EQUIFASE 99. V Conferencia Iberoamericana sobre
Equilibrio entre Fases para el Diseño de Procesos
Vigo del 20 al 24 de Junio de 1999

A GROUP CONTRIBUTION MODEL FOR ACTIVITY COEFFICIENTS IN ASSOCIATING SOLUTIONS

M.O. Ferreira, E.A. Brignole and S.B. Bottini

PLAPIQUI, UNS-CONICET, C.C. 717, 8000 Bahía Blanca, Argentina

ABSTRACT

A group contribution model is presented for the prediction of activity coefficients in associating mixtures. The new model adds an association term to the traditional UNIFAC residual and combinatorial contributions to the activity coefficients. The association term is based on Wertheim's theory for fluids with highly directed attractive forces, as applied in the SAFT equation, and it follows the group contribution approach proposed by Gros et al. in the GCA-EOS model. Good predictions of both, vapor-liquid and liquid-liquid equilibria are achieved in the whole concentration range, with a single set of group interaction parameters.

INTRODUCTION

Local composition models do not describe properly the behaviour of liquid mixtures when associating components are present. This is also the case for group contribution local composition models, such as UNIFAC [1]. The limitations of these models to deal with associating components are more serious when the prediction of both, vapor-liquid and liquid-liquid equilibria is attempted, using a unique set of interaction parameters. In the present work, an extended UNIFAC model for the prediction of activity coefficients in associating solutions is presented. An association term, based on Wertheim´s first order thermodynamic perturbation theory [2] has been added to the traditional combinatorial and residual UNIFAC contributions. The association term was derived from the corresponding expression for the residual Helmholtz energy applied in the SAFT equation of state [3-7], as it was done by Fu et al. [8] for the UNIQUAC model. The group contribution approach followed by Gross et al. [9,10] in the GCA-EOS model was adopted, in order to allow a straight forward extension of the method to multicomponent solutions, overcoming the computational difficulties inherent to the molecular approach, when dealing with cross association problems.

GROUP CONTRIBUTION ACTIVITY COEFFICIENT

The derivation of the model is given elsewhere [11]. The non ideal behaviour is described by the addition of three different contributions to the excess Gibbs energy function and activity coefficients:

$$G^{E} = G^{comb} + G^{res} + G^{assoc} \tag{1}$$

$$\gamma = \gamma^{comb} \ \gamma^{res} \ \gamma^{assoc} \tag{2}$$

In these expressions the combinatorial (comb) and residual (res) contributions are those of the UNIFAC model and the association (assoc) term is derived from an expression for the residual Helmholtz energy due to association.

In the model, the energy of association is a function of the number and type of associating groups present in the solution.

Each associating group is characterised through a volume (κ^*) and energy (ε) related parameters, which define the association strength (Δ^*). The values of the association strength and the molar density of the solution determine the degree of association, which is quantified through the fraction X^A of molecules not bonded at associating site A.

The final expression of γ^{assoc} will depend on the amount and type of associating sites and species present in the solution [11]. The simplest expression correspond to mixtures in which only one associating group with two bonding sites is present. A typical example is hydrogen bonding between an electropositive site H and an electronegative site O in alcohols and water. In the present work we have assumed that all association effects in alcohols, water, their mixtures and mixtures with other inert components, are due to the presence of a unique OH associating group, the same for all alcohols and water. Therefore, these solutions will be characterised by a single Δ^{*OH} association strength, of energy ε^{OH} and volume κ^{*OH} parameters, for the non zero hydroxyl O-H interactions, giving rise to a fraction ($1-X^{OH}$) of hydrogen-bonded molecules. On the basis of these assumptions, the association contribution to the activity coefficient of component i in a solution with hydrogen bonding effects is [11]:

$$\ln\gamma_i^{assoc} = \nu^{OH,i}\left[2\ln\left(\frac{X^{OH}}{X_i^{OH}}\right)+X_i^{OH}-X^{OH}\right]-\left(\frac{2}{X^{OH}}-1\right)\frac{\left(X^{OH}\right)^2\rho_{OH}^{*}\Delta^{*OH}\left(\nu^{OH,i}-r_i\rho_{OH}^{*}\right)}{\left(1+2\rho_{OH}^{*}\Delta^{*OH}X^{OH}\right)} \qquad (3)$$

