

# On the Thermodynamics of Concentrated Strong Electrolytes Aqueous Solutions

## The System $\text{NaNO}_3\text{--NaCl--H}_2\text{O}$

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A simple analytical function is proposed for the calculation of molar excess Gibbs energy of binary solutions of strong electrolytes in water. Empirical parameters can be easily determined from experimental data reported in the literature.

The treatment is extended to ternary solutions and to solid liquid equilibria using an empirical equation. Absence of solid solutions is assumed.

The correlations are applied to the common ion ternary system  $\text{NaNO}_3\text{--NaCl--H}_2\text{O}$  in the temperature range from 0 to 100°C.

Predictions of activity coefficients of the binary systems and saturation curves of the ternary system are in good agreement with experimental data.

Knowledge of the behaviour of concentrated aqueous solutions of strong electrolytes at different temperatures is necessary for rational design of separation equipment used in chemical engineering.

Recently interest in this field has increased, especially in the treatment of electrolytes mixtures in solution<sup>(1-6)</sup>.

The traditional approach is given in several excellent books<sup>(7-9)</sup>. Scatchard<sup>(10)</sup> has reviewed and commented on the main advances up to 1967. Of the later works related with the present study, it is of interest to consider briefly those of Hala<sup>(11)</sup>; of Kusik, Meissner and Tester<sup>(12-15)</sup> and those of Funk and Vega<sup>(16)</sup>.

Hala was interested in vapor-liquid equilibria of systems of electrolytic components and proposed an analytical expression for the molar excess Gibbs free energy as a function of composition. Kusik, Meissner and Tester have developed a graphical method to predict the mean ionic activity coefficient of strong electrolytes in solution at 25°C and extended its application to other temperatures by means of an empirical correction. Funk and Vega, with a different approach, give analytical empirical correlations for the activity coefficient of strong electrolytes in concentrated aqueous solutions at temperatures between 0 and 50°C.

The present work is oriented to the prediction of solid-liquid equilibria. It proposes a semi-empirical analytical function for the molar excess Gibbs free energy of concentrated solutions of strong electrolytes in water, which permits its treatment in a fashion similar to that of non-electrolytes by the Redlich-Kister<sup>(17)</sup> expression.

On propose une fonction analytique simple pour calculer l'énergie molaire en excès de Gibbs dans le cas de solutions aqueuses et binaires de forts électrolytes. On peut facilement déterminer des paramètres empiriques à partir des résultats expérimentaux déjà publiés.

En employant une équation empirique, on fait une extension du processus à des solutions ternaires et à des équilibres entre solides et liquides. On suppose l'absence de solutions solides.

On applique les corrélations au système ternaire ayant un ion en commun  $\text{NaNO}_3\text{--NaCl--H}_2\text{O}$ , pour une échelle de températures comprises entre 0°C et 100°C.

Les prévisions relatives aux coefficients d'activité des systèmes binaires et aux courbes de saturation dudit système ternaire concordent bien avec les résultats expérimentaux.

The activity coefficient for the salt is defined considering saturation as the reference state. For water, however, pure water is considered as the reference state.

The proposed function for the molar excess Gibbs free energy gives Debye-Huckel type expressions for the mean ionic activity coefficient of the salt in the dilute region and extremely simple expressions for the logarithm of the activity coefficient of water.

For determination of the empirical parameters that appear in the proposed function, accurate experimental information of vapor pressure over aqueous solutions is necessary. Alternatively, data of the mean ionic activity coefficient up to saturation can be used. Recently<sup>(18-20)</sup> a renewed interest in these measurements has been observed.

Consequently with the adopted binary model, the extension to ternary systems is made by considering the perturbation caused in the activity coefficient of one salt, in its own aqueous solution, by the presence of the other salt with a common ion.

Two interaction parameters are introduced, one for each salt of the ternary system, and both are evaluated from a single experimental point: the concentrations of the solution saturated in the two salts. The knowledge of this double saturation point, at each temperature, allows prediction of the saturation curve for each salt in presence of the other.

Initially the method is applied to the system  $\text{NaNO}_3\text{--NaCl--H}_2\text{O}$  in the temperature range from 0 to 100°C. The study of other systems is under preparation.

In the following treatment the subindex 1 refers always to water and subindexes 2, 3, ... refer to the salts. For binary systems salt-water, the saturation

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properties are indicated with an asterisk (\*), and for the ternary systems with the superindex(s). The superindex(ss) stands for the properties of the double saturated point.

## 1. Thermodynamics of concentrated aqueous solutions of strong electrolytes

### Binary systems water (1) — salt (i)

For simplicity this section is limited to the discussion of 1:1 type electrolytes. Equations, however, can be easily adapted to other types of electrolytes by using the appropriate expression for the fugacity as a function of the mean ionic activity coefficient,  $\gamma_{\pm}$ .

