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Activity of Water in the KI + KNO_3 + H_2O Ternary System at 298.15 K

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The activities of water in the KI + KNO_3 + H_2O system were determined with an electronic hydrometer. The experimental study was carried out at 298.15 K and constant ionic strengths of 2.0, 2.5, and 3.0 $mol \cdot kg^{-1}$. Different ionic strength fractions of KNO_3, $y_B = m_B/(m_A + m_B)$, were studied for each ionic strength. The experimental values were fit to three thermodynamic models (Pitzer, Scatchard, Lim); each of these models required only two fitted parameters in order to obtain deviations within experimental uncertainty. In addition, mean ionic activity coefficients were determined for KI and KNO_3 as well as the Gibbs excess energy of mixing.

Introduction

Data on the thermodynamic properties of aqueous electrolyte systems are useful in varied fields such as water desalinization, recovery of geothermal energy, geochemistry, oceanography, hydrometallurgy, pulp and paper chemicals, and drilling for petroleum.

Furthermore, experimental determination of thermodynamic properties, especially at moderate or high concentrations, is of interest because it provides information needed to determine interaction parameters in thermodynamic models.[1,2] These models are valuable tools in the study of optimization and simulation of industrial processes for the recovery of salts from naturally occurring multicomponent brines. Thermodynamic models such as that of Pitzer[3−7] are continually used for predicting and simulating solid−liquid equilibria of multicomponent saline systems. Despite extensive information on parameters for the presently discussed mixture model, no information has been found regarding the interaction parameters for the ions in this ternary system. This system is of great interest to us, since it is present in the extraction process that is used for iodine and other ions originating in salt deposits found in northern Chile which contain high levels of nitrate and iodate salts.

The objective of the present study was to determine the activities of the solvent for the potassium iodide + potassium nitrate + water system, which had not been previously measured, and represent the thermodynamic behavior of the system by means of the Pitzer,[8] Scatchard,[9] and Lim[10] models. This was done to obtain basic thermodynamic information for this system and broaden our reference database with regard to parameters of ionic interaction, particularly for the Pitzer model.

Experimental Section

All reagents used in this research were of analytical grade and used directly without further purification (potassium iodide, Merck Co., ≥99.7 mass %; potassium nitrate, Merck Co., ≥99 mass %). Potassium iodide and potassium nitrate were dried to constant weight in an oven for 48 h at 393.15 K before use. Distilled water passed through a Millipore Corp. ultrapure cartridge kit was used in all measurements.

Stock solutions of KI and KNO_3 were prepared by mass, using an analytical balance having a precision of $\pm 10^{-4}$ g. Working solutions for each given ionic strength fraction were prepared by weighing stock solutions and solvent. Total ionic strengths of solutions were prepared having an accuracy in the composition of $\pm 2 \times 10^{-4}$ $mol \cdot kg^{-1}$. Activities of the water (a_w) of the solutions were simultaneously measured in triplicate using a Novasina Corp. model AW-Center 500 electronic hydrometer, with temperature controlled at ±0.2 K. The hydrometer was calibrated prior to making each set of measurements by using standard saturated salt solutions supplied by the manufacturer of the instrument. Each set of triplicate measurements took about 12 h; an uncertainty of 0.002 a_w units was obtained.

Results and Discussion

Experimental values for the activity of the water (a_w) in the KI + KNO_3 + H_2O system at 298.15 K are presented in Table 1. This table shows y_B as a fraction of ionic strength of KNO_3 in the mixture, while I represents the total ionic strength of the ternary system.

For each ionic strength determined, the values of a_w for $y_B = 0$ represent the values of "pure" KI (KI + H_2O). The values of a_w for the three ionic strengths reported in the prior table as well as two others ($I = 4.0$ and 4.5 $mol \cdot kg^{-1}$) are comparable to those reported by Robinson and Stokes[11] for the KI + H_2O system. The average deviation between these two sets of data was ±0.003 a_w units. The greatest deviation reached $I = 2$ $mol \cdot kg^{-1}$ with a deviation of 0.005 a_w units. The deviation decreased with greater ionic strengths. Despite the observed deviation, our experimental data are in good agreement with those from the literature which were obtained by a different experimental method.