The fraction of monomers in the solution (X^{OH}) and in pure component i (X_i^{OH}) can be calculated explicitly from a quadratic expression:

$$X^{OH} = \frac{-1+\sqrt{1+4\,\rho_{OH}^{*}\Delta^{*OH}}}{2\,\rho_{OH}^{*}\Delta^{*OH}} \qquad (4)$$

$$X_i^{OH} = \frac{-1+\sqrt{1+4\,(\rho_{OH}^{*})_i\Delta^{*OH}}}{2\,(\rho_{OH}^{*})_i\Delta^{*OH}} \qquad (5)$$

In these equations ρ_{OH}^{*} and $\left(\rho_{OH}^{*}\right)_i$ represent a density number for the hydroxyl OH group in the solution and in pure associating component i, respectively:

$$\rho_{OH}^{*} = \frac{\sum_{i=1}^{NC}\nu^{OH,i}x_i}{\sum_{i=1}^{NC}r_i x_i} \qquad (6)$$

$$(\rho_{OH}^{*})_i = \frac{\nu^{OH,i}}{r_i} \qquad (7)$$

where $\nu^{OH,i}$ represents the number of OH groups present in molecule i and r_i is the UNIQUAC volume parameter (evaluated from UNIFAC group parameters R_k in the usual way $r_i = \Sigma\, \nu^{k,i} R_k$) Eqn. 3 satisfies the Gibbs-Duhem equation. In mixtures of an associating and an inert component, there will be a non- zero association contribution to the activity coefficients for both, the associating as well as the non-associating compound. The number of hydroxyl associating groups is $\nu^{OH} = 0$ for the pure non-associating component, and $\nu^{OH} = 1$ for water and alcohols.

PARAMETERIZATION

The model was applied to mixtures of alcohols, water and alkanes, under conditions of low pressure vapor-liquid (VLE) and liquid-liquid (LLE) equilibria.

ASSOCIATION PARAMETERS

The values of the volume κ^{*OH} and energy ε^{OH} association parameters for the hydroxyl group were obtained by adjusting the expression proposed in this paper for X^{OH} (eqn. 4), to the fraction of monomers predicted by the SAFT equation [5], for ethanol and water at liquid densities. The results are reproduced in Figures 1 and 2. There are two curves shown in each figure for the SAFT equation: one corresponds to the fractions of monomer predicted at saturated liquid densities, and the other at a constant density (the saturated liquid density at 298 K). The SAFT variable-density curves show how the monomer fraction increases (i.e. how association decreases), as the liquid density decreases towards its critical value. The curves for the present association model were obtained with the following values for the association parameters: $\kappa^{*OH} = 0.025$ and $\varepsilon^{OH}/k = 3000$ K. As shown in the figures, this unique set of group parameters was able to reproduce reasonably well the monomer fractions of water and ethanol predicted by the more complex, molecular based, SAFT expressions.

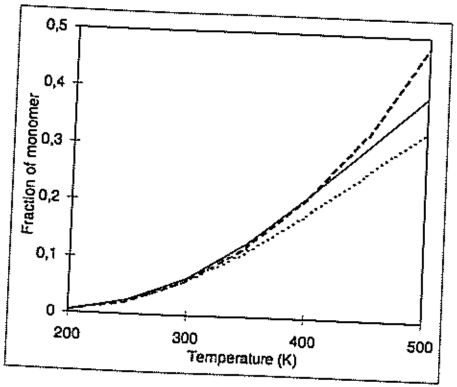

Fig.1: Ethanol monomer fractions: · SAFT (saturated liquid densities); ······ SAFT (liquid density at 298K); —— present work.

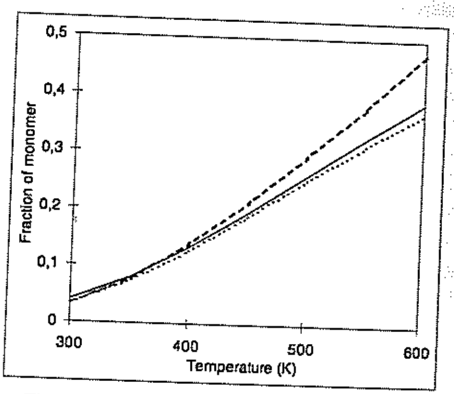

Fig.2: Water monomer fractions: SAFT (saturated liquid densities); ······ SAFT (liquid density at 298K); —— present work.

