

UNIFAC PREDICTION OF VAPOR-LIQUID EQUILIBRIA IN MIXED SOLVENT-SALT SYSTEMS

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(First received 31 May 1990; accepted in revised form 13 March 1991)

Abstract—The Sander model for correlation and prediction of salt effects on vapor-liquid equilibria (VLE) of mixed solvents combines a term of the Debye-Hückel type with a modified UNIQUAC equation with concentration dependent parameters. In this work the UNIQUAC equation has been substituted by the original UNIFAC group-contribution model with concentration independent group interaction parameters. Group interaction parameters have been estimated between ions (Li^+ , Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Sr^{2+} , Cu^{2+} , Ni^{2+} , Hg^{2+} , F^- , Cl^- , Br^- , J^- , NO_3^- and CH_3COO^-), and solvent groups (CH_2 , OH , CH_2OH , H_2O , CH_3CO), while previously published group interaction parameters between solvent groups have been maintained. It is shown that the proposed model represents VLE for solvent-water-salt mixtures with an expected average accuracy of the total pressure around 9% and of the vapor-phase mole fractions around 4%. Since it is a predictive group-contribution method it has a much broader range of applicability than the Sander model.

INTRODUCTION

Sander *et al.* presented in 1986 a model for the description of salt effects on vapor-liquid equilibria (VLE) of water-solvent mixtures. The model combines a Debye-Hückel term with a modified UNIQUAC term with concentration dependent parameters. It was shown that the model could represent changes in vapor phase composition on the addition of salt to alcohol-water mixtures with good accuracy. Cardoso and O'Connell (1987) showed that the Sander model contained an inconsistency in the Debye-Hückel term for a solvent in a mixed solvent system. Macedo *et al.* (1990) have recently used a modified Debye-Hückel term to ensure a more correct representation of long range forces. This modification required a re-estimation of previously published interaction parameters. At the same time Macedo *et al.* also extended the range of applicability of the Sander model by including some more ions and solvents.

In this work the Sander model has been modified: (1) the Debye-Hückel term is calculated according to the McMillan-Mayer solution theory as described by Cardoso and O'Connell (1987) and (2) the UNIQUAC term has been substituted by a UNIFAC term (Fredenslund *et al.*, 1977).

UNIFAC group-interaction parameters between ions and solvent groups have been estimated, while the values of the group-interaction parameters between solvent groups are the same as those which have been published previously for nonelectrolyte solutions (Gmehling *et al.*, 1982).

THEORY

In this work the activity coefficient γ_n of a solvent n in a liquid-solvent mixture is calculated as:

$$\ln \gamma_n = \ln \gamma_n^{D-H} + \ln \gamma_n^C + \ln \gamma_n^R \quad (1)$$

where γ_n^{D-H} is the Debye-Hückel term and γ_n^C and γ_n^R represent the UNIFAC combinatorial and residual contributions.

The Debye-Hückel term is calculated from eq. (2) as described by Macedo *et al.* (1990).

$$\ln \gamma_n^{D-H} = \frac{2AM_n d_s}{b^3 d_n} \left[1 + b\sqrt{I} - \frac{1}{1 + b\sqrt{I}} - 2 \ln(1 + b\sqrt{I}) \right] \quad (2)$$

In eq. (2) M_n is the molar mass of solvent n , I is the ionic strength, d_n is the density of pure solvent n , while the density of the solvent mixture d_s is calculated as

$$d_s = \frac{M_s}{\sum_n x'_n M_n / d_n} \quad (3)$$

where x'_n is the salt-free mole fraction of solvent n and $M_s = \sum_n x'_n M_n$ is the molar mass of the liquid mixture. The pure solvent densities are evaluated from the *DIPPR Tables* (1984).

$$A = 1.327757 \times 10^5 d_s^{1/2} / (\epsilon T)^{3/2} \quad (4)$$

$$b = 6.359696 d_s^{1/2} / (\epsilon T)^{1/2} \quad (5)$$

The dielectric constant ϵ of the solvent mixture is obtained from the pure solvent values ϵ_n (Maryott and Smith, 1951) and Oster's empirical mixing rule (Franks, 1973) which for a binary aqueous mixture

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(water is solvent 1) can be approximated to:

$$\varepsilon \approx \varepsilon_1 + [(\varepsilon_2 - 1)(2\varepsilon_2 + 1)/2\varepsilon_2 - (\varepsilon_1 - 1)] \times x'_2 V_2/V \quad (6)$$

where the molar volume of the mixture V is calculated from the pure solvent molar volumes V_1 and V_2 as

$$V = x'_1 V_1 + x'_2 V_2. \quad (7)$$

The UNIFAC contributions γ_n^C and γ_n^R in eq. (1) are calculated as described by Fredenslund *et al.* (1977). The group volume and surface area parameters, R_k and Q_k , needed for the UNIFAC calculations are shown in Table 1. The values of R_k and Q_k for the ions are taken from Macedo *et al.* (1990) and for the solvent groups from Gmehling *et al.* (1982). Table 1 comprises the solvent groups which are needed to build up the solvents included by Macedo *et al.* (1990) and which occur in the database used for the parameter estimations. The sample group assignment is shown in Table 1 for the pertinent solvents.

