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Prediction of Multiphase Equilibria in Associating Fluids by a Contact-Site Quasichemical Equation of State[1]

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A contact-site quasichemical equation of state has been used for the modeling of different kinds of fluid phase equilibria (between a gas phase and one or more liquids) over a wide range of conditions. Among the systems of interest are the ternary mixtures water + alkanols + hydrocarbons (alkanes or alkynes), water + alkanols (or acetone) + CO_2, water + polyoxyethyleneglycol ethers + heavy alkanes. The model has been applied to describing the thermodynamic properties of the binary subsystems and to predict the phase behavior of the ternary systems. For longer-chain alkanols and hydrocarbons a group-contribution approach is implemented, which allows the modeling when no experimental data are available. The model gives reasonable predictions of phase behavior and the correct trends in the calculated phase diagrams in most cases. The concentrations of associates in liquid and gas phases are estimated by the model and compared with some experimental and computer simulation data. The predictive abilities of the model, its limitations, and possible ways of its improvement are discussed.

KEY WORDS: associating fluids; contact-site model; equation of state; group contribution; monomer fraction; multiphase equilibria.

1. INTRODUCTION

Many mixtures of practical importance containing associating components exhibit complex phase behavior with several fluid phases forming, coexisting,

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and disappearing under certain conditions. Mixtures of alkanols with hydrocarbons and water, aqueous mixtures of organic compounds with near-critical solvents, and water + oil + nonionic surfactant systems are typical examples of multiphase high- or low-pressure equilibria between a gas and several liquid phases. The presence of associating components imposes strong limitations on the possible choices of the equations of state for modeling such mixtures. Apart from empirical equations of the Huron–Vidal family [1], the appraoches to model associating fluids are the "chemical theory" equations [the associated perturbed anisotropic chain theory (APACT) [2] being one of the most elaborated equations of the kind], the statistical associated fluid theory (SAFT) [3, 4], and the lattice-fluid quasichemical equations of state [5, 6]. The latter equations and the SAFT employ the idea of molecules having strongly attracting specific sites to model association, while the chemical theories consider association equilibria directly and operate with association constants. The different approaches have been carefully compared and tested against computer simulations for associating hard spheres [7]. This analysis has shown that, although having quite different theoretical background, these approaches lead to similar results in the description of association equilibria, the differences being mainly due to physical interaction terms of the equations of state.

The performance of the hole model (HM) [6], a lattice-gas contact-site quasichemical equation of state, has been tested recently for alkanol-alkane mixtures over a wide range of temperatures and pressures [8, 9] and compared with that of the APACT [8]. Despite the fact that the HM has a typical lattice-gas repulsion term, which is known to be basically incorrect [10] and gives a poor description of dense single-phase states [11], the model describes the saturation curves for associating fluids surprisingly well [8] and often better than the APACT, which has more refined nonspecific (repulsion and long-range attraction) interaction terms. While the reasons of the observed behavior are not quite clear, and might well be a topic of a separate study, a demanding task is the application of the model for the prediction of complex phase equilibria in mixtures of practical importance.

Table I contains a list of mixtures considered in this work. The common feature of these mixtures is that they exhibit multiphase equilibria at certain conditions. The types of experimentally studied equilibria are indicated in the table. The mixtures belong to different classes. The first seven systems contain a near-critical solvent (CO_2, C_4) and are examples of high-pressure equilibria. The phase behavior of these mixtures is important to know for applications such as supercritical fluid extraction and supercritical fluid chromatography. The mixtures of the second class