RESIDUAL PARAMETERS

The residual group interaction parameters were determined by fitting information on low pressure vapor-liquid (VLE) and liquid-liquid equilibria (LLE) of some binary systems.

Table 1 shows the values of the residual parameters for the interactions between the OH, CH_2 and H_2O groups. The average errors in the correlation of data and the source of experimental data are reported in Table 2.

Table 1 - Residual group interaction parameters

Am,n	CH_2	OH	H_2O
CH_2	0.0	48.3	145.9
OH	96.0	0.0	-165.2
H_2O	314.8	-76.6	0.0

RESULTS AND DISCUSSION

Figures 3 to 10 show some of the results of the correlation of VLE and LLE of alkane-alcohol, alkane-water, alcohol-alcohol and water-alcohol mixtures. Good representation of both, vapor-liquid and liquid-liquid equilibria is achieved, with a single non-adjustable pair of associating parameters and a unique set of group interaction parameters.

Table 3 compares the predictions of activity coefficients at infinite dilution for some binaries. It is interesting to analyse the effect of composition on the values of the association and residual contributions to the activity coefficients of associating compounds. Figure 11 shows the variation of the association and the residual activity coefficient terms, for ethanol diluted in hexane. The association curve was obtained with the expression given in eqn. 3, using the parameters adopted in this work for the OH associating group ($\kappa^{*OH} = 0.025$; $\varepsilon^{OH}/k = 3000$ K). As it can be inferred from this figure, the association term is able to follow, in the very diluted region, the sharp increase of the ethanol activity coefficient towards its value at infinite dilution (it should be remembered that the association parameters were not adjusted to this γ^{∞} value). This sharp variation is not followed by UNIFAC residual contribution, as shown by the dotted line in Fig. 11, which was obtained using the UNIFAC VLE parameter table [17].

Finally, Figures 12 and 13 show the prediction of liquid-liquid equilibria for the ternary ethanol - water - hexane. Though the model seems to overpredict the region of partial liquid miscibility, there is an excellent agreement between the experimental and predicted tie lines and ethanol distribution coefficients, even at low ethanol concentrations.

The introduction of a specific term to account for the highly directed association forces seems to have added flexibility to the traditional UNIFAC model. No new adjustable parameters have been introduced in the model, and a good representation of both, vapor-liquid and liquid-liquid equilibria was achieved in the whole concentration range, using a unique set of residual group interaction parameters.

Table 2- Average errors in the correlation of data and source of experimental data.

