Mean Activity Coefficients Measurements and Thermodynamic Modeling of the Ternary Mixed Electrolyte KCl + Lactose + Water System at T = 298.15 K

N.Z. Norouzi and M.A. Bagherinia*

Department of Chemistry, Faculty of Science, Lahijan Branch, Islamic Azad University, Lahijan, Iran
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In this work, the mean activity coefficients of KCl in the KCl + lactose + water system were determined using the potentiometric method. The electromotive force measurements were carried out on the galvanic cell without liquid junction of the type: Ag|AgCl|KCl (m), lactose (wt.%), H_2O (1 - wt.)%|K-ISE, in various mixed solvent systems containing 0, 5, 7.5, 10 and 12.5% mass fractions of lactose. The ionic strengths range was from 0.0003-2.000 kg mol^{-1}. The modeling of this ternary system was made based on the Pitzer ion-interaction model. The mean activity coefficients were correlated with Pitzer model and the adjustable Pitzer parameters (β^o, β^1 and C^{ϕ}) were determined for the series under investigated system. Then, these parameters were used to calculate the amounts of thermodynamic properties such as osmotic coefficients and excess Gibbs free energies for under investigated systems. The results clearly indicated that a good correlation was obtained with the Pitzer model to describe this system.

Keywords: Thermodynamic properties, KCl, Lactose, Pitzer model, Potentiometric method

INTRODUCTION

The most biological systems of interest contain ionic solutes such as Na^+ and K^+ which play a vital role in various metabolic activities. So, the measurement and modeling of mean activity coefficients of electrolyte systems of the type (electrolyte + sugar + water) are especially important for understanding the behavior of sugars in living organisms [1-4]. Saccharides and their derivatives are important compounds within biological systems. They are directly involved in the biology processes. For example, intestinal lactic acid transformed from lactose fermentation can improve the absorption and utilization of calcium, phosphorus, potassium, iron, and other mineral elements in food. Thermodynamic properties of electrolytes in saccharide solutions are important not only for studying the nature of interactions of saccharides with ions, but also for providing significant information on the stereo-structure of saccharide molecules and the action mechanism of their biological activity.

Hernandez-Luis [5-6], Zhou [4,7] and Ghalami [1,3,8-9] have determined activity coefficients of many electrolytes in aqueous saccharide solutions by electrochemical method. In our previous work [2], thermodynamic properties for ($MgCl_2$ + glocuse + water) system have been studied. Since the structure of disaccharides is very complicated, and their conformations can be influenced by many factors, thermodynamic properties such as activity coefficients of electrolytes in (disaccharide + water) mixtures are seldom reported, especially at high concentrations.

The present study includes the determination of mean ionic activity coefficients in aqueous KCl solutions containing lactose in an attempt to provide fundamental knowledge on ionic interactions in (electrolyte + sugar + water) solutions. The main goal of this work is to give scientific literature and precise thermodynamic data about the ternary system (KCl + Lactose + H_2O) which may allow modeling its behavior.

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*Corresponding author. E-mail: mabagherinia@liau.ac.ir

One ion-interaction model for electrolyte solution has been proposed to predict activity coefficients of each solute and osmotic coefficients of the aqueous systems by Pitzer [10-12]. To measure the thermodynamic properties of electrolytes in solutions such as (electrolyte + sugar + water), the most common methods are the isopiestic vapour pressure [13-14] and potentiometric techniques [1-7]. The electromotive force (emf) methods have the characteristics of simplicity and convenience in comparison with the other mentioned techniques.

In this work, the results pertaining/related to the thermodynamic properties of (KCl + Lactose + water) system using the potentiometric method are reported at T = 298.15 K. Thermodynamic properties of the mixed solvent solutions are useful in the prediction of the behavior of salt electrolyte in biological systems, development of the electrolyte solutions models, estimation of the interactions occurring in these solutions and so on. To our survey, there was not any report regarding the thermodynamic properties of KCl + Lactose + H_2O system. The potentiometric measurements reported in this work were carried out with a galvanic cell containing a solvent polymeric membrane K^+-ion selective electrode (K^+-ISE) and Ag-AgCl electrode that both of them were prepared in our laboratory and showed a reasonably good Nernst response. We have reported in our previous papers the ability of the solvent polymeric membrane electrodes for the determination of the activity coefficient for binary and ternary electrolyte solutions [2,15]. The stock solution of electrolyte was prepared by adding weighted amounts of KCl into the proportion volume of the Lactose-water as a mixed solvent. It can be noted that all of the Lactose-water mixed solvents were separately prepared by direct weighting. The determination of the activity coefficients of KCl in various Lactose-water mixed solvent systems containing 0.0, 5.0, 7.5, 10.0 and 12.5% mass fractions of Lactose were performed over ionic strength ranging from 0.0003-2.0000 mol kg^{-1}. The modeling of this ternary system was made based on the Pitzer ion-interaction model. Then, the Pitzer ion-interaction parameters (β^0, β^1 and C^o) for the series under investigated system were estimated by fitting experimental results with the model. Finally the excess Gibbs free energies and osmotic coefficients of water were calculated using the Pitzer ion-interaction parameters.

