphi - \frac{\sqrt{2}}{6}C_{\text{MgCl}_2}^\varphi + B'_{\text{KCl}} - \frac{1}{3}B'_{\text{MgCl}_2} \right) + \frac{1}{3}(1-y)I \left( \theta + \frac{1}{3}(1+2y)I\psi \right),
 \end{aligned} \tag{14}$$

$$G^{\text{EX}} = RT[v_1m_1(1 - \varphi + \ln \gamma_{\text{MgCl}_2}) + v_2m_2(1 - \varphi + \ln \gamma_{\text{KCl}})]. \tag{15}$$

The values of these thermodynamic properties were illustrated for different series of salt molal ratios in Table 4. Figure 3 shows the plot of the osmotic coefficient against the square root of the total ionic strength. It can be seen that the osmotic coefficient of water is reduced by increasing the ionic strength fraction ( $y$ ) of KCl in the mixture. Further, Figures 4 and 5 show the mean activity coefficients of KCl ( $\gamma_{\text{KCl}}$ ) and the excess Gibbs energy plots as a function of the square root of the total ionic strength for all of the investigated mixed electrolyte systems, respectively (Table 5).

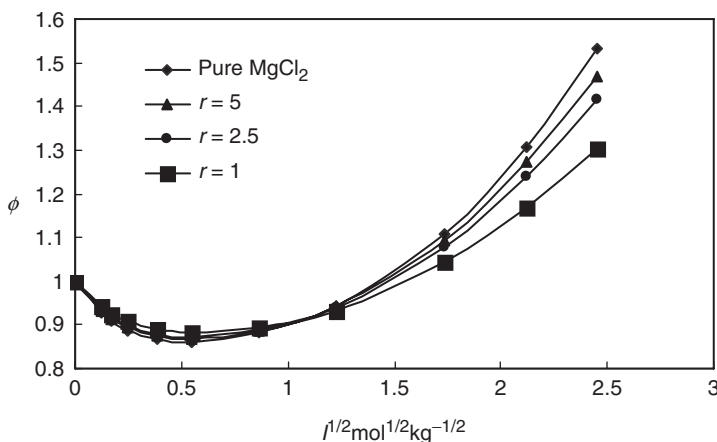


Figure 3. The osmotic coefficients of water against the square root of the total ionic strength at different molal ratios ( $r = m_{\text{MgCl}_2}/m_{\text{KCl}}$ ) at 298 K.

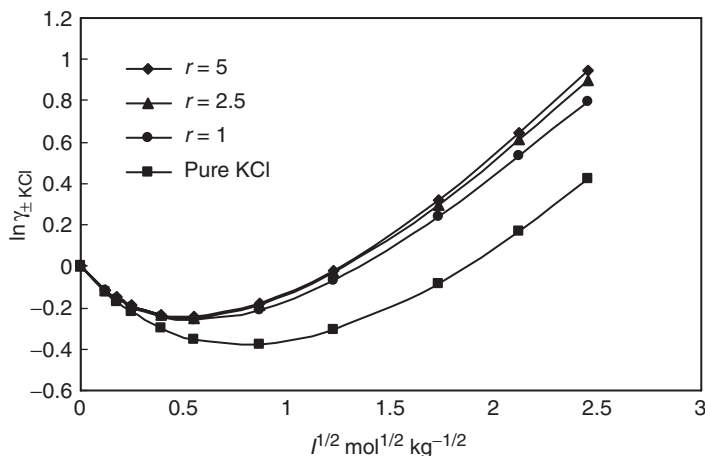


Figure 4. The mean activity coefficients for KCl vs. the square root of the total ionic strength at different molal ratios ( $r = m_{\text{MgCl}_2}/m_{\text{KCl}}$ ) at 298 K.

## 5. Conclusions

We have presented for the first time results concerning the use of a new type of sol-gel-based ion selective electrode for the thermodynamic study of the ternary aqueous mixed electrolyte solutions. The galvanic cell containing a Mg-ISE based on sol-gel membrane combined with an Ag/AgCl electrode was used for the determination of activity coefficients of  $\text{MgCl}_2$  in mixed electrolyte solution  $[(1-y)\text{MgCl}_2 + y\text{KCl}]_{(\text{aq})}$  at 298 K. The experimental mean activity coefficients were correlated based on the Pitzer ion-interaction model and the mixing Pitzer parameters were determined for this system. These parameters are  $\theta_{\text{MgK}} = 0.1249$  and  $\psi_{\text{MgKCl}} = -0.0572$ . The excess Gibbs free energy, which is one of the most important thermodynamic properties, was calculated using our mixing Pitzer parameters. It can be concluded that the excess Gibbs free energy rises with increasing ionic strength fractions  $y$  at the same total ionic strength.

