Regular Article

Determination and Modeling of Activity Coefficients of Sodium Chloride in (Glycerol + Water) Mixtures Based on Potentiometric Measurements

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In this work, the results concerning to the mean activity coefficient measurements for NaCl in the (glycerol + water) system using the potentiometric method are reported. The potentiometric measurements were performed on the galvanic cells without liquid junction of the type: Ag|AgCl|NaCl (m), glycerol (wt%), H$_2$O (1 - wt)%|Na-ISE, in various mixed solvent systems containing 0, 5, 10, 20 and 30 mass fraction percents of glycerol over ionic strength ranging from 0.0020-3 mol kg^{-1} at T = 298.2 K. The sodium ion selective electrode and Ag-AgCl electrode as self-made electrodes had a reasonably Nernst response. The modified zeolite was used to fabricate the sodium ion selective electrode as electrochemical sensor. The modeling of the investigated system was made based on an extended Debye-Hückel equation, the Pitzer and Pitzer-Simonson-Clegg models. The unknown parameters were determined for each model. The resulting values of the mean activity coefficients, osmotic coefficients and excess Gibbs energy are reported for the studied system.

INTRODUCTION

In recent years, there has been a growing interest in the measurement or prediction of the thermodynamic properties of electrolyte in mixed solvent systems because of their applications in various areas like in industry, biochemistry, environmental chemistry, oceanography, geochemistry and separation processes [1-3]. Thermodynamic study of (salt + alcohol + water) system is useful to understand several biodiesel post-production processes [4,5]. Production of biofuels has been widely studied in recent years because of its potential to solve many of the current social problems and concerns, from air pollution and global warming to other environmental improvements and sustainability issues [6-8]. For instance, Glycerol is a byproduct of biodiesel industry [4]. Generally the crude glycerol is also generated together with biodiesel productions in a large quantity, but most of the glycerol from biodiesel fuel due to its impurities is disposed without utilization [9]. These impurities include low amounts of alcohol, water and also some salt residues

[10,11]. Because of the wide applications of pure glycerol in food, pharmaceutical, cosmetics and many other industries [9], it is too costly to refine the crude glycerol to a highly pure matter. Among various separation techniques used to recover the crude glycerol, distillation is certainly the most cited in literature. So, knowledge of the thermodynamic properties of (salt + glycerol + water) system can be useful for this process.

To measure the thermodynamic properties of electrolytes in mixed solvent, the most common methods are the isopiestic vapor pressure [12,13] and potentiometric techniques [14-16]. The electromotive force (emf) method presents advantages such as rapidity and relative simplicity to generate experimental data in comparison with the other techniques [17-19]. The incorporation of zeolites into electrochemical systems has received increasing attention in recent years [20]. Zeolites are narrowly defined, porous crystalline aluminosilicates with a uniform pore structure, exhibiting ion-exchange behavior. Their ion-exchange properties can make them the candidates for preparing ion-selective membranes [21].

In our previous papers, we reported the ability of the

solvent polymeric membrane electrode for determination of the activity coefficient for binary, ternary and quaternary electrolyte solutions [22-24]. In this work, the results concerning to the thermodynamic properties of (NaCl+glycerol+water) system using the potentiometric method are reported at T = 298.2 K. The potentiometric measurements were performed on the galvanic cell using self-made electrodes. New sodium ion selective electrode (Na - ISE) was fabricated using the modified zeolite Y as an ionophore. The activity coefficients are reported for NaCl in various glycerol + water mixed solvent systems containing 0, 5, 10, 20 and 30 mass percentage of glycerol over ionic strength ranging from 0.0020 to 3 mol kg^{-1}. This ternary system was designed based on an extended Debye-Hückel equation, the Pitzer and Pitzer-Simonson-Clegg (PSC) ion-interaction models. The resulting values of the mean activity coefficients, osmotic coefficients and excess Gibbs energy, together with the Pitzer ion-interaction model parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^{φ}), PSC model parameters (W_{2NaCl}, U_{2NaCl}, V_{2NaCl}, Z_{12NaCl}) and extended Debye-Hückel model parameters (a, c and d), are reported for the investigated systems.

EXPERIMENTAL

Chemicals Used

Silica powder, $Al_2(SO_4)_3.16H_2O$, sodium hydroxide, aluminum powder, glycerol, Dibuthyl phthalate (DBP), cetyltrimetylammoniumbromide (CTMABr), potassium tetrakis (*p*-chlorophenyl) borate (KTp CIPB), high molecular weight polyvinylchloride (PVC), tetrahydrofuran (THF), sodium chloride (NaCl) and all other reagents used were purchased from Merck and Fluka chemical company, which all of them were of analytical reagent grade. Double distilled water was also used throughout all experiments. The stock aqueous solutions of electrolyte were prepared from NaCl, glycerol and double-distilled water whose specific conductance was less than 2.0×10^{-4} S m^{-1} by adding weighted amounts of NaCl and glycerol into the proportion volume of double-distilled water.

Apparatus

The zeolite Y was characterized for crystallinity and phase purity by a Philips PW1840 X-ray diffractometer with Cu Kα radiation. All of the potentiometric measurements

were made using a multimeter (Martini instruments Mi 180) whose resolution was 0.1 mV. The output of the multimeter was connected to a personal computer by the RS232 connector for data acquisition. The Mi 5200 software together with Microsoft Excel (Office 2007) software were used for data acquisition and calculations. The magnetic stirrer (Delta Model HM-101) was employed to avoid concentration gradients in the test solutions. Samples were centrifuged by a Hettich EBA 20 and the Fourier transformation infrared (FT-IR) spectra of samples were recorded on KBr pellets using a Perkin-Elmer spectrometer in the range of 400-4000 cm^{-1} at room temperature.