Table I. Experimental Studies of Ternaries Showing Multiphase Equilibria

No.	System	Conditions	Type	Ref. No.
1	$CO_2 + \text{acetone} + H_2O$	313, 333 K 2.93–9.26 MPa	LLG	12
		313 K 4, 10 MPa	LLG	13
2	$CO_2 + \text{MeOH} + H_2O$	305–311 K 7.2–8.1 MPa	LLG	14
3	$CO_2 + \text{EtOH} + H_2O$	304 K 6.87 MPa	LLG	15
4	$CO_2 + \text{i-PrOH} + H_2O$	323, 333 K 9.4–12.2 MPa	LLLG LLG	16
		334 K 12.2 MPa	LLG	17
		303–333 K 6.8–12.4 MPa	LLLG LLL LLG	18
5	$CO_2 + \text{BuOH} + H_2O$	313, 333 K 3–15 MPa	LLLG LLG	19
6	$C_4 + \text{i-BuOH} + H_2O$	448 K 4.48 MPa	LLG	20
7	$CO_2 + \text{MeOH} + C_2$	288, 298 K 3.3–6.0 MPa	LLG	21
8	$C_7 + H_2O + \text{MeOH}$	298 K 0.1 MPa	LL	22
9	$C_7 + H_2O + \text{EtOH}$			
10	$C_7 + H_2O + \text{PrOH}$			
11	$C_7 + H_2O + \text{BuOH}$			
12	$C_7 + H_2O + C_5OH$			
13	$C_7 + H_2O + C_6OH$			
14	$\text{Heptyne} + H_2O + \text{EtOH}$	298 K 0.1 MPa	LL	23
15	$\text{Heptyne} + H_2O + \text{PrOH}$			
16	$\text{Heptyne} + H_2O + \text{BuOH}$			
17	$C_8 + H_2O + \text{BuOH}$	298 K 0.1 MPa	LLL	24
18	$C_{10} + C_4E_1 + H_2O$	303–325 K 0.1–30 MPa	LLL	25
19	$C_{12} + C_7E_5 + H_2O$	335–395 K 0.1 MPa	LLL	26

(systems 8–16) are composed of water, hydrocarbons, and alkanols and are of importance in the fuel industry. They exhibit two liquid phases in equilibrium with a vapor. For these systems, however, only the liquid–liquid equilibrium at normal pressures has been studied experimentally, as indicated in Table I. A special case of mixtures with multiphase equilibria is mixtures 18 and 19, which represent the water + oil + nonionic surfactant systems. They reveal rather complex phase behavior and structural properties [26, 27]. It was interesting to see to what extent these mixtures could be modeled with a relatively simple equation of state. The results of phase equilibria modeling are presented in Section 2. Section 3 is devoted to the prediction of the concentrations of associates and to the discussion of the abilities of the model.

2. RESULTS OF PHASE EQUILIBRIA MODELING

The HM has been described in detail in previous papers [6, 9]. According to the HM the molecules have different contact sites (functional groups). The model parameters are the effective temperature-dependent dimensionless interchange energies between groups of different kinds ($\Delta\varepsilon_{st} = W_{st} + H_{st}(T_0 - T)/T + C_{st}[\ln(T_0 T) - (T_0 - T)/T]$ for a pair of groups of kinds s and t [6]) and parameters reflecting the geometry of groups (a size parameter, r_s, and the bulkiness factor, l_s, for a group of kind s). If the same parameter values are used for functional groups of the same kind in different substances, then the group-contribution approach follows. For the majority of mixtures in Table I the parameters have been estimated earlier [8, 9, 28]. Some additional parameters necessary to perform calculations are estimated in the present work and listed in Table II.