EXPERIMENTAL

Apparatus and Reagents

All of the potentiometric measurements were made using a digital multimeter (Eutech 2100) with a resolution of 0.1 mV. The solutions were continuously stirred using a magnetic stirrer (Delta Model HM-101) at a slow constant rate to avoid concentration gradients in the test solutions. A GFL model of circulation water bath was used to control the temperature of the test solution at 298.15 K ± 0.1. The conductivity measurements were carried out with a Metrohm 660 conductivity meter. An analytical balance (Sartorius GMBH 2842) with accuracy of 0.1 mg was used throughout all experiments. Acetophenone, potassium tetrakis(p-chlorophenyl) borate (KT_PClPB), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF), potassium choride (KCl), lactose and all other reagents used were purchased from Merk and Fluka and all of them were of analytical reagent grade (Table 1). All aqueous solutions were prepared by using doubly distilled water whose specific conductance was less than 2.0×10^{-4} s m^{-1}.

Preparation of the PVC Membrane Electrode and the Ag-AgCl Electrode

The general procedure used to prepare the PVC membrane was mixing thoroughly optimized amounts of 32.2 mg of powdered PVC, 61.6 mg plasticizer acetophenone and 1.2 mg additive KT_PClPB in 2 ml of dry freshly distilled THF. To this solution, for fabrication of the K^+-selective electrodes, 5 mg of valinomaycin as an ionophore was added and mixed very well. Valinomycin acted as a neutral carrier in plasticized polymeric membranes for the fabrication of K^+-selective electrods. The resulting clear mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated at the room temperature. 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 K^+-selective electrodes were backfilled each time with a KCl internal filling solution of 0.01 mol dm^{-3}. Then, the electrodes were conditioned in 0.01 mol dm^{-3} solution of KCl for 48 h. The K^+-selective electrode was calibrated

Table 1. Provenance and Mass Fraction Purity of the Components

IUPAC compound names	Abbreviations	Company	Mass fraction purity
Dibutyl phthalate	DBP	Fluka	≥0.99
Potassium tetrakis(*p*-chlorophenyl) borate	KT$_P$ClPB	Fluka	≥0.99
Poly(vinyl chloride)	PVC	Fluka	High molar
Tetrahydrofuran	THF	Fluka	≥0.99.5
Potassium chloride	KCl	Merck	≥0.99
Lactose	$C_{12}H_{22}O_{11}$	Merck	≥0.97

Table 2. Debye-Huckel Parameter Values for the Osmotic Coefficient ($A_{\emptyset}$), Solvent Relative Permittivity (ε_r) and Density (ρ) in Different Mass Fractions (wt.) of Lactose-water Mixed Solvent Systems at 298.15 K[a]

Lactose (wt.%)	$A_{\emptyset}$ (kg$^{1/2}$ mol$^{-1/2}$)	ε_r	P (kg m^{-3})
0	0.3915	78.38	997.2
5	0.4125	76.2	1016.962
7.5	0.4245	75.0	1027.178
10	0.4380	73.7	1037.578
12.5	0.4521	72.4	1048.161

[a]Standard uncertainties u with 0.68 level of confidence are: u(T) = 0.1 K, u(wt.) = 0.1 wt%. data (A_{ϕ}, ε_r and ρ) were taken from literature [18].

versus a saturated calomel reference electrode in the 1-10^{-4} mol dm^{-3} concentration range of a solution of pure KCl before using each series of measurements.

For fabrication of the Ag-AgCl electrode, an Ag wire was electrolyzed in 0.1 mol dm^{-3} HCl solution, as described in literature [16]. The Ag-AgCl electrode prepared was used as both internal reference and chloride selective electrode. The Ag-AgCl electrode was conditioned overnight in the appropriate mixed electrolyte system before each series of measurements. The Ag-AgCl electrode was calibrated

versus a saturated calomel reference electrode in the 1-10^{-4} mol dm^{-3} concentration range of a solution of pure KCl before using each series of measurements.

Potentiometric Measurements

The cell arrangement used in this work is described as follows:

(A) K-ISE|KCl (m), lactose (wt.%), H$_2$O (100-wt.)%|Ag-AgCl

where wt. was the mass fraction of lactose in the mixed solvent. The emf measurements of the galvanic cell (A) were made by using standard addition procedure. For this purpose, certain volumes of the concentrated electrolyte solutions were added into the cell containing a specified volume of Lactose-water as a mixed solvent, step by step. 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 during 20 min by using a multimeter. As usual, all measurements were performed under stirring conditions and the temperature was kept constant at 298.15 K (±0.1 K), employing a double-wall container enabling the circulation of thermostat water from a GFL model circulation.

PITZER ION INTERACTION MODEL

The Pitzer ion interaction model was used for the experimental data correlation and calculation of thermodynamic properties for the under investigated system [17]. According to the Pitzer model, the mean molal activity coefficient (γ±) for KCl in the mixed solvent was inscribed as:

$$\ln\gamma^o_{\pm KCl} = f^\gamma + B^\gamma_{KCl}I + 1.5C^\phi_{KCl}I^2 \tag{1}$$

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

$$B^\gamma_{MX} = 2\beta^\circ_{MX} + \frac{2\beta^1_{MX}}{\alpha^2_1 I}[1-(1+\alpha_1\sqrt{I} - \frac{\alpha^2_1}{2}I)e^{-\alpha_1\sqrt{I}}] \tag{3}$$