System	Number of points	δY	δP	Source of data: DECHEMA Series
VLE Methanol - Butane* 50°C	11	4.28	6.95	Vol. I, Part 2c; pg. 126
VLE Methanol - Hexane* 45°C	13	5.82	4.26	Vol. I, Part 2a; pg. 252
VLE Methanol* - Octane 1 atm.	13	1.29	3.16	Vol. I, Part 2c; pg. 249
VLE Ethanol - Pentane* 20°C	21	1.62	5.31	Vol. I, Part 2c; pg. 375
VLE Ethanol - Hexane* 25°C	9	1.85	3.05	Vol. I, Part 2a. pg. 456
VLE Ethanol - Hexane* 35°C	11	2.11	2.08	Vol. I, Part 2a; pg. 450
VLE Ethanol* - Heptane 40°C	15	3.29	2.53	Vol. I, Part 2c; pg. 457
VLE Ethanol* - Octane 45°C	17	2.99	5.30	Vol. I, Part 2c; pg. 462
VLE Ethanol* - Isooctane 25°C	10	2.78	2.75	Vol. I, Part 2a; pg. 502
VLE 1-Propanol - Hexane* 45°C	5	1.32	4.00	Vol. I, Part 2a; pg. 584
VLE 1-Propanol* - Heptane 60°C	16	14.00	3.10	Vol. I, Part 2c; pg. 564
VLE 1-Butanol - Pentane* 30°C	15	3.58	15.78	Vol. I, Part 2b; pg. 169
VLE 1-Butanol - Hexane* 1 atm.	21	1.44	1.72	Vol. I, Part 2b; pg. 200
VLE 1-Butanol - Heptane* 50°C	8	1.85	4.34	Vol. I, Part 2b; pg. 217
VLE 1-Pentanol - Pentane* 30°C	15	2.06	19.28	Vol. I, Part 2b; pg. 330
VLE 1-Pentanol - Hexane* 25°C	11	0.43	9.38	Vol. I, Part 2b; pg. 337
VLE 2-Propanol*-Isooctane atm.	14	25.94	12.46	Vol. I, Part 2b; pg. 116
VLE 2-Butanol - Hexane* 60°C	11	2.85	3.78	Vol. I, Part 2b; pg. 250
VLE t-Butanol - Hexane* 1 atm.	24	5.01	5.00	Vol. I, Part 2b; pg. 262
VLE Ethanol* - 1-Butanol 1 atm.	14	1.04	0.63	Vol. I,. Part 2a; pg. 365
VLE Ethanol* - Isobutanol 60°C	11	3.51	4.24	Vol. I, Part 2a; pg. 378
VLE 1-Propanol* - Isobutanol 80°C	11	0.92	0.15	Vol. I, Part 2a; pg. 542
VLE 1-Propanol*- 1-Butanol 1atm.	9	0.36	1.22	Vol. I, Part 2a; pg. 539
VLE 1-Butanol - Isobutanol* 1atm.	17	0.51	0.93	Vol. I, Part 2b; pg. 161
VLE 2-Propanol - Ethanol* 1 atm.	13	1.28	0.43	Vol. I, Part 2a; pg. 341
VLE 2-Butanol*-1-Butanol .66 atm	11	0.40	0.22	Vol. I, Part 2b; pg. 153
VLE t-Butanol - Ethanol* 1 atm.	16	3.01	1.91	Vol. I, Part 2a; pg. 367
VLE Water - Methanol* 1 atm.	12	6.22	7.80	Vol. I, Part 1; pg. 65
VLE Water - Ethanol* 100 mmHg.	11	6.93	8.10	Vol. I, Part 1; pg. 167
VLE Water - Ethanol* 40°C	13	6.99	8.47	Vol. I, Part 1; pg. 172
VLE Water- 1-Propanol* 60°C	15	11.34	9.19	Vol. I, Part 1; pg. 297
VLE Water* - 1-Butanol 1 atm.	15	5.82	4.53	Vol. I, Part 1; pg. 406
VLE Water - 1-Butanol* 60°C	9	12.74	8.31	Vol. I, Part 1; pg. 411
VLE Water - Isopropanol* 1 atm.	20	15.51	4.73	Vol. I, Part 1; pg. 317
VLE Water - Isopropanol* 45°C	8	8.35	7.13	Vol. I, Part 1; pg. 321
VLE Water - t-Butanol* 25°C	14	50.69	32.56	Vol. I, Part 1; pg. 422
		δX1	δX2	
LLE Water - Pentane 0 - 25°C	4	187.18	0.0257	Vol. V, Part 1; pg. 305
LLE Water - Hexane 0 - 40°C	6	145.53	0.0185	Vol. V, Part 1; pg. 414
LLE Water - Heptane 0 - 40°C	6	213.71	0.0178	Vol. V, Part 1; pg. 470
LLE Water - Octane 0 - 30°C	5	126.45	0.0163	Vol. V, Part 1; pg. 493
LLE Water - 1-Butanol 0 -120°C	8	49.25	48.95	Vol. V, Part 1; pg. 236
LLE Water - 2-Butanol 20 - 100°C	6	76.48	79.56	Vol. V, Part 1; pg. 240
LLE Water - Isobutanol 0 - 120°C	8	64.20	29.19	Vol. V, Part 1; pg. 244
LLE Water - 1-Pentanol 20 - 90°C	6	35.75	6.21	Vol. V, Part 1; pg. 312
LLE Water - 2-Pentanol 20 - 30°C	3	78.84	5.88	Vol. V, Part 1; pg. 312
LLE Water - 1-Hexanol 25°C	1	53.84	0.73	Vol. V, Part 1; pg. 419
LLE Water - 2-Hexanol 20 - 30°C	3	80.49	1.13	Vol. V, Part 1; pg. 422
LLE Water - 1-Heptanol 30°C	1	49.84	2.46	Vol. V, Part 1; pg. 472
LLE Water - 1-Octanol 20 - 60°C	4	67.84	4.30	Vol. V, Part 1; pg. 501