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Table 1. Experimental Data for the System KI + KNO_3 + H_2O at 298.15 K

$I = 2.000$ mol·kg^{-1}		$I = 2.500$ mol·kg^{-1}		$I = 3.000$ mol·kg^{-1}	
y_B	a_w	y_B	a_w	y_B	a_w
0	0.938	0	0.920	0	0.901
0.1998	0.944	0.1998	0.925	0.2000	0.908
0.3998	0.948	0.4001	0.932	0.4002	0.917
0.6000	0.953	0.6000	0.940	0.5998	0.925
0.8000	0.956	0.8001	0.945	0.8000	0.935

Table 2. Values of the Pitzer Parameters for KI and KNO_3 a 298.15 K

electrolyte	β^0/kg·mol^{-1}	β^1/kg·mol^{-1}	C^ϕ/kg^2·mol^{-2}
KI	0.074 60	0.251 70	−0.004 14
KNO_3	−0.081 60	0.049 40	0.006 60

Our measurements were carried out at $I = 2$, 2.5, and 3 mol·kg^{-1}, given the high experimental uncertainty at $I <$ 2 mol·kg^{-1} and the limited solubility of KNO_3 (the KNO_3 solubility[12] at 293.15 K is 3.12 mol·kg^{-1}).

The experimental values for the activity of the water were fit by means of the equation

$$a_w = \exp\left(\frac{-2I\phi 18.015}{1000}\right) \tag{1}$$

where I is the total ionic strength and ϕ is the osmotic coefficient of the water in the ternary mixture, expressed by the equation[13,14]

$$\phi = y_A\phi_A^0 + y_B\phi_B^0 + \frac{1}{2}Iy_Ay_B[g_0 + Ig_0' + 2g_1IY] \tag{2}$$

This equation is valid for 1:1 ternary electrolyte mixtures. The terms y_A and y_B are ionic strength fractions of KI and KNO_3, respectively; $Y = 1-2y_B$; $g_0' = \partial g_0/\partial I$; g_0 and g_1 are the coefficients of the Friedman mixtures, modified by Lim[15] [$g_n^F = g_n^L(-I)^n$]; ϕ_A^0 and ϕ_B^0 are the osmotic coefficients of the “pure” electrolytes KI and KNO_3, respectively, evaluated at the same total ionic strength of the mixture. These osmotic coefficients were calculated using the Pitzer[8] equation, the expression of which for 1:1 electrolytes is given by

$$\phi^0 = 1 + f^\phi + IB^\phi + I^2C^\phi \tag{3}$$

where

$$f^\phi = -A_\phi\left[\frac{I^{1/2}}{1 + bI^{1/2}}\right] \tag{4}$$

$$B^\phi = \beta^0 + \beta^1 \exp(-\alpha I^{1/2}) \tag{5}$$

The value of A_ϕ is 0.3915 kg$^{1/2}$·mol$^{-1/2}$ at 298.15 K, while the values of the parameters b and α are 1.2 kg$^{1/2}$·mol$^{-1/2}$ and 2.0 kg$^{1/2}$·mol$^{-1/2}$, respectively. The values of the Pitzer[16] parameters β^0, β^1, and C^ϕ for the KI and KNO_3 electrolytes at 298.15 K are listed in Table 2.

The g_n coefficients of eq 2 can have different behavior with the ionic strength of the mixture, depending on the model employed. Models employed in the present study include those of Pitzer, Scatchard, and the High Order Limit Law (HOLL) of Lim.[15] The fit with the Pitzer model was carried out considering three alternatives: (1) mixing parameters θ and ψ independent of I; (2) parameter θ dependent on I; and (3) parameter θ dependent on I, but with the limit necessary to remain in compliance with HOLL. The following is a summary of the dependence of g_n on I for each model.

Pitzer 1 (P1) Model

$$g_0 = 2\theta + \psi I \tag{6}$$

$$g_0' = \psi \tag{7}$$

$$g_1 = 0 \tag{8}$$

where θ and ψ are parameters of the mixture which represent the interionic interactions of I + NO_3 and K + I + NO_3, respectively, and their values are obtained by fitting of the experimental a_w data.