In these equations, α and b were assumed to be constant with the values of 2.0 and 1.2 kg$^{1/2}$ mol$^{-1/2}$, respectively, both in water and in lactose-water mixtures; I indicated the total ionic strength on a molality scale. The parameters β^0, β^1 and C$^\phi$ were interaction Pitzer parameters for a single salt electrolyte solution and they showed solute-specific interaction that their amounts should be determined for KCl in lactose-water mixtures. A$_\phi$ denoted the Debye-Huckel parameter for the osmotic coefficients defined by:

$$A_\phi = \frac{1.4006 \times 10^6 \rho^{\frac{1}{2}}}{(\varepsilon_r T)^{\frac{3}{2}}} \quad kg^{\frac{1}{2}}.mol^{-\frac{1}{2}} \tag{4}$$

where ρ was the solvent density (kg m^{-3}); ε$_r$ was the solvent relative permittivity; and T was the kelvin temperature. The Debye-Huckel parameter for the osmotic coefficients (A$_\phi$) of pure water and the mixture (lactose-water), together with the values of the physical properties (ρ and ε$_r$) was taken from the literature [18] and are shown in Table 2.

RESULTS AND DISCUSSION

Calibration of K$^+$-ISE and Ag/AgCl Electrode Pairs

For this purpose, the molalities of KCl in solutions (m) were selected from 0.0003 to 2.0000 mol kg^{-1} to determine the corresponding potentials (E$_A$) using the cell (A). The Nernst equation for the cell (A) was:

$$E_A = E' + k\log m^2_{A_0}.\gamma^{o2}_{\pm KCl} = E^0 + s\log I.\gamma^0_{\pm KCl} \tag{5}$$

where $k = (\ln10)$ RT/ZF represented Nernst slope. R, F, Z and T were the universal gas constant, Faraday constant, charge of ion, and absolute temperature, respectively. In this work, Z was equal to 1. $\gamma^0_{\pm KCl}$ was the mean activity coefficient of KCl in water as a pure solvent which can be calculated from Pitzer equation. The E° and s referred to the experimental standard potential and the Nernst slope, respectively. Also, the phrase of $I.\gamma^0_{\pm KCl}$ was equivalent of the activity of KCl (a_{KCl}) in solution.

The mean activity coefficients of KCl ($\gamma^0_{\pm KCl}$) in water were calculated based on Pitzer equation using the Pitzer parameters taken from the literature [19]. Then, the potentials determined were plotted against loga_{KCl} to check the efficiency of the respective electrode pair to determine the mean activity coefficients of KCl (Fig. 1). The amount of linear correlation coefficient (R^2 = 0.9999) showed that results obtained are in good agreement with the literature, [19] and the electrode pair used was well suitable for our measurements. The mean activity coefficients of KCl in pure water determined in this work were compared with the literature [19] in Fig. 2. As shown in the Fig. 2, there was a good agreement between them. In the other word,
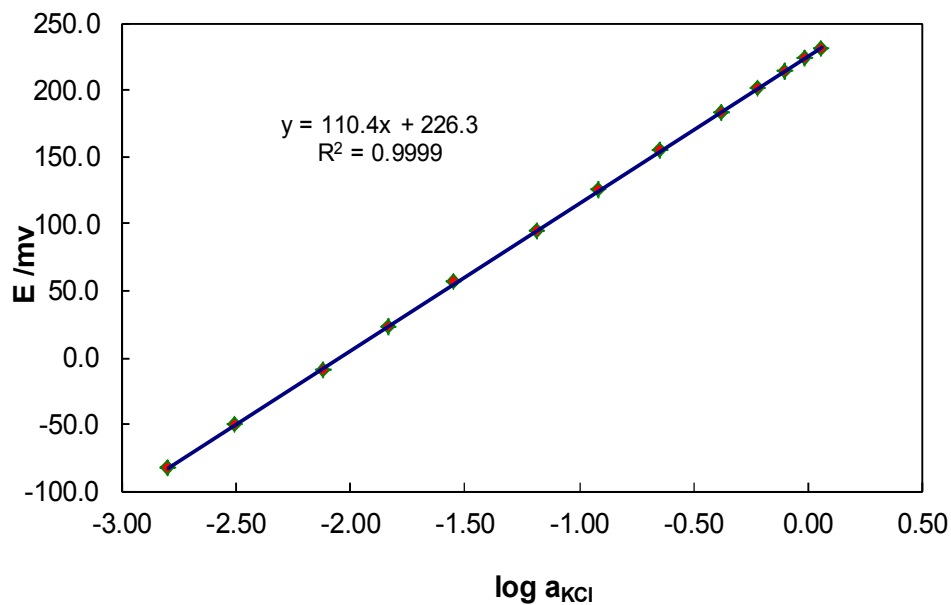
Fig. 1. The plot of emf *vs*. loga_{KCl} to check the efficiency of the respective electrode pair at 298.15K.
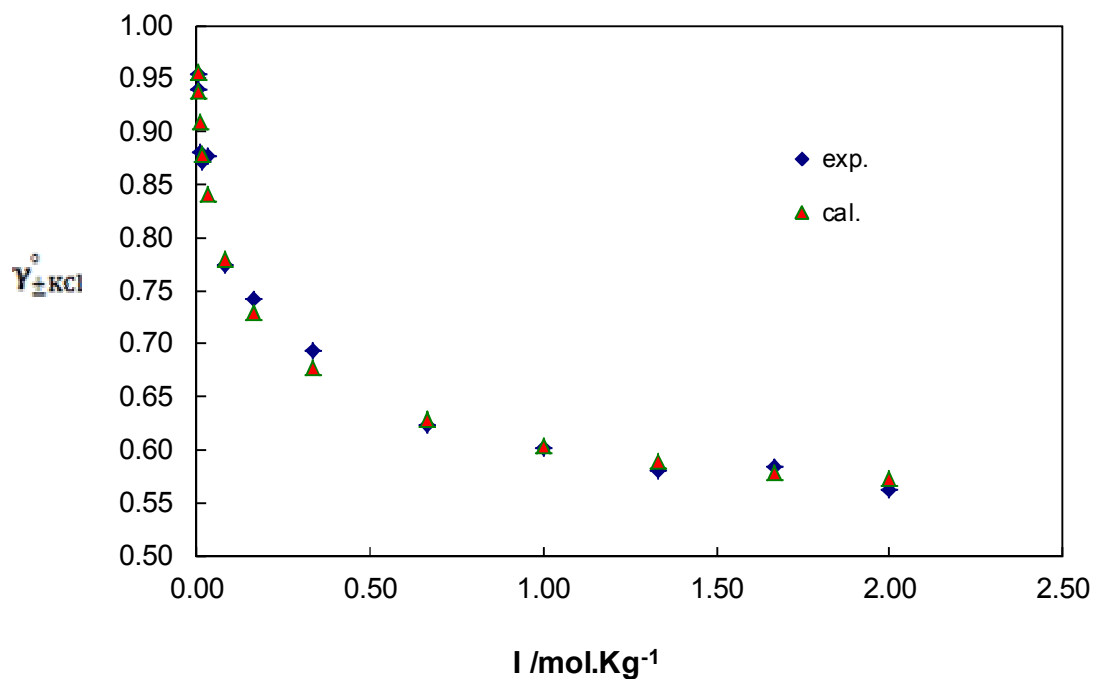
Fig. 2. Correlation of the experimental mean activity coefficients of KCl (exp.) with the calculated mean activity coefficients (cal.).

