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BINARY AND TERNARY PHASE BEHAVIOUR OF THE SYSTEM WATER-ETHANOL-CARBON DIOXIDE

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ABSTRACT

A perturbed-dipolar-hard-spheres equation of state for multicomponent mixtures of polar compounds, which was applied to the correlation of thermodynamic properties of pure fluids and of several binary systems containing at least one polar component is applied here to the correlation of thermodynamic properties of the system ethanol-carbon dioxide up to the critical pressure and to prediction of phase behaviour of the ternary system water-ethanol-carbon dioxide over pressure, temperature and concentration ranges of potential industrial interest.

New experimental data are given for the system water-ethanol-carbon dioxide.

Our data are compared with data from literature, and with ethanol loading in supercritical carbon dioxide and solvent selectivity predicted by the model.

INTRODUCTION

Supercritical and near critical carbon dioxide can be considered as a suitable solvent for downstream processing of dilute aqueous solutions of ethanol obtained by fermentation of renewable materials (McHugh and Krukonis, 1986; van Ejis et al., 1988). In fact, when the ethanol to water ratio in the liquid phase is lower than one, the same ratio in the carbon dioxide is one or two order of magnitude higher. Several sets of experimental data for the ternary system water-ethanol-carbon dioxide have been reported in the literature in the last decade (Paulaitis et al., 1981; Kuk and Montagna, 1983; Takishima et al., 1986; Feng et al., 1988; Inomata et al., 1988; Nagahama et al.,

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1988).

Since abundant information is also available on the vapor-liquid equilibrium of the binary system water-ethanol, and on the gas-liquid of the two binary systems water-carbon dioxide, and ethanol-carbon dioxide, the most general procedure for calculating the ternary phase behaviour is to use this information along with a predictive model.

We use a perturbed-dipolar-hard sphere EOS which gives satisfactory results in correlating vapor-liquid equilibrium data of several binary mixtures of polar fluids over a wide range of temperature and pressure (Brandani et al., 1989).

The purpose of this study is to evaluate the predictive capability of this model and to verify the quality of different sets of ternary data reported in the literature for the system water-ethanol-carbon dioxide at supercritical conditions of carbon dioxide. Since significant difference were observed between different sets of data, experimental values of ethanol solubility and solvent selectivity at 313.2 K and for pressures up to 200 bar were also measured.

EXPERIMENTAL

A single pass flow apparatus schematically shown in Fig. 1 and previously described by Di Giacomo et al. (1989) was used for the measurement of the GLE of the system water-ethanol-carbon dioxide.

The same procedure and instrumentation described in the above cited paper was used in this study.

At the end of each run all the extracted solute was recovered from glass traps using propanol as solvent. The resulting liquid solution was then analyzed using a gas chromatograph equipped with a thermoconductivity detector.

The substances used were distilled deionized water and ethanol >99% purity, while the carbon dioxide (Matheson) has >99.95% purity. About 40 g of carbon dioxide was used for each experimental run along with 40 g of aqueous solution of ethanol. Carbon dioxide was fed at a constant mass flow rate of about 0.5 g/min.

The raw experimental data are listed in Table 1. The solvent selectivity of ethanol between the liquid and the gas phase is defined by the ratio of the distribution coefficient of ethanol and water:

$$\text{selectivity} = \left(Y_{\text{ethanol}} \big/ X_{\text{ethanol}} \right) \Big/ \left(Y_{\text{water}} \big/ X_{\text{water}} \right) \qquad (1)$$

while the ethanol loading is defined by the ratio of ethanol and carbon dioxide in the gas phase:

$$\text{loading} = 104.55 \left(Y_{\text{ethanol}} \Big/ Y_{\text{carbon dioxide}} \right) \qquad (2)$$

Y_i and X_i are the mole fraction of component i on a carbon dioxide free basis in the gas and liquid phase respectively.