Synthesis and Modification of Zeolite

Preparation of zeolite Y was performed based on our previous work [25] with some modification in according to the literature [26]. But in this work, CTMABr as surfactant was used instead of hexadecyltrimethylammonium bromide. The Na-Y zeolite (2 g) was mixed with 100 ml of 100 mMCTMAB solutions, and stirred for 24 h on a magnetic stirrer. The mixture was then centrifuged at 5000 rpm for 20 min and the resulting zeolite was dried in air.

Electrodes Preparation

The Na - ISE was prepared in accordance with the general procedure of PVC membrane construction. To this aim, an optimized mixture containing of 30 mg of powdered PVC, 38.8 mg of plasticizer DBP, 4.2 mg of additive KTpCIPB and 31.3 mg of modified zeolite Y as ionophore was dissolved in 3 ml of dry freshly distilled THF. The resulting clear mixture was transferred into a glass dish of 2 cm in diameter. The solvent was evaporated. After 2 h the polymer membrane could be easily removed from the plate. Then, the transparent PVC membrane was taken up from the plate and attached to the end of a glass tube with a diameter of 1 cm and height of 5 cm by means of PVC-THF viscose solution. The Ag-AgCl wire electrodes were prepared basically as described elsewhere by electrolysis [27]. Both Na-ISE and Ag-AgCl electrodes were conditioned overnight in the appropriate electrolyte system prior to each series of measurements.

Potentiometric Measurements

The activity coefficients for NaCl in the mixed solvent system were determined from the emf measurements using

the following cell:

Ag|AgCl|NaCl(m), glycerol (wt%), H$_2$O (1-wt)%|Na-ISE

(A)
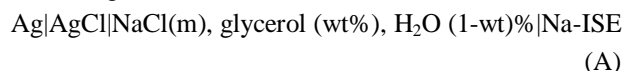
where wt is the mass fraction of glycerol in the mixed solvent system. The emf measurements of the galvanic cell were made by using standard addition procedure. For this purpose, the concentrated electrolyte solutions were added into the cell containing a specified volume of the glycerol-water as a mixed solvent. The standard addition steps were carried out using proper burette and suitable Hamilton syringes (CH-7402 Bonaduz). In each series and for each standard addition step, data collection was performed every 10 s interval and during 15 (for concentrated solutions) to 20 min (for dilute solutions) by using a multimeter connected to personal computer. As usual, all measurements were performed under stirring conditions and the temperature was kept constant at 298.2 K ($\pm$0.1 K), employing a double-wall container enabling the circulation of thermostat water from a Model GFL circulation.

THERMODYNAMIC MODEL

Pitzer Model

The Pitzer ion interaction model was used for the experimental data correlation and calculation of thermodynamic properties for under investigated system [28]. According to the Pitzer model, the mean activity coefficient in molal based ($\gamma_\pm$) for NaCl in the mixed solvent is described as:

$$\ln \gamma_{\pm NaCl} = f^\gamma + B^\gamma_{NaCl} I + 1.5 C^\varphi_{NaCl} I^2 \tag{1}$$

Where

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

$$B^\gamma_{NaCl} = 2\beta^{(0)}_{NaCl} + \frac{2\beta^{(1)}_{NaCl}}{\alpha^2 I} [1 - (1 + \alpha\sqrt{I} - \frac{\alpha^2 I}{2})e^{-\alpha\sqrt{I}}] \tag{3}$$

In these equations, α and b are assumed to be constant with values of 2.0 and 1.2 kg$^{1/2}$ mol$^{1/2}$, respectively, both in water and in glycerol-water mixtures; I indicates the total ionic strength on a molality scale. $\beta^{(0)}$, $\beta^{(1)}$ and C^φ show solute-specific interaction Pitzer parameters for electrolyte solution that their values should be determined for NaCl in glycerol + water mixtures . A_φ (kg$^{1/2}$ mol$^{-1/2}$) denotes the Debye-Hückel (DH) parameter for the osmotic coefficients defined by

$$A_\varphi = \frac{1.4006 \times 10^6 d^{1/2}}{(\varepsilon_r T)^{3/2}} \tag{4}$$

where d is the solvent density (kg m^{-3}); ε_r the solvent relative permittivity; and T the Kelvin temperature. The Debye-Hückel osmotic coefficient parameter values of pure water and the mixture (glycerol + water), together with the values of the physical properties (d and ε_r) are shown in Table 1 [29].

PSC Model

The PSC model was also applied to correlate with the experimental data. In according to the PSC model, an extended DH expression for long-range forces including composition-dependent terms together with a four-suffix Margules expansion for short-range forces including parameters for the interactions of both the solvent-anion and solvent-cation is employed [30,31]. Based on PSC model, the natural logarithm of mean activity coefficient in mole fraction based ($lnf_\pm$) for NaCl in the mixed solvent is assumed to consist of long-range Debye-Hückel ($lnf_\pm^{DH}$) and short range forces ($lnf_\pm^s$) as:

$$\ln f_\pm = \ln f_\pm^{DH} + \ln f_\pm^s \tag{5}$$

$$\ln f_\pm^{DH} = -A_x [(\frac{2}{\rho}) \ln(1 + \rho I_x^{1/2}) + \frac{I_x^{1/2}(1 - 2I_x)}{1 + \rho I_x^{1/2}}] + X_x B_{MX} g(\alpha I_x^{1/2}) - X_x X_M B_{MX}$$
$$[\frac{g(\alpha \rho I_x^{1/2})}{2I_x} + (1 - \frac{1}{2I_x}) \exp(-\alpha I_x^{1/2})]$$

(6)

$$\ln f_\pm^s = (1 - X_s)(X_1 W_{1MX} + X_2 W_{2MX}) + 2X_s(1 - X_s)(X_1 U_{1MX} + X_2 U_{2MX}) + X_s(2 - 3X_s)$$

$$(X_1^2 V_{1MX} + X_2^2 V_{2MX}) + X_1 X_2 (W_{12} + 2(X_1 - X_2)u_{12} + X_1 X_2(1 - 2X_s)Z_{12MX} - W_{1MX}$$

(7)

In equations 5-7, x_1, x_2, I_x, x_x, x_M and A_x are the water mole fraction, glycerol mole fraction, ionic strength, anion mole faction, cation mole fraction and DH parameter for the osmotic coefficient on a mole fraction basis, respectively.