The UNIFAC group-interaction parameters between the solvent groups have not been changed in this work and we use the values presented by Gmehling *et al.* (1982) and shown in Table 2. The interaction parameters between the solvent groups and the ions have been estimated as described in the following section.

ESTIMATION OF UNIFAC PARAMETERS

The database for parameter estimation is the same as the one used by Macedo *et al.* (1990). It consists of binary and ternary data sets for mixtures with the solvents water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and acetone; the cations of lithium, sodium, potassium, calcium, barium, strontium, copper, nickel and mercury; the anions of

fluoride, chloride, bromide, iodide, nitrate and acetate. Binary salt-solvent data for which ternary salt-mixed solvent data for the same components are not available have not been included in the database.

The experimental VLE data fall in three categories: (1) x, T, y, P ; (2) x, T, P and (3) x, T, Φ . Here x and y represent mole fractions in the liquid and vapor phases respectively, T is the temperature, P the total pressure and Φ the osmotic coefficient. The osmotic coefficient Φ is only used for binary aqueous solutions and it is calculated as:

$$\Phi = x_n \ln(x_n \gamma_n)/(1 - x_n). \quad (8)$$

The UNIFAC group interaction parameters have been estimated by minimization of the following objective function:

$$F = \sum_{NDP} \sum_{NDT} (D_{exp} - D_{calc})^2 W_D \quad (9)$$

where D represents P, y and Φ and/or γ depending on the type of available experimental data. W_D is a weight factor for data type D . NDP and NDT are the numbers of data points and data types. The subscripts exp and calc refer to experimental and calculated data.

In principle, it would be necessary to estimate all ion-solvent group-interaction parameters simultaneously in order to obtain the optimal values of the parameters. In practice, it has however turned out that it is more efficient to split the database and to estimate the parameters in groups from more limited databases. In the first estimation we have for example estimated most of the interaction parameters with Li^+, K^+ and Br^- and in the second estimation most of the parameters involving Na^+, Ca^{2+} and Cl^- . The application of limited databases has significantly reduced the rather lengthy computer times for the

Table 1. Group volume (R_k) and surface area (Q_k) parameters

Cations									
Type	Li^+	Na^+	K^+	Ca^{2+}	Ba^{2+}	Sr^{2+}	Cu^{2+}	Ni^{2+}	Hg^{2+}
R_k	1.0	3.0	3.0	1.0	3.0	1.0	1.0	1.0	3.0
Q_k	1.0	3.0	3.0	1.0	3.0	1.0	1.0	1.0	3.0
Anions									
Type	F^-	Cl^-	Br^-	I^-	NO_3^-	CH_3COO^-			
R_k	0.4195	0.9861	1.2331	1.6807	1.64	2.05			
Q_k	0.5597	0.9917	1.1510	1.4118	1.60	1.90			
Solvent groups									
No.	Main group	No.	Subgroup	R_k	Q_k	Sample group assignment			
1	CH_2	1	CH_3	0.9011	0.848	Ethanol	1 CH_3 , 1 CH_2 , 1 OH		
		2	CH_2	0.6744	0.540	1-Propanol	1 CH_3 , 2 CH_2 , 1 OH		
		3	CH	0.4469	0.228	2-Propanol	2 CH_3 , 1 CH, 1 OH		
5	OH	15	OH	1.000	1.200	1-Butanol	1 CH_3 , 3 CH_2 , 1 OH		
		16	CH_3OH	1.4311	1.432	Methanol	1 CH_3OH		
6	CH_3OH	16	CH_3OH	1.4311	1.432	Water	1 H_2O		
7	H_2O	17	H_2O	0.92	1.40	Acetone	1 CH_3 , 1 CH_3CO		
9	CH_2CO	19	CH_3CO	1.6724	1.488				

Table 2. UNIFAC-group interaction parameters a_{ij} in Kelvin'

	Ba^{2+}	Ca^{2+}	K^+	Na^+	Li^+	CH_3CO	H_2O	CH_3OH	OH	CH_2
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parameter estimation. The estimated interaction parameters are shown in Table 2. Lack of experimental data has prevented the estimation of some parameters. In the table they are marked "n.a.", i.e. not available. Parameters of the type $a_{cc'}$ and $a_{aa'}$ where cc' and aa' represent pairs of cations and anions of different types cannot be obtained from single-salt data. In Table 2 these parameters are marked "N.C.". And it is suggested (Sander *et al.*, 1986) that these parameters in calculations on mixed electrolyte solutions are set equal to zero.