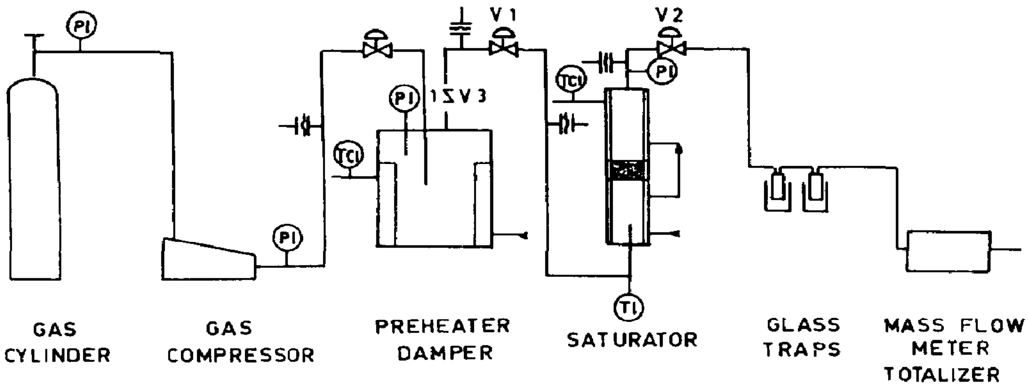

Fig. 1. Schematic diagram of the single pass flow experimental apparatus.

The experimental values of ethanol loading reported in Table 1 are in good agreement with those reported by Kuk and Montagna (1983) under the same P and T conditions and with those obtained by experimental GLE data of Nagahama et al. (1988) at the same temperature and at 99.8 bar.

Our experimental selectivity values at 100 bar and 313.2 K are almost double those reported by Kuk and Montagna (1983) while they are in satisfactory agreement with those obtained from GLE data reported by Nagahama et al. (1988) at the same temperature and at 99.8 bar. Our experimental selectivity values at 200 bar and 313.2 K are still significantly higher (about 35%) than those reported by Kuk and Montagna (1983) at low liquid ethanol concentration, while at higher concentration the agreement is much better. However the pressure dependence of our selectivity is different from that found by Kuk and Montagna (1983).

TABLE 1

Experimental GLE data for the system water-ethanol-carbon dioxide at 313.2 K.

P [bar]	x_{H_2O}	x_{EtOH}	y_{H_2O}	y_{EtOH}	y_{CO_2}	LOAD.	SEL.
100	0.7356	0.2644	0.0076	0.0381	0.9543	4.2	13.9
100	0.7486	0.2514	0.0073	0.0368	0.9559	4.0	15.0
100	0.7505	0.2495	0.0071	0.0358	0.9571	3.9	15.2
100	0.7617	0.2383	0.0069	0.0354	0.9577	3.9	16.4
100	0.7751	0.2249	0.0066	0.0347	0.9587	3.8	18.1
100	0.7768	0.2232	0.0062	0.0341	0.9597	3.7	19.1
100	0.7892	0.2108	0.0056	0.0322	0.9622	3.5	21.5
100	0.8101	0.1899	0.0050	0.0295	0.9655	3.2	25.2
100	0.8226	0.1744	0.0047	0.0264	0.9688	2.9	26.0
100	0.9134	0.0866	0.0044	0.0144	0.9812	1.5	34.5
100	0.9155	0.0845	0.0043	0.0140	0.9817	1.5	35.3
100	0.9160	0.0840	0.0042	0.0137	0.9821	1.5	35.6
100	0.9222	0.0778	0.0036	0.0117	0.9846	1.3	38.5
100	0.9233	0.0767	0.0034	0.0111	0.9855	1.2	39.3
200	0.7432	0.2568	0.0190	0.0610	0.9200	6.9	9.3
200	0.7446	0.2554	0.0183	0.0606	0.9211	6.9	9.5
200	0.7640	0.2360	0.0170	0.0555	0.9275	6.3	10.6
200	0.7674	0.2326	0.0161	0.0536	0.9303	6.0	11.0
200	0.7855	0.2145	0.0142	0.0494	0.9364	5.5	12.7
200	0.7896	0.2104	0.0141	0.0492	0.9367	5.5	13.1
200	0.8050	0.1950	0.0132	0.0428	0.9440	4.8	13.4
200	0.8309	0.1691	0.0107	0.0366	0.9527	4.0	16.8
200	0.8368	0.1632	0.0101	0.0345	0.9553	3.8	17.5
200	0.9179	0.0821	0.0067	0.0204	0.9729	2.2	34.0
200	0.9282	0.0718	0.0064	0.0187	0.9750	2.0	37.8
200	0.9343	0.0657	0.0059	0.0162	0.9779	1.7	39.0
200	0.9400	0.0600	0.0058	0.0152	0.9790	1.6	41.1

