

Choice of a model for calculation and critical evaluation of solide-liquid electrolyte phase diagrams. Application to the ternary system NaCl-KCl-H₂O

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Abstract - In order to find expressions for fitting equations that could be applied to any type of electrolyte phase diagram and easily extended from binary to ternary systems, we were led to proceed in two steps : first, find fitting equations for solubilities along convenient isoplethic sections of the diagram ; and second extend the calculation to isothermal sections. The model is applied to the calculation of solubilities in the ternary system NaCl-KCl-H₂O.

INTRODUCTION

The present paper deals with the critical evaluation of solid-liquid equilibria at constant pressure in aqueous multicomponent electrolyte systems, in the frame of the Solubility Data Project (S.D.P.) of the International Union of Pure and Applied Chemistry. This project, one of the most ambitious of IUPAC, has been initiated and developed by the late Professor Steven Kertes.

The main purpose of the S.D.P. is the collection and critical evaluation of solubility data, the selection of best values and calculation of solubilities for rounded values of temperatures, i.e. calculation of the phase diagram. In order to calculate the phase diagram, a rational treatment of data is needed, which is based on appropriate models of liquid and solid phases. The scope of this paper will be limited to the case where the solid phase is stoichiometric.

CHOICE OF A MODEL

As already stated in a previous publication concerning the critical evaluation of binary systems (ref. 1), the models used for fitting equations of solubility surfaces must never be in contradiction with thermodynamic laws and, consequently, they must comply with several constraints. If *i* is a constituent (ion or molecule) of the system in phase α :

- under constant pressure:

$$d \left(\frac{\mu_i^\alpha}{T} \right) = - \frac{H_i^\alpha}{T^2} dT + R d \ln (a_i^\alpha) \quad (1)$$

- each phase is in equilibrium with respect to each chemical reaction *r* in that phase:

$$\sum_i v_i^{(r)} \mu_i^\alpha = 0 \quad (2)$$

where μ_i^α = chemical potential of component *i* in phase α
 v_i = stoichiometric coefficient of *i* in solid phase

- any two phases are in mutual equilibrium all along the solubility surface:

$$\mu_i^\alpha = \mu_i^\beta \quad ; \quad d\mu_i^\alpha = d\mu_i^\beta \quad (3)$$

- the Gibbs-Konovalov relation is satisfied at stable or metastable congruent melting points

- activities are consistent with de Gibbs-Duhem relation:

$$SdT + \sum_i x_i d\mu_i = 0 \quad (P \text{ constant}) \quad (4)$$

- the variation of the enthalpy for phase change follows Kirchoff's law:

$$\frac{d\Delta H}{dT} = \Delta C_p \quad (5)$$

Equation of liquidus surface of ternary systems

In expressing the chemical potentials as functions of the activities of the constituents of the system, the liquidus surface can then be written, by integration of relation (3), in the form:

$$Y - Y_m = Z - Z_m \quad (6)$$

Z is a function of temperature:

$$Z - Z_m = \int_{T_m}^T \frac{\Delta H_m}{RT^2} dT \quad (7)$$

which may be developed in a series:

$$Z - Z_m = \frac{A}{T} + B \ln(T) + C + DT + ET^2 + \dots \quad (8)$$

The subscript m concerns the coordinates of a particular point of the solubility surface, taken as the limit of integration (usually the congruent melting point of the solid phase involved in solid-liquid equilibrium). According to the case under consideration, A, B, C, D, E are considered as adjustable coefficients or deduced from thermodynamic data such as congruent melting point, enthalpy or heat capacity change at the melting point, or other constraints such as coordinates of characteristic points, eutexy, peritexy.

