PREDICT THE PROPERTIES OF AQUEOUS MIXED ELECTROLYTE SOLUTIONS FROM PROPERTIES OF THE INDIVIDUAL ELECTROLYTE SOLUTION

Kh. Nasrifar	**Sh. Ayatollahi**	**M. Moshfeghian**
Institute of Petroleum Engineering	**Dept. of Chemical Engineering**	**Dept. of Chemical Engineering**
University of Tehran	**Shiraz University**	**University of Qatar**
Iran	**Shiraz, Iran**	**Doha, Qatar**

ABSTRACT

For calculating the thermodynamic properties of mixed electrolyte solutions, a thermodynamic framework is developed. The vapor pressure, density and osmotic coefficient of several mixed electrolyte solutions are predicted and compared with the experimental data and the prediction of other models. The agreement is quite good. The average of absolute error is 0.1 % for predicting the vapor pressure and density of electrolyte solutions and 1.3 % for predicting the osmotic coefficient.

Key words: Electrolyte, Mixing Rule, Density, Vapor Pressure, Osmotic Coefficient

INTRODUCTION

For design of processes dealing with the phase equilibria of systems containing salts, the thermodynamics of electrolyte solutions plays an important role. Often, the most important property is the excess Gibbs energy of single or mixed electrolyte solution [1]. Equally important is, however, the vapor pressure and density of the electrolyte solutions.

Although the measuring and correlation of single salt solutions for a wide range of conditions are not easy tasks, the measuring and correlation of mixed electrolyte solutions are more cumbersome. The more salts in a system, the wider rang of experimental data is needed. Consequently, developing predictive methods for calculating the thermodynamic properties of mixed electrolyte solutions is needed.

Few thermodynamic models have been developed to calculate the properties of mixed electrolyte solutions. Patwardhan and Kumar [2,3] introduced an empirical framework based on ionic strength corresponding states. Later, they improved their model for systems having unlike ions [4]; however, it has no generality.

In this paper, a semi-theoretical framework based on mean ionic charge corresponding state is introduced. Equations for calculating properties like vapor pressure, density and osmotic coefficient are obtained. The predictions are compared to the experimental data and other models.

II. THERMODYNAMIC FRAMEWORK

Let a mixed electrolyte solution be consisted of $1000/MW_w$ moles of water and m_j moles of electrolyte j. The Gibbs-Duhem equation is then expressed by:

$$\frac{1000}{MW_w} d\overline{M}_w + \sum_j^{nel} m_j d\overline{M}_j = 0 \tag{1}$$

where nel is the number of electrolytes and $\overline{M}$ is the partial molar property. Then, assume that each electrolyte is separated from the others and confined in an imaginary cell. Each cell will contain m_j moles of the electrolyte and n_{wj} moles of water. The number of moles of water in the cells are subjected to the constraint,

$$\sum_k^{nel} n_{w,k} = 1000/MW_w \tag{2}$$

Eq. (2) implies that the total number of moles of water in the mixed electrolyte solution is proportioned to the

cells. A further assumption is that the short-range and long-range interactions are neglected among the various cells. This means that only the interactions in the interior of each cell are considered. Using the above-mentioned assumptions, the Gibbs-Duhem relation can be written for each cell,

$$n_{w,j} d\overline{M}^{\circ}_{w,j} + m_j d\overline{M}_j = 0 \tag{3}$$

where $\overline{M}^{\circ}_{w,j}$ is the partial molar property of water in cell j. Combining Eqs. (1) and (3) gives:

$$d\overline{M}_w = \sum_j^{nel} \Phi_j d\overline{M}^{\circ}_{w,j} \tag{4}$$

with

$$\Phi_j = \frac{n_{w,j}}{1000 / MW_w} \tag{5}$$

where Φ_j is the fraction of total moles of water in cell j. When electrolytes are dissolved in water, ions are produced. Assuming complete dissociation, the ions are hydrated by water molecules in different proportions. In other words, cationic charges are hydrated by more water molecules than anionic charges [5]. Consequently, one would expect that the fraction of water molecules in each cell is proportional to the charge number. In order to consider both the anionic and cationic charges, we define mean ionic charge by:

$$Mean\ ionic\ charge = m_{\pm} z_{\pm} = m \left(v_+^{v_+} v_-^{v_-} \right)^{\frac{1}{v}} \left(z_+^{z_+} z_-^{z_-} \right)^{\frac{1}{z}} \tag{6}$$

where $v = v_+ + v_-$ and $z = z_+ + z_-$. Now we propose that the faction of water molecules in each cell is proportional to the mean ionic charge of the electrolyte in the cell,

$$\frac{n_{w,j}}{1000 / MW_w} = K\, m_{\pm,j} z_{\pm,j} \tag{7}$$

where K is the proportionality constant. Substituting Eq. (7) into Eq.(2) yields:

$$K = \frac{1}{\sum_k^{nel} m_{\pm,k} z_{\pm,k}} \tag{8}$$

Comparing Eqs. (7), (8) and (5) gives:

$$\Phi_j = \frac{m_{\pm,j} z_{\pm,j}}{\sum_k^{nel} m_{\pm,k} z_{\pm,k}} \tag{9}$$

Eqs. (4) and (9) are our thermodynamic framework. The parameter $\overline{M}^{\circ}_{w,j}$ is to be calculated for a cell containing m_j moles of electrolyte and $n_{w,j}$ moles of water. Thus, noting to Eqs. (5) and (9), the molality of the electrolyte j in its cell (m_j°) is calculated from

$$m_j^{\circ} = \frac{m_j}{n_{w,j}} \times \frac{1000}{MW_w} = m_j \frac{\sum_k^{nel} m_{\pm,k} z_{\pm,k}}{m_{\pm,j} z_{\pm,j}} \tag{10}$$

Eq. (10) along with Eqs. (4) and (9) complete our formulation. Eq. (10) can be rearranged to obtain:

$$m_{\pm,j}^{\circ} z_{\pm,j} = \sum_k^{nel} m_{\pm,k} z_{\pm,k} \tag{11}$$

Eq. (11) has a simple interpretation, i.e., each cell must have the same mean ionic charge as the mixed electrolyte solution. In other words, the cells are in corresponding states with respect to mean ionic charge.

III. RESULTS AND DISCUSSION

In this section, equations for predicting the vapor pressure, osmotic coefficient and density of mixed electrolyte solutions are derived.

1. Vapor pressure

At low and moderate pressures, the vapor pressure of an aqueous electrolyte solution might be related to pure water vapor pressure as:

$$a_w = \frac{p}{p_w} \tag{12}$$

where a_w is the activity of water, p is the vapor pressure of solution and p_w is the pure water vapor pressure. Having predicted a_w, the vapor pressure of aqueous solution is predicted. If we take $M=G$ and noting that,

$$d\overline{G}_w = RTd\ln a_w \tag{13}$$

Eq. (4) is reduced to:

$$d\ln a_w = \sum_j^{nel} \Phi_j d\ln a_{w,j}^o \tag{14}$$

Integrating Eq. (14) from pure water to real state yields:

$$\ln a_w = \sum_j^{nel} \Phi_j \ln a_{w,j}^o \tag{15}$$

In this work the activity of water in cell j ($a_{w,j}^o$) is calculated from the equation given by Pitzer and Mayorga [6].

In Table 1 the vapor pressures of 9 binary electrolyte solutions and 1 ternary electrolyte solution are compared with the experimental data and the results obtained from the equation of Patwardhan and Kumar [2]. The average of absolute deviations was found to be 0.11%. Comparison with the equation of Patwardhan and Kumar [2] shows that both models predict the vapor pressures of solutions with the same accuracy. Figure 1 shows a deviation plot for predicting the vapor pressure of mixed electrolyte solutions given in Table 1. As can be seen, with increasing the ionic strength, the deviations increase. However, most of the deviations are between -0.2% and 0.2%.