EQUATION OF STATE FOR MIXTURES OF POLAR COMPONENTS

To generalize the equation of state described in a previous work (Brandani et al., 1989) to multicomponent mixtures of polar or non polar compounds, we take into account the results of the perturbation theory for a mixture of hard spheres with ideal dipole moment at their centers (Winkelman, 1983). The compressibility factor is given by the sum of two contributions, one from the reference system and one from a perturbation:

$$z = Pv/RT = z^{ref} + z^{per} \qquad (3)$$

The reference term of the compressibility factor is given by a Carnaham-Starling (1972) expression:

$$z^{ref} = \left(1+f^{[1]}\eta+f^{[2]}\eta^2 f^{[3]}\eta^3 \right)/\left(1-\eta \right)^3 \qquad (4)$$

where the reduced density is:

$$\eta = b_m \rho/4 \tag{5}$$

here ρ is density and

$$b_m = \Sigma_j \Sigma_i \; w_i w_j b_{ij} \tag{6}$$

$$b_{ij} = (1+l_{ij}) \; [(b_{ii}^{1/3} + b_{jj}^{1/3})/ 2]^3 \tag{7}$$

where w is either x or y, and l_{ij} is a binary adjustable parameter. The expressions for the coefficients $f^{[1]}$, $f^{[2]}$ and $f^{[3]}$ are given by :

$$f^{[1]} = 1 - 9.5670 \; 10^{-3} \; \tilde{\mu}^4 - 1.95606 \; 10^{-4} \; \tilde{\mu}^6 \tag{8}$$

$$f^{[2]} = 1 + 26.3279 \; 10^{-3} \; \tilde{\mu}^4 + 4.7746 \; 10^{-4} \; \tilde{\mu}^6 \tag{9}$$

$$f^{[3]} = 1 + 19.8052 \; 10^{-3} \; \tilde{\mu}^4 + 2.09945 \; 10^{-4} \; \tilde{\mu}^6 \tag{10}$$

The coefficients are functions of temperature through the reduced dipole moment, $\tilde{\mu}$, defined by:

$$\tilde{\mu}^4 = \frac{95.96^4}{b_m \; T^2} \; [\; \Sigma_i \; \Sigma_j \; w_i w_j \hat{\mu}_i^2 \; \hat{\mu}_j^2 \; / \; b_{ij} \;] \tag{11}$$

$$\tilde{\mu}^6 = \frac{95.96^6}{b_m^2 \; T^3} [\; \Sigma_i \; \Sigma_j \; \Sigma_k \; w_i w_j w_k \; \hat{\mu}_i^2 \hat{\mu}_j^2 \hat{\mu}_k^2 \; / \; (\; b_{ij} b_{ik} b_{jk} \;)^{1/3}] \tag{12}$$

The perturbation term of the compressibility factor is given by an equation of the van der Waals form:

$$z^{per} = - \; a_m/[\; RT(\; v+0.2b_m \;)] \tag{13}$$

where, according to the two fluid theory of Whiting and Prausnitz (1982):

$$a_m = \Sigma_i \; w_i [(\; \Sigma_j \; w_j a_{ji} G_{ji} \;)/(\; \Sigma_K \; w_k \; G_{ki} \;)] \tag{14}$$

where:

$$a_{ji} = (\; 1-k_{ij} \;)(\; a_{ii} a_{jj} \;)^{1/2} \tag{15}$$

$$G_{ji} = \exp[\; \alpha \; a_{ji} \ln(\; 1+0.2\rho \; b_m \;)/(\; 0.2TRb_m \;)] \tag{16}$$

where the non-randomness factor α is assumed to be 0.10 for all the systems here examined and k_{ij} is the usual binary parameter.