The polyoxyethyleneglycol ether molecules were subdivided into the CH_3 and CH_2 groups (same as in *n*-alkanes [9]), an "oxy" group ($O\text{–}CH_2\text{–}CH_2$), and the hydroxyl group with O and H subgroups (same as in alkanols [9]). The parameters for this new oxy group (Table II) were estimated from saturated liquid density and vapor pressure of pure butoxyethanol [29]. As shown in Table II, only two energetic parameter values are adjusted independently, most of the values being preset equal to zero. The interaction parameters for the oxy group with water (Table II) were regressed from VLE data on water + C_4E_1 [29] at 358–368 K and allowed us to reproduce these data with an average bubble pressure error $\Delta P = 1.4\%$. The model correctly predicts the existence of liquid immiscibility in this binary system. New interaction parameters for alkynes ("yne" group) have been determined as well (Table II). The water–yne parameters have been found from mutual solubility data [30], and those for alkanols were estimated from low-pressure VLE in octyne + butanol [31] ($\Delta P = 0.6\%$). New individual parameters were obtained for pure i-PrOH treated as a combination of an alkyl tail and a hydroxyl group (Table II). The parameters for water + i-PrOH were regressed from VLE at 308–348 K [32] ($\Delta P = 1.1\%$). In CO_2 + i-PrOH the high-pressure data [33] have been used for the estimation of the hydroxyl group–CO_2 parameters ($\Delta P = 2.5\%$; Table II), and the alkyl tail–CO_2 interaction

Table II. HM Parameters Estimated in the Present Work

Type of groups, s and t	W_{st}	H_{st}	C_{st}
Pure polyoxyethyleneglycol ethers[a]			
Oxy–H(OH)	−3.0325	−3.0325	0
Oxy–O(OH)	0	0	0
Oxy–CH_3	0	0	0
Oxy–CH_2	0	0	0
Oxy–hole	0.1956	0.1956	0
Pure isopropanol[b]			
Alkyl–OH	0	0.606	2.7619
Alkyl–hole	0.1647	0.1425	0.6602
Polyoxyethyleneglycol ethers + water			
Oxy–O(H_2O)	−0.2099	−0.2099	0
Oxy–H(H_2O)	−2.7472	−2.7472	0
Alkynes + water			
yne–H_2O	0.1110	0.1110	0
Alkynes + Normal alkanols			
yne–OH	−0.0462	0.2003	0
Isopropanol + water			
Alkyl–H_2O	−0.0611	−0.1523	0
H(OH)–O(H_2O)	−4.7658	−8.8982	0
O(OH)–H(H_2O)	−5.0999	−5.4926	0
H(OH)–H(H_2O)	0	0	0
O(OH)–O(H_2O)	0	0	0
Isopropanol + CO_2			
O(CO_2)–H(OH)	−2.4949	−2.3275	0
O(CO_2)–O(OH)	−0.1443	0.3868	0
C(CO_2)–H(OH)	−0.1443	0.3868	0
C(CO_2)–O(OH)	−0.1443	0.3868	0

[a] $R_{oxy} = 2.5038$, $l_{oxy} = 1$ for the "oxy" group.

[b] $R_{alk} = 4.0006$, $l_{alk} = 0.5$ for the alkyl tail.

parameters were taken to be the same as for CO_2 + alkane systems [9]. The parameters reported in Table II together with those obtained previously suffice to predict phase behavior for all the mixtures in Table I.

For the systems with a near-critical solvent (mixtures 1 – 7) a typical example of three-phase equilibria prediction is given in Fig. 1. In agreement with the experiment the model predicts the existence of the LLG region, the trend in its shift with pressure, and its final disappearance at high pressures. The model gives the correct slope of tie lines and reasonable estimates of the binodal loci. For other mixtures of this type the accuracy of LLGE prediction is quite similar in *all* the cases, when these mixtures exhibit only one three-phase region (the exceptions are systems 4 and 5). In contrast to experiment no four-phase equilibrium regions have been found