RESULTS AND DISCUSSION

Table 3 gives some examples of deviations between experimental and calculated pressures and vapor-phase mole fractions for a number of ternary systems. All the systems listed in Table 3 were included in the database for the parameter estimation with the exception of the systems marked by † which are predicted from the parameters reported in Table 2. Deviations are given for calculations with UNIFAC parameters of this work and UNIQUAC parameters of Macedo *et al.* (1990).

It can be seen that the deviations in pressure predicted by UNIFAC are, in general, comparable to, even though normally somewhat larger than the deviations obtained from UNIQUAC. The UNIFAC

predictions of the vapor-phase mole fractions are of reasonable accuracy but the deviations are, in general, three times as large as the UNIQUAC deviations.

Considering that the UNIFAC method is a group-contribution method and that the group-interaction parameters are concentration independent it seems fair to say that the UNIFAC predictions are quite good. It should be recalled that the UNIQUAC parameters in the Sander model are concentration dependent, and that UNIQUAC can only be used for specific solvents while UNIFAC as a group-contribution method is much more flexible.

For ethanol-water-KNO₃ the UNIFAC deviations for both the pressure and vapor-phase mole fractions are very large. The reason is that UNIFAC as a group-contribution method cannot be expected to work very well on this system which shows a liquid-liquid phase split. One can of course make a nice fitting with the UNIQUAC method. Furthermore, the experimental data set (Rieder and Thompson, 1950) may not be too reliable since the authors apparently did not measure the pressure, and the system was saturated without measured salt concentrations.

The database comprised in total 123 binary and ternary data sets. Based on all the data sets the absolute deviations are around 9% in pressure and 0.042 in vapor-phase mole fractions.

Table 3. Some comparisons of ternary VLE calculations using UNIQUAC parameters from Macedo *et al.* (1990) and UNIFAC parameters from this work

System	P (mm Hg) or t (°C)	Number of data points	UNIQUAC		UNIFAC	
			ΔP [†] (mm Hg)	Δy [‡]	ΔP (mm Hg)	Δy
Methanol-water-NaBr	760	23	22.0	0.029	19.1	0.025
-NaCH ₃ COO	760	21	16.4	0.011	34.5	0.070
-CaCl ₂	752	15	21.7	0.012	43.0	0.076
-LiCl	700 [§]	23	20.5	0.008	22.2	0.017
Ethanol-water-NaF	700	13	10.9	0.010	12.8	0.007
-NaCl	700	32	21.9	0.008	32.6	0.024
-NaI	700	17	4.7	0.004	19.4	0.022
-KI	700	19	10.9	0.010	26.3	0.025
-KNO ₃	760	8	7.9	0.012	114.6	0.089
-KCH ₃ COO	756	12	47.6	0.013	24.4	0.042
1-Propanol-water-KCl	753	10	20.9	0.020	27.93	0.044
-Ca(NO ₃) ₂	700	16	30.9	0.007	37.0	0.020
2-Propanol-water-LiCl	75.1	22	18.5	0.007	40.6	0.083
-NaBr	760	11	36.2	0.043	8.0	0.030
-CaCl ₂	760	16	9.4	0.008	13.4	0.013
1-Butanol-water-KI	700	17	6.0	0.014	15.0	0.032
-Ca(NO ₃) ₂	700 [§]	28	24.4	0.019	44.4	0.048
Acetone-water-KCl	760	28	21.9	0.018	62.8	0.030
Acetone-methanol-CaCl ₂	760	28	16.3	0.029	25.2	0.010
		Average	19.4	0.015	32.8	0.037

$$^{\dagger}|\Delta P| = (1/N) \sum_N |P_{\text{exp}} - P_{\text{calc}}|$$

$$^{\ddagger}|\Delta y| = (1/N) \sum_N |y_{\text{exp}} - y_{\text{calc}}|$$

[§]Systems not included in the parameter estimation data base.