Therefore, the proposed equation of state for multicomponent mixtures is:

$$z = [(\; 1+f^{[1]}\eta + f^{[2]}\eta^2 - f^{[3]}\eta^3 \;)/(\; 1-\eta \;)^3] - [\; a_m/RT(\; v+0.2b \;)] \tag{17}$$

The expressions for the Helmholtz energy, A, and for the chemical potential of component "i", μ_i, in a multicomponent mixture are reported in APPENDIX.

RESULTS AND DISCUSSION

The pure component parameters a and b for water, ethanol and carbon dioxide were found by fitting density, vapor pressure and second virial coefficient (Dymond and Smith, 1980; International Critical Tables, 1928; Kennedy and Thodos, 1960; Medici, 1969) of the pure components at temperatures ranging from 303 to 373 K.

We used an analytical equation proposed by Bryan and Prausnitz (1987) to describe the relationship between a and temperature, while for b we found it was better to use a linear relationship:

$$a = [(a_1+a_2T^{0.5}+a_3T)(1-\phi)+(a_4+a_5T)(1+\phi)]^2 \tag{18}$$

$$b = (b_1+b_2T)(1-\phi)+(b_3+b_4T)(1+\phi) \tag{19}$$

TABLE 2

Values of the coefficients expressing the temperature dependence of a and b.

Pure component	a_1	a_2	a_3	a_4	a_5
Water	0.5088	-10.1827	-0.5451	1.1243	-0.00016
Ethanol	-9.6403	-19.3858	1.0814	-2.9296	0.00241
Carbon dioxide	1.2158	-0.0064	-0.0004	0.6982	0.00110
	b_1	b_2	b_3	b_4	
Water	30.4074	55.6944	22.2415	-0.0149	
Ethanol	16.0938	-1.8022	69.5515	-0.0519	
Carbon dioxide	28.0929	-0.0105	18.0894	0.0249	

and

$$\phi = \tanh[10(T_c/T-1)] \tag{20}$$

where T_c is the critical temperature, in Kelvin. Table 2 gives the numerical values of the coefficients of equations (18) and (19).

To find the numerical values of the adjustable parameters k_{ij} and l_{ij} we minimized the following function for each set of isothermal binary PTxy experimental data (Gillespie and Wilson, 1982; Gmehling and Onken, 1977; Nagahama et al., 1988; Feng et al, 1988; Shen et al., 1988) :

$$SSQ = \sum [(P_{exp} -P_{cal})/\sigma_p]^2 + \sum [(y_{exp} -y_{cal})/\sigma_y]^2 \tag{21}$$

where σ_p equals 1.0 bar and σ_y equals 0.01 except for the system ethanol-water for which σ_p equals 1 tor and σ_y equals 0.001.

In all the above calculations l_{ij} was found to be temperature independent, while k_{ij} is a linear function of temperature, as can be seen in Fig. 2:

$$k_{ij} = k_{ij}^0 + k_{ij}^1 \, T \tag{22}$$

Table 3 gives numerical values of l_{ij}, k_{ij}^0 and k_{ij}^1 for all the binary systems examined.

TABLE 3

Values of the parameter l_{ij} and of the coefficients k_{ij}^0 and k_{ij}^1 of the three binary systems.

System	l_{ij}	k_{ij}^0	k_{ij}^1
water-carbon dioxide	-0.30	-0.359	0.0015
ethanol-carbon dioxide	0.15	0.316	-0.0008
ethanol-water	-0.05	0.076	-0.0004

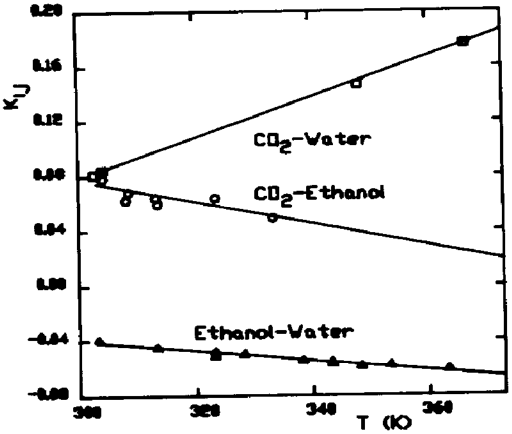

Fig. 2. Temperature dependence of the adjustable binary parameter k_{ij}.