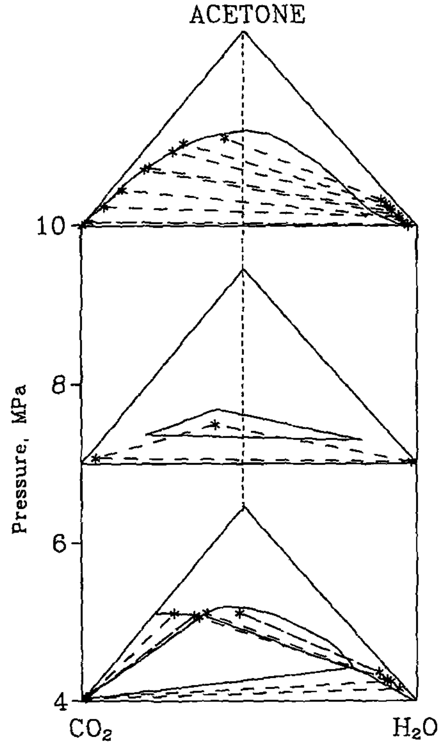

Fig. 1. Prediction by HM (solid curves and lines) of the phase diagram (pressure–mole fractions) for the system CO_2 + acetone + H_2O at 313 K. Triangles represent three-phase regions. (–––) Experimental tie lines; (∗) experimental equilibrium compositions.

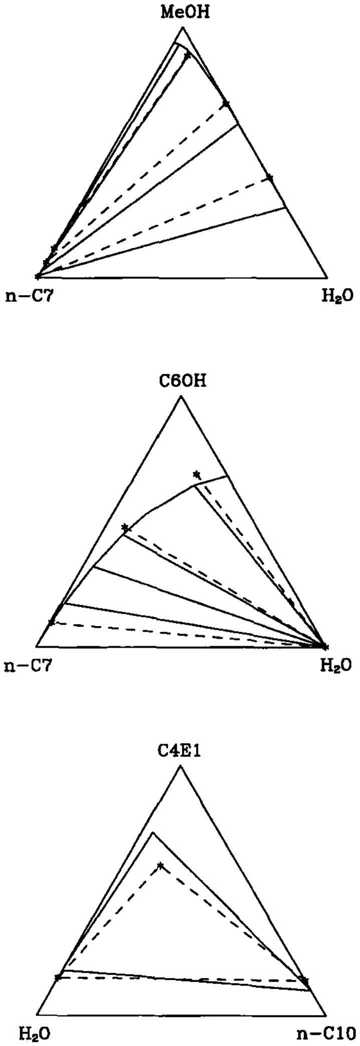

Fig. 2. The predicted liquid miscibility gaps (solid curves and lines) for systems 8 and 13 (at 298 K, 0.1 MPa, mole fractions) and 18 (at 313 K, 20 MPa, weight fractions). Triangles represent three-phase regions. (−−−) Experimental tie lines; (∗) experimental equilibrium compositions.

applying the model for these systems. Thus, for system 4 the HM predicts the existence of only one LLG region and did not predict the second one, which merge to form an LLLG equilibrium. Consequently, the predicted slope of LL tie lines at very high pressures is qualitatively incorrect. No third liquid phase (with the composition close to that of the gas phase) has been found in our predictions for system 5.

For the systems of the second type (8–16) all the LLE diagrams were reproduced quite well (Fig. 2). The model predicts correctly the change in the slope of tie lines (from alkanol-rich to water-rich liquid) from lower to higher alkanols, the errors in calculated liquid composition being typically no more than 4 mol%. The only exception is system 14, for which the errors are somewhat larger.

In mixtures 17–19 three liquid phases were predicted (Fig. 2), in agreement with experiment. However, the model gives very weak dependence of the predicted diagram on temperature and pressure for the systems with polyoxyethylene glycol ethers, in contrast to the experimental data. The inability of the model to reflect correctly this pressure dependence is due to the shortcoming of the lattice-gas repulsive term.