$\delta z=100\sqrt{(\sum_i \{[zi(exp)-zi(calc)]/zi(exp)\}^2/NP)}$, NP: number of points; z: x, y or P; *: component for which δy was calculated; x_1: Water in Alkane or Alkanol. x_2: Alkane or Alkanol in Water.

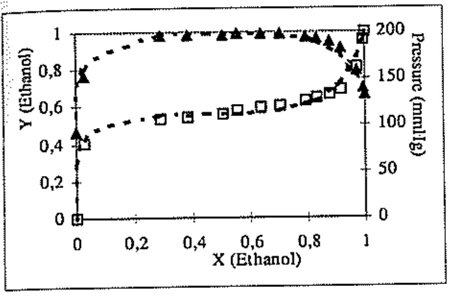

Fig.3: Vapor-Liquid Equilibrium of Ethanol-Heptane at 313K: experimental data (vapor composition and pressure respectively): Dechema Series, Vol. I,. Part 2c, pg. 457; ········ calculated.

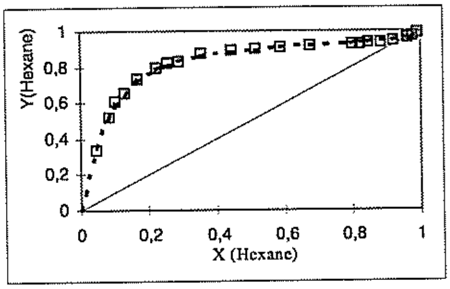

Fig.4: Vapor-Liquid Equilibrium of 1-Butanol-Hexane at 1atm: experimental data (vapor composition): Dechema Series, Vol. I, Part 2b, pg. 200; ········ calculated.

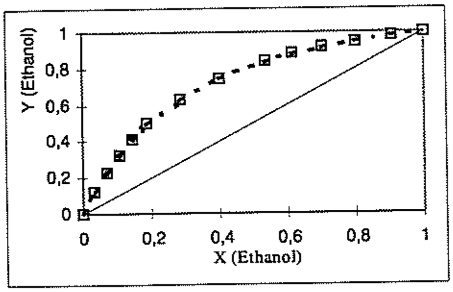

Fig.5: Vapor-Liquid Equilibrium of Ethanol- 1-Butanol at 1atm: experimental data (vapor composition): Dechema Series, Vol. I, Part 2a, pg. 365; ········ calculated.

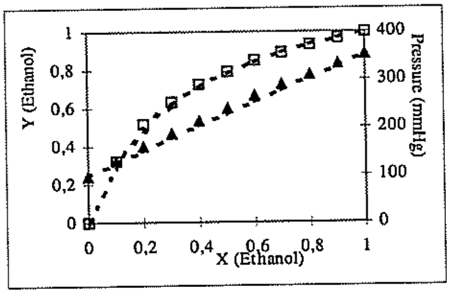

Fig.6: Vapor-Liquid Equilibrium of Ethanol - Isobutanol at 333 K: experimental data (vapor composition and pressure, respectively): Dechema Series, Vol. I, Part 2a, pg. 378; ········ calculated.

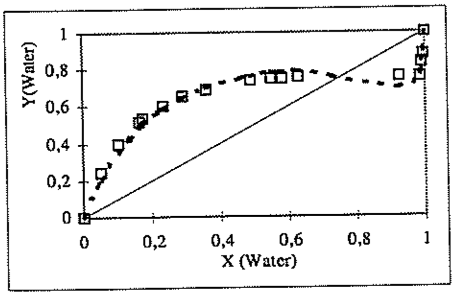

Fig.7: Vapor-Liquid Equilibrium of Water - 1-Butanol at 1atm: experimental data (vapor composition): Dechema Series, Vol. I, Part 1, pg. 406; ········ calculated.