The general expression for the fugacity  $f_i$  of an electrolyte  $i$  which dissociates completely, giving  $\nu_+$  cations and  $\nu_-$  anions, can be written<sup>(21)</sup>

$$f_i = m^{\nu} \nu_+^{\nu_+} \nu_-^{\nu_-} \gamma_{\pm}^{\nu} H \quad \text{I.1}$$

where  $m$  is the molality of the solute,  $\nu = \nu_+ + \nu_-$ , and  $H$  is Henry's constant. The mean ionic activity coefficient  $\gamma_{\pm}$  has been normalized to unity for the infinitely dilute solution reference state.

Thus, for a 1:1 type electrolyte

$$f_i = m^2 \gamma_{\pm}^2 H \quad \text{I.2}$$

Funk<sup>(16)</sup> has proposed that the reference state for the salt is better chosen as its behaviour in the saturated solution, mentioning two main advantages for this choice. First, the logarithm of the mean ionic activity coefficient is a highly non-linear function of composition, usually showing a minimum. By contrast, the logarithm of the activity coefficient  $\Gamma_i$ , which results with the new reference state, is a monotonic function of the composition expressed as mole fraction and it is essentially linear in the concentrated region. Second, the normalization of the activity coefficient to unity at saturation permits solubilities to be calculated with better accuracy and greater simplicity.

Additionally it can be observed that the new reference state is a real one in contrast with the hypothetical state of ideal solution, infinitely dilute, at unit molality, required for the determination of Henry's constant. Also it should be pointed out that there is no loss of generality with the use of this new convention because neither this nor the classical treatment gives information about the individual activity coefficients of the ions.

Conveniently modifying the original expression of Funk, the fugacity of the electrolyte  $i$  in aqueous solution, can be written in the form

$$f_i = (X_i/X_i^*) \Gamma_i f_i^* \quad \text{I.3}$$

where  $X_i$  is the mole fraction of the electrolyte  $i$  in the binary solution,  $X_i^*$  is its mole fraction at saturation at the absolute temperature  $T$  of the system, and  $f_i^*$  is the value of the fugacity of component  $i$  in the saturated solution at the same temperature  $T$ . Obviously,

$$\Gamma_i = 1 \quad \text{for} \quad (X_i/X_i^*) = 1 \quad \text{I.4}$$

From Equations I.2 and I.3, the activity coefficients  $\gamma_{\pm}$  and  $\Gamma_i$  can be directly related

$$\Gamma_i = (HX_i^*/f_i^*) (m^2/X_i) \gamma_{\pm}^2 \quad \text{I.5}$$

Equation I.5 will be frequently used in this work. It is useful to notice that, when applied to saturation conditions, it takes the form

$$H/f^* = 1/(m^* \gamma_{\pm}^*)^2 \quad \text{I.5.a}$$

For water, considering pure water at the temperature of the system as the reference state, the fugacity is given by

$$f_1 = X_1 \Gamma_1 f_1^{\circ} \quad \text{I.6}$$

or

$$a_1 = f_1/f_1^{\circ} = X_1 \Gamma_1 \quad \text{I.6.a}$$

where  $f_1^{\circ}$  is the pure water fugacity at the temperature of the system,  $a_1$  is the activity and  $X_1$  is the mole fraction of water in the binary solution. The activity coefficient of water  $\Gamma_1$  meets the normalization condition

$$\Gamma_1 \rightarrow 1 \quad \text{for} \quad X_1 \rightarrow 1 \quad \text{I.7}$$

In contrast with the activity coefficient of the salts, the activity coefficient of water does not change drastically from the dilute region up to saturation. This experimental fact is the reason for considering pure water as the reference state for water.

Since operating conditions of interest are usually at pressures near atmospheric, the ratio of fugacity coefficients is close to unity, and the effect of the Poynting correction is negligible<sup>(22)</sup>, then Equation I.6 takes the form

$$\bar{p}_1 = X_1 \Gamma_1 p_1^{\circ} \quad \text{I.8}$$

where  $\bar{p}_1$  stands for the partial pressure of water over the aqueous solution in equilibrium, and  $p_1^{\circ}$  for the pressure of pure water at the temperature of the system.

The next step is to have an expression for the molar excess Gibbs free energy of the binary system Water (1)-Salt (i),  $g_{ii}^E$ , in order to obtain the activity coefficients in an analytical form with the general equation

$$\ln \Gamma_j = -\frac{\partial}{\partial n_j} (n_T g_{ii}^E/RT)_{p, T, n_k (k \neq j)} \quad \text{I.9}$$

where  $n_j$  is the number of moles of component  $j$  (water or salt),  $n_T$  is the total number of moles of the system, and  $R$  stands for the Gas Constant.

The molar excess Gibbs free energy is defined as difference between the molar Gibbs free energy of the real solution and that of the ideal solution at the same concentration, temperature and pressure formed from the components in their reference states.