Pitzer 2 (P2) Model

$$g_0 = 2\left\{\theta^0 + \frac{2\theta^1}{\alpha^2 I}[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]\right\} + \psi I \tag{9}$$

$$g_0' = \frac{4\theta^1}{\alpha^2 I^2}\left[-1 + \left(1 + \alpha I^{1/2} + \frac{1}{2}\alpha^2 I\right)\exp(-\alpha I^{1/2})\right] + \psi \tag{10}$$

$$g_1 = 0 \tag{11}$$

where θ^0, θ^1, and ψ are the parameters to be obtained by fitting with the experimental data.

Pitzer 3 (P3) Model

$$g_0 = 2\left\{\theta^0 + \frac{2\theta^1}{\alpha^2 I}[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]\right\} + \psi I \tag{12}$$

$$g_0' = \frac{4\theta^1}{\alpha^2 I^2}\left[-1 + \left(1 + \alpha I^{1/2} + \frac{1}{2}\alpha^2 I\right)\exp(-\alpha I^{1/2})\right] + \psi \tag{13}$$

$$g_1 = 0 \tag{14}$$

with θ^0 and θ^1 related using the expression[17]

$$\theta^1 = -\frac{\theta^0}{\left(1 + \dfrac{\alpha}{9z^2A_\phi}\right)} \tag{15}$$

where z^2 represents the product of the charges between the cation and the anion.

Scatchard (S) Model

$$g_0 = b_{01} + \frac{1}{2}b_{02}I + \frac{1}{3}b_{03}I^2 \tag{16}$$

$$g_0' = \frac{1}{2}b_{02} + \frac{2}{3}b_{03}I \tag{17}$$

$$g_1 = \frac{1}{2}b_{12} \tag{18}$$

where the parameters b_{nk} are mixture parameters, which may be related to the different types of interactions present in the system[18] and whose values are obtained from the fit.

Lim-HOLL (L) Model

$$g_0 = g_0(0)\exp(\lambda_S I^{1/2}) + \mu I + \nu I^{3/2} \tag{19}$$

$$g_0' = \frac{\lambda_S g_0(0)}{2I^{1/2}}\exp(\lambda_S I^{1/2}) + \mu + \frac{3}{2}\nu I^{1/2} \tag{20}$$

$$g_1 = \text{constant} \tag{21}$$

where $\lambda_S = 6z^2A_\phi$. The mixture parameters $g_0(0)$, μ, ν, and

Table 3. Mixing Parameters for the System KI + KNO_3 + H_2O

P1	θ/kg·mol^{-1}	ψ/kg^2·mol^{-2}	$\sigma(a_w)$	Δ_{max}	n/m	$\bar{\Delta}$
	−0.572 88	0.173 91	0.002 32	0.004 64	5/15	0.000 89
	−0.097 63		0.003 43	0.004 64	11/15	0.001 53

P2	θ^0/kg·mol^{-1}	θ^1/kg·mol^{-1}	ψ/kg^2·mol^{-2}	$\sigma(a_w)$	Δ_{max}	n/m	$\bar{\Delta}$
	0.654 07	−11.196 01	−0.119 81	0.002 34	0.004 64	4/15	0.000 87
	0.156 44	−6.704 05		0.002 26	0.004 64	4/15	0.000 87

P3	θ^0/kg·mol^{-1}	ψ/kg^2·mol^{-2}	$\sigma(a_w)$	Δ_{max}	n/m	$\bar{\Delta}$
	−0.615 09	0.183 92	0.002 33	0.004 64	5/15	0.000 90
	−0.099 66		0.003 45	0.004 64	11/15	0.001 55

S	b_{01}/kg·mol^{-1}	b_{02}/kg^2·mol^{-2}	b_{03}/kg^3·mol^{-3}	b_{12}/kg^2·mol^{-2}	$\sigma(a_w)$	Δ_{max}	n/m	$\bar{\Delta}$
	−2.805 14	1.670 02	−0.257 31	0.039 54	0.002 24	0.004 64	3/15	0.000 87
	−2.804 89	1.669 92	−0.257 38		0.002 34	0.004 64	4/15	0.000 87
	−1.146 13	0.347 96			0.002 32	0.004 64	5/15	0.000 89

L	$g_0(0)$/kg·mol^{-1}	μ/kg^2·mol^{-2}	ν/kg$^{1/2}$·mol$^{-1/2}$	g_1/kg^2·mol^{-2}	$\sigma(a_w)$	Δ_{max}	n/m	$\bar{\Delta}$
	−0.024 52	−1.353 94	0.951 78	0.019 77	0.002 24	0.004 64	3/15	0.000 87
	−0.024 53	−1.353 93	0.951 81		0.002 34	0.004 64	4/15	0.000 87
	0.007 21	−0.229 92			0.002 53	0.004 64	7/15	0.000 99