As an example Figs. 3, 4 and 5 show a comparison between calculated isothermal Pxy curves and experimental data for the three binary systems water-carbon dioxide, ethanol-carbon dioxide and ethanol-water, respectively. As can be seen in these figures there is a satisfactory agreement for all the three binary systems between the experimental and calculated data. The agreement between experimental and calculated data holds at other temperatures into the 303-373 K range studied.

Table 4 gives numerical values of Average Absolute Percent Deviations (AAPD) of predicted and experimental P and y for several isothermal sets of data of binary systems.

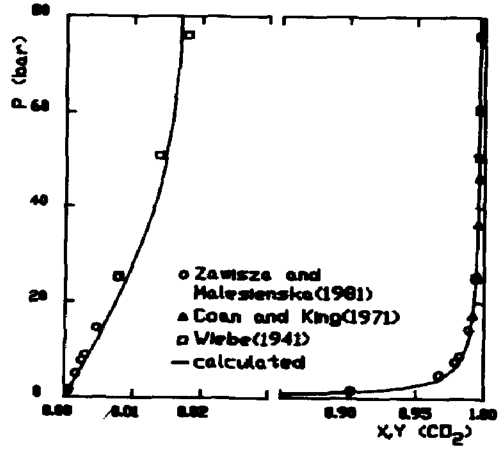

Fig. 3. GLE for the system water-carbon dioxide at 323.2 K.

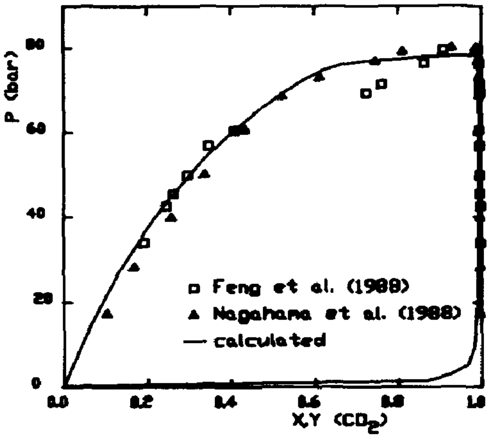

Fig. 4. GLE for the system ethanol-carbon dioxide at 313.3 K

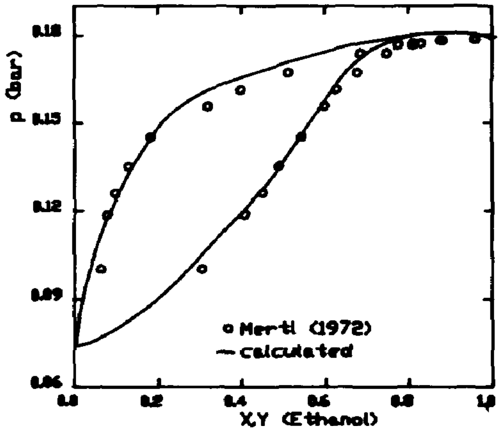

Fig. 5. VLE for the system ethanol-water at 313.2 K.

TABLE 4

Average Absolute Percent Deviations of predicted and experimental data for binary systems.

System	No. of data points	T, K	AAPD(P)	AAPD(y)	data source
water-carbon dioxide	3	302.6	6.3	22.8	a
	5	304.2	21.5	24.7	a
	5	348.2	3.0	3.1	a
	5	366.5	6.4	5.8	a
ethanol-carbon dioxide	9	304.2	2.4	28.0	b
	5	308.2	2.0	31.7	c
	7	308.6	2.5	11.6	b
	10	313.2	4.1	42.0	b
	10	313.5	6.0	37.7	d
	5	323.4	2.8	49.0	b
	12	333.3	12.1	11.9	d
ethanol-water	5	303.2	1.7	3.0	e
	15	313.2	2.6	2.7	f
	14	323.2	1.6	1.7	g
	13	328.2	1.1	1.7	f
	17	338.2	2.0	4.7	h
	13	343.2	0.7	7.9	f
	17	343.2	2.3	5.0	h
	16	343.2	0.6	3.8	i
	9	348.2	1.1	1.5	h
	12	353.2	0.9	9.1	h
	15	363.2	0.6	3.1	i