The Debye-Hückel Law, modified by Brönsted and Guggenheim, suggests the following expression for the molar excess Gibbs free energy

$$g_{ii}^E/RT = A X \ln X + BX^{\frac{1}{2}} + KX + CX^{\frac{3}{2}} + DX^2 + \dots \quad \text{I.10}$$

where  $X$  is the mole fraction of salt  $i$  and  $A, B, C, D, \dots$  are adjustable parameters, functions of the temperature and nature of the salt but not of composition.  $K$  is not an independent parameter and it can be evaluated as a function of the adjustable parameters and the saturation mole fraction of the salt,  $X^*$ , by the normalization of the activity coefficient  $\Gamma_i$ .

Applying Equation I.9 to Equation I.10, the activity coefficient of water takes the simple form

$$\ln \Gamma_1 = aX + bX^{\frac{1}{2}} + cX^{\frac{3}{2}} + dX^2 + \dots \quad \text{I.11}$$

with  $A = -a$ ;  $B = 2b$ ;  $C = -2c$  and  $D = -d$

Independently of the assumed form of  $g_{ii}^E$ , for a

binary solution at low pressure, the following general relationship holds

$$g_{ii}^E/RT = (1 - X) \ln \Gamma_1 + X \ln \Gamma_2 \dots \dots \dots \text{I.12}$$

Combining Equations I.10, I.11 and I.12, when applied to saturation, and remembering that  $\Gamma_1^* = 1$ , it can be shown that

$$K = a + a \ln X^* - bX^{*-1} - \alpha_1 X^* - \alpha_2 X^{*1} - cX^{*3/2} - dX^{*2} - \dots \dots \dots \text{I.13}$$

where  $\alpha_1 = a - 2d$  and  $\alpha_2 = b - 3c$ .

Finally, applying Equation I.9 to Equation I.10, in order to obtain  $\ln \Gamma_1$

$$\ln \Gamma_1 = (K - a) - a \ln X + bX^{-1} + \alpha_1 X + \alpha_2 X^1 + cX^{3/2} + dX^2 + \dots \dots \dots \text{I.14}$$

Equations I.11 and I.14 satisfy the Gibbs-Duhem Equation at constant temperature and pressure. As for isothermal binary systems the equilibrium pressure changes with composition, its effect on the activity coefficients has to be considered<sup>(23)</sup>. However, for the system  $\text{Na NO}_3\text{-H}_2\text{O}$  at 20°C was verified that the term that accounts for the change in vapor-pressure of the solution with composition can be neglected in comparison with the other terms. Density data as a function of composition given in the literature<sup>(24)</sup> were used for this calculation.

In order to compare Equation I.14 with the expression obtained from Debye-Hückel Law, modified by Brönsted and Guggenheim, for a 1:1 type electrolyte<sup>21</sup>

$$\ln \gamma_{\pm} = A_{\pm} m^{1/2} / (1 + b_{\pm} m^{1/2}) + B_{\pm} m \dots \dots \dots \text{I.15}$$

it is necessary to obtain the quotient of the first term of the right hand side of Equation I.15. Considering that in dilute electrolyte solutions the molality is proportional to the mole fraction and applying Equation I.15, it can be obtained an expression of the form

$$\ln \Gamma_1 = K' + \ln X + \alpha_1' X + \alpha_2' X^1 + \alpha_3' X^{3/2} + \alpha_4' X^2 + \dots \dots \dots \text{I.16}$$

Comparison of Equation I.16 with Equation I.14, shows that, qualitatively, the parameter  $a$  should be negative close to unity. Notably the term in  $X^{-1/2}$  does not appear in Equation I.16. This fact suggests a low value of the parameter  $b$ , close to zero. In concentrated solutions the empirical fit of the parameters, and mainly the failure of the approximation made considering the mole fraction proportional to molality, will affect the estimated values of the parameters  $a$  and  $b$ . For concentrated solutions, Equation I.10 represents an empirical extension of Debye-Hückel model, only justified by its usefulness in engineering design.

#### Extension to ternary and higher solutions

One simple form of considering the interaction effect between two electrolytes in solution is to assume, as a first approximation, that the activity coefficient of electrolyte  $i$  in presence of electrolyte  $j$ , in a ternary aqueous solution, is given by

$$\ln \Gamma_i(X_i, X_j) = \ln \Gamma_i^{\circ}(X_i^{\circ}) + A_{ij} X_j \dots \dots \dots \text{I.17}$$

where  $X_i^{\circ}$  stands for the mole fraction of salt  $i$  in its own binary solution with water, free of the other salt.

$$X_i^{\circ} = X_i / (X_i + X_1) \dots \dots \dots \text{I.18}$$

The values of  $\ln \Gamma_i^{\circ}(X_i^{\circ})$  are obtained by substitution of  $X_i^{\circ}$  in place of  $X$  in Equation I.14 with the respective binary parameters. The parameters  $A_{ij}$  represent the perturbation caused by the presence of salt  $j$  on the activity coefficient of salt  $i$ . They are functions of temperature and nature of the salts but not of composition.