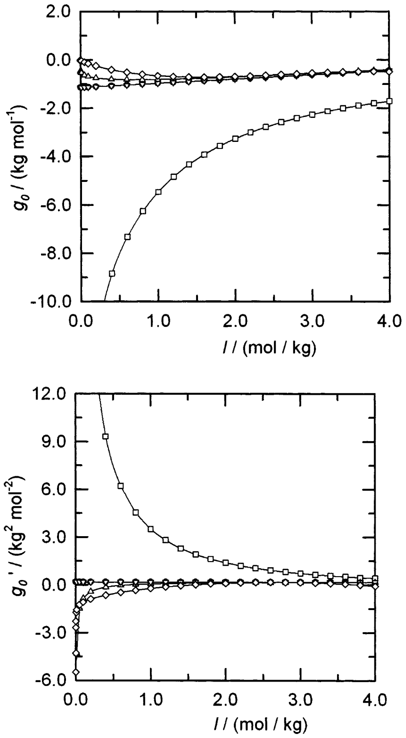

Figure 1. Variation of g_0 and g_0' with ionic strength: ○, Pitzer 1 model; □, Pitzer 2 model; △, Pitzer 3 model; ▽, Scatchard model; ◇, Lim model.

g_1 are obtained by fitting a_w experimental data. The parameter $g_0(0)$ represents the Friedman mixing coefficient evaluated when the ionic strength of the medium tends toward zero.

Table 3 shows the parameters of the mixture obtained for each model as well as the standard deviation of the fit, $\sigma(a_w)$, the maximum deviation Δ_{max}, the number of points n of the total of fitted m for those for which the deviation is greater than 0.002 (estimated experimental error), and the average deviation $\bar{\Delta}$. Different combinations of parameters have been assayed within each method to observe their effects on the standard deviations of the fit. In general, the number of parameters required for us to fit experimental data of this type depends on, among other factors, the concentration range studied. Thus, the higher the concentration range, the more parameters need to be taken into account. On the other hand, if too many parameters are taken, it is possible that these may improve the fit, but physical significance is lost. For this reason, a compromise situation must be obtained which permits reaching a deviation near to the estimated experimental error, but using the least possible number of parameters.

Table 4. Rounded Values for the KI + KNO_3 + H_2O System at 298.15 K

y_B	γ_{KI}	γ_{KNO_3}	ϕ	a_w
		I = 1.5 mol·kg^{-1}		
0.0	0.6355 [a]	0.2441[b]	0.9410	0.9504
0.2	0.5477	0.2743	0.8189	0.9567
0.4	0.4647	0.3035	0.7342	0.9611
0.5	0.4255	0.3174	0.7059	0.9626
0.6	0.3882	0.3306	0.6869	0.9636
0.8	0.3192	0.3545	0.6771	0.9641
1.0	0.2584[b]	0.3742[a]	0.7047	0.9626
		I = 2.0 mol·kg^{-1}		
0.0	0.6364[a]	0.1981[b]	0.9571	0.9334
0.2	0.5409	0.2316	0.8264	0.9422
0.4	0.4471	0.2635	0.7317	0.9486
0.5	0.4022	0.2781	0.6979	0.9509
0.6	0.3594	0.2914	0.6731	0.9527
0.8	0.2810	0.3135	0.6504	0.9542
1.0	0.2137[b]	0.3281[a]	0.6637	0.9533
		I = 2.5 mol·kg^{-1}		
0.0	0.6419[a]	0.1699[b]	0.9736	0.9160
0.2	0.5471	0.2067	0.8494	0.9263
0.4	0.4465	0.2407	0.7528	0.9344
0.5	0.3969	0.2555	0.7149	0.9376
0.6	0.3489	0.2683	0.6839	0.9403
0.8	0.2610	0.2865	0.6425	0.9438
1.0	0.1870[b]	0.2928[a]	0.6288	0.9449
		I = 3.0 mol·kg^{-1}		
0.0	0.6503[a]	0.1536[b]	0.9899	0.8985
0.2	0.5652	0.1941	0.8872	0.9086
0.4	0.4615	0.2304	0.7967	0.9175
0.5	0.4073	0.2452	0.7561	0.9215
0.6	0.3539	0.2570	0.7185	0.9253
0.8	0.2549	0.2692	0.6526	0.9319
1.0	0.1725[b]	0.2648[a]	0.5990	0.9373
		I = 3.5 mol·kg^{-1}		
0.0	0.6603[a]	0.1458[b]	1.0056	0.8809
0.2	0.5951	0.1914	0.9392	0.8883
0.4	0.4926	0.2307	0.8629	0.8969
0.5	0.4340	0.2453	0.8209	0.9016
0.6	0.3744	0.2553	0.7765	0.9067
0.8	0.2613	0.2595	0.6801	0.9178
1.0	0.1675[b]	0.2423[a]	0.5736	0.9302