Table 1
Average absolute percent deviation (%AAD)[a] for predicting the vapor pressure of aqueous systems at 298.15 K

Aqueous System	n	I_{max} (mol.kg^{-1})	Ionic Strength of the second salt (%)	Ref.	%AAD[a]	
					This work	PK
LiCl+BaCl$_2$	20	4	20-80	[7]	0.074	0.159
CsCl+BaCl$_2$	24	4	20-80	[7]	0.131	0.122
MgCl$_2$+Mg(NO$_3$)$_2$	9	4	14-63	[8]	0.042	0.042
MgCl$_2$+Ca(NO$_3$)$_2$	8	5.7	28-52	[8]	0.239	0.239
Mg(NO$_3$)$_2$+CaCl$_2$	13	4.2	29-79	[8]	0.243	0.243
Mg(NO$_3$)$_2$+Ca(NO$_3$)$_2$	6	6	21-75	[8]	0.098	0.098
CaCl$_2$+Ca(NO$_3$)$_2$	6	5.9	15-90	[8]	0.089	0.089
HClO$_4$+UO$_2$(ClO$_4$)$_2$	21	5.1	25-75	[9]	0.066	0.019
NaClO$_4$+UO$_2$(ClO$_4$)$_2$	20	6	25-75	[9]	0.112	0.178
HClO$_4$+LiCLO$_4$+NaClO$_4$	27	4.4	10-45	[10]	0.104	0.104

a

$$\%AAD = (100/n)\sum_j^{nel} \left| p_{cal,j} - p_{exp,j} \right| / p_{exp,j}$$
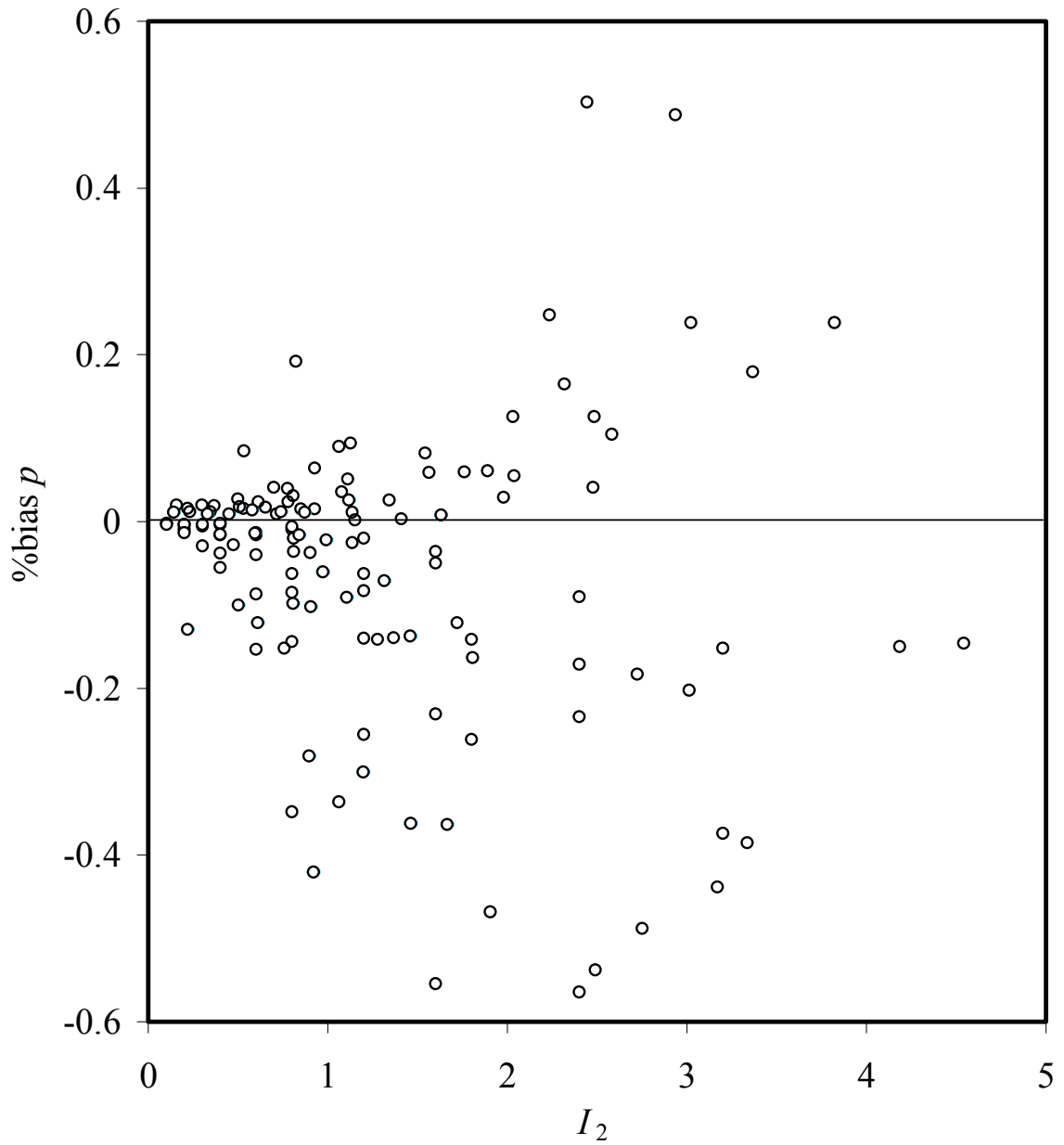
Fig. (1) Percent of deviations for predicting the vapor pressure of aqueous systems given in Table 1 as a function of the ionic strength of the second salt