For multicomponent solutions Equation I.17 can be easily extended since Equation I.18 is not restricted to ternary solutions. Further, it should be noticed that  $X_i^{\circ}$  is directly related to the molality of salt  $i$  in a multicomponent aqueous solution by

$$X_i^{\circ} = m_i / (m_i + 55.51) \dots \dots \dots \text{I.19}$$

When the solution is saturated in salt  $i$ ,  $X_i^{\circ s}$  is related to the solubility  $Si$ , defined as the grams of salt  $i$  dissolved in 100 grams of water, by

$$X_i^{\circ s} = Si / (Si + 5.55 M_i) \dots \dots \dots \text{I.20}$$

where  $M_i$  is the molecular weight of the salt  $i$ .

It has not been attempted to test the validity of the assumption of independence of composition of the interaction parameters  $A_{ij}$ . However, as the present study is oriented to the concentrated region, the failure of this assumption in the dilute region will only affect the value of the activity coefficient of water calculated through the Gibbs-Duhem Equation. If more terms were needed to describe the behaviour in the dilute region, it would always be possible to develop an expansion of terms around the double saturation point, the first term being  $A_{ij} X_j$ .

The advantage of this simple assumption is that that parameters  $A_{23}$  and  $A_{32}$ , for a ternary system, can be obtained, at each temperature, with the only information of the composition of the aqueous solution saturated in both salts. Then the equilibrium curves of saturation, needed for fractional crystallization processes design, can be easily predicted. The double saturation point is the simplest to measure experimentally.

#### Solid-liquid equilibria

The rational design of fractional crystallization processes requires a knowledge of the saturation curves of the different salts involved in the process. Fitch<sup>(25)</sup> has systematized the graphical procedures used in design of this kind of process.

The present study is limited to Type I systems in Fitch's classification. These are systems in which "solutes crystallize without forming either solid solutions or compounds among themselves (double salts). They may, however, form compounds with the solvent (hydrates)"<sup>(25)</sup>. A typical diagram for this kind of system is given in Figure I.1. It shows the saturation curves of salt 2 (S2) and of salt 3 (S3), and the double saturation point (SS). For a point  $P$  in curve S2, the relative positions of the composition variables are shown.

With the aim to predict the saturation curves of Figure I.1, for a ternary solution, the fugacity of salt  $i$  can be written as

$$f_i = (X_i^{\circ} / X_i^*) \Gamma_i(X_i, X_j) f_i^* \dots \dots \dots \text{I.21}$$

where  $\Gamma_i(X_i, X_j)$  is given by Equation I.17 and the other symbols have their usual meaning.

If the ternary solution is saturated in salt  $i$ , the fugacity of component  $i$ ,  $f_i^s$ , in the solution will be the same as in the binary water-salt  $i$  system saturated at the same temperature,  $f_i^*$ , so Equation I.21 will reduce to

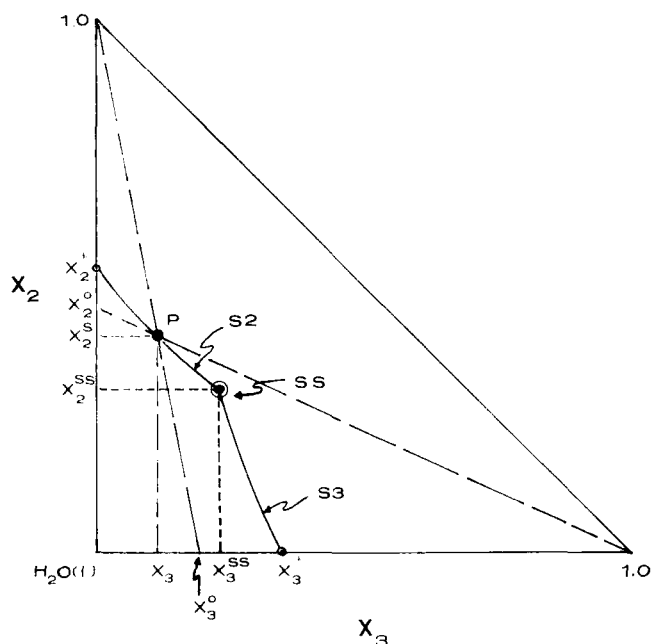


Figure 1(1) - Typical solubility diagram for a Type I system of Fitch.

$$\Gamma_i^* = (X_i^*/X_i^{os}) \dots \dots \dots \text{I.22}$$

Applying Equation I.17 to each salt, for example electrolytes  $i$  and  $j$ , in the double saturation point and substituting the respective value of the activity coefficient given by Equation I.22, the values of the parameters  $A_{ij}$  and  $A_{ji}$  can be obtained simultaneously.

Equation I.22 clearly shows that  $\Gamma_i^*$  is a measure of the solubility variation of the component  $i$  due to the presence in the solution of the other salt.

The comparison of Equation I.17 with Equation I.22 shows that if the solubility of salt  $i$  does not change with the presence of salt  $j$ ,  $A_{ij} = 0$ ; if it increases,  $A_{ij} < 0$ ; and if it decreases,  $A_{ij} > 0$ .