Table 3. The Values of Measured emf in Different Mass Fractions of Lactose (wt.) at 298.15 K[a]

m (mol Kg^{-1})	E (mV) wt.% = 0.0	E (mV) wt.% = 5.0	E (mV) wt.% = 7.5	E (mV) wt.% = 10.0	E (mV) wt.% = 12.5
0.0003	-74.5	-93.5	-87	-82	-91.1
0.0008	-53.7	-72.1	-66.1	-60.7	-66.5
0.0017	-39.3	-55.9	-57.5	-45.3	-49.2
0.0033	-26.1	-39.9	-42.1	-29.1	-38.4
0.0083	-3.8	-18.9	-18.7	-10.9	-16.8
0.0167	11.1	-4.9	-2.8	0.6	-3.5
0.0333	24.9	11.2	12.2	13.2	7.6
0.0833	44.5	31.2	32.6	32.8	28.2
0.1667	60.0	47.0	49.0	48.4	45.1
0.3333	75	61.8	64.7	63.3	61.8
0.6667	89.4	76.3	79.9	79.4	81.3
1.0000	97.6	84.8	89.0	89.2	92.8
1.3333	104.5	91.3	95.4	96.4	100.7
1.6667	109.9	96.5	100.9	102.5	107.7
2.0000	114.2	100.6	105.2	107.4	113.8

[a]Standard uncertainties, u, with 0.68 level of confidence are: $u(T) = 0.1$ K, $u_r(m) = 0.0001$, $u(E) = 0.1$ mV, and $u(wt.) = 0.1$ wt%.

Table 4. The Slope of Pair Electrode (s) and the Experimental Standard Potential (E°) for KCl Electrolyte in Different Mass Fractions of Lactose (wt.) at 298.15 K

Lactose (wt.%)	0.0	5.0	7.5	10.0	12.5
s (mV decade^{-1})	110.4	109.7	115.6	114.3	117.1
u(s) (mV decade^{-1})	0.12	0.15	0.16	0.14	0.17
E° (mV)	226.3	254.8	262.3	248.9	255.6
u(E°) (mV)	0.22	0.19	0.26	0.17	0.21