Table 1. Values of the Mean Molar Weight (Ms), Density (ds), Relative Permittivity (εr), and Debye-Hückel Constants (A, B and Aφ), Debye-Hückel Paramour on the Mole-Fraction Basis (Ax) and the Parameter Related to the Closest Approach Distances (ρ) for Glycerol+Water Mixtures at 298.2 K

wt.%	Ms (g mol^{-1})	d (kg m^{-3})	ε_r[a]	A $(\text{kg}^{1/2}\,\text{mol}^{-1/2})$	B $(\text{kg}^{1/2}\,\text{mol}^{-1/2}\,\text{A}^{\circ-1})$	$A\varphi$[a] $(\text{kg}^{1/2}\,\text{mol}^{1/2})$	A_x	ρ
0	18.02	997.2	78.24	0.5114	0.3288	0.3915	2.9180	14.0571
5	18.75	1000.8	76.9	0.5279	0.3336	0.4051	2.9580	14.2620
10	19.57	1020.7	75.5	0.5458	0.3386	0.4190	2.9948	14.4776
20	21.45	1045.2	72.9	0.5822	0.3487	0.4469	3.0512	14.9096
30	23.72	1070.7	70.0	0.6262	0.3602	0.4807	3.1207	15.3994

[a]The values are taken from [29].

B_{MX} is a specific parameter for each electrolyte; The α is assumed to be constant with values of 13.0, both in water and in glycerol + water mixtures; W_{1MX}, U_{1MX}, V_{1MX} W_{12} and U_{12} parameters were calculated by using the reported data in the literatures [32,4]. The W_{2MX}, U_{2MX} and V_{2MX} are binary solute-solvent interaction parameters for NaCl with glycerol and Z_{12MX} is the triple interaction parameter that their values should be determined. Also, X_s, I_x, $g(x)$, A_x and ρ are defined by

$$X_s = 1 - X_1 - X_2 \tag{8}$$

$$I_x = \frac{1}{2}(X_M + X_X) \tag{9}$$

$$g(X) = 2[1 - (1+X)\exp(-X)]/X^2 \tag{10}$$

$$A_x = (1000/M_s)^{1/2} A^\phi \tag{11}$$

$$\rho = 2150(d_s/\varepsilon T)^{1/2} \tag{12}$$

The values of the physical properties (A_x and ρ_r) are shown in Table 1. In addition, the relation between the activity coefficient in mole fraction, f_i, with corresponding value in molal based, γ_i. would be established through the equation

$$f_i = \gamma_i (1 + M_s/1000)\sum_i m_i \tag{13}$$

where M_S and m_i are the mean molar mass of the mixed solvent and the molality of species i, respectively [30].

Extended Debye-Hückel Theory

The extended Debye-Hückel theory can be considered as the first ion-interaction model, which introduces the electrolyte-specific regression parameters [4]. For 1-1 type electrolytes, such as NaCl, the extended Debye-Hückel equation for the mean activity coefficients is given as:

$$\log \gamma_\pm = -\frac{A\sqrt{I_m}}{1 + Ba\sqrt{I_m}} + cI_m + dI_m^2 - \log(1 + 0.002 I_m M_s) \tag{14}$$

where a is the ion size parameter, c and d are the ion-interaction parameters, M is the average molecular mass of the mixed solvent. A $(\text{kg}^{1/2}\,\text{mol}^{-1/2})$ and B $(\text{kg}^{1/2}\,\text{mol}^{1/2}\,A^{-1})$ are the extended Debye-Hückel constants given by:

$$A = \frac{1.8247 \times 10^6 d^{1/2}}{(\varepsilon_r T)^{1/2}} \tag{15}$$

$$B = \frac{50.2901 d^{1/2}}{(\varepsilon_r T)^{1/2}} \tag{16}$$

The A and B values of the pure water and the mixture (glycerol + water) at T = 298.2 K are shown in Table 1.

RESULTS AND DISCUSSION

Synthesized Zeolite and Modified Zeolite Characterization

X-ray diffraction studies. X-ray diffraction patterns of

the prepared samples before and after modification are shown in Fig. 1. Figure 1a shows the XRD pattern of the synthesized zeolite Y. Figure 1b shows the XRD pattern of the modified zeolite Y. The characteristic diffraction peaks for zeolite Y are confirmed by comparing the XRD data with those reported in standard reference source [34]. The main XRD reflections for zeolite Y appear at around $2\theta = 6.27°$, $10.20°$, $11.95°$, $15.71°$, $18.74°$, $20.40°$, $23.68°$ and $27.07°$ (attributed to (111), (220), (311), (331), (333), (440), (533) and (642) crystal planes, respectively). Figure1 also shows that the structure of zeolite Y does not change before and after modification.

FT-IR studies. Infrared (IR) spectroscopy was used to characterize the synthesized and modified zeolites Y samples. The IR results show adsorption of an appropriate amount of surfactant on the zeolite Y. FTIR spectra of the synthesized and modified zeolite are shown in Fig. 2. The IR pattern of modified zeolite Y (Fig. 2b) shows characteristic peaks at 2921 and 2852 cm^{-1}, indicating the incorporation of CTMABr into the zeolite Y structure. They are related to C-H and C-C vibrations in the surfactants, that are absent in Synthesized zeolite spectrum. It can be seen, both patterns of the synthesized and modified zeolites are nearly the same. Therefore, the zeolite structure does not change after modification.