Once the value of  $A_{ij}$  is known, the saturation curve of salt  $i$  (SI) can be constructed in a simple way giving values to  $X_i^{os}$  between  $X_i^{os}/(1 - X_j^{os})$  and  $X_i^*$ , and directly evaluating  $X_j$  with Equations I.17 and I.22.  $X_i$  is then obtained as  $X_i^{os} (1 - X_j)$  accordingly to Equation I.18. If  $X_i^*$  is to be determined starting from  $X_j$ , a standard optimization computer program is needed.

### Binary systems forming hydrates

Even when the present stage of development of

this work is restricted to 1:1 type electrolytes, for which there is experimental evidence that no hydrates are formed, it is convenient to notice that, in principle, systems forming hydrates can be treated in a similar way as the systems considered above. If, for example, salt  $i$  forms a hydrate (salt  $i \cdot n \cdot H_2O$ ), Equation I.3 would be valid considering now that  $f_i^*$  is the fugacity of salt  $i$  in the aqueous solution in equilibrium with the hydrated solid-phase and  $X_i^*$  is the mole fraction of salt  $i$  in the same solution.

For water, Equation I.8 would be equally valid and therefore the treatment of this kind of system, in the temperature range where the particular hydrate is formed, would be identical to the one previously described.

## II. The system $NaNO_3$ - $NaCl$ - $H_2O$

This system has been chosen to begin this study because of its practical interest in the Nitrate industry.

Both binaries  $NaNO_3(2)$ - $H_2O(1)$  and  $NaCl(3)$ - $H_2O(1)$  and the ternary  $NaNO_3(2)$ - $NaCl(3)$ - $H_2O(1)$  were studied using experimental data reported in the literature. No new measurements were made.

The results obtained are satisfactory for practical application in fractional crystallization processes design.

### The binary system $NaNO_3(2)$ - $H_2O(1)$

Vapor pressure data of water over aqueous solutions of  $NaNO_3$ , at different temperatures, available in the literature<sup>(26)</sup>, were reduced accordingly to Equation I.8 in order to obtain values of  $\Gamma_1$ . For each isotherm between 0 and 100°C the data range from  $X_2 = 0.0105$  up to saturation but unfortunately are of low quality and a smoothing procedure was needed.

The binary parameters obtained, fitting Equation I.11, and the saturation mole fraction for the use of Equation I.14 are given in Table 1 for five temperatures. Notably at 25°C only one parameter suffices to describe the behaviour of the system and at other temperatures two parameters are needed. For intermediate temperatures, linear interpolation of the values given in Table 1 is enough to reproduce the experimental values of the vapor pressure of water by means of Equation I.11 and I.8.

For the system  $NaNO_3$ - $H_2O$  at 25°C, Robinson and Stokes<sup>(27)</sup> reported a value of 0.735 for the activity of water in the saturated solution. The calculated value using Equation I.6.a and Equation I.11 is 0.743.

For this system, literature data<sup>(9)</sup> of the mean ionic activity coefficient refers only to 25°C. The ratio  $H/f^*$

TABLE 1  
BINARY PARAMETERS AND SATURATION MOLE FRACTION OF THE SALT

System	Temp., °C	$a$	$b$	$c$	$d$	$X^*$
$NaNO_3(2) - H_2O(1)$	0	-0.3516	-0.0607	—	—	0.1407
	25	-0.7265	0.0000	—	—	0.1633
	50	-0.9019	0.0314	—	—	0.1943
	75	-1.0262	0.0551	—	—	0.2310
	100	-1.1518	0.0854	—	—	0.2715
$NaCl(3) - H_2O(1)$	0	-0.9156	-0.0107	2.463	-16.53	0.0990
	25	-1.5304	0.0250	6.500	-23.98	0.1000
	50	-1.8620	0.0363	8.131	-25.39	0.1018
	75	-2.2454	0.0528	9.985	-27.29	0.1046
	100	-2.6603	0.0727	11.988	-29.51	0.1079

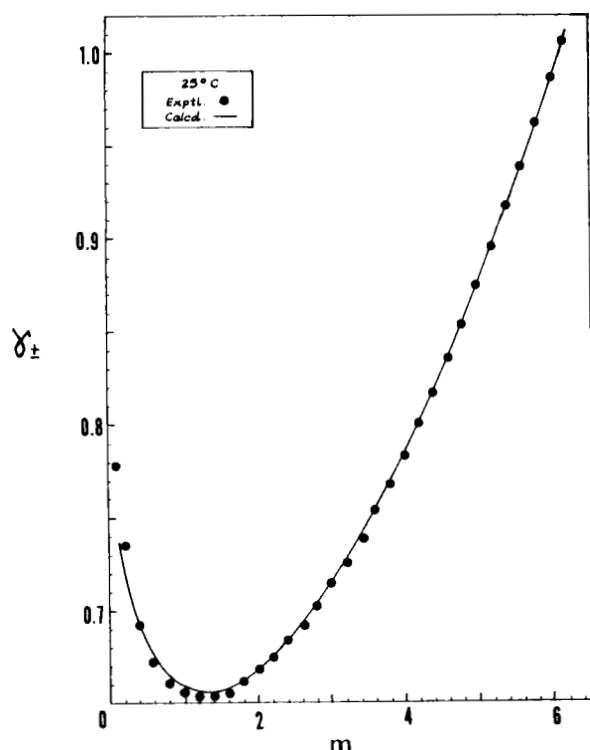


Figure II.(1) — Mean ionic activity coefficient of NaCl in aqueous solution at 25°C.