2. Osmotic coefficient

Osmotic coefficient is related to the activity of water by:

$$\phi = -1000 \ln a_w / [MW_w \nu m] \tag{16}$$

Combining Eqs. (16) and (15) yields:

$$\phi = \frac{\sum_{j}^{nel} \Phi_j \nu_j m_j^{\circ} \phi_j^{\circ}}{\sum_{j}^{nel} \nu_j m_j} \tag{17}$$

In Figure 2 the predicted osmotic coefficients are compared with the observed values. The parameter ϕ_j° is calculated from the equation given by Pitzer and Mayorga [6]. As can be seen there are good agreements between the predicted and experimental values. The average of absolute error was found to be 1.3%.
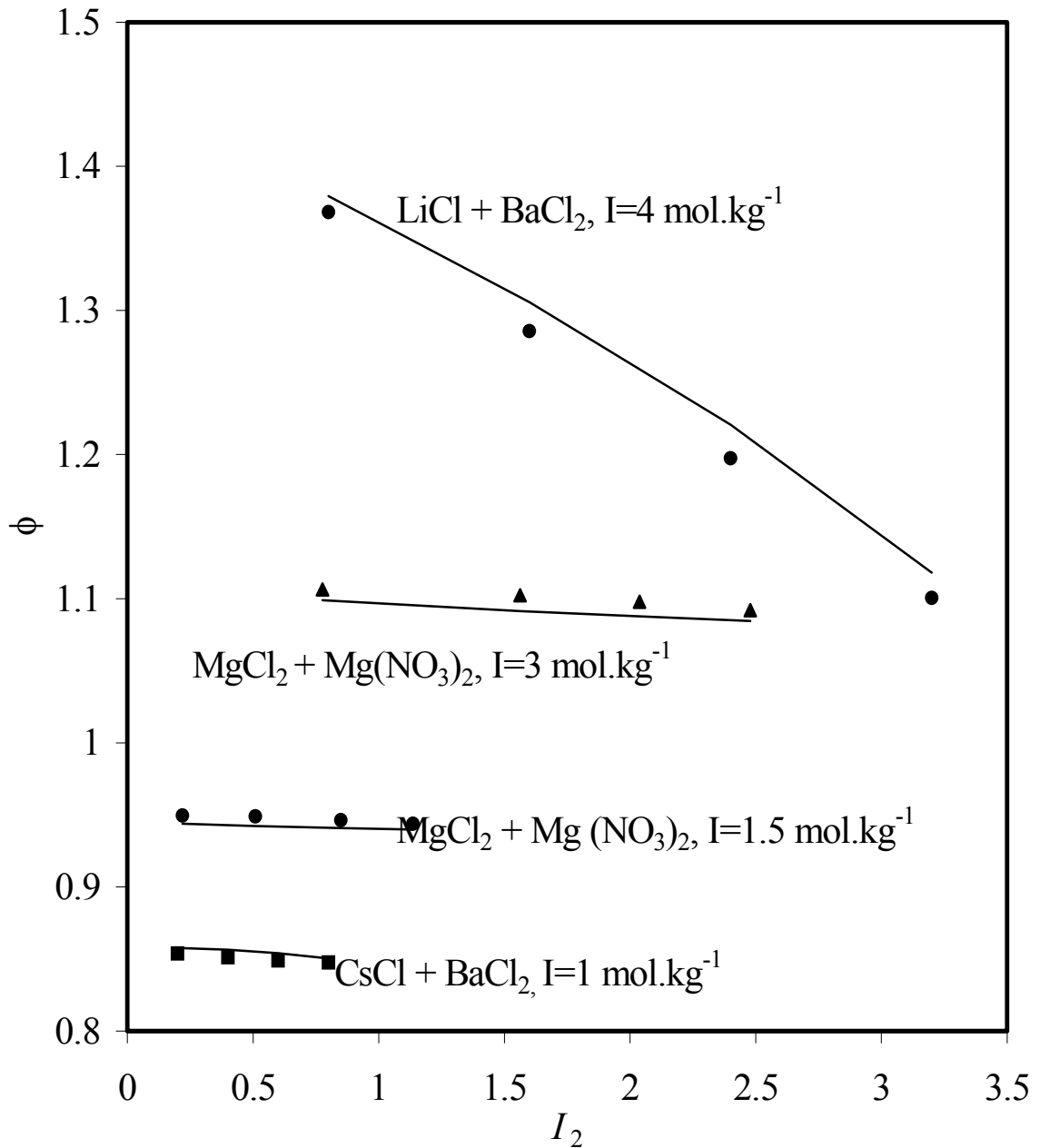

Fig. (2) Experimental (symbols) [7,8] and predicted (solid lines) osmotic coefficient of some aqueous systems as a function of the ionic strength of the second salt

3. Density

For $M=v$, Eq. (4) reduces to:

$$d\overline{v}_w = \sum_j^{nel} \Phi_j dv_{w,j}^o \tag{18}$$

For a mixed electrolyte solution, the volume change of mixing can be written as:

$$V - V' = \frac{1000}{MW_w}(\overline{v}_w - v_w) + \sum_j^{nel} m_j(\overline{v}_j - v_j) \tag{19}$$

where V' is the volume of solution at standard state. The summation term of Eq. (19) is zero because there are no volume changes of mixing for electrolytes. Integrating Eq. (18) from pure water to real state and combining the resulting equation with Eq. (19) gives:

$$V - V' = \sum_j^{nel} \Phi_j(V_j^o - V_j') \tag{20}$$

In terms of density, Eq. (20) is rewritten as

$$\frac{1000 + \sum_j^{nel} m_j MW_j}{\Delta} - \frac{1000}{\rho_w} - \sum_j^{nel} \frac{m_j MW_j}{\rho_j} = \sum_j^{nel} \Phi_j \left(\frac{1000 + m_j^o MW_j}{\Delta_j^o} - \frac{1000}{\rho_w} - \frac{m_j MW_j}{\rho_j} \right) \tag{21}$$

where Δ is the density of the electrolyte solution. Solving for Δ, we will obtain the following equation for density of electrolyte solutions.