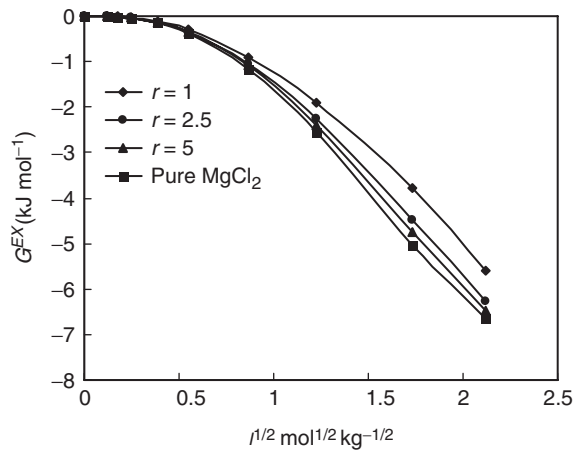


Figure 5. The excess Gibbs energy for mixed electrolyte solution  $[(1-y)\text{MgCl}_2 + y\text{KCl}]_{(\text{aq})}$  opposed to the square root of the total ionic strength at different molal ratios ( $r = m_{\text{MgCl}_2}/m_{\text{KCl}}$ ) at 298 K.

Table 5. Calculated values of natural logarithm of mean activity coefficients for KCl ( $\ln \gamma_{\pm\text{KCl}}$ ), osmotic coefficients ( $\phi$ ), excess Gibbs free energies ( $G^E$ ) as a function of ionic strength, for the investigated mixed electrolyte systems at 298 K.

$I$ (mol kg <sup>-1</sup> )	$\ln \gamma_{\pm\text{KCl}}$	$\phi$	$G^{EX}$ (J mol <sup>-1</sup> )	$I$ (mol kg <sup>-1</sup> )	$\ln \gamma_{\pm\text{KCl}}$	$\phi$	$G^{EX}$ (J mol <sup>-1</sup> )
$r = 1$				$r = 5$			
0.0150	-0.118	0.9411	-5	0.0150	-0.1163	0.9314	-6
0.0300	-0.1539	0.9249	-14	0.0300	-0.1507	0.9131	-16
0.0600	-0.1941	0.9079	-37	0.0600	-0.1884	0.8941	-42
0.1500	-0.2437	0.8886	-125	0.1500	-0.2319	0.8738	-146
0.3000	-0.2618	0.8814	-302	0.3000	-0.2426	0.8682	-358
0.7500	-0.2139	0.8923	-901	0.7500	-0.1796	0.8867	-1098
1.5000	-0.0689	0.9331	-1917	1.5000	-0.0172	0.9426	-2400
3.0000	0.242	1.0426	-3794	3.0000	0.3237	1.0922	-4752
4.5000	0.5336	1.1695	-5608	4.5000	0.6474	1.2715	-6490
6.0000	0.7979	1.3035	-7738	6.0000	0.9475	1.4684	-7531
$r = 2.5$				Pure <sup>a</sup>			
0.0150	-0.1167	0.9346	-6	0.0150		0.9273	-6
0.0300	-0.1516	0.9170	-16	0.0300		0.9080	-17
0.0600	-0.19	0.8988	-41	0.0600		0.8881	-44
0.1500	-0.2353	0.8789	-140	0.1500		0.8671	-152
0.3000	-0.2481	0.8729	-342	0.3000		0.8617	-374
0.7500	-0.1894	0.8893	-1041	0.7500		0.8826	-1158
1.5000	-0.032	0.9406	-2258	1.5000		0.9438	-2554
3.0000	0.2999	1.0777	-4472	3.0000		1.1086	-5040
4.5000	0.6136	1.2401	-6262	4.5000		1.3085	-6659
6.0000	0.9021	1.4166	-7705	6.0000		1.5310	-7113

Note: <sup>a</sup>Values taken from [13].

### Acknowledgement

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