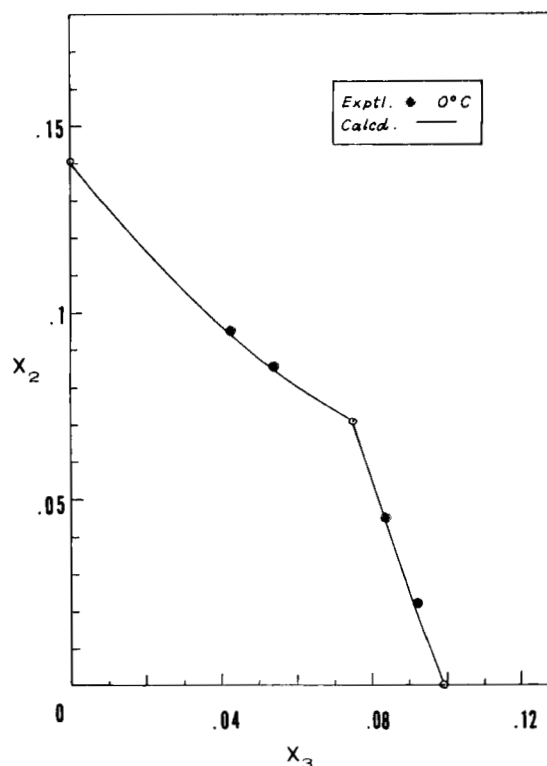


Figure II.(2) — Saturation curves of the system  $\text{NaNO}_3(2)\text{-NaCl}(3)\text{-H}_2\text{O}(1)$  at 0°C.

was estimated applying Equation I.5 for each reported value. Equation I.5.a is not useful because the data covers only up to a molality of six whereas the saturation molality is 10.83. A reasonable estimation appears to be  $H/f^* = 0.087$ . Accordingly to Equation I.5.a this value corresponds to a mean ionic activity coefficient  $\gamma_{\pm}^* = 0.313$  for the saturated solution.

The comparison of calculated and experimental values of  $\gamma_{\pm}$ , not reported here, is satisfactory considering that only one adjustable parameter has been used and that the value of  $H/f^*$  was roughly estimated.

### The binary system $\text{NaCl}(3)\text{-H}_2\text{O}(1)$

For this system high precision data of water vapor pressure as a function of composition at 25°C were available<sup>(9)</sup>. At other temperatures there is wider information in the literature<sup>(26)</sup> but the quality is considerably inferior.

Also there are data of the mean ionic activity coefficient at 25°C from the dilute region up to saturation<sup>(9)</sup> and at other temperatures in the low concentration region<sup>(7,9)</sup>. Extrapolations for the concentrated region from 40 to 80°C have been made recently<sup>(19)</sup>.

The binary parameters were obtained in the same way as in the previous system. These parameters and the saturation mole fraction of the salt, are given in Table 1.

The use of four parameters is justified by the high precision of the data at 25°C. Four parameters are also given at other temperatures, even when the accuracy of the data is lower, to allow interpolation.

For this system, Robinson and Stokes<sup>(27)</sup> report a value of the activity of water in the saturated solution, at 25°C, of  $a_{1E}^* = 0.753$ . The calculated value, using Equation I.6.a and Equation I.11, with  $X_2^* = 0.100$ , is  $a_{1E}^* = 0.752$ .

TABLE 2

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUE OF  $\bar{p}/p^*$  AND  $\gamma_{\pm}$  FOR THE SYSTEM  $\text{NaCl-H}_2\text{O}$  AT 25°C