$$\Delta = \frac{\sum_j^{nel} \delta_j}{\sum_j^{nel} \dfrac{\delta_j}{\Delta_j^o}} \tag{22}$$

with

$$\delta_j = 1000\Phi_j + m_j MW_j \tag{23}$$

In Table 2 the density of several binary electrolyte solutions are compared with the observed values and the model of Patwardhan and Kumar [3]. The average of absolute deviations was found to be within 0.1%. The density of single salt solutions was calculated from the correlation of Novotny and Sohnel [11]. Comparison with the model of Patwardhan and Kumar [3] shows that both models predict with the same extent, however, this work is a little better. Figure 3 presents a deviation plot for predicting the density of solutions given in Table 2. The deviations are scatter, but the model usually predicts higher than the experimental data. Figure 4 shows the experimental and predicted densities of a binary solution at different temperatures. As can be seen even at temperatures other than 298.15 K, the agreement is quite good.

Table 2
Average absolute percent deviation (%AAD)[a] for predicting the density of aqueous systems at 298.15 K

Aqueous System	n	I_{max} (mol.kg^{-1})	Ionic Strength of the second salt (%)	Ref.	%AAD[a]	
					This work	PK
$MgCl_2+Na_2SO_4$	18	3	10-90	[12,13]	0.038	0.038
$NaCl+Na2SO4$	17	3	10-90	[12,13]	0.063	0.065
$MgSO_4+Na_2SO_4$	15	3	24-84	[12,13]	0.084	0.088
$NaCl+MgCl_2$	18	3	10-90	[12,13]	0.057	0.062
$MgCl_2+MgSO_4$	18	3	10-90	[12,13]	0.061	0.061
$KCl+NaBr$	31	4	12-90	[14]	0.018	0.018
$NaCl+KCl$	5	1.5	20-80	[15]	0.008	0.008
$KCl+K_2SO_4$	9	1.5	10-90	[15]	0.023	0.028
$K_2SO_4+Na_2SO_4$	9	1.5	10-90	[15]	0.019	0.019
$NaCl+Na_2SO_4$	8	1.5	10-90	[15]	0.031	0.033
$NaCl+K_2SO_4$	9	1.5	10-90	[15]	0.044	0.048
$KCl+Na2SO4$	9	1.5	10-90	[15]	0.049	0.050

a

$$\%AAD = (100/n)\sum_{j}^{nel}\left|\Delta_{cal,j} - \Delta_{\exp,j}\right|/\Delta_{\exp,j}$$

