PREDICTION OF VLE BEHAVIOR IN CONCENTRATED ELECTROLYTE SOLUTIONS

T. HAUG-WARBERG[*] and S. SKOGESTAD

Norsk Hydro, Research Centre, N-3901 Porsgrunn, Norway

ABSTRACT
    A new hybrid electrolyte VLE model is suggested. By extending
the theoretical Debye-Hückel-Pitzer expression with the empirical
Redlich-Kister term, a highly flexible model has been developed
which is well suited for representing VLE behavior for specific
systems. The system $H_2O-HCl-MgCl_2$ is accurately described in
a temperature and concentration range of 273-423 K, 0-30 mole%
HCl and 0-12 mole% $MgCl_2$. 6 binary parameters (totally 11 when
the temperature dependency is included) were used in the fit.

INTRODUCTION
    Throughout this paper an electrolyte is interpreted as a mixture
(solution) of ionic and molecular compounds. During the past 60
years several attemps have been made to obtain theoretical electro-
lyte activity models. All of these models are based upon the well-
known Debye-Hückel (1923) equation, which is commonly accepted as
the "limiting law" expression for the activity of an ionic compound
in a dielectric continum. However, due to the very complex nature
of electrolytes, none of these general models are capable of hand-
ling concentrated solutions.
    To get a satisfactory activity prediction in a concentrated
solution, Chen (1980) and Pitzer (1980) suggests that an electro-
lyte should be treated with a hybrid equation, e.g. as a sum of a
pure ionic and a molecular model. The contribution from the ionic
term will dominate in the diluted region (here the electrolyte is
almost completely dissociated) and the molecular term in the con-
centrated region. These kinds of equations have been shown to be
very flexible.

---

[*] Author to whom correspondence should be adressed.

Chen (1980) used a hybrid model consisting of the Debye-Hückel equation and an NRTL model based upon <u>all species</u> in the electrolyte (ions and molecules). Pitzer (1980) used an extended Debye-Hückel equation and a van Laar type model which only included the <u>main components</u> in the system (components in the sense of the phase rule). Pitzer´s treatment seems to be more convenient for multicomponent mixtures because of the reduced number of components. This paper is to be regarded as an extension of Pitzer´s work, with special attention to the thermodynamics behind hybrid models.

VLE IN ELECTROLYTES

From the basic equation for vapor-liquid equilibrium (1), the definition of activity (2) and fugacity (3):

$$\mu_i^\ell = \mu_i^g \tag{1}$$

$$\mu_i^\ell = \mu_i^{*\ell} + RT \ln a_i \tag{2}$$

$$\mu_i^g = \mu_i^{\cdot g} + RT \ln f_i / f_i^{\cdot} \tag{3}$$

it is straightforward thermodynamics to establish the equilibrium criterion (4). Here the pressure dependency of the chemical potential is neglected.

$$f_i = f_i^* a_i \tag{4}$$

The fugacity is commonly related to the pressure by introducing a fugacity coefficient:

$$f_i = \varphi_i y_i P \tag{5}$$

There are several ways to relate the activity to the liquid composition, but in the case of electrolytes it is convenient to use a hypothetical mole fraction based upon a completely dissociated electrolyte. Let i be any molecular and j any ionic component in the solution and assume that j dissociates according to the following equation:

$$j = \nu+ \; j+ \; + \; \nu- \; j- \tag{6}$$

$\nu+$ are the number of cations (j+), and $\nu-$ the number of anions (j-) in one formula unit of j.