<i>m</i>	$\bar{p}/p^*$		$\gamma_{\pm}$	
	Exptl.	Calcd.	Exptl.	Calcd.
0.2	0.9934	0.9935	0.735	0.720
0.4	0.9868	0.9867	0.693	0.694
0.6	0.9802	0.9801	0.673	0.675
0.8	0.9736	0.9735	0.662	0.664
1.0	0.9669	0.9667	0.657	0.659
1.2	0.9601	0.9599	0.654	0.657
1.4	0.9532	0.9531	0.655	0.656
1.6	0.9461	0.9461	0.657	0.658
1.8	0.9389	0.9389	0.662	0.662
2.0	0.9316	0.9316	0.668	0.668
2.2	0.9242	0.9243	0.675	0.674
2.4	0.9166	0.9168	0.683	0.682
2.6	0.9089	0.9091	0.692	0.692
2.8	0.9011	0.9012	0.702	0.702
3.0	0.8932	0.8931	0.714	0.714
3.2	0.8851	0.8850	0.726	0.727
3.4	0.8769	0.8768	0.739	0.740
3.6	0.8686	0.8684	0.753	0.754
3.8	0.8600	0.8598	0.768	0.769
4.0	0.8515	0.8513	0.783	0.785
4.2	0.8428	0.8426	0.800	0.801
4.4	0.8339	0.8338	0.817	0.819
4.6	0.8250	0.8249	0.835	0.837
4.8	0.8160	0.8157	0.854	0.856
5.0	0.8068	0.8068	0.874	0.875
5.2	0.7976	0.7973	0.895	0.897
5.4	0.7883	0.7881	0.916	0.918
5.6	0.7788	0.7790	0.939	0.939
5.8	0.7693	0.7696	0.962	0.962
6.0	0.7598	0.7600	0.986	0.986
6.17			1.006	1.006

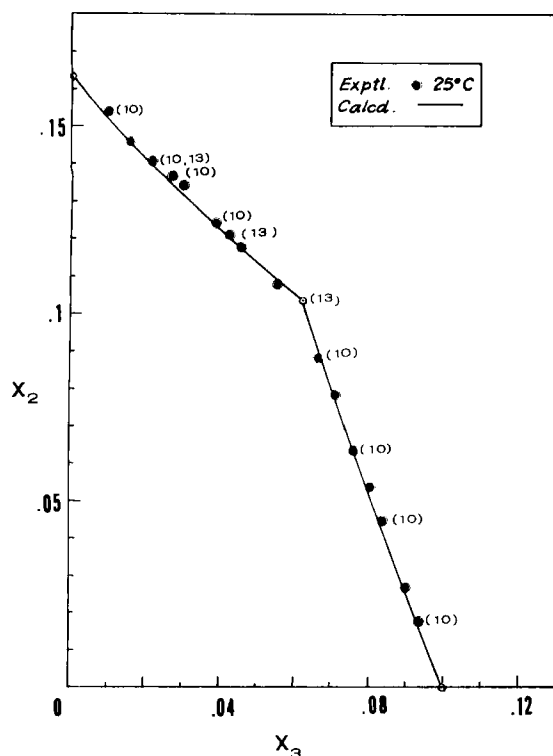


Figure II.(3) — Saturation curves of the system  $\text{NaNO}_3(2)\text{-NaCl}(3)\text{-H}_2\text{O}(1)$  at 25°C.

The more drastic comparison between the calculated values of  $\Gamma_3$  and the experimental value of  $\gamma_{\pm}$  can be made more precisely at 25°C for this system. The reported data<sup>9</sup> range from the dilute region up to a molality of six, being the saturation molality of 6.167. A slight extrapolation gives, for the mean ionic activity coefficient of  $\text{NaCl}$  at saturation, a value of  $\gamma_{\pm}^* = 1.006$ .

Equation I.15.a then gives a value for the ratio  $H/f^*$  of 0.026. Replacing values of  $\Gamma_3$ , calculated with Equation I.14, in Equation I.5, values of the mean ionic activity coefficient of the  $\text{NaCl}$  can be obtained for the concentrations reported in the literature. Table 2 presents the comparison between the experimental and calculated values and they are shown in Figure II.1.

It can be noticed that only in the extremely dilute region ( $m < 0.5$ ), where the Debye-Hückel Law gives good results, the agreement is not satisfactory. The proposed correlation correctly predicts the minimum of the mean ionic activity coefficient as a function of molality.

At higher temperatures, experimental data of the mean ionic activity coefficient are reported only up

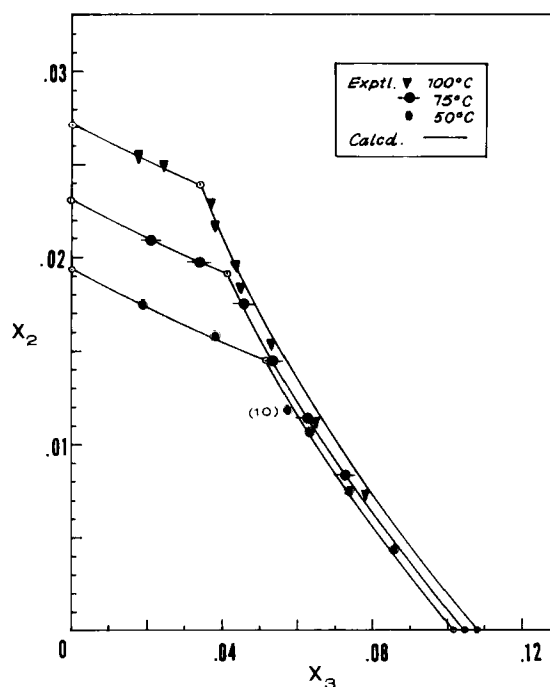


Figure II.(4) — Saturation curves of the system  $\text{NaNO}_3(2)\text{-NaCl}(3)\text{-H}_2\text{O}(1)$  at 50, 75 and 100°C.

to a molality of four<sup>(7,9)</sup>. Estimates for the concentrated region, based on heat of solution measurements<sup>(19)</sup>, show that the value of the mean ionic activity coefficient at saturation decreases and the molality of saturation increases as the temperature rises. This behaviour, according to Equation 1.5.a gives a minimum for the ratio  $H/f^*$  around 60°C.