a-Gillespie,P.C.;Wilson G.M. RR-48 (GPA) 1982, 11.
b-Feng,Y.S.;Du,X.Y.;Li,C.F.;Hou,Y.J. Proc.Int.Symp. SCF (Nice) 1988, Vol.1,75.
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To verify the predictive capabilities of the model at supercritical conditions of carbon dioxide, we calculated the GLE of the ternary system water-ethanol-carbon dioxide at 313 K. As a result we found that our model can be used to describe with acceptable accuracy the GLE behaviour of this system for ethanol concentration in the liquid phase up tu 40% by weight.

Table 5 gives numerical values of Average Absolute Percent Deviations of predicted and experimental liquid and gas compositions for the ternary system at different pressures. The AAPD values corresponding to our experimental data were obtained at fixed values of the ratio of ethanol to water in the liquid phase.

TABLE 5
Average Absolute Percent Deviations of predicted and experimental data for the ternary system water-ethanol-carbon dioxide.

No. of data points	P, bar	T, K	AAPD(x,X)	AAPD(Y)	data source
6	38.6	312.9	7.2	9.3	a
3	57.9	312.9	8.0	16.1	a
3	99.8	313.3	6.9	10.0	a
14	100.0	313.2	0.07	13.6	b
13	200.0	313.2	0.03	12.1	b

a-Nagahama,K.;Suzuki,J.;Suzuki,T. Proc. Int. Symp.SCF (Nice) 1988, Vol.1, 149.
b-This work.

From an engineering point of view, the most important properties in the evaluation of a separation process based on a phase equilibria are the solvent selectivity and the ethanol loading in the extractant phase. As can be seen in Figs. 6 and 7 both selectivity and loading can be satisfactorily predicted by the proposed model.

Fig. 6 shows that ethanol loading in supercritical carbon dioxide increases with increasing pressure and increasing ethanol concentration in the liquid phase. Calculated curves at 100 and 200 bar are in agreement with our data as well as with experimental data from literature at the same temperature.

Fig. 7 shows that calculated solvent selectivity at 313.2 K and at 100 and 200 bar decreases with increasing pressure and with increasing ethanol concentration in the liquid phase. The same behaviour is shown by our experimental data while experimental selectivity data at 313.2 K and 100

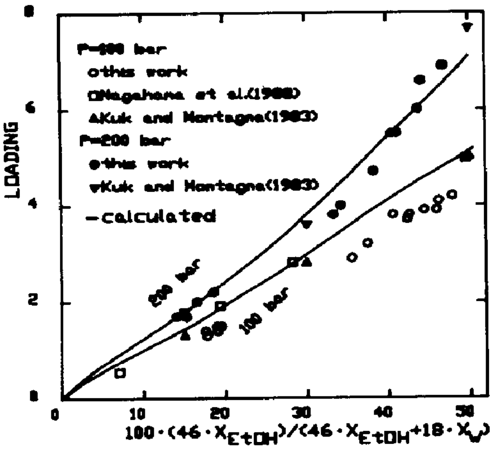

Fig. 6. Ethanol loading in supercritical carbon dioxide at 313.2 K.

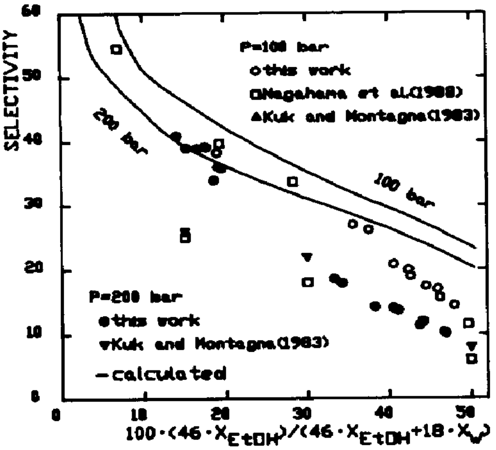

Fig. 7. Solvent selectivity for the system water-ethanol-carbon dioxide at 313.2 K.

and 200 bar reported by Kuk and Montagna (1983) show different behaviour. Fig. 7 also shows that the solvent selectivity calculated from the model agrees quantitatively with our experimental data and with those obtained from GLE data of Nagahama et al. (1988) up to about 20% by weight of liquid ethanol concentration on a solvent free basis.