Y is the natural logarithm of an activity product, expressed for any stoichiometric solid phase $A_p B_q C_r \cdot nH_2O$ of the system, by:

$$Y = \ln(a_A^p a_B^q a_C^r a_{H_2O}^n) \quad (9)$$

The logarithm of the rational solubility product for solid phase $A_p B_q C_r \cdot nH_2O$ can be written (ref. 2):

$$S = \ln(x_A^p x_B^q x_C^r x_{H_2O}^n) = Y - \ln(\Gamma) \quad (10)$$

where $\Gamma = f_B^q f_C^r f_{H_2O}^n$ and f_i is the rational activity coefficient of species i .

The different models used in the treatment of solubility data will differ by the expressions of mole fractions x_i and activity coefficients f_i according to the nature of the particular phase diagram. For instance, in strongly solvated electrolytes the mole fractions can be corrected in order to take into account the free and associated water. Similarly the Debye-Hückel model may be used for the calculation of activity coefficients of slightly soluble salts. It is clear that a single model for the activity coefficient will not allow description of all types of solutions and several models have been proposed in the literature for the calculation of activity coefficients in multicomponent aqueous electrolyte systems. They are very useful and well adapted to the study of the liquid state, in dilute as well as in concentrated aqueous solutions. Some of the most usual are presented in bibliography (ref. 3 to 22).

It is not very easy to use the classical expressions of activity in critical evaluation of multicomponent phase diagrams since the evaluation must be performed over a very large range of temperature and composition, on the solubility surfaces where temperature and composition vary simultaneously. In order to find expressions that could be applied to any type of electrolyte and easily extended from binary to ternary systems, we were led to proceed in two steps: first, find fitting equations for solubilities along convenient isoplethic sections of the diagram (ref. 23); and second extend the calculation to isothermal sections. Such calculations depend upon the choice of two different reference states, one for the activity coefficients and one for the calculation of isothermal solubility. Along the solubility surface of any solid $A_p B_q C_r \cdot nH_2O$ which occurs in the phase diagram, the pure compound is chosen as reference state for the evaluation of activity coefficients.

Choice of reference sections of the diagram

In an isoplethic section of a ternary system, at constant pressure, solubility, activity coefficients along the solubility curve and consequently $\ln(\Gamma)$ can be expressed as functions of a single variable T . Activity coefficients can be expanded in the same series as Z

relation (8) since the derivative of $\ln(f_i)$ versus T is a function of excess enthalpy:

$$\frac{\partial \ln(f_i)}{\partial T} = \frac{H_i^{ex}}{RT^2} \tag{11}$$

and may be written for any species of the solution:

$$\ln(f_i) = \frac{\alpha_i}{T} + \beta_i \ln(T) + \gamma_i + \delta_i T + \epsilon_i T^2 + \dots \tag{12}$$

For a solid phase $A_p B_q C_r \dots nH_2O$ in equilibrium with liquid:

$$\ln(\Gamma) = \frac{\alpha}{T} + \beta \ln(T) + \gamma + \delta T + \epsilon T^2 + \dots \tag{13}$$

with $\alpha = p\alpha_A + q\alpha_B + r\alpha_C + n\alpha_{H_2O} + \dots$

with $\beta = p\beta_A + q\beta_B + r\beta_C + n\beta_{H_2O} + \dots$

The relation (13) is a generalisation to ternary systems of the equation derived by Tenu and Counioux (ref. 24) for binary systems. In most cases, the development of $\ln(\Gamma)$ can be limited to two or three terms. Sometimes, it may be reduced to a single term $\ln(\Gamma) = \alpha/T$ as if the solution could be considered as regular (ref. 25).

A vertical section of the phase diagram containing the representative point of a pure compound can then be chosen as reference in the calculation of the solubility surface of that compound. For instance, in the ternary system NaCl-KCl-H₂O the reference section used in critical evaluation for the solubility surfaces of NaCl, NaCl.2H₂O and ice is the limiting binary system NaCl-H₂O. In the same way the binary system KCl-H₂O is used as reference for the calculation of the solubility surface of KCl. In a system involving a ternary compound M, the reference isoplethic section used for critical evaluation of M's solubility surface would be the quasibinary section M-H₂O.