Calibration of Na-ISE and Ag/AgCl Electrode Ppairs

As a preliminary step, the amount of NaCl molality (m) from 0.0010-1.000 mol kg^{-1} was selected to determine each corresponding potential (E_A) using the cell (A). The Nernstian Equation for cell (A) is:

$$E_A = E^{'} + k \log_{10}(m^{\ 2}\gamma^2_{\pm NaCl}) = E^o + s \log(\gamma_{\pm NaCl}I) \qquad (17)$$

where $k = (ln10)RT/ZF$ represents Nernstian slope. The R, F, Z and T are the universal gas constant, Faraday constant, the charge of ion and absolute temperature, respectively. In this work Z is equal to 1. The $\gamma_{\pm}$ is the mean activity coefficient of NaCl in pure water or mixed solvents. The E° is the experimental standard potential of cell (A).

Then, the measured potentials were plotted against $log(\gamma_{\pm}I)$ to check the slope (s) and the linear correlation coefficient (R^2). The activity coefficients of NaCl in pure

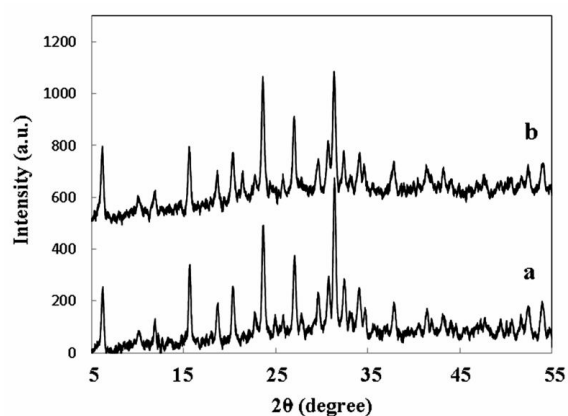**Fig. 1.** XRD patterns of the synthesized zeolite Y before (a) and after (b) modification with surfactant.
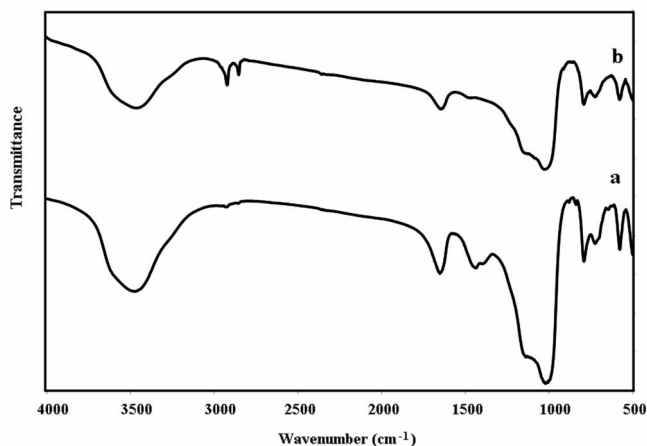

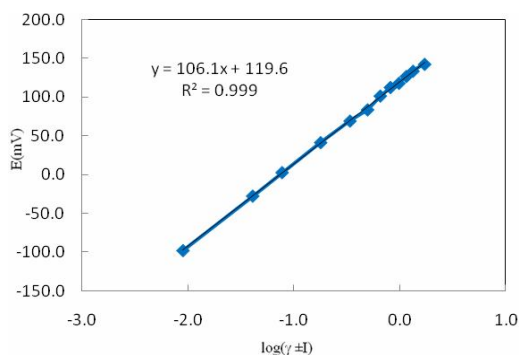**Fig. 2.** FTIR patterns of the synthesized zeolite Y before (a) and after (b) modification with surfactant.

Fig. 3. The plot of cell (A) emf *vs.* log(y $_{NaCl}$I) for calibration of Na-ISE and Ag-AgCl electrode pair at 298.2 K.

water were taken from literature [18] and were calculated according to Eq. (1). Figure 3 shows the electrode pair used here has a slope (s = 106.1 mV decade^{-1}), and linear correlation coefficient (R^2 = 0.999) and it can be proper for our measurements.
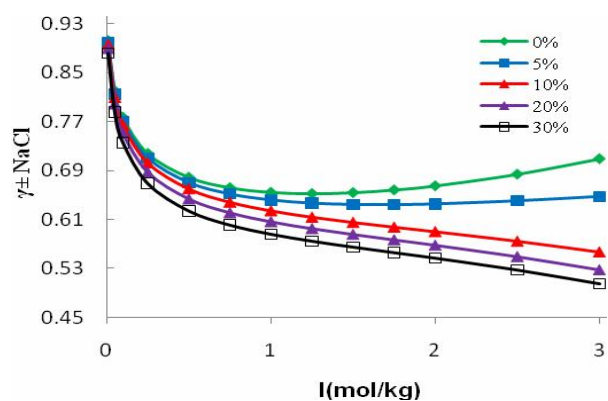
Determination of the Mean Activity Coefficients and Pitzer Parameters