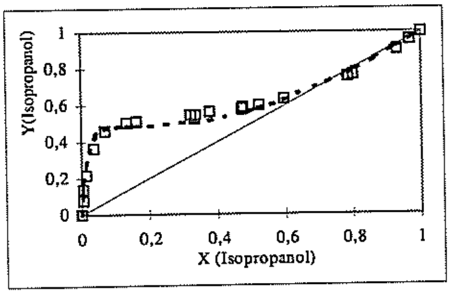

Fig.8: Vapor-Liquid Equilibrium of Water - Isopropanol at 1 atm: experimental data (vapor composition): Dechema Series, Vol. I, Part 1, pg. 317; ········ calculated.

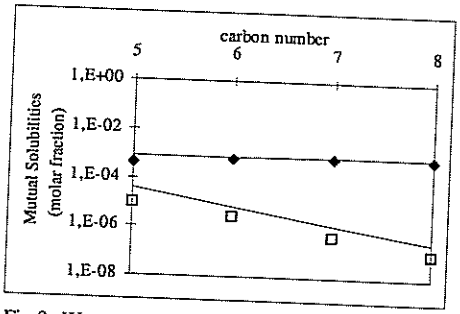

Fig.9: Water - hydrocarbons mutual solubilities at 298K. Experimental (Dechema Series, Vol. V, 1979, pgs. 305, 414, 470 and 493): water sol.; hydrocarbons sol.; —— calculated.

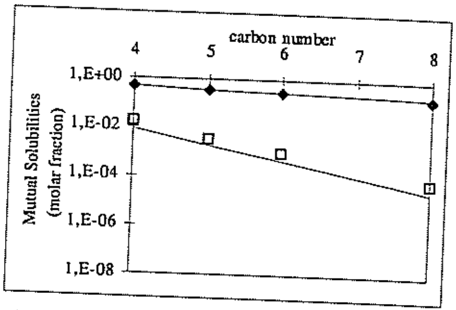

Fig.10: Water - alkanols mutual solubilities at 298K. Experimental (Dechema Series, Vol. V, 1979, pgs. 236, 312, 419, 472 and 501): water sol.; alkanols sol.; —— calculated

Table 3 -Infinite dilute activity coefficients predicted for some binaries.

System	References	γ^{∞}	γ^{∞}calculated
Ethanol(1)+Hexane(2) Calculated from experimental ethanol distribution coefficient between hexane and water and γ^{8} of ethanol in water;	J.Roddy and C. Coleman, Ind. Eng. Chem. Fundam., 20(1981) 250-254; R.E. Pecsar and J.J.Martin, Anal. Chem. 38 (1966) 1661.	$\gamma^{\infty}(1)=103$ at 303K	$\gamma^{\infty}(1)=106.1$
Ethanol(1)+Hexane(2)	E.R.Thomas, B.A.Newman, G.L. Nicolaides and C.A.Eckert, J. Chem. Eng. Data, 27 (1982) 233-240.	$\gamma^{\infty}(2)=8.1$ at 351K	$\gamma^{\infty}(2)=6.7$
Hexane(1)+Water(2) Calculated from liquid - liquid equilibrium data	J.M.Sorensen and W. Arlt, Liquid-Liquid Equilibrium Data Collection. Binary Systems, DECHEMA Series, Vol. V, 1979, Part 1, pg.414.	$\gamma^{\infty}(1)=3.6\mathrm{x}10^{5}$ at 298K $\gamma^{\infty}(2)=1.6\mathrm{x}10^{3}$ at 298K	$\gamma^{\infty}(1)=1.4\mathrm{x}10^{5}$ $\gamma^{\infty}(2)=1.5\mathrm{x}10^{3}$
Ethanol(1)+Water(2)	R.E. Pecsar and J.J.Martin, Anal. Chem. 38 (1966) 1661.	$\gamma^{\infty}(1)=6.15$ at 303K	$\gamma^{\infty}(1)=5.93$
Ethanol(1)+Water(2) Extrapolated value;	J. Gmehling and U. Onken, Vapor Liquid Equilibrium Data Collection. Aqueous Organic Systems, DECHEMA Series, Vol.V, 1977, Part 1, pg.167.	$\gamma^{\infty}(2)=2.6$ at 307K	$\gamma^{\infty}(2)=1.7$