3. LOCAL ORDERING EFFECTS IN QUASICHEMICAL APPROXIMATION

For modeling of the mixtures considered here one of the main problems is to describe correctly the local ordering effects. In Fig. 3 we compare, for pure saturated liquid ethanol, the model prediction with

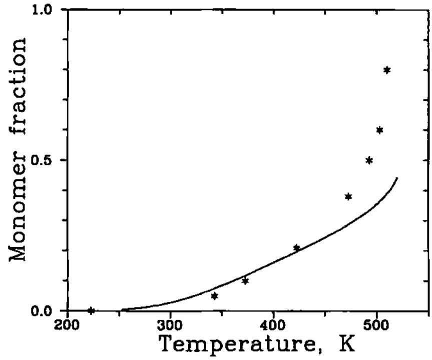

Fig. 3. The fraction of molecules nonbonded by hydrogen bonds (monomer fraction) in saturated liquid ethanol. Prediction by HM (curve) and spectroscopic experimental data (*) [34].

the spectroscopically determined fraction of molecules not engaged in hydrogen bonds. It can be seen that the HM predicts this structural property reasonably well. For mixtures the comparison has been made with the computer simulation results for systems of Lennard–Jones molecules with conical specific sites that mimic association [35]. Two types of binary mixtures were considered in these computer experiments: a solvating mixture (association occurs between unlike molecules only, each of the components having one specific site per molecule) and an associating mixture (one component has two specific sites per molecule and associates, while the other component is inert). We modeled both systems with the aid of HM, using the original values [35] for the interaction energies between the sites. The results (Fig. 4) show good agreement with the computer experiment for both types of systems and are comparable with those

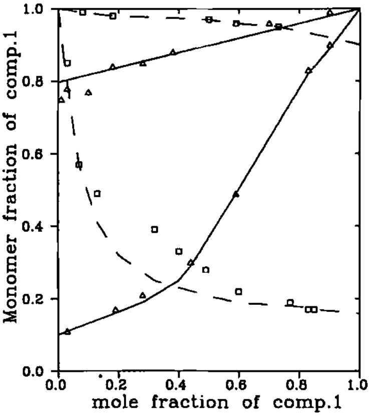

Fig. 4. The prediction (curves) of the monomer fraction and the results of computer simulation [35] (points) for binary mixtures. The upper and the lower curves represent equilibrium vapor and liquid phases, respectively. The HM parameters were chosen according to Ref. 35. In a solvating mixture (——; Δ) $e^{\text{bond}} = 10e$, $e_{11} = e_{22} = e_{12} = e$ for the interaction energies between specific and nonspecific sites of the components 1 and 2 ($r_1 = r_2 = 1$). $T^* = kT/e = 1.0$. For an associating mixture (---; □) $e^{\text{bond}} = 8e_{11}$, $e_{22} = 1.2e_{11}$, $e_{12} = (e_{11}e_{22})^{0.5}$, $r_1 = r_2 = 1$, $T^* = 1.1$. The bulkiness factor for specific sites was calculated from their conic geometry [35].

obtained by SAFT [35]. It confirms that the contact-site quasichemical model is a simple approach to capturing the basic structural features of an associating fluid. However, for describing complex systems like water + polyoxyethyleneglycol ether + hydrocarbon mixtures (e.g., mixtures 18 and 19; Fig. 2), a more detailed consideration of local ordering effects (inhomogeneties due to the formation of large molecular aggregates of varying shape leading to spatial variations of concentration) than given by an ordinary bulk-fluid equation of state, as applied in this paper, seems to be quite useful.

Undoubtedly, the introduction of a better repulsive term [10] into HM would improve the results of phase equilibria prediction. Nevertheless, it is quite clear that these improvements will still leave the model being apt to the limitations of classical equations of state in modeling critical behavior and, hence, will not remove all the limitations in the abilities to predict complex multiphase equilibria.