From relations (6),(8) and (10) and taking the pure compound $A_p B_q C_r \dots nH_2O$ as reference state for the calculation of activity coefficients the logarithm of the solubility product of a solid phase can be expressed:

$$S - S_m = \ln(x_A^p x_B^q x_C^r x_{H_2O}^n) - \ln\left(\frac{p^p q^q r^r n^n}{(p+q+r+n)^{p+q+r+n}}\right) = Z - Z_m - \ln(\Gamma) \tag{14}$$

It can be expanded in the same way as the activity product and a treatment of data will allow, by an iterative method (ref. 1, 26), the calculation of a set of adjustable coefficients A', B', C', D', E' constant all along the reference section

$$S - S_m = \frac{A'}{T} + B' \ln(T) + C' + D'T + E'T^2 + \dots \tag{15}$$

with $A' = A - \alpha$, $B' = B - \beta \dots$

The products $(-RA')$, (RB') are molar partial quantities and can be identified with melting enthalpy and melting heat capacity of the pure compound if (but only if) ideal conditions are fulfilled.

Isothermal section of the diagram

In a ternary system the isothermal solubility of a species $A_p B_q C_r \dots nH_2O$ is represented by a monovariant curve along which the coefficients A', B', C', D', E'... are no more constant and can be expanded in series of a single composition variable ζ . As often as possible simple polynomial developments have been used for A', B', C', D', E' and they revealed sufficient in most cases. Anyway, a comparison has been made in some cases with classical expressions of activity coefficients given in the literature.

$$\begin{aligned} A' &= A^0 + \alpha_1 (\zeta - \zeta^0) + \alpha_2 (\zeta - \zeta^0)^2 + \dots \\ B' &= B^0 + \beta_1 (\zeta - \zeta^0) + \beta_2 (\zeta - \zeta^0)^2 + \dots \end{aligned} \tag{16}$$

A^0, B^0, \dots, ζ^0 are the values of adjustable coefficients and of the variable on the isoplethic section taken as reference. $\alpha_1, \alpha_2 \dots$ are calculated from experimental data at different temperatures by a linear regression.

APPLICATION TO THE CRITICAL EVALUATION OF THE SYSTEM NaCl-KCl-H₂O

Four solid phases (ice, NaCl, KCl, NaCl.2H₂O) are observed, but the equations of solubility surfaces have been developed, in the present paper, only for NaCl and KCl, using the data of Cornec and Krombach (ref. 28) at temperatures between 0 and 100°C.

Solubility surfaces of NaCl and KCl

If x_1 and x_2 are respectively the mole fractions of NaCl and KCl, the mole fractions of ions and molecules are:

$$\begin{aligned} x_{\text{Na}} &= \frac{x_1}{1+x_1+x_2} & x_{\text{K}} &= \frac{x_2}{1+x_1+x_2} \\ x_{\text{Cl}} &= \frac{x_1+x_2}{1+x_1+x_2} & x_{\text{H}_2\text{O}} &= \frac{1-x_1-x_2}{1+x_1+x_2} \end{aligned} \quad (17)$$