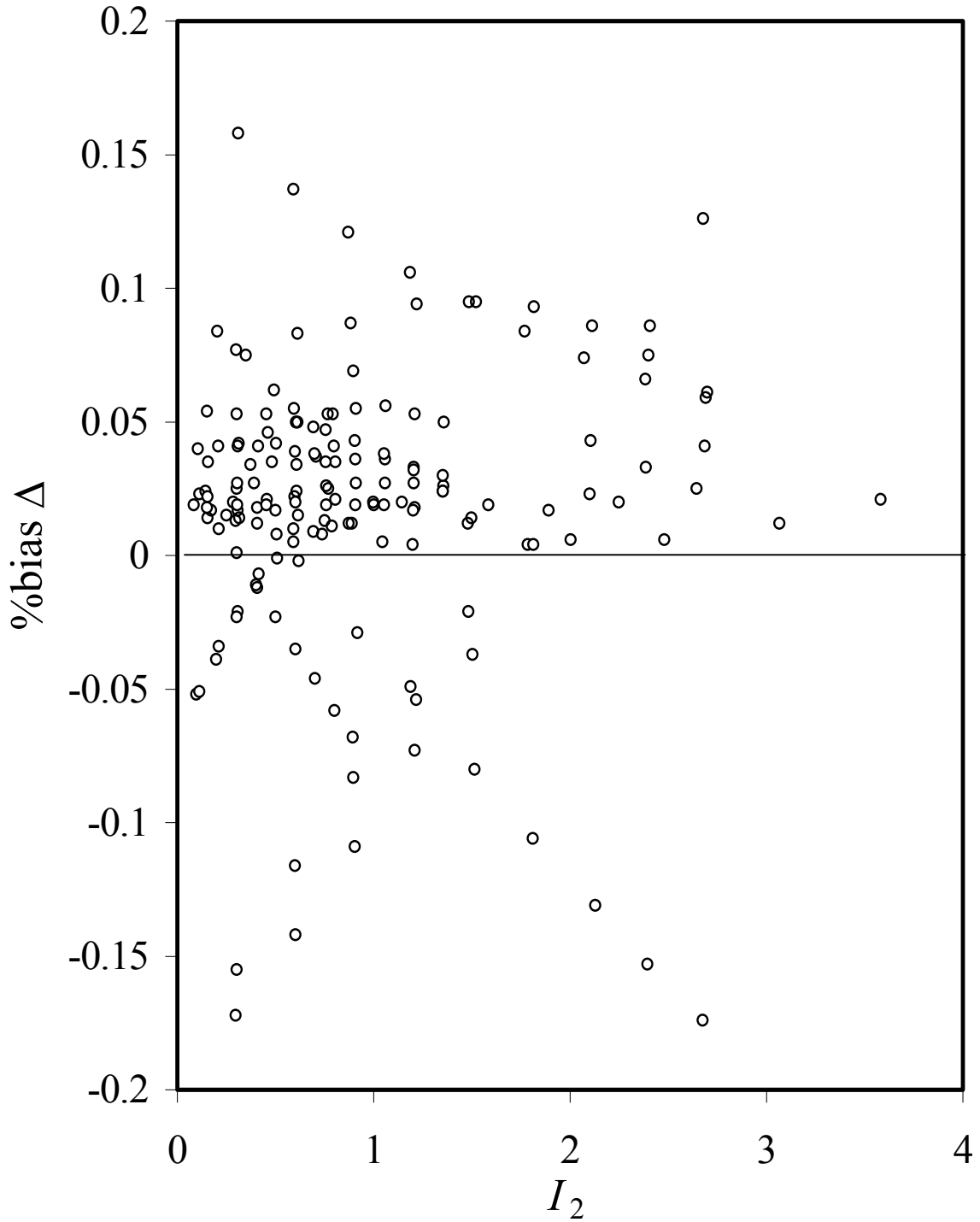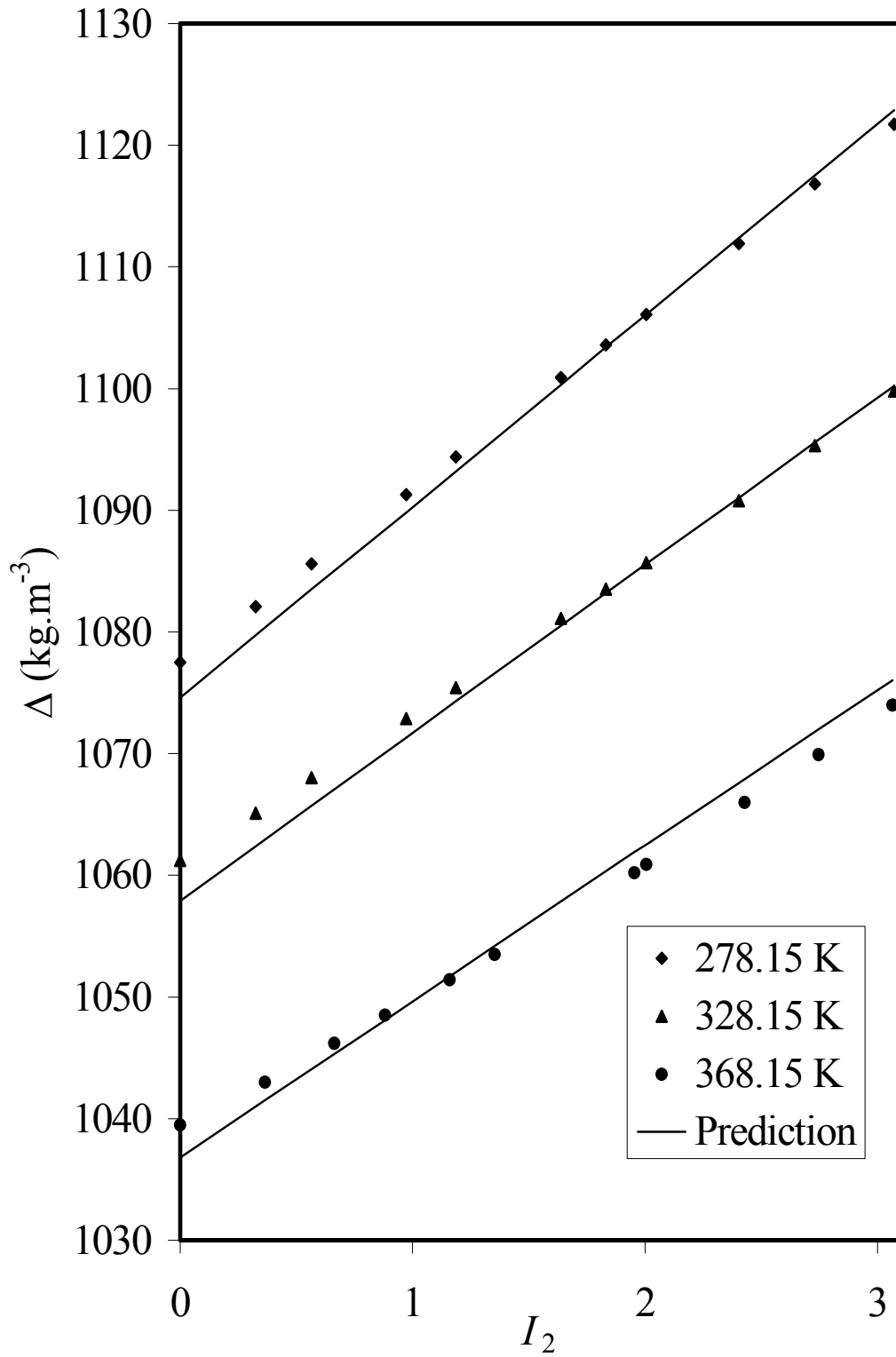**Fig. (3) Percent of deviations for predicting the density of aqueous systems given in Table 2 as a function of the ionic strength of the second salt**