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REFERENCES

1. D. S. H. Wong, H. Orbey, and S. I. Sandler, *Ind. Eng. Chem. Res.* **31**:2033 (1992).
2. I. G. Economou and M. D. Donohue, *Ind. Eng. Chem. Res.* **31**:2388 (1992).
3. W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, *Ind. Eng. Chem. Res.* **29**:1709 (1990).
4. S. H. Huang and M. Radosz, *Ind. Eng. Chem. Res.* **30**:1994 (1991).
5. R. B. Gupta, C. G. Panyiotou, I. C. Sanchez, and K. P. Johnston, *AIChE J.* **38**:1243 (1992).
6. N. A. Smirnova and A. I. Victorov, *Fluid Phase Equil.* **34**:235 (1987).
7. I. G. Economou and M. D. Donohue, *AIChE J.* **37**:1875 (1991).
8. A. Deak, A. I. Victorov, and Th. W. de Loos, *Fluid Phase Equil.* **107**:277 (1995).
9. A. I. Victorov and Aa. Fredenslund, *Fluid Phase Equil.* **66**:77 (1991).
10. K. G. Honnell and C. K. Hall, *J. Chem. Phys.* **90**:1841 (1989).
11. N. A. Smirnova and A. I. Victorov, *Fluid Phase Equil.* **82**:333 (1993).
12. A. Z. Panagiotopoulos and R. C. Reid, *ASC Symp. Ser.* **329**:115 (1987).
13. P. Traub and K. Stephan, *Chem. Eng. Sci.* **45**:751 (1990).
14. Ji-Ho Yoon, M.-K. Chun, W.-Hi Hong, and H. Lee, *Ind. Eng. Chem. Res.* **32**:2881 (1993).
15. S. Takishima, K. Saiki, K. Arai, and S. Saito, *J. Chem. Eng. Japan* **19**:48 (1986).
16. I. R. Di Anderth and M. E. Paulaitis, *Fluid Phase Equil.* **32**:261 (1987).
17. M. Radosz, *Ber. Buns. Phys. Chem.* **88**:859 (1984).
18. M. Wenderland, H. Hasse, and G. Maurer, *J. Supercrit. Fluids* **6**:211 (1994).
19. A. Z. Panagiotopoulos and R. C. Reid, *Fluid Phase Equil.* **29**:525 (1986).

20. M. Radosz, *Fluid Phase Equil.* **29**:515 (1986).
21. S. P. Hong, C. L. Patton, and K. D. Luks, *J. Chem. Eng. Data* **39**:90 (1994).
22. T. M. Letcher, S. Wooten, B. Shuttleworth, and C. Heward, *J. Chem. Thermodyn.* **18**:1037 (1986).
23. T. M. Letcher, M. B. Bricknell, S. E. Radloff, and J. D. Shewry, *J. Chem. Thermodyn.* **25**:1183 (1993).
24. S. Backlund, H. Hoiland, E. Ljosland; and I. Vikholm, *Fluid Phase Equil.* **20**:249 (1985).
25. C. L. Sassen, Th. W. de Loos, and J. de Swaan Arons, *J. Phys. Chem.* **95**:10760 (1991).
26. C. L. Sassen, A. Conzalez Casielles, Th. W. de Loos, and J. de Swaan Arons, *Fluid Phase Equil.* **72**:173 (1992).
27. M. Kahlweit, R. Strey, P. Firman, D. Haase, J. Jen, and R. Schomacker, *Langmuir* **4**:499 (1988).
28. H. S. Abdulkadirova, *Russ. J. Phys. Chem.* **66**:2133 (1992).
29. O. Chiavone-Filho, P. Proust, and P. Rasmussen, *J. Chem. Eng. Data* **38**:128 (1993).
30. C. McAuliffe, *J. Phys. Chem.* **70**:1267 (1966).
31. L. Kudryavtseva, M. Grinchak, E. Kirjanen, and I. Balashova, *Proc. Acad. Sci. Estonian SSR Chem.* **38**:34 (1989).
32. E. Sada and T. Morisue, *J. Chem. Eng. Japan* **8**:191 (1975).
33. M. Radosz, *J. Chem. Eng. Data* **31**:43 (1986).
34. W. A. P. Luck, *Disc. Faraday Soc.* **43**:115 (1967).
35. J. K. Johnson and K. E. Gubbins, *Mol. Phys.* **77**: 1033 (1992).