[a] γ_i^0 values. [b] γ_i^{tr} values.

To describe the accuracy of the different models, we may refer to the mathematical form of g_0[19] as

$$g_0(I) = f_1(I) + f_2(I)I + f_3(I)I^2 \tag{22}$$

It can be seen that model S is the only one in which all the f_i are constant, but it is also the only one in which f_3 is different from zero. For this reason this method may be somewhat better than the Pïtzer methods. The P2, P3, and L methods use f_1 dependent on I and f_2 constant, but the extra term in $I^{3/2}$ considered in the Lim-HOLL model makes it somewhat more precise than the others.

It can be stated that, in all cases of the system studied in the present research, two parameters are required to obtain a deviation near to the experimental error. It can be assumed that inclusion of more parameters would not appreciably improve the results. Regarding compliance with the High Order Limiting Law, Lim[20] affirms that the HOLL may be satisfied by the S model only if b_{01} and b_{02} have the same sign. Similarly, the P1 model must show equality of signs between the parameters θ and ψ. Table 3 shows that this is not the case. For the P2 and P3 models the condition is that $-1 < k < 0$ (with $k = \theta^1/\theta^0$), and this is verified only for P3. Finally, the L method also fulfills the HOLL, as this has been imposed in it's deduction.

We have compared both g_0 and g_0' in Figure 1 with ionic strength. It is observed that the range of ionic strength with which we have worked using all the methods except for P2 leads to similar values. Extrapolating to values of I near to zero, we observe that g_0 tends toward zero in the P3 and L methods, as predicted by Scatchard and Prentiss,[21] while in the P1 and S models they tend toward an finite value (2θ and b_{01}, respectively). The P2 method deviates broadly from the other methods.

Once the parameters for the mixture have been obtained, it is possible to evaluate the mean ionic activity coefficients of KI (γ_A) and of KNO3 (γ_B), using the following expresions:[13,14]

$$\log \gamma_A = \log \gamma_A^0 + \frac{y_B I}{2 \ln 10}\left[g_0 + g_1\left(\frac{I}{2} + \frac{3YI}{2}\right) + g_0'\left(\frac{I}{2} + \frac{YI}{2}\right) - \Phi\right] \tag{23}$$

$$\log \gamma_B = \log \gamma_B^0 + \frac{(1 - y_B)I}{2 \ln 10}\left[g_0 + g_1\left(-\frac{I}{2} + \frac{3YI}{2}\right) + g_0'\left(\frac{I}{2} - \frac{YI}{2}\right) + \Phi\right] \tag{24}$$

where $\Phi = 2(\phi_A^0 - \phi_B^0)/I$ and γ_A^0 and γ_B^0 are the mean ionic activity coefficients of "pure" KI and "pure" KNO3, respectively, evaluated at the same ionic strength of the mixture. All the other symbols retain their typical meaning.

Table 4 lists values for γ_A, γ_B, and ϕ as calculated using P1. The effect of one electrolyte on another in a ternary mixture may be obtained by comparing the values of the activity coefficients in two limiting situations—"pure" electrolyte and using a trace quantity. In eq 25 when $y_B = 0$ and $y_B = 1$, $\log \gamma_A^0$ and $\log \gamma_A^{tr}$ are obtained, respectively. In analogous form, in eq 26 when $y_B = 0$ and $y_B = 1$, $\log \gamma_B^{tr}$ and $\log \gamma_B^0$ are obtained, respectively. In ternary mixtures the values of $\log \gamma_i^{tr}$ relative to $\log \gamma_i^0$ depend on two factors:[22] ion−ion interactions and ion−solvent interactions. An increase in ion−solvent interactions normally results in a rise in $\log \gamma_i$, whereas an increase in ion−ion interactions causes a fall in $\log \gamma_i$.