Table 4. Prediction of vapor-phase mole fraction deviation for two systems not included in the database[†]

Ethanol-water-CaCl ₂ at 298 K		
RAMD [‡]		
Salt concentration (wt%)	Sander model	UNIFAC of this work
5	1.19	3.70
10	0.90	2.67
15	2.76	5.40
Methanol-ethanol-CaCl ₂ at 298 K		
RAMD		
Salt concentration (wt%)	Sander model	UNIFAC of this work
5	2.55	0.85
10	1.53	0.35
15	3.52	3.05

[†]Experimental data: Mishima *et al.* (1986).

$$^{\ddagger}\text{RAMD} = (1/N) \sum_N \left(\frac{|y_{\text{exp}} - y_{\text{calc}}|}{y_{\text{exp}}} \right) \times 100.$$

Table 4 shows some predictions of vapor-phase mole fractions for two systems which were not included in the database for parameter estimation. The experimental data are given by Mishima *et al.* (1986) for ethanol-water-CaCl₂ and methanol-ethanol-CaCl₂ at 298 K. Figures 1 and 2 show *y*-*x* diagrams for the two systems. It is seen from the figures and Table 4 that UNIFAC gives quite accurate predictions.

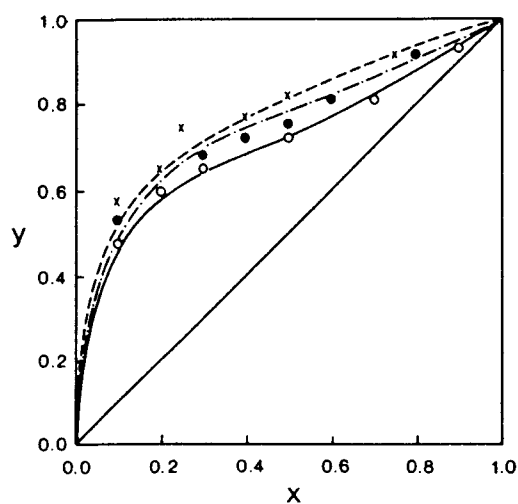


Fig. 1. Ethanol-water-CaCl₂ at 298 K. Experimental data from Mishima *et al.* (1986): (o) 5 wt%, (●) 10 wt%, (×) 15 wt%. UNIFAC predictions (—) 5 wt%, (---) 10 wt%, (· · ·) 15 wt%.

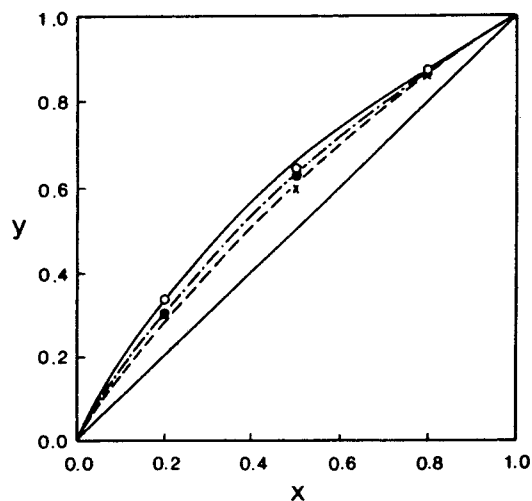


Fig. 2. Methanol-ethanol-CaCl₂ at 298 K. Experimental data from Mishima *et al.* (1986): (o) 5 wt%, (●) 10 wt%, (×) 15 wt%. UNIFAC predictions (—) 5 wt%, (---) 10 wt%, (· · ·) 15 wt%.

CONCLUSIONS

This paper has shown that it is possible to use a model which combines a Debye-Hückel contribution for long range electrostatic forces and a UNIFAC contribution for short range physical interactions to predict VLE for salt-mixed solvent systems.

UNIFAC group-interaction parameters are given for 9 cations, 6 anions and 5 solvent groups. VLE predictions for systems which contain these ions and solvent groups can be made with an expected average accuracy of the total pressure around 9% and of the vapor phase mole fractions around 4%.

Acknowledgements—The authors gratefully acknowledge the financial support to this work by NATO and CNR. In addition we thank Professor P. Alessi (Trieste, Italy) and Aa. Fredenslund (Lyngby, Denmark) and Dra. E. Macedo (Porto, Portugal), who have in different ways contributed to this work.

NOTATION

<i>A</i>	Debye-Hückel parameter
<i>b</i>	Debye-Hückel parameter
<i>d</i>	density, kg/m ³
<i>F</i>	objective function
<i>I</i>	ionic strength
<i>M_n</i>	molar mass of component <i>n</i>
<i>P</i>	pressure
<i>T</i>	absolute temperature in Kelvin
<i>V</i>	molar volume, m ³ /mol
<i>x'_n</i>	liquid phase salt-free mole fraction
<i>y_n</i>	vapor-phase mole fraction

Greek letters

ϵ	dielectric constant
γ	activity coefficient
Φ	osmotic coefficient

Subscripts

calc calculated
 exp experimental
 n component *n*
 s solvent mixture

Superscripts

C combinatorial
 D-H Debye-Hückel
 R residual.

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