CONCLUSIONS

With some simplifying assumptions, a thermodynamic framework has been developed to predict the thermodynamic properties of mixed electrolyte solutions. This method is classified among the corresponding state methods, i.e., a mixed electrolyte solution is divided into a number of cells each having an electrolyte with a mean ionic charge equal to the mean ionic charge of the mixed electrolyte solution. The equations derived are accurate for dilute and moderate solutions up to a molality of 6 mol.kg^{-1}, however, the predictions get worse with increasing the ionic strength.

Symbols

a	activity
G	Gibbs energy (kj)
I	ionic strength (mol.kg^{-1})
I_2	ionic strength of the second salt
K	proportionality constant
m	molality (mol.kg^{-1})
M	molar property
$\overline{M}$	partial molar property
MW	molecular weight
n	number of moles
nel	number of electrolytes (number of cells)
p	pressure (kPa)
R	universal gas constant (8314 m^3.Pa.K^{-1}.kmol^{-1})
T	temperature (K)
v	molar volume of a compound (m^3.kmol^{-1})
$\overline{v}$	partial molar volume of a compound (m^3.kmol^{-1})
V	molar volume of a solution (m^3.kmol^{-1})
z	number of charges

Greek letter

δ	parameter defined by Eq. (23)
Δ	density of an aqueous electrolyte solution (kg.m^{-3})
ϕ	osmotic coefficient
Φ	molar fraction of water in a cell
ν	stoichiometric number of ions
ρ	density of a compound (kg.m^{-3})

Subscripts

j, k	dummy indexes
w	water
$+$	positive ion
$-$	negative ion
$\pm$	mean ionic property

Superscripts

o	indicating the property of a cell
'	indicating the standard state property

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