The mean activity coefficients of NaCl in the mixed solvent (glycerol + water) were determined from the emf measurements using the galvanic cell (*A*) in according to equation 17 (Table 2). Also, Fig. 4 presents the variation of the NaCl mean activity coefficients *vs.* the ionic strength in water, and different mass fraction of glycerol in mixed solvents at T = 298.2 K. It can be observed that the values of the mean activity coefficients decrease with increasing the ionic strength of electrolyte. Also, the values of the mean activity coefficients decrease with increasing the mass fraction of glycerol in glycerol + water mixed solvent when the ionic strength is fixed. This phenomenon can be interpreted as ion-ion and ion-solvent interactions in the mixture. For glycerol-water mixed solvents, the relative permittivity of the mixed solvent decreases with an increase of glycol content, while the ion-ion interaction is more significant than other interactions.
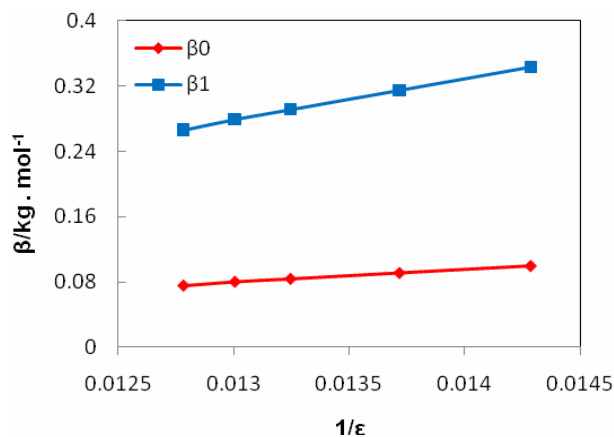
The Pitzer ion interaction parameters were determined by combining Eqs. (1) and (17) by an iteration minimization procedure employing the Microsoft Excel (solver) program. The resulting $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} Pitzer ion-interaction parameters, E^0, the cell constant potential and s, the electrode slope obtained from iteration minimization procedure for the investigated systems at T = 298.2 K are illustrated in Table 3. The values of $\beta^{(0)}$ and $\beta^{(1)}$ obtained are plotted in Fig. 5 against the reciprocal value of the relative permittivity of the glycerol-water mixture. As observed, both $\beta^{(0)}$, identified by the total binary ionic interactions, and $\beta^{(1)}$, identified by the interactions between unlike-charged ions change linearly with $1/\varepsilon$. The linear dependence observed in this study is reasonable, following behavior similar to the other electrolytes in different aqueous mixtures of organic solvents.

Estimation of Debye-Hückel Parameters

The extended Debye-Hückel was also used to correlate

Fig. 4. The mean activity coefficients ($\gamma\pm$) for NaCl *vs.* ionic strength (I) of electrolyte in various glycerol-water mixed solvent systems containing 0,5, 10, 20 and 30% mass fraction of glycerol at 298.2 K.

Fig. 5. Variation of Pitzer parameters ($\beta^{(0)}$and $\beta^{(1)}$) for NaCl against the reciprocal value of relative permittivity ($1/\varepsilon$) of the glycrol + water mixtures at 298.2 K.

the experimental activity coefficient data for under investigated electrolyte system at T = 298.2 K. The adjustable parameters (a, c and d) were obtained by an iteration minimization procedure employing the Microsoft Excel (solver) program. The parameters found for NaCl in various glycerol-water mixed solvent system containing 0, 5, 10, 20 and 30% mass fraction are illustrated in Table 3. The results of this table show that the extended Debye-

Table 2. The Molality of NaCl, Experimental Mean Activity Coefficients of NaCl and emf Data for All of the Investigated Electrolyte System at T = 298.2 K

I^a (mol kg^{-1})	E^b (mV)	$\gamma^c_{\pm NaCl}$	I (mol kg^{-1})	E^b (mV)	$\gamma^c_{\pm NaCl}$
wt% = 0			wt%=5		
0.0100	-98.0	0.9023	0.0100	-117.6	0.8991
0.0500	-27.6	0.8204	0.0500	-41.4	0.8150
0.1000	2.8	0.7768	0.1000	-12.3	0.7705
0.2500	41.5	0.7182	0.2500	21.6	0.7106
0.5000	69.4	0.6796	0.5000	52.7	0.6704
0.7500	83.9	0.6628	0.7500	69.1	0.6518
1.0000	101.7	0.6555	1.0000	78.8	0.6419
1.2500	112.8	0.6537	1.2500	85.9	0.6367
1.5000	118.2	0.6556	1.5000	95.8	0.6345
1.7500	127.0	0.6603	1.7500	102.6	0.6342
2.0000	133.8	0.6673	2.0000	105.0	0.6353
2.5000	142.7	0.6870	2.5000	115.0	0.6403
			3.0000	126.6	0.6474
wt% = 10			wt%=20		
0.0100	-100.3	0.9627	0.0100	-100.0	0.8895
0.0500	-29.8	0.8959	0.0500	-26.6	0.7985
0.1000	1.4	0.8095	0.1000	-2.2	0.7509
0.2500	41.1	0.7639	0.2500	37.8	0.6870
0.5000	69.6	0.7023	0.5000	64.8	0.6431
0.7500	87.6	0.6598	0.7500	78.2	0.6205
1.0000	99.0	0.6380	1.0000	90.2	0.6057
1.2500	107.0	0.6240	1.2500	99.7	0.5945
1.5000	117.6	0.6136	1.5000	106.3	0.5849
1.7500	123.4	0.6050	1.7500	112.3	0.5760
2.0000	129.7	0.5973	2.0000	117.4	0.5672
2.5000	139.4	0.5898	2.5000	125.2	0.5484
3.0000	145.4	0.5742	3.0000	132.0	0.5267
wt% = 30					
0.0100	-96.5	0.8817			
0.0500	-28.9	0.7855			
0.1000	0.0	0.7354			
0.2500	38.2	0.6690			
0.5000	63.6	0.6239			
0.7500	80.0	0.6009			
1.0000	94.6	0.5859			
1.2500	103.2	0.5745			
1.5000	111.2	0.5648			
1.7500	118.6	0.5557			
2.0000	124.7	0.5467			
2.5000	131.4	0.5273			
3.0000	140.9	0.5048			

[a]The error in ionic strength and molality values were ±0.0001 mol kg^{-1}. [b]The error in emf value was ±0.1 mV. [c]Th eaverage standard deviation in mean activity coefficient value was ±0.0064