CONCLUSIONS.

A new model for multicomponent mixtures of polar compounds which has been obtained by a modification of the equation of state for pure components proposed by Bryan and Prausnitz (1987) was applied to the correlation of VLE of the binary system ethanol- water, and of GLE of the two binary systems water-carbon dioxide and ethanol-carbon dioxide,at temperatures from 303 to 373 K. Satisfactory results have been obtained for all the systems examined.

Predictive capabilities of the model have been verified successfully for the ternary system water-ethanol-carbon dioxide at low ethanol concentration (≤50% wt), 313.2 K and 100 and 200 bar.

Under the same conditions, the prediction of ethanol loading in supercritical carbon dioxide as well as the prediction of selectivity can be performed satisfactorily.

Consequently, we believe that the model may substantially facilitate the task of process design and optimization for the extraction of ethanol from dilute aqueous solutions using supercritical carbon dioxide.

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APPENDIX

A). Helmholtz free energy.

$$A - A^{id} = A^{ref} + A^{per} \qquad (A1)$$

where

$$A^{ref} = -nRT\left[C_1 \ln(1-\eta) - \frac{C_2\,\eta}{(1-\eta)} + \frac{C_3\,\eta\,(2-\eta)}{(1-\eta)^2}\right] \qquad (A2)$$

with

$$C_1 = 1-f^{[1]} \qquad (A3)$$

$$C_2 = 1-f^{[2]}+2f^{[3]} \qquad (A4)$$

$$C_3 = 1+f^{[1]}+f^{[2]}-f^{[3]} \qquad (A5)$$

and

$$A^{per} = -(nRT/\alpha)\left[\textstyle\sum_i w_i \ln\left(\sum_j w_j G_{ji}\right)\right] \qquad (A6)$$

with

$$G_{ji} = \exp\left[\alpha\, a_{ji} \ln(1+0.2\rho\, b_m)/(0.2RTb_m)\right] \qquad (A7)$$

B). Chemical potential of component "i".

$$\mu_k - \mu_k^{id} = \mu_k^{ref} + \mu_k^{per} \qquad (A8)$$

where

$$\mu_k^{ref} = -C_1 \ln(1-\eta) + \frac{C_2\,\eta}{(1-\eta)} + \frac{C_3\,\eta\,(2-\eta)}{(1-\eta)^2} + \left[\frac{C_1}{(1-\eta)} + \frac{C_2}{(1-\eta)^2} + \frac{2\,C_3}{(1-\eta)^3}\right]\frac{\partial \eta}{\partial n_k} + \left[-\frac{\partial C_1}{\partial n_k}\ln(1-\eta) + \frac{\partial C_2}{\partial n_k}\,\frac{\eta}{(1-\eta)} + \frac{\partial C_3}{\partial n_k}\,\frac{\eta\,(2-\eta)}{(1-\eta)^2}\right] \qquad (A9)$$

$$\frac{\partial C_1}{\partial n_k} = -C_{31}\frac{\partial \tilde{\mu}^4}{\partial n_k} - C_{32}\frac{\partial \tilde{\mu}^6}{\partial n_k} \tag{A10}$$

$$\frac{\partial C_2}{\partial n_k} = (-C_{21}+2C_{31})\frac{\partial \tilde{\mu}^4}{\partial n_k} + (-C_{22}+2C_{32})\frac{\partial \tilde{\mu}^6}{\partial n_k} \tag{A11}$$

$$\frac{\partial C_3}{\partial n_k} = (C_{11}+C_{21}-C_{31})\frac{\partial \tilde{\mu}^4}{\partial n_k} + (C_{12}+C_{22}-C_{32})\frac{\partial \tilde{\mu}^6}{\partial n_k} \tag{A12}$$

$$\bar{\bar{C}} = \begin{vmatrix} -9.5670\ 10^{-3} & -1.95606\ 10^{-4} \\ 26.3279\ 10^{-3} & 4.7746\ 10^{-4} \\ 19.8052\ 10^{-3} & 2.09945\ 10^{-4} \end{vmatrix} \tag{A13}$$