[a]Standard uncertainties, u, with 0.68 level of confidence are $u(T) = 0.1$ K, and $u(wt.) = 0.1$ wt%.
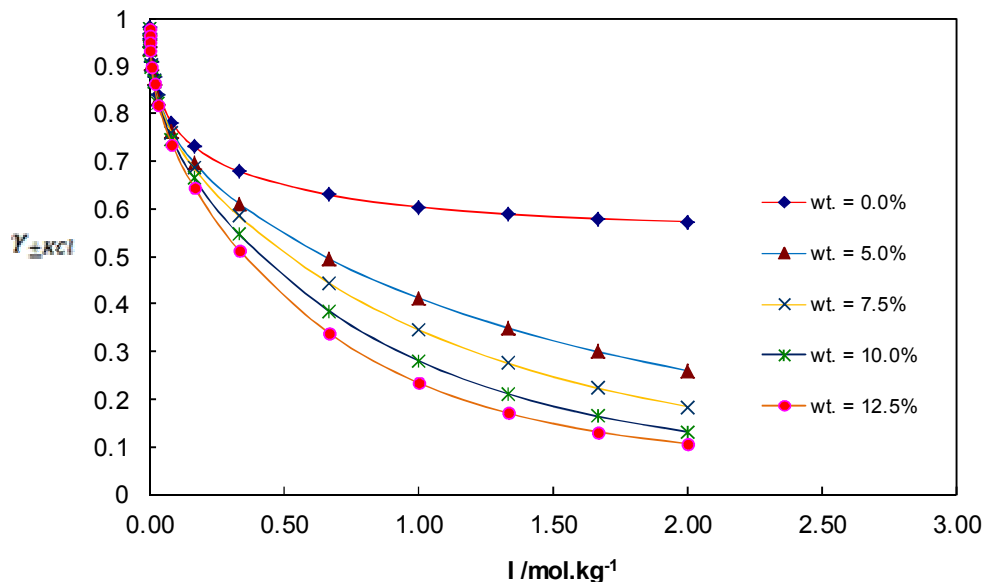
Fig. 3. The plot of the values of mean activity coefficients of KCl *vs.* total ionic strength at different mass fractions of Lactose at 298.15 K.
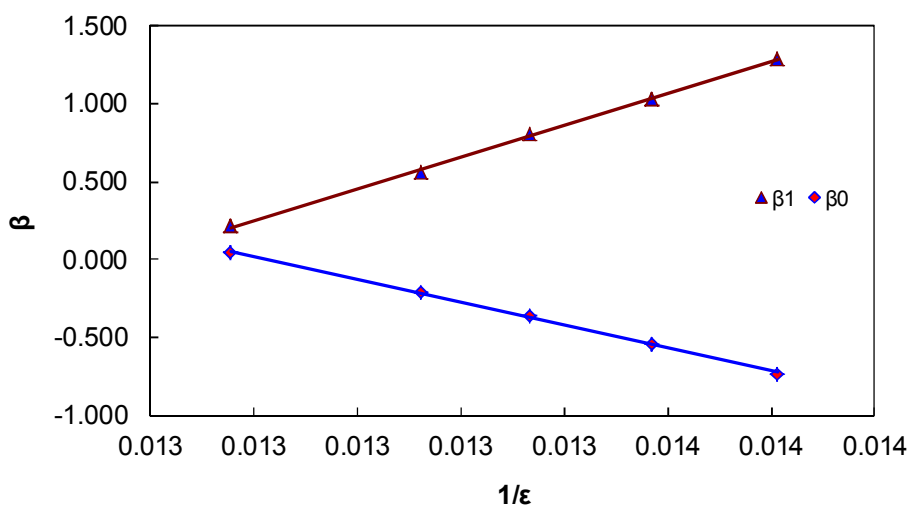
Fig. 4. Variation of β^o and β^1 *vs.* the reciprocal value of the relative permittivity of the lactose-water mixture in different mass fractions of lactose at 298.15 K.

correlation of the experimental mean activity coefficients with the mean activity coefficients calculated based on the Pitzer equation using the Pitzer parameters taken from ref. [19] supported this subject.

Determination of the Mean Activity Coefficients and Pitzer Parameters

The emf measurements of the cell (A) were measured at different series of electrolyte molalities in lactose-water

Table 5. The Values Obtained for Pitzer Ion Parameters and Standard Deviation (σ) of the Fits for KCl Electrolyte in Different Mass Fractions of Lactose (wt.) at 298.15 K[a]

Lactose (wt.%)	β^0	β^1	$C^{\o}$	σ
0[b]	0.04835	0.2122	-0.0008	-
5.0	-0.2155	0.5599	0.02154	0.0041
7.5	-0.3668	0.8101	0.04809	0.0083
10.0	-0.5413	1.0289	0.09445	0.0243
12.5	-0.7320	1.2897	0.1698	0.0256

[a]Standard uncertainties, u, with 0.68 level of confidence are: u(T) = 0.1 K, and u(wt.) = 0.1 wt%.
[b]Taken from the literature [19].

Table 6. The Values of Osmotic Coefficients ($\emptyset$) and the Excess Gibbs Free Energy (G^E) for Different Series of Lactose Mass Fraction (wt.) in Mixed Solvents at 298.15 K[a]

M (mol Kg^{-1})	$\emptyset$	G^E/RT	m (mol Kg^{-1})	$\emptyset$	G^E/RT
wt.% = 0.0			wt.% = 5.0		
0.0003	0.9934	0.0000	0.0003	0.9931	0.0000
0.0008	0.9894	0.0000	0.0008	0.9889	-0.0001
0.0017	0.9850	-0.0001	0.0017	0.9843	-0.0005
0.0033	0.9797	-0.0002	0.0033	0.9788	-0.0017
0.0083	0.9697	-0.0010	0.0083	0.9683	-0.0036
0.0167	0.9597	-0.0051	0.0167	0.9576	-0.0090
0.0333	0.9478	-0.0104	0.0333	0.9439	-0.0241
0.0833	0.9298	-0.0352	0.0833	0.9185	-0.0700
0.1667	0.9159	-0.0752	0.1667	0.8890	-0.1418
0.3333	0.9039	-0.1889	0.3333	0.8439	-0.2908
0.6667	0.8975	-0.4795	0.6667	0.7876	-0.6150
1.0000	0.8999	-0.8190	1.0000	0.7762	-1.0139
1.3333	0.9073	-1.1488	1.3333	0.8119	-1.4326
1.6667	0.9184	-1.4871	1.6667	0.8959	-2.0498
2.0000	0.9328	-1.8806	2.0000	1.0285	-2.9885