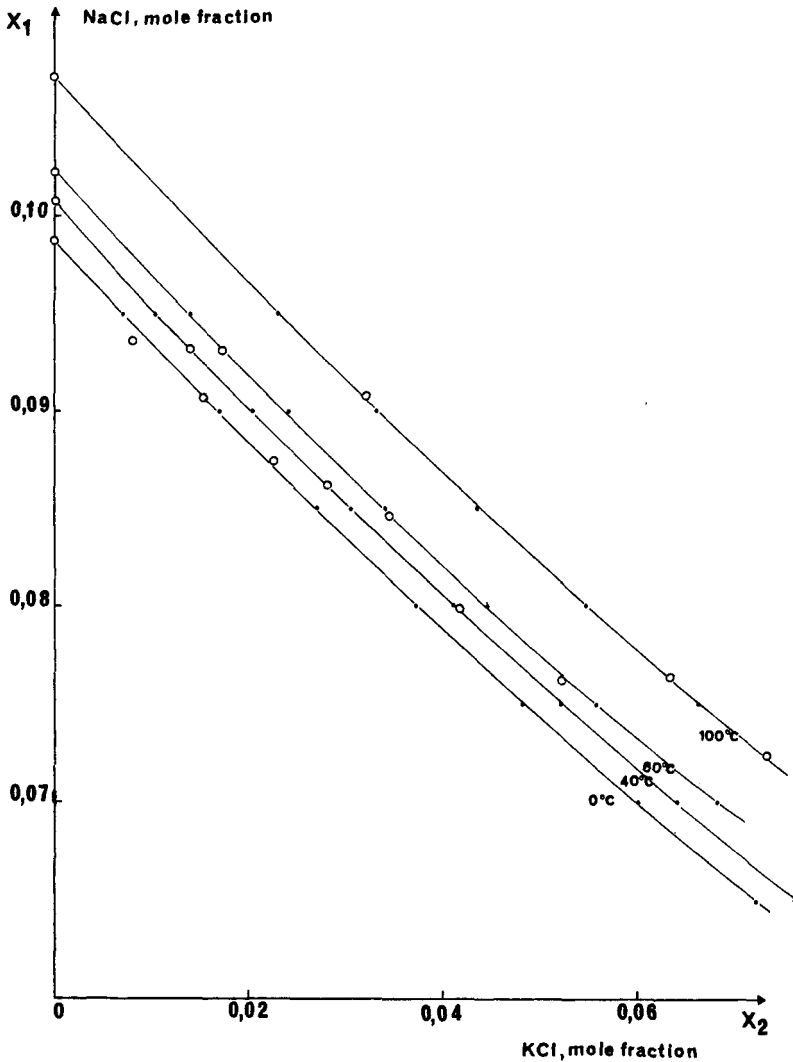


Fig. 1. Isothermal section of ternary system NaCl-KCl-H₂O

Solubility of NaCl ○ experimental — calculated values

Due to the reference taken in evaluation of activity coefficients, the solubility surface of NaCl can be represented by:

$$\ln \left(\frac{4x_1(x_1+x_2)}{(1+x_1+x_2)^2} \right) = \frac{A_1}{T} + B_1 \ln(T) + C_1 + D_1 T + E_1 T^2 \quad (18)$$

In order to take account of the variation of ionic strength of the solution, the coefficients A_1, B_1, C_1, \dots have been expanded in function of $x_1+x_2-x_1^\circ$ and a linear development have been found sufficient for the calculation of solubility between 0 and 100°C. As already seen the reference state for the isothermal solubility curves of NaCl and KCl are the binary systems NaCl-H₂O and KCl-H₂O which have been compiled and evaluated in the S.D.P series (ref. 28).

TABLE 1. Coefficients of fitting equations for binary systems

Solid phase	Coefficients	Conditions introduced in calculation	Range/K
NaCl	$A_1^\circ = 99.14456 \text{ K}$	melting point	273-1073
	$B_1^\circ = -1.53935 \text{ K}$	peritectic pt. NaCl.2H ₂ O	
	$C_1^\circ = 2.86411$		
	$D_1^\circ = 7.24959 \cdot 10^{-3} \text{ K}^{-1}$		
KCl	$A_2^\circ = -7262.7 \text{ K}$	melting point	202-1044
	$B_2^\circ = -36.0456$	eutectic pt ice + KCl	
	$C_2^\circ = 208.489$		
	$D_2^\circ = 0.06294 \text{ K}^{-1}$		
	$E_2^\circ = -1.355519 \cdot 10^{-5} \text{ K}^{-2}$		