$$\frac{\partial \tilde{\mu}^4}{\partial n_k} = -\frac{95.54^4}{b_m T^2}\left[2\sum_{j\neq k}\sum_i w_i w_j \hat{\mu}_i^2\left(\frac{\hat{\mu}_j^2}{b_{ij}} - \frac{\hat{\mu}_k^2}{b_{ik}}\right)\right] - \tilde{\mu}_j^4 / b_m \frac{\partial b_m}{\partial n_k} \tag{A14}$$

$$\frac{\partial \tilde{\mu}^6}{\partial n_k} = -\frac{95.59^6}{b_m^2\ T^3}\left[-3\sum_i\sum_j\sum_{l\neq k} w_i w_j w_l \frac{\hat{\mu}_i^2 \hat{\mu}_j^2}{(b_{ij} b_{il})^{1/3}}\left(\frac{\hat{\mu}_l^2}{b_{jl}^{1/3}} - \frac{\hat{\mu}_k^2}{b_{jk}^{1/3}}\right)\right] +$$

$$- 2 / b_m \tilde{\mu}^6 \frac{\partial b_m}{\partial n_k} \tag{A15}$$

$$\frac{\partial b_m}{\partial n_k} = -2\sum_j\sum_{i\neq k}[w_i w_j (b_{ij} - b_{kj})] \tag{A16}$$

$$\mu_k^{per} = -1/\alpha \ln\left(\sum_j w_j G_{jk}\right) - 1/\alpha \sum_i \left[\frac{w_i}{\sum_j w_j G_{ji}}\sum_{j\neq k}(G_{ki} - G_{ji})\right] +$$

$$- 1/\alpha \sum_i \left[\frac{w_i}{\sum_j w_j G_{ji}}\sum_j w_j \frac{\partial G_{ij}}{\partial n_k}\right] \tag{A17}$$

$$\frac{\partial G_{ij}}{\partial n_k} = \frac{G_{ij}\ \alpha\ a_{ij}}{(0.2\ RTb_m)}\frac{\partial b_m}{\partial n_k}\left[-\frac{1}{b_m}\ln(1+0.2\ b_m) + \right.$$

$$\left. + \frac{0.2\ \rho}{(1+0.2\ \rho\ b_m)b_m}\frac{\partial b_m}{\partial n_k}\right] \tag{A18}$$

LIST OF SYMBOLS

A	Helmholtz free energy.
a	equation of state constant reflecting attractive forces.
a_n	(n=1-5) adjustable coefficient in eqn. (18).

b	equation of state constant reflecting repulsive forces.
b_n	(n=1-4) adjustable coefficient in eqn. (19).
C_c	(c=1,2,3) quantities defined in APPENDIX.
$f^{[f]}$	(f=1,2,3) coefficients dependent on reduced dipole moment.
G_{ij}	dimensionless group defined in eqn. (16).
k_{ij}	binary adjustable parameter.
k^0_{ij}	coefficient of kij linear function on temperature.
k^1_{ij}	coefficient of kij linear function on temperature.
l_{ij}	binary adjustable parameter.
n	total number of moles.
N_A	Avogradro's number.
P	pressure.
R	gas constant.
SSQ	quantity defined in eqn. (21).
T	absolute temperature.
T_c	Critical temperature.
v	molar volume.
x	liquid mole fraction
X	liquid mole fraction on a carbon dioxide free basis.
y	vapor mole fraction.
Y	vapor mole fraction on a carbon dioxide free basis.
w	liquid or vapor mole fraction.
z	compressibility factor.

Greek symbols.

α	non-randomness parameter.
ϕ	dimensionless function defined in eqn. (20).
ρ	molar density.
η	dimensionless density.
σ_p	estimated standard deviation for P.
σ_y	estimated standard deviation for y.
$\hat{\mu}$	dipole moment.
$\tilde{\mu}$	reduced dipole moment.
μ_i	chemical potential of component "i".

Superscripts and subscripts.

i, j, k	components "i", "j" and "k", respectively
id	ideal gas.
m	mixture.

per perturbation part of equation of state.
ref reference part of equation of state.

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