The activity of i and j may now be expressed in terms of the completely dissociated electrolyte mole fraction (χ) and activity coefficients:

$$a_i = \gamma_i \chi_i \tag{7}$$

$$a_j = (\gamma_{j+} \chi_{j+})^{\nu+} (\gamma_{j-} \chi_{j-})^{\nu-} = (\gamma_{j\pm} \chi_{j\pm})^{\nu} \tag{8}$$

$j\pm$ denotes the mean ionic properties, and $\nu = \nu+ + \nu-$. For any ion or molecule k, χ is related to the analytical mole fractions of i and j by:

$$\chi_k = \frac{n_k}{\sum_i n_i + \sum_j \nu n_j} \tag{9}$$

One way to get an expression of the activity coefficients is to make a model of the excess Gibbs free energy for the mixture:

$$\Delta G^E = G^{\text{real mix}} - G^{\text{ideal mix}} \tag{10}$$

Partial differentiation with respect to a molecular component yields the activity coefficient according to eqn. (7):

$$\left(\frac{\partial \Delta G^E}{\partial n_i}\right)_{P,T,n_k} = RT \ln \gamma_i \tag{11}$$

Partial differentiation with respect to an ionic compound yields the mean ionic activity coefficient according to eqn. (8):

$$\left(\frac{\partial \Delta G^E}{\partial n_j}\right)_{P,T,n_k} = RT \ln \gamma_{j+}^{\nu+} + RT \ln \gamma_{j-}^{\nu-} = RT \ln \gamma_{j\pm}^{\nu} \tag{12}$$

Equation (8) and (12) give the relationship between the fictitious ionic activity coefficients ($\gamma+$, $\gamma-$) and the observable mean activity coefficient $\gamma\pm$. Although $\gamma+$ and $\gamma-$ are physically unrealistic, they play an important role in the electrolyte theory. This is due to the fact that every electrolyte is completely dissociated at infite dilution, and in this case the _true_ mole fractions of the free ions (χ_{j+} and χ_{j-}) may be calculated according to eqn. (9). Knowing the concentrations of the free ions it is possible to develop a theoretical activity expression by means of statistical thermodynamics. These kinds of equations may give the ionic activities although they are not physically measurable.

In concentrated solutions the theoretical activity expressions will, however, fail to work because of significant ion - ion interaction, and some kind of correction has to be used. In our opinion the best way to make this correction is to express the mean ionic activity coefficient $(\gamma_{j\pm})$ in terms of x_j without any knowledge of the true values of x_{j+} or x_{j-}. This leads to the mixing of two excess-functions, one in terms of χ and one in terms of x. The way this problem may be solved is to combine eqns. (10) and (12):

$$(\frac{\partial \Delta G^E}{\partial n_j})_{P,T,n_i} = \nu + (\frac{\partial \Delta G^E}{\partial n_{j+}})_{P,T,n_i} + \nu - (\frac{\partial \Delta G^E}{\partial n_{j-}})_{P,T,n_i} \tag{13}$$

The last equation is very important because it utilizes a direct mixing of a theoretical ionic model in terms of χ_i, χ_{j+}, χ_{j-} and a molecular model in terms of x_i, x_j.

PROPOSED ELECTROLYTE MODEL

To represent the activity coefficients in electrolyte solutions we propose to use a hybrid model consisting of the Debye-Hückel-Pitzer (DHP) equation for the electrostatic forces (Pitzer, 1980), and the Redlich-Kister (RK) 3 parameter model for the residual part (Redlich and Kister, 1948). This combination is justified by the simple form of DHP and the great flexibilty of RK. The excess expression now becomes (pure components as reference states):

$$\frac{\Delta G^E}{RT} = (\sum_i n_i + \sum_j \nu_j n_j)(\frac{1000}{M_s})^{1/2} \frac{4A_\gamma \ln 10}{3\rho} \; I \ln(1 + \rho I^{1/2}) \tag{DHP}$$

$$+ \sum_i n_i (\sum_i \sum_k x_i x_k (b_{ik} + c_{ik}(x_i - x_k) + d_{ik}(x_i - x_k)^2)/2) \tag{RK}$$

$$- \sum_j \nu_j n_j RT \ln \gamma_{j\pm, x_j = 1} \tag{14}$$

In the summations above, j may be any ionic component and i,k any ionic or molecular component.

VLE IN THE SYSTEM H_2O - HCl - $MgCl_2$

In most of the temperature range of interest, this system consist of one subcritical ($1-H_2O$), one supercritical ($2-HCl$), and one solid component ($3-MgCl_2$).