Table 6. Continued

wt.% = 7.5			wt.% = 10.0		
0.0003	0.9928	0.0000	0.0003	0.9926	0.0000
0.0008	0.9885	-0.0002	0.0008	0.9881	-0.0001
0.0017	0.9835	-0.0015	0.0017	0.9829	-0.0006
0.0033	0.9775	-0.0035	0.0033	0.9766	-0.0015
0.0083	0.9655	-0.0087	0.0083	0.9638	-0.0070
0. 0167	0.9523	-0.0195	0.0167	0.9492	-0.0219
0. 0333	0.9333	-0.0448	0.0333	0.9277	-0.0557
0.0833	0.8909	-0.1251	0.0833	0.8767	-0.1565
0.1667	0.8318	-0.2483	0.1667	0.8027	-0.3172
0.3333	0.7309	-0.4827	0.3333	0.6739	-0.6241
0.6667	0.5936	-0.9158	0.6667	0.4991	-1.1046
1.0000	0.5530	-1.3931	1.0000	0.4527	-1.6126
1.3333	0.6157	-2.1257	1.3333	0.5441	-2.4141
1.6667	0.7844	-3.2479	1.6667	0.7770	-3.7471
2.0000	1.0602	-5.0585	2.0000	1.1531	-5.9677
wt.% =12.5					
0.0003	0.9925	0.0000			
0.0008	0.9880	-0.0001			
0.0017	0.9830	-0.0004			
0.0033	0.9771	-0.0027			
0.0083	0.9654	-0.0089			
0. 0167	0.9524	-0.0247			
0. 0333	0.9332	-0.0676			
0.0833	0.8848	-0.1902			
0.1667	0.8076	-0.3833			
0.3333	0.6619	-0.7307			
0.6667	0.4503	-1.1683			
1.0000	0.386	-1.6071			
1.3333	0.4872	-2.4220			
1.6667	0.7615	-3.8463			
2.0000	1.2120	-6.2687			

[a]standard uncertainties, u, with 0.68 level of confidence are: $u(T) = 0.1$ K, $u_r(I) = 0.0001$, $u(\o)$ = 0.001, $u(G^E/RT) = 0.001$, and u(wt.) = 0.1 wt%.
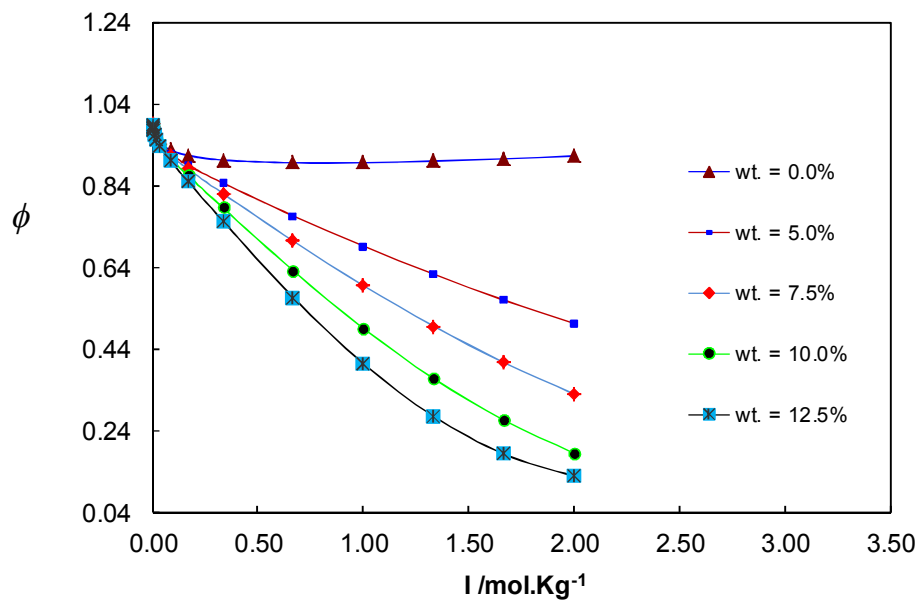
Fig. 5. The plot of the osmotic coefficients of water against total ionic strength at different mass fractions of Lactose at 298.15 K.
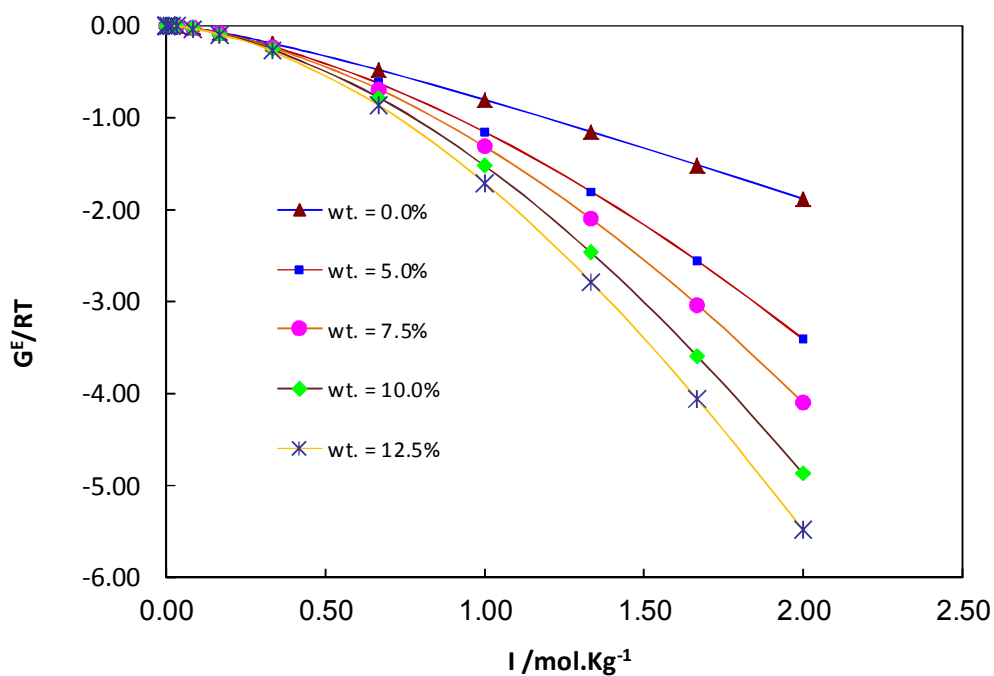
Fig. 6. The plot of the excess Gibbs energy for the solution against total ionic strength at different mass fractions of Lactose at 298.15 K.