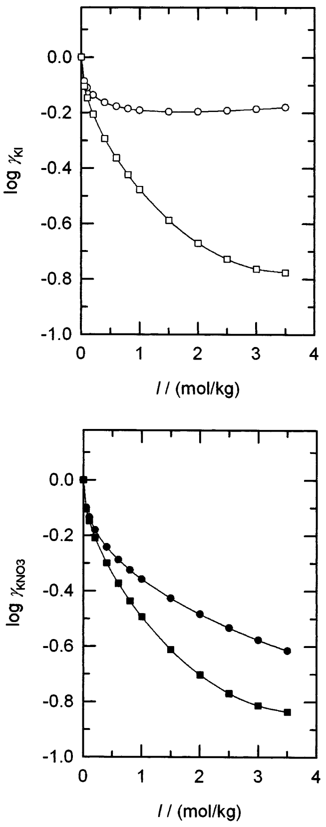

Figure 2. Variation of $\log \gamma$ with ionic strength: ○, $\log \gamma_{KI}^0$; □, $\log \gamma_{KI}^{tr}$; ●, $\log \gamma_{KNO_3}^0$; ■, $\log \gamma_{KNO_3}^{tr}$.

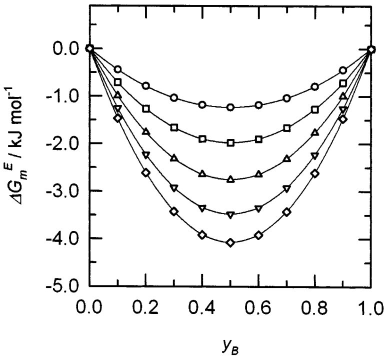

Figure 3. Excess Gibbs energy of mixing versus y_B at constant ionic strength: ○, $I = 1.5$ mol·kg^{-1}; □, $I = 2$ mol·kg^{-1}; △, $I = 2.5$ mol·kg^{-1}; ▽, $I = 3$ mol·kg^{-1}; ◇, $I = 3.5$ mol·kg^{-1}.

Figure 2 shows the values of $\log \gamma$ as a function of I. Examination of Figure 2, for KI, shows that $\log \gamma_{KI}^0 > \log \gamma_{KI}^{tr}$, indicating that the substitution of iodide ions by ions of nitrate intensifies the ion−ion interactions in the mixture over the ion−solvent interaction, producing an increment in free water in the medium, and thus a decrease in the KI concentration. This is equivalent to an increase in the solubility of the KI; that is, there is the promotion of a salting-in effect of NO_3^- anion toward the I^- anion. Similar conclusions are obtained when comparing the values of the activity coefficients of "pure" KNO3 and those in trace quantities.

Figure 3 shows the excess Gibbs free energy of the mixture ΔG_m^Eas a function of ionic strength fraction, the values of which were determined using the equation[13,14]

$$\Delta G_m^E = RTI^2 y_B(1 - y_B)[g_0 + g_1(1 - 2y_B)I] \tag{25}$$

where R is the universal gas constant and T is the absolute temperature. From Figure 3 it can be seen that the shapes of the curves are parabolic and show a minimum of about $y_B = 0.5$, due to the fact that g_1 has a value equal to zero. The values of ΔG_m^E are always negative and decrease with an increase in I. The negative values of ΔG_m^E imply that in a mixture of KI and KNO_3 the formation of $I + NO_3$ pairs is more favored than would be expected from a statistical encounter.[22] This fact may be explained in accord with Robinson et al.,[18] if we consider as important only the binary interactions,

$$g_0 \approx b_{01} \approx K_{I-I} + K_{NO_3-NO_3} - K_{I-NO_3} \tag{26}$$

where K_{i-j} represents the association constant between the i and j ions. Table 3 shows that the value of b_{01} is negative, for which it is concluded that $K_{I-NO_3} > K_{I-I} + K_{NO_3-NO_3}$. The latter would indicate that the $I + NO_3$ interactions would be more intense than the $I + I$ interactions and $NO_3 + NO_3$ in the present ternary system.

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