The choice of suitable reference states then becomes quite diffi-
cult, but it appears to be convenient to use pure H_2O, HCl in azeo-
tropic H_2O-HCl mixture (az), and an infinite dilute solution of
$MgCl_2$ in H_2O (∞) as reference solutions for the 3 components re-
spectively. Since $MgCl_2$ is nonvolatile the VLE criterion now
becomes:

$$\varphi_1 y_1 P = \gamma_1 x_1 \varphi_1^* P_1^* \tag{15}$$

$$\varphi_2 y_2 P = \gamma_{2\pm}^2 x_{2\pm}^2 \varphi_2^* y_2^* P_2^* \tag{16}$$

Normalizing the activity coefficient of HCl to 1 in an azeotropic
solution of H_2O-HCl fixes the hypothetical reference state of HCl:

$$\varphi_2^* P_2^* y_2^* = \frac{\varphi_{2,az} y_{2,az} P_{az}}{x_{2\pm,az}^2} \tag{17}$$

By introducing the azeotropic mole fraction of HCl the final VLE
expression for HCl becomes:

$$\varphi_2 y_2 P = \varphi_{2,az} \gamma_{2\pm}^2 x_{2\pm}^2 \frac{(1+x_{2,az})^2}{x_{2,az}} P_{az} \tag{18}$$

Vapor phase fugacities are calculated from the second virial
coefficients given by Wozny (1979). The following H_2O vapor
pressure and H_2O-HCl azeotropic data have been used:

$$\ln P_1^* = 77.78 - \frac{7376}{T} + .007044T - 9.072 \ln(T) \tag{19}$$

$$\ln P_{az} = -225.8 + \frac{1060}{T} - .06964T + 43.161 \ln(T) \tag{20}$$

$$x_{2,az} = .1325 + .002941T - .9151 \cdot 10^{-6} T^2 \tag{21}$$

By introducing eqn. (13) in (14) the normalized activity coeffici-
ents of H_2O, HCl and $MgCl_2$ may be written as:

$$\ln \gamma_1 = \ln \gamma_1^{DHP} + \ln \gamma_1^{RK} \tag{22}$$

$$\ln \gamma_{2\pm}^2 = (\ln \gamma_{2+} + \ln \gamma_{2-} - \ln \gamma_{2+,az} - \ln \gamma_{2-,az})^{DHP}$$
$$+ (\ln \gamma_{2\pm}^2 - \ln \gamma_{2\pm,az}^2)^{RK} \tag{23}$$

$$\ln \gamma_{3\pm}^3 = (\ln \gamma_{3+} + 2 \ln \gamma_{3-}^2)^{DHP} + (\ln \gamma_{3\pm}^3 - \ln \gamma_{3\pm,\infty}^3)^{RK} \tag{24}$$

The final activity coefficient expressions are given in appendix 1. Comparison of reported and calculated isotherms is shown in Figs. 1 and 2. The model has three adjustable Redlich-Kister parameters for each binary; the two lower-order parameters (b_{ij} and c_{ij}) were assumed to be linear functions of temperature. The resulting 15 parameters were found by a regression analysis of experimental x, y, P, T data. Due to the limited concentration range, 4 of these parameters were found to be insignificant and therefore fixed equal to 0. The optimal parameters are listed below:

$$b_{12} = -.636 + .222\,T, \quad c_{12} = -51.699 - .0505\,T, \quad d_{12} \approx 24.25$$
$$b_{13} = 1001.315 + 1.955\,T, \quad c_{13} = 313.702 - .6340\,T, \quad d_{13} \approx 0.00$$
$$b_{23} = -287.914 + .625\,T, \quad c_{23} = 0.000 - .0000\,T, \quad d_{23} \approx 0.00$$