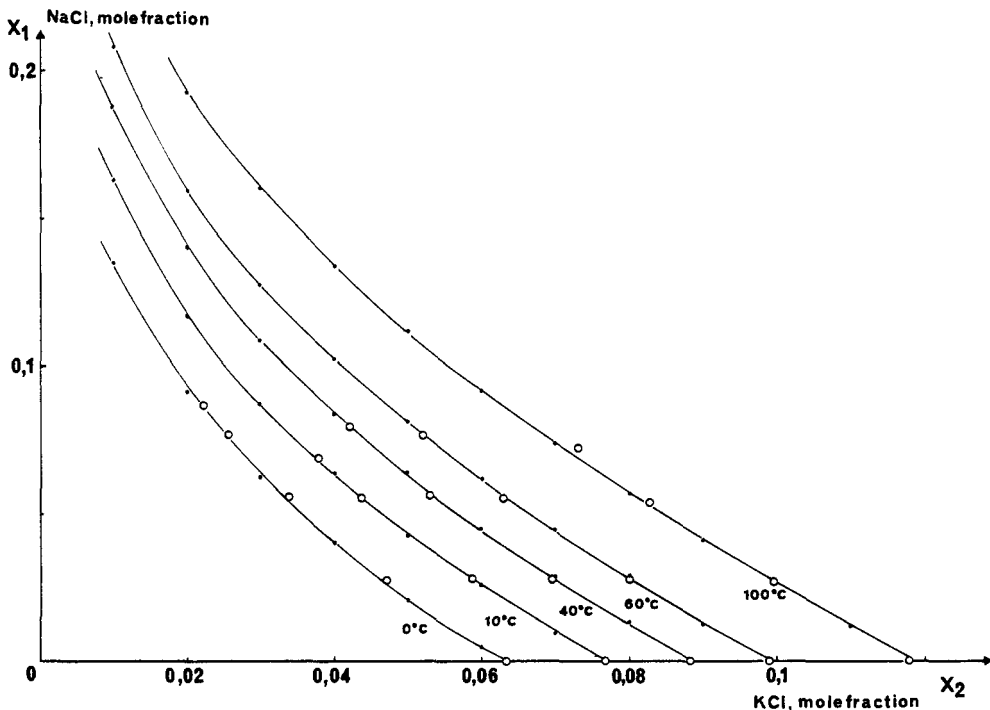


Fig. 2. Isothermal section of ternary system NaCl-KCl-H₂O

Solubility of KCl ○ experimental — calculated values

Taking into account the values of coefficients A_1° , B_1° ... for the binary systems given in table 1, the equation (18) becomes:

$$\ln \left(\frac{x_1(x_1+x_2)}{(1+x_1+x_2)^2} \right) - 2 \ln \left(\frac{x_1^\circ}{1+x_1^\circ} \right) = F_1 (x_1+x_2-x_1^\circ) \quad (19)$$

$$\text{with } 2 \ln \left(2 \frac{x_1^\circ}{1+x_1^\circ} \right) = \frac{A_1^\circ}{T} + B_1^\circ \ln(T) + C_1^\circ + D_1^\circ T \quad (20)$$

Similarly, the solubility of KCl is given by:

$$\ln \left(\frac{x_2(x_1+x_2)}{(1+x_1+x_2)^2} \right) - 2 \ln \left(\frac{x_2^\circ}{1+x_2^\circ} \right) = F_2 (x_1+x_2-x_2^\circ) \quad (21)$$

$$\text{with } 2 \ln \left(2 \frac{x_2^\circ}{1+x_2^\circ} \right) = \frac{A_2^\circ}{T} + B_2^\circ \ln(T) + C_2^\circ + D_2^\circ T + E_2^\circ T^2 \quad (22)$$

x_1° , x_2° are the solubilities of NaCl and KCl in water at temperature T.