mixture as solvents through changing of electrolyte concentration by standard addition method (Table 3). Then, the mean activity coefficients of KCl in solutions were determined from the emf measurements in according to Eq. (5). In order to achieve the accuracy of the mean activity coefficient values, the corresponding slope (s) and the experimental standard potential (E^o) were determined before performing each series of measurements in systems for concentration range 10^{-1}-10^{-4} mol kg^{-1} (Table 4). Figure 3 presents the variation of the mean activity coefficients of KCl *vs.* the ionic strength in water, and different mass fractions of lactose in mixed solvents at T = 298.15 K. It can be observed that the values of the mean activity coefficients decrease with increasing the ionic strength of electrolyte. At the same time, when the ionic strength is fixed, the values of the mean activity coefficient decrease with increasing the mass fraction of lactose in lactose-water mixed solvent. This trend of changes for the mean activity coefficient showed that electrostatic interactions were stronger than other interactions.

The Pitzer ion interaction parameters were determined by an iteration minimization procedure employing the Microsoft MATLAB program. Table 5 shows the resulting β^0, β^1 and $C^\varnothing$ Pitzer ion-interaction parameters, from iteration minimization procedure for the investigated systems at T = 298.15 K. The values of β^o and β^1 obtained were plotted against the reciprocal value of the relative permittivity of the lactose-water mixture solvent (Fig. 4). As observed, both β^o, which could be identified with the total binary ionic interactions, and β^1, which could be identified with the interactions between unlike-charged ions, changed linearly with $1/\varepsilon$.

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Calculation of Thermodynamic Properties by the Pitzer Model

The Pitzer parameters obtained were used to calculate the thermodynamic properties of under investigation system by the Pitzer model. The osmotic coefficients (ø) and the excess Gibbs free energy (G^E) for all of the under investigation series can be calculated using the following equations:

$$\phi - 1 = 2f^\phi + IB_{KCl}^\phi + I^2 C_{KCl}^\phi \tag{6}$$

$$f^\phi = -\frac{A_\phi \sqrt{I}}{1 + b\sqrt{I}} \tag{7}$$

$$B_{KCl}^\phi = \beta_{KCl}^0 + \beta_{KCl}^1 \exp(-\alpha_1 \sqrt{I}) \tag{8}$$

$$\frac{G^E}{RT} = 2I\,(1 - \phi + \ln \gamma_{\pm KCl}) \tag{9}$$

The values of these thermodynamic properties were illustrated in Table 6 for different series of lactose mass fraction in mixed solvents. Figures 5 and 6 showed the plot of osmotic coefficients (ø) and the excess Gibbs free energy (G^E) *vs.* the ionic strength, respectively. It can be seen that the excess Gibbs free energy is increased by increasing the mass fraction of lactose in mixed solvent.

CONCLUSIONS

The mean activity coefficients of KCl in the (KCl + Lactose + water) system were determined by a potentiometric method using a solvent polymeric ion-selective membrane electrode and Ag-AgCl electrodes at T = 298.15 K. We used the Pitzer ion-interaction model to get the Pitzer parameters (β^0, β^1 and $C^\varnothing$) and the thermodynamic properties such as the osmotic coefficients (ø) and excess Gibbs free energy (G^E). The results showed that the Pitzer adjustable parameters linearly change with the reciprocal value of the relative permittivity of the lactose-water mixed solvent. The results showed that the Pitzer ion-interaction model satisfactorily describes the system under investigation.

ACKNOWLEDGMENTS

REFERENCES

[1] Ghalami-Choobar, B.; Shafaghat-Lonbar, M.; Mossayyebzadeh-Shalkoohi, P., Activity coefficients determination and thermodynamic modeling of (NaCl + Na$_2$HCit + glucose + H$_2$O) system at T =

(298.2 and 308.2) K, *J. Mol. Liq.* **2015**, *212*, 922-929, DOI:10.1016/j.molliq.2015.10.051.