The model has been tested thoroughly against all available literature data, and the range of validity seems to be 273-423 K, 0-30 mole% HCl and 0-12 mole% $MgCl_2$. The calculated phase diagram for the system H_2O-HCl-$MgCl_2$ is shown in Fig. 3.
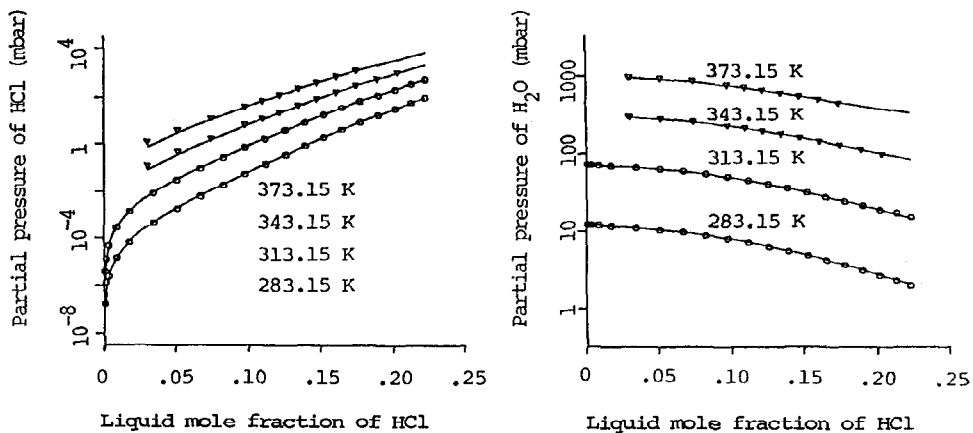

Fig.1. Data fitting in the system H_2O-HCl. o experimental data from Fritz and Fuget (1956). ∇ experimental data from Perry (1975). Full lines are calculated values.
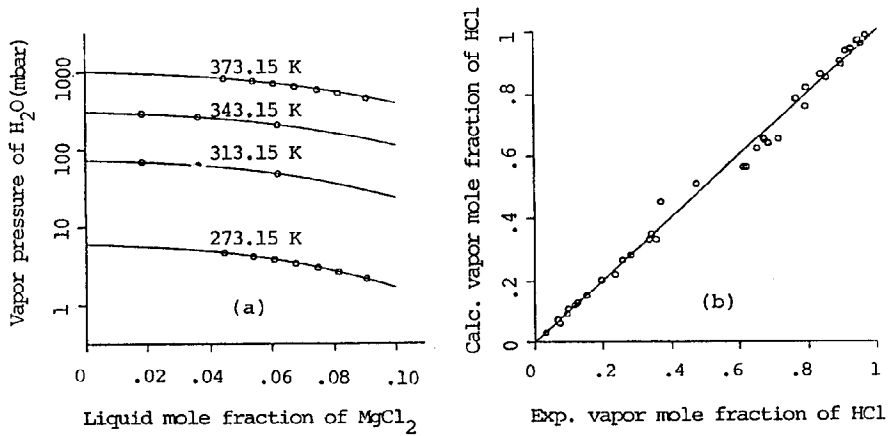
Fig.2. Data fitting in the system H_2O-$MgCl_2$ (a) and H_2O-HCl-$MgCl_2$ (b). o experimental values from Gmelin (1939) and Mirsch (1958) respectively. Full lines are calculated values.
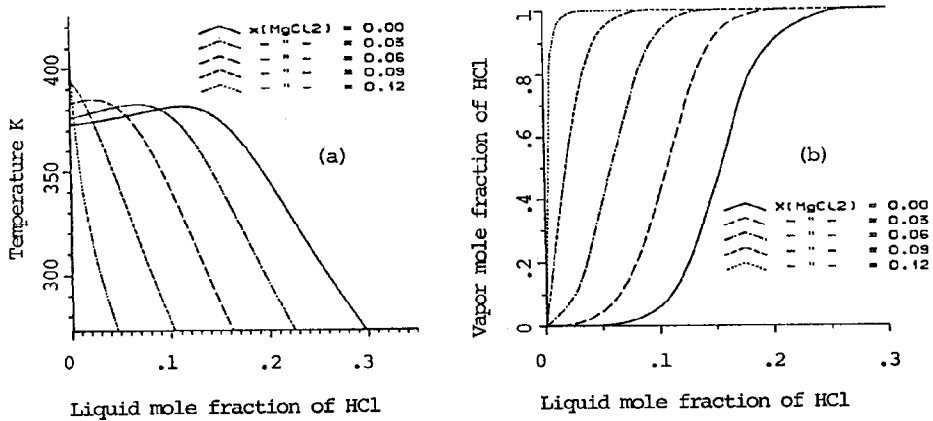