Table 3. The Values Obtained of Pitzer and Debye-Hückel Parameters for NaCl Electrolyte in the Different Glycerol-Water Mixtures Together with Values of the Slope (s) and the Cell Constant Potential (E^0) at T = 298.2 K

wt%	$\beta^{(0)}$ (kg mol^{-1})	$\beta^{(1)}$ (kg mol^{-1})	C^{φ} (kg^2 mol^{-2})	$\sigma \gamma$	a	c	d	$\sigma \gamma$	S	$E^{(0)}$ (mV)
	Pitzer				Debye-	Hückel				
0	0.0756	0.2664	0.00127	0.0015	4.2459	0.0412	0.0034	0.0391	106.1	119.6
5	0.0803	0.2795	-0.00566	0.0001	4.1789	0.0450	-0.0010	0.0383	102.2	97.7
10	0.0839	0.2916	-0.01644	0.0403	4.1275	0.0474	-0.0080	0.0002	108.2	121.6
20	0.0911	0.3152	-0.01953	0.0002	4.0329	0.0524	-0.0099	0.0452	102.9	113.9
30	0.0996	0.3436	-0.02147	0.0001	1.9303	0.1685	-0.0291	0.0374	105.5	119.4

Table 4. Values of PSC's Parameters for NaCl in the Different Glycerol + Water Solvent Mixtures at 298.2 K

W_{12}[a]	U_{12}[a]	W_{1mx}[b]	B_{mx}[b]	U_{1mx}[b]	V_{1mx}[b]	W_{2mx}	U_{2mx}	Z_{12mx}	V_{2mx}	$\sigma \gamma$
-0.8901	0.0200	-7.4354	16.2622	-2.2831	1.0289	-21.3454	-337.1070	13.78149	4174.6350	0.0870

[a]The values are taken from [32]. [b]The values are taken from [4].

Hückel also is suitable in the case of the mixed solvent system. However, it should be noted that the explicit relation between adjustable parameters (*a* and *d*) and physical properties is not observed by the extended Debye-Hückel. Also, Fig. 6 shows the performance of the extended Debye-Hückel and Pitzer model for NaCl activity coefficients in aqueous solvent. As seen, Pitzer model is better than the extended Debye-Hückel to correlate the activity coefficients data.

Evaluation of PSC Parameters

The continuation of this work, the PSC mode was used to correlate the mean activity coefficient. For this aim, the W_{12} and U_{12} parameters was firstly calculated using vapor liquid equilibrium data of water + glycerol mixtures in according to margules equation [32]. Then, B_{MX}, W_{1mx}, U_{1MX} and V_{1MX} parameters were taken from literature [4]. Finally, W_{2MX}, U_{2MX}, Z_{12MX} and V_{2MX} parameters were determined by combining equations. 5, 13 and 17. The obtained parameters were illustrated in Table 4. As well, Fig. 7 shows the variation of the activity coefficient (*f*±) for NaCl versus the
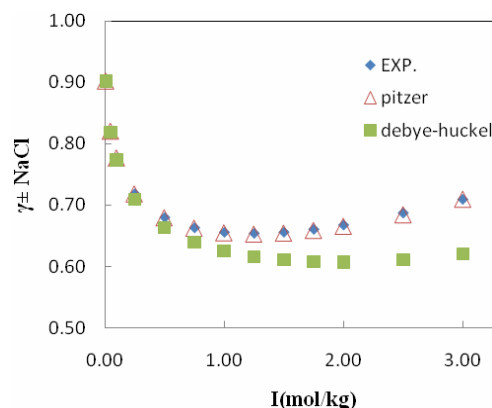
Fig. 6. The comparison of the extended Debye-Hückel and Pitzer model to correlate the NaCl activity coefficients data in aqueous solvent.

mole fraction of the total ions (*Xs*) in various glycerol + water mixtures at 298.2 K.

Calculation of the Thermodynamic Properties

The obtained parameters were used to calculate the

thermodynamic properties of under investigated system by the Pitzer and PSC models. Based on Pitzer model, the osmotic coefficients (ϕ), solvent activity and the excess Gibbs free energy for all of the under investigated series can be calculated using the following equations:

$$\phi = 1 - \frac{A_\phi \sqrt{I}}{1 + b\sqrt{I}} + B_{NaCl}^\phi I + C_{NaCl}^\phi I^2 \tag{18}$$

$$B_{NaCl}^\phi = B_{NaCl}^{(0)} + B_{NaCl}^{(1)} \exp(-\alpha\sqrt{I}) \tag{19}$$

$$G^E = 2IRT(1 - \varphi + ln\gamma_\pm) \tag{20}$$

$$a_s = \exp(\frac{-\phi M I}{500}) \tag{21}$$

The values of these thermodynamic properties are illustrated in Table 5 for different series of glycerol mass fraction in mixed solvents. Figure 8 shows the plot of the excess Gibbs free energy versus the ionic strength. It can be seen that the excess Gibbs free energy is decreased by increasing the mass fraction of glycerol in mixed solvent. It can be interpreted in terms of the interaction model. For the system presented here, polar groups in glycerol can interact with Na^+ and Cl^-.

In addition, The PSC parameters obtained were used to calculate the thermodynamic properties of under investigation system. According to the PSC model, the excess Gibbs free energy per mole can be written:

$$\frac{g^E}{RT} = (\frac{-4I_x A_X}{\rho}) \ln[\frac{(1 + \rho\sqrt{I_x})}{1 + \rho\sqrt{I_x^0}}] + X_s^2 B_{MX} g(\alpha\sqrt{I_x}) + X_s(X_1 W_{1MX} + X_2 W_{2MX}) +$$

$$X_s^2(X_1 U_{1MX} + X_2 U_{2MX}) + X_s^2(X_1^2 V_{1MX} + X_2^2 V_{2MX}) + X_1 X_2[W_{12} + (X_1 - X_2)u_{12} + X_s Z_{12MX}]$$
$$\tag{22}$$

The values of the excess Gibbs free energy per mole are illustrated for different series of glycerol mass fraction in mixed solvents in Table 6. Figure 9 shows the plot of the excess Gibbs free energy versus the mole fraction of the total ions in the solution. It can be seen that the excess Gibbs free energy is reduced by increasing the mass fraction of glycerol in mixed solvent. As observed, both Pitzer and PSC models, show the similar variations.