[2] Rouhi, A.; Bagherinia, M. A., Mean activity coefficient measurement and thermodynamic modeling of the ternary mixed electrolyte (MgCl₂ + glucose + water) system at T = 298.15 K, *J. Chem. Thermodyn.* **2015**, *91*, 286-291, DOI: 10.1016/j.jct.2015.07.049.

[3] Ghalami-Choobar, B.; Mohammadian, M., Thermodynamic modeling of the KCl + glucose + water system based on potentiometric measurements at 298.15 K, *J. Mol. Liq.* **2010**, *154*, 26-30, DOI: 10.1016/j.molliq.2010.03.008.

[4] Zhuo, K.; Liu, H.; Zhang, H.; Liu, Y.; Wang, J., Activity coe-cients of CaCl₂ in (maltose + water) and (lactose + water) mixtures at 298.15 K, *J. Chem. Thermodyn.* **2008**, *40*, 889-896, DOI: 10.1016/j.jct.2007.12.008.

[5] Herna´ndez-Luis, F.; Galleguillos, H. R.; Vazquez, M. V., Activity coefficients of NaF in (glucose + water) and (sucrose + water) mixtures at 298.15 K, *J. Chem. Thermodyn.* **2004**, *36*, 957-964. DOI: 10.1016/j.jct.2004.07.002.

[6] Herna´ndez-Luis, F.; Grandoso, D.; Lemus, M., Activity coefficients of NaCl in fructose + water at 298.15 K, *J. Chem. Eng. Data,* **2004**, *49*, 668-674. DOI: 10.1021/je034240g.

[7] Zhuo, K.; Wang, Y. P.; Liu, Q.; Zhang, H.; Wang, J., Thermodynamic and conductivity properties of Cd(NO₃)₂ in monosaccharide (D-glucose, D-galactose, D-xylose, D-ribose) + water systems at 298.15 K, *J. Solution Chem.* **2006**, *35*, 753-768. DOI 10.1007/s10953-006-9022-4.

[8] Ghalami-Choobar, B. A.; Ghalami-Choobar, B. E., Thermodynamic modeling of the KCl + formamide/glucose/proline + water ternary systems and activity coefficient prediction based on artificial neural network, *J. Mol. Liq.* **2015**, *207*, 136-144, DOI:10.1016/j.molliq.2015.03.028.

[9] Ghalami-Choobar, B.; Mirzaie, S., Thermodynamic study of (KCl + proline + water) system based on potentiometric measurements at T = (298.2 and

303.2) K, *J. Mol. Liq.* **2012**, *169*, 124-129, DOI: 10.1016/j.molliq.2012.02.009.

[10] Pitzer, K.S.; Thermodynamics of electrolytes. I. Theoretical basis and general equations, *J. Phys. Chem.* **1973**, *77*, 268. DOI: 10.1021/j100621a026

[11] Pitzer, K. S.; Mayorga, G., Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent, *J. Phys. Chem.* **1973**, *77*, 2300-2308, DOI: 10.1021/j100638a009.

[12] Pitzer, K. S., Activity Coefficients in Electrolyte Solutions, Second ed., CRC Press, Boca Raton, FL, 1991, p. 99.

[13] Lay, W. K.; Miller, M. S.; Elcock, A. H., Reparameterization of solute-solute interactions for amino acid-sugar systems using isopiestic osmotic pressure molecular dynamics simulations, *J. Chem. Theory Comput.* **2017**, *13*, 1874-1882, DOI: 10.1021/acs.jctc.7b00194.

[14] Shinde, S. P.; Dagade, D. H., Osmotic and activity coefficients for binary aqueous solutions of 1-butyl-3-methylimidazolium based amino acid ionic liquids at 298.15 K and at 0.1 MPa, *J. Chem. Eng. Data,* **2015**, *60*, 635-642, DOI: 10.1021/je500772z.

[15] Bagherinia, M. A.; Giahi, M.; Pournaghdy, M.; Vaghar, G. R., Thermodynamic investigation of the ternary mixed aqueous electrolyte (MgCl₂ + MgSO₄) system by potentiometric method at T = 298.15 K, *J. Chem. Thermodyn.* **2012**, *44*, 169-176. DOI: 10.1016/j.jct.2011.08.020

[16] Bates, R. G., Determination of pH, Theory and Practice, Second ed., John Wiley, New York, 1964.

[17] Pitzer, K. S.; Thermodynamics, 3 rd Ed., McGraw-Hill, New York, 1995, p. 291.

[18] Hernandez-Luis, F.; Galleguillos, H. R.; Vazquez, M. V., Activity coefficients of NaF in (glucose + water) and (sucrose + water) mixtures at 298.15 K, *J. Chem. Thermodyn.* **2004**, *36*, 957, DOI: 10.1016/j.jct.2004.07.002.

[19] Kim, H. T.; Frederick, W. J., Evaluation of Pitzer ion interaction parameters of aqueous electrolytes at 25.degree.C. 1. Single salt parameters, *J. Chem. Eng. Data,* **1988**, *33*, 177-184. DOI: 10.1021/je00052a035.