Again, to avoid excessive extrapolation of the experimental data, the value of the ratio  $H/f^*$  was obtained by simple comparison, as explained for the previous system. Reasonable estimates are  $H/f^* = 0.024$  at 60°C and  $H/f^* = 0.026$  at 100°C.

At 60°C, from the estimated value of  $H/f^*$  and Equation I.5.a, it is possible to predict a mean ionic activity coefficient at saturation of  $\gamma_{\pm}^* = 1.015$ . From Ensor data<sup>19</sup>, the extrapolated value is  $\gamma_{\pm}^* = 1.015$ , which coincides with the previous prediction.

#### The ternary system $\text{NaNO}_3(2)\text{-NaCl}(3)\text{-H}_2\text{O}(1)$

Wide experimental information of the saturation curves can be found in the literature<sup>(28-31)</sup> for this ternary system. Some of this information has been plotted in Figures II.2 to II.4. Most of the data have been reported by Cornec and Chretien<sup>(28)</sup>. Those data pertaining to other authors are specifically identified in each figure.

Interaction parameters  $A_{23}$  and  $A_{32}$  were determined from the double saturation points and are given together with the mole fractions of double saturation, at each temperature of interest, in Table 3.

Surprisingly the parameter  $A_{32}$  increases from 0 to 25°C and then decreases for higher temperatures.

The available information<sup>(28)</sup> on double saturation points at intermediate temperatures of 5, 10, 13, 15, 17 and 20°C on one side, and 30 and 40°C on the other, confirms this behaviour of  $A_{32}$ . The maximum is attained near 25°C so linear interpolation of the values given in Table 3 is enough to reproduce saturation curves at intermediate temperatures.

TABLE 3

INTERACTION PARAMETERS AND MOLE FRACTION OF SALTS AT THE DOUBLE SATURATION POINT FOR THE SYSTEM  $\text{NaNO}_3(2) - \text{NaCl}(3) - \text{H}_2\text{O}(1)$

Temp., °C	$A_{23}$	$A_{32}$	$X_2^{ss}$	$X_3^{ss}$
0	11.48	10.26	0.0703	0.0751
25	10.15	11.98	0.1034	0.0627
50	8.03	11.61	0.1448	0.0515
75	6.34	11.19	0.1907	0.0414
100	4.91	10.28	0.2389	0.0341

The saturation curves were predicted by the method previously described in Section I, for five equally spaced values of the free basis mole fraction of the component in which the solution is saturated. The predicted curves are compared with available experimental data in Figures II.2 to II.4 at the temperatures of interest.

## Conclusions

The molar excess Gibbs energy of binary systems of strong electrolytes in concentrated aqueous solutions can be described by a simple analytical expression. A maximum number of four parameters were needed for the systems under consideration.

A coherent link can be established between binary and ternary equations by means of the definition of the mole fraction of a salt in its own binary solution with water  $X^\circ$ , in place of using molalities.

The introduction of interacting parameters, that can be obtained from a single, easy to measure, experimental point allows to consider the perturbation produced in the activity coefficient of one salt by the presence of other salt (with a common ion) and to predict saturation curves.

The advantages of having analytical functions for computer calculations of equilibrium conditions is evident.

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## Nomenclature

$A, B, C, D, a, b, c, d, \alpha_1, \alpha_2$	= numerical parameters
$a_1$	= activity of water
$f$	= fugacity
$f^v$	= pure component fugacity
$g^E$	= molar excess Gibbs free energy
$H$	= Henry's constant
$K$	= normalization parameter at each temperature
$m$	= molality
$n$	= number of moles
$n_T$	= total number of moles
$p$	= absolute pressure
$\bar{p}$	= partial pressure
$p^\circ$	= pure component vapor pressure
$R$	= Gas constant
$T$	= absolute temperature
$X$	= mole fraction
$X^\circ$	= free basis mole fraction
$\Gamma$	= activity coefficient
$\gamma_{\pm}$	= mean ionic activity coefficient
$v_+, v_-$	= stoichiometric number of ions
$v$	= $v_+ + v_-$

## General superscripts

*	= saturation properties in binary solutions
**	= supersaturation properties in binary solutions
.	= saturation properties in ternary solutions
..	= properties at the double saturation point

## General subscripts

1	= water
2, 3, ... i	= salts
j	= general component (water or salt)
c	= calculated property
E	= experimental property

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