Fig.3. Calculated bubble point curves (a) and the corresponding xy - diagram (b) for the system H_2O-HCl-$MgCl_2$ at 1000 mbar.

PARTIAL MOLAR ENTHALPIES FOR THE SYSTEM H_2O-HCl-$MgCl_2$

The use of classical thermodynamics give the relationship between activity coefficients and partial molar enthalpies in the liquid:

$$\left(\frac{\partial \ln \gamma_k}{\partial T}\right)_{P,x} = - \frac{\bar{h}_k - \bar{h}_k^*}{RT^2} \qquad (25)$$

Enthalpies have been <u>predicted</u> from the previously described VLE model (which was based on VLE data only) to check the temperature dependency of the activity coefficients. Comparison of reported and calculated enthalpies are shown in Fig. 4. The agreement is very good.
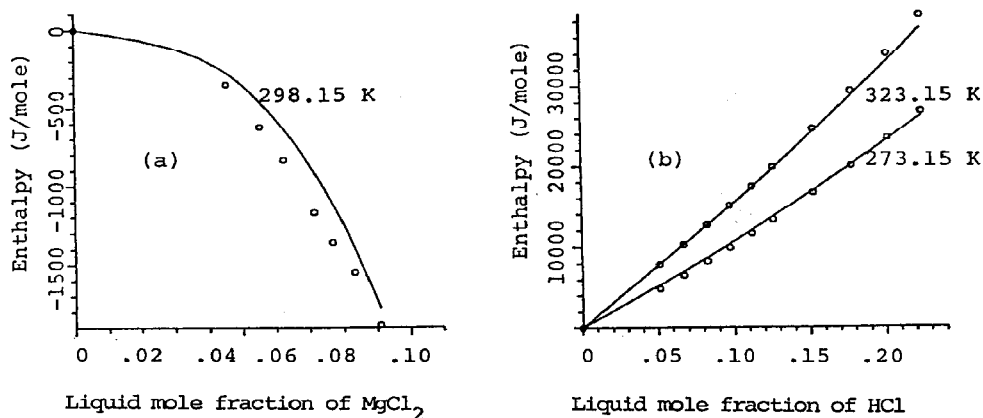

Fig.4. Partial molar enthalpy of (a) H_2O in H_2O-$MgCl_2$, and (b) HCl in H_2O-HCl. o experimental data from Gmelin (1939). Full lines are values predicted from the VLE model.

CONCLUSION

A new semiempirical, hybrid, electrolyte activity model has been developed and successfully applied to the system H_2O-HCl-$MgCl_2$. The model is highly flexible, and should be well suited for industrial applications where the objective often is to get a good fit for a specific system. The model is not a general predictive one, and its use must be based on experimental data. The model has a sound physical basis, however, and safe extrapolations may be made to some extent beyond the range of experimental data.

APPENDIX 1

Activity coefficient of component k according to eqn. (14) and (22)-(23). (i,j and k may be any ionic or molecular component):

$$\ln\gamma_k = -(\frac{1000}{M_s})^{1/2} \frac{A_\gamma \ln 10}{3} \left(\frac{2\nu z_{k\pm}^2}{\rho} \ln(1+\rho I^{1/2}) + \frac{\nu z_{k\pm}^2 I^{1/2} - 2\nu I^{3/2}}{1 + \rho I^{1/2}} \right)$$

$$+ \sum_{j=1}^{N} x_j (b_{kj} + c_{kj}(2x_k-x_j) + d_{kj}(x_k-x_j)(3x_k-x_j))$$

$$- \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{2} x_i x_j (b_{ij} + 2c_{ij}(x_i-x_j) + 3d_{ij}(x_i-x_j)^2)$$