CONCLUSIONS

The mean activity coefficients of NaC in the NaCl +
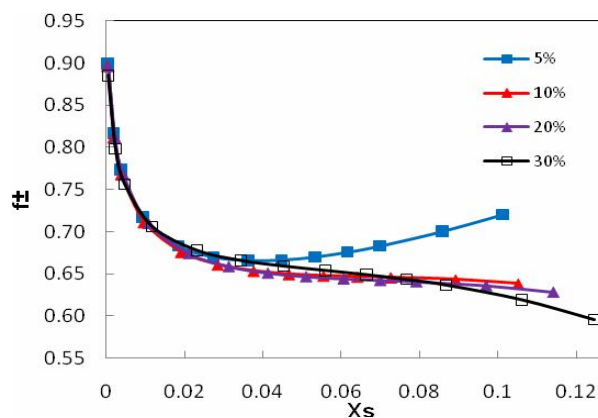
Fig. 7. The plot of the activity coefficient($f_\pm$) for NaCl *vs.* the mole fraction of the total ions (Xs) in various glycerol + water mixed solvent systems containing 5, 10, 20 and 30% mass fraction of glycerol at 298.2 K.
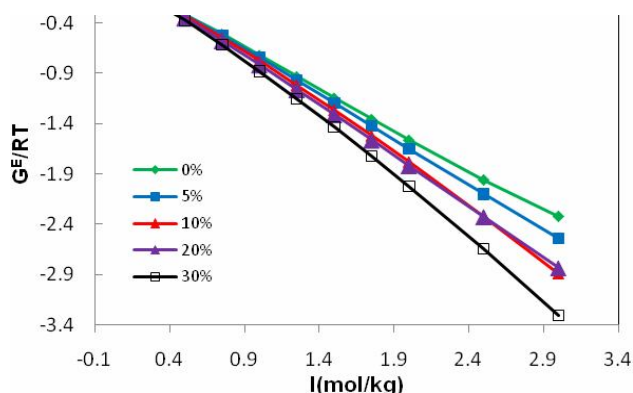
Fig. 8. Variation of excess Gibbs free energy (G^E/RT) calculated using Pitzer model with the ionic strength of NaCl electrolyte in various glycerol + water mixed solvent system containing 0, 5, 10, 20 and 30% mass fraction of glycerol at 298.2 K.

glycerol + water system were determined by potentiometric method using the modified zeolite as ionophore to fabricate the sodium ion selective electrode and Ag-AgCl electrodes at T = 298.2 K. We used the extended Debye-Hückel equation, the Pitzer and PSC ion-interaction model to get

Table 5. The Values Calculated of Osmotic Coefficients (φ), Excess Gibbs Free Energies (G^E) and Solvent Activity (a_s) as a Function of NaCl Molalities in Glycerol + water Mixtures at T = 298.2 K

I (mol kg^{-1})	φ	G^E/RT	a_s	I (mol kg^{-1})	φ	G^E/RT	a_s
wt% = 0				wt% = 5			
0.0100	0.9680	-0.0014	0.9997	0.0100	0.9669	-0.0015	0.9996
0.0500	0.9433	-0.0141	0.9983	0.0500	0.9415	-0.0146	0.9982
0.1000	0.9320	-0.0369	0.9967	0.1000	0.9300	-0.0381	0.9965
0.2500	0.9211	-0.1263	0.9917	0.2500	0.9188	-0.1303	0.9914
0.5000	0.9207	-0.3079	0.9836	0.5000	0.9178	-0.3176	0.9829
0.7500	0.9265	-0.5086	0.9753	0.7500	0.9221	-0.5254	0.9744
1.0000	0.9350	-0.7182	0.9669	1.0000	0.9284	-0.7437	0.9658
1.2500	0.9452	-0.9314	0.9584	1.2500	0.9355	-0.9676	0.9571
1.5000	0.9566	-1.1447	0.9497	1.5000	0.9432	-1.1944	0.9483
1.7500	0.9691	-1.3556	0.9408	1.7500	0.9510	-1.4221	0.9395
2.0000	0.9825	-1.5623	0.9317	2.0000	0.9588	-1.6494	0.9306
2.5000	1.0115	-1.9572	0.9130	2.5000	0.9743	-2.0993	0.9127
				3.0000	0.9888	-2.5395	0.8947
wt% = 10				wt% = 20			
0.0100	0.9658	-0.0015	0.9996	0.0100	0.9636	-0.0016	0.9996
0.0500	0.9396	-0.0151	0.9982	0.0500	0.9358	-0.0161	0.9980
0.1000	0.9277	-0.0394	0.9964	0.1000	0.9232	-0.0419	0.9960
0.2500	0.9158	-0.1346	0.9911	0.2500	0.9106	-0.1430	0.9903
0.5000	0.9130	-0.3289	0.9823	0.5000	0.9068	-0.3482	0.9807
0.7500	0.9145	-0.5460	0.9735	0.7500	0.9066	-0.5756	0.9712
1.0000	0.9165	-0.7766	0.9648	1.0000	0.9062	-0.8148	0.9619
1.2500	0.9182	-1.0169	0.9561	1.2500	0.9045	-1.0609	0.9527
1.5000	0.9189	-1.2647	0.9475	1.5000	0.9009	-1.3110	0.9437
1.7500	0.9186	-1.5193	0.9390	1.7500	0.8954	-1.5634	0.9350
2.0000	0.9170	-1.7802	0.9307	2.0000	0.8875	-1.8170	0.9267
2.5000	0.9095	-2.3214	0.9148	2.5000	0.8647	-2.3254	0.9114
3.0000	0.8957	-2.8914	0.9001	3.0000	0.8319	-2.8337	0.8985
wt% = 30							
0.0100	0.9609	-0.0017	0.9995				
0.0500	0.9312	-0.0173	0.9978				
0.1000	0.9178	-0.0450	0.9957				
0.2500	0.9049	-0.1535	0.9893				
0.5000	0.9023	-0.3741	0.9788				
0.7500	0.9041	-0.6202	0.9683				
1.0000	0.9061	-0.8815	0.9579				
1.2500	0.9073	-1.1539	0.9476				
1.5000	0.9072	-1.4353	0.9375				
1.7500	0.9054	-1.7250	0.9276				
2.0000	0.9019	-2.0228	0.9180				
2.5000	0.8888	-2.6442	0.8999				
3.0000	0.8674	-3.3053	0.8838				