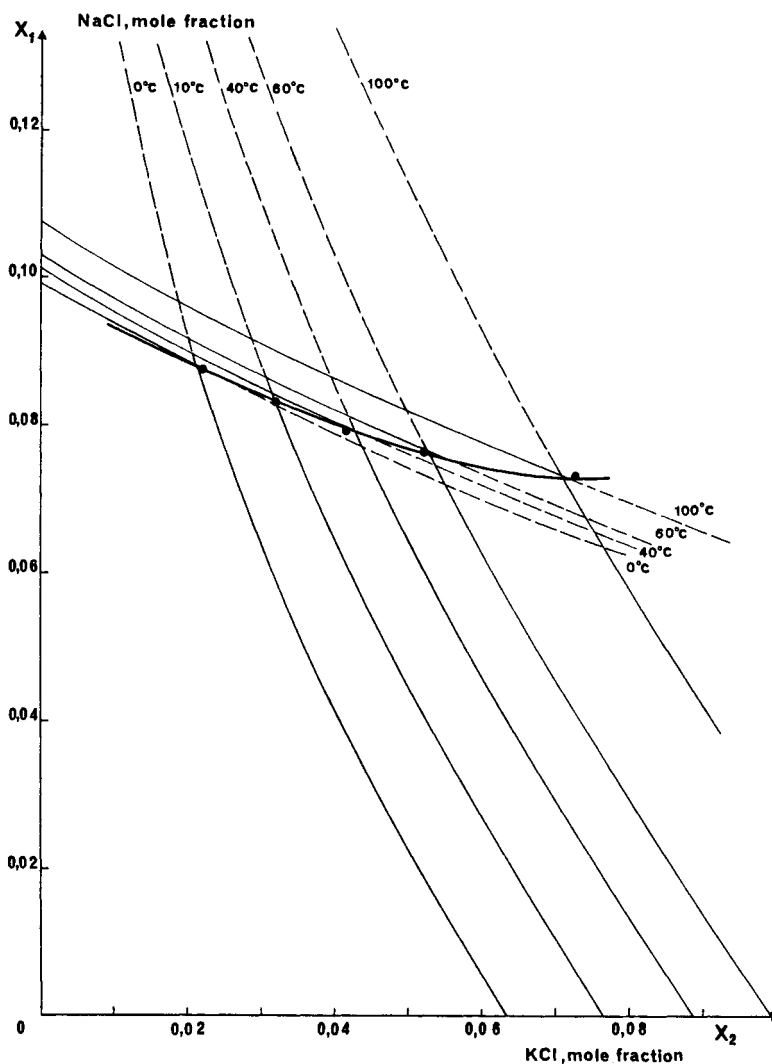


Fig. 3. Ternary system NaCl-KCl-H₂O

Calculated monovariant line — experimental ●

The coefficients F_1 and F_2 were found practically independent of the temperature between 0 and 100°C:

$$F_1 = -4.2491 \quad ; \quad F_2 = -14.3408$$

so that, in the range of temperature 0-100°C, any solid-liquid equilibrium of the ternary system NaCl-KCl-H₂O can be deduced from relations (19) to (22).

At a given temperature the values of x_1^0 and x_2^0 are deduced first from eq. (20), (22) and the solubilities of NaCl or KCl are then evaluated by an iterative method. The calculated and experimental data at 0, 10, 40, 60 and 100°C are in very good agreement as shown in figures 1, 2 and 3.

CONCLUSIONS

A semi empirical model is proposed for critical evaluation of solid-liquid equilibria in aqueous electrolyte multicomponent systems and applied to the ternary system NaCl-KCl-H₂O. It is based first on the choice of a fitting equation for a convenient isoplethic section of the phase diagram and then on the modelisation of isothermal sections.

The application to the solubility of NaCl and KCl shows that the representation of each solubility surface requires three or four adjustable parameters (two or three for the binary system and one for the isothermal section).

The relative simplicity of the representation seems due to the fact that, in concentrated solution, the mean activity coefficient involved in the expression of the activity product varies slowly with the ionic strength of the medium and with temperature.

As already seen in binary systems a more complex development of activity coefficients is required for modelisation of the solubility of ice, on account of the great variation of ionic strength along the solubility surface.

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