$$- \ln\gamma_{k,x_k=x_{norm}}$$

$$\nu z_{k\pm}^2 = \nu_{k+} z_{k+}^2 + \nu_{k-} z_{k-}^2 \qquad (=0 \text{ for molecular components})$$

$$A_\gamma = \frac{(2\pi N_o d_s)^{1/2}}{\ln 10} (\frac{e^2}{\epsilon_o DkT})^{3/2} = 57708.995 (\frac{d_s^{1/3}}{DT})^{3/2}$$

$$I = \frac{1}{2} \sum_k (z_{k-}^2 x_{k-} + z_{k+}^2 x_{k+})$$

LIST OF SYMBOLS

a   : Liquid activity.
A_γ : Debye-Hückel constant.
b,c,d : Redlich-Kister parameters ($b_{ij} = b_{ji}, c_{ij} = -c_{ji}, d_{ij} = d_{ji}$)
d   : Density
D   : Dielectric constant.
e   : Elementary charge = $1.60219 \cdot 10^{-19}$ (C).
f   : Vapor fugacity.
G   : Gibbs free energy.
I   : Ionic strength.
k   : Boltzmanns constant = $1.38062 \cdot 10^{-23}$ (J·K^{-1}).
M   : Molecular weight.
n   : Number of moles.
N_o : Avogadros number = $6.022 \cdot 10^{23}$ (mol^{-1}).
P   : Pressure
T   : Temperature (K)
x   : Analytical liquid mole fraction.
X   : Hypothetical electrolyte mole fraction.
y   : Analytical vapor mole fraction.
z   : Ionic charge.

GREEK LETTERS

ε_o : Permittivity of free space = $4\pi \cdot 8.85419 \cdot 10^{-12}$ $(C \cdot V^{-1} \cdot m^{-1})$.
γ : Liquid activity coefficient.
φ : Vapor fugacity coefficient.
ν : Number of ions in one formula unit of an ionic compound.
ρ : Closest approach parameter = 14.9 for water systems.
μ : Chemical potential.

SUPERSCRIPT

ℓ : Liquid phase.
g   : Vapor phase.
*   : Reference state, function of both P and T.
$\cdot$: Standard state, function of T only (P fixed).
s   : Solvent
RK,DHP : Redlich-Kister, Debye-Hückel-Pitzer activity model.

SUBSCRIPT

+, -   : Cation, anion
i,j,k   : Pertaining to component i,j,k.
1,2,3   : H_2O, HCl, $MgCl_2$
az,∞,norm : Azeotropic mixture, infinite dilute component in H_2O,
          mixture to which an activity coefficient is normalized.

REFERENCES

Chen, C.C., 1980. Computer Simulation of Chemical Processes with
    Electrolytes, D.Sc., Massachucetts Institute of Technology.
Fritz, J.J. and C.R. Fuget, 1956. Ind.Eng.Chem.Data.Ser., 1: 10-12.
Gmelins Handbuch der Anorganischen Chemie, 1939. Syst. nr. 27 B.,
    114-29.
Mirsch, E., 1958. Chem. Tech., 10: 540-41.
Mirsch, E. and M. Tittel, 1958. Chem. Tech., 10: 539-40.
Perry, R.H. and C.H. Chilton, 1975. Chemical Engineer's Handbook,
    5th.ed., McGraw-Hill Kogakusha LTD., New York.
Pitzer, K.S., 1980. J. of. Am. Chem. Soc., 102: 2902-06.
Redlich, O. and A.T. Kister, 1948. Ind. Eng. Chem., 40: 345-48.
Wozny, G., 1979. Phasengleichgewichte starker Electrolyte aus
    Dampfdruckmessungen und deren Anwendung zur Auslegung von
    Trennkolonnen bei Thermochemischen Wasserzersetzungprozessen,
    Dr.Ing., RWTH Aachen, .