Table 6. Total Mole Fraction of Ions (X_S), Ionic Strength on the Mole Fraction Scale (I_X), Mean activity Coefficient Based on Mole Fraction and the Excess Gibbs Free Energy Calculated Using PSC Model for NaCl Electrolyte in Various Glycerol + Water Mixed Solvent Systems Containing 5, 10, 20 and 30% Mass Fraction of Glycerol at 298.2 K

X_s	I_x	$f_{\pm,NaCl}$	g^{E}/RT	X_s	I_x	$f_{\pm,NaCl}$	g^{E}/RT
wt% = 5				wt% = 10			
0.0004	0.0001	0.8994	0	0.0004	0.0002	0.8964	0
0.0018	0.0009	0.8165	-0.0003	0.0019	0.0009	0.8118	-0.0003
0.0037	0.0018	0.7734	-0.0007	0.0039	0.0019	0.6780	-0.0008
0.0093	0.0046	0.7172	-0.0024	0.0097	0.0048	0.7113	-0.0026
0.0184	0.0092	0.6830	-0.0059	0.0192	0.0096	0.6758	-0.0062
0.0273	0.0136	0.6701	-0.0096	0.0285	0.0142	0.6607	-0.0102
0.0361	0.0180	0.6659	-0.0135	0.0377	0.0188	0.6533	-0.0143
0.0448	0.0224	0.6665	-0.0173	0.0460	0.0233	0.6495	-0.0148
0.0533	0.0266	0.6701	-0.0212	0.0555	0.0277	0.6475	-0.0228
0.0616	0.0308	0.6758	-0.0251	0.0641	0.0320	0.6464	-0.0270
0.0698	0.0349	0.6829	-0.0288	0.0726	0.0363	0.6456	-0.0312
0.0858	0.0429	0.7003	-0.0360	0.0892	0.0446	0.6431	-0.0396
0.1012	0.0506	0.7201	-0.0429	0.1051	0.0525	0.6382	-0.0479
wt% = 20				wt% = 30			
0.0004	0.0002	0.8962	0	0.0005	0.0002	0.8850	0
0.0021	0.0010	0.8112	-0.0003	0.0024	0.0012	0.1978	-0.0004
0.0042	0.0021	0.7671	-0.0008	0.0047	0.0023	0.7559	-0.0010
0.0106	0.0053	0.7098	-0.0028	0.0177	0.0058	0.7058	-0.0033
0.0210	0.0105	0.6739	-0.0068	0.0231	0.0115	0.6775	-0.0078
0.0312	0.0156	0.6585	-0.0112	0.0343	0.0172	0.6657	-0.0126
0.0411	0.0205	0.6507	-0.0158	0.0453	0.0226	0.6589	-0.0176
0.0509	0.0254	0.6464	-0.0204	0.0560	0.0280	0.6538	-0.0227
0.0605	0.0302	0.6439	-0.0251	0.0665	0.0332	0.6488	-0.0279
0.0698	0.0349	0.6421	-0.0298	0.0767	0.0383	0.6432	-0.0332
0.0790	0.0395	0.6403	-0.0344	0.0867	0.0433	0.6365	-0.0386
0.0969	0.0484	0.6357	-0.0436	0.1061	0.0530	0.6191	-0.0498
0.1141	0.0510	0.6280	-0.0527	0.1247	0.0623	0.5954	-0.0617

the associated parameters and calculation of thermodynamic properties. The results show that the Pitzer adjustable parameters linearly change with reciprocal value of the relative permittivity of the glycerol-water mixed solvent. Whereas, there is no an explicit relation between Debye-

Hückel parameters (a and d) and physical properties. It can be concluded that, although the PSC model describes the experimental data with less parameters (4 parameters) than those of Pitzer model (with 12 parameters), the Pitzer ion-interaction model satisfactorily describes the system under
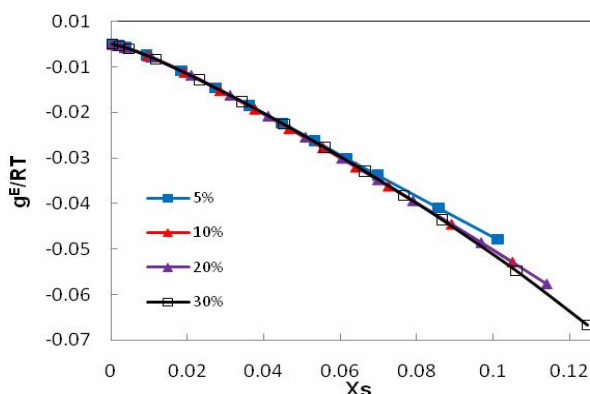
Fig. 9. Variation of excess Gibbs free energy (g^E/RT) calculated using PSC model *vs*. the mole fraction of the total ions (Xs) in various glycerol + water mixed solvent systems containing 5, 10, 20 and 30% mass fraction of glycerol at 298.2 K.

investigation.

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