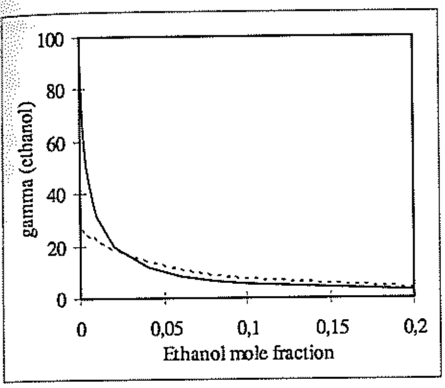

Fig.11: Activity coefficients of ethanol in hexane ········at 298K:—— Association contribution; residual contribution (UNIFAC parameters $A_{CH2,OH}$=986.5K and $A_{OH,CH2}$=156.4K).

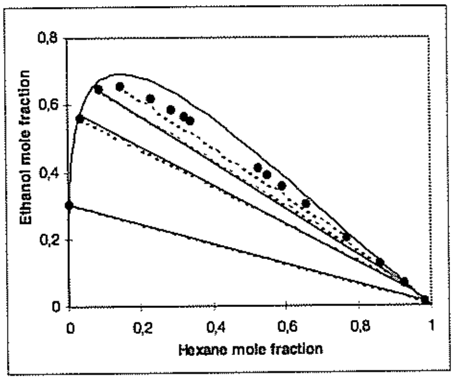

Fig. 12: Liquid-liquid equilibria for ethanol-hexane-water at 298K. Binodal curve and Tie lines: experimental (Dechema Series, Vol. V, Part 2, pg 364); —— calculated; ....
Tie lines: experimental; calculated.

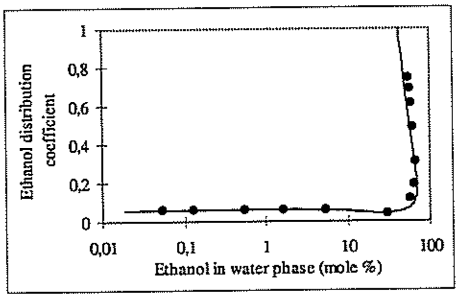

Fig. 13: Ethanol Distribution Coefficients between hexane and water phases at 298K:

experimental data (J.Roddy and C. Coleman. Ind. Eng. Chem. Fundam., 20 (1981) 250-254 and Dechema, Vol. V, Part 2, pg. 364);
calculated.

REFERENCES

[1] Aa. Fredenslund, R.L. Jones and J.M. Prausnitz, AIChE J., 21 (1975) 1086-1098.
[2] M. Wertheim, Journal of Statistical Physics, 35 (1984) 19-47; 42 (1986) 459-492.
[3] W. Chapman, K. Gubbins, J. Jackson and M. Radosz, Fluid Phase Equilibria, 52 (1989) 31-38.
[4] W. Chapman, K. Gubbins, J. Jackson and M. Radosz, Ind. & Eng. Chem. Res., 29 (1990) 1709-1721.
[5] S. Huang and M. Radosz, Ind. Eng. Chem. Res., 29 (1990) 2284-2294.
[6] S. Huang and M. Radosz, Ind. Eng. Chem. Res., 30 (1991) 1994-2005.
[7] S. Suresh and J. Elliot, Ind. Eng. Chem. Res., 31 (1992) 2783-2794.
[8] Y-H Fu, S. Sandler and H. Orbey, Ind. Eng. Chem. Res., 34 (1995) 4351-4363.
[9] H. Gros, M. Zabaloy, S. Bottini and E. Brignole, Proc. 3rd. International Symposium on Supercritical Fluids, Strasbourg, France, 1994, pgs. 113-118.
[10] H. Gros, S. Bottini and E. Brignole, Fluid Phase Equilibria, 116 (1996) 537-544.
[11] A. Mengarelli, E.A. Brignole and S.B. Bottini, sent for publication to Fluid Phase Equilibria.