

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231392352>

Liquid–Liquid Equilibrium Modeling of Ternary Hydrocarbon + Water + Alkanol Systems†

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · SEPTEMBER 1997

Impact Factor: 2.59 · DOI: 10.1021/ie970007y

CITATIONS

16

READS

13

3 AUTHORS, INCLUDING:



Igor V. Prihodko

Saint Petersburg State University

9 PUBLICATIONS 74 CITATIONS

SEE PROFILE



Trevor Letcher

University of KwaZulu-Natal

240 PUBLICATIONS 4,707 CITATIONS

SEE PROFILE

Liquid–Liquid Equilibrium Modeling of Ternary Hydrocarbon + Water + Alkanol Systems[†]

Igor V. Prikhodko,* Trevor M. Letcher,[‡] and Theo W. de Loos[§]

Department of Chemistry, St. Petersburg State University, Universitetsky pr. 2, 198904 St. Petersburg, Russia, Department of Chemistry and Applied Chemistry, University of Natal, King George V Avenue, Durban 4001, South Africa, and Faculty of Chemical Engineering and Materials Science, Laboratory of Applied Thermodynamics and Phase Equilibria, Delft University of Technology, Julianalaan 116, 2628 BL Delft, The Netherlands

The associated perturbed anisotropic chain theory (APACT) and the hole quasilattice group-contribution model (HM) have been used to model liquid–liquid equilibria at low pressure in ternary systems composed of hydrocarbons (*n*-heptane, heptene-1, heptyne-1, benzene, toluene), water, and alkanols (methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol). Calculations of phase diagrams have been carried out and compared with experimental data. Both equations of state (EOS) tested describe the phase diagrams reasonably well and give the correct slope to the tie lines. However, the HM reproduces the binodal curves better than does the APACT model. In most cases the EOS predict the correct type of phase diagram. The results show that the HM is not only able to fit the experimental data but can be recommended also to predict the liquid–liquid equilibria for the systems under consideration.

1. Introduction

Knowledge about liquid–liquid equilibrium (LLE) in binary and multicomponent systems is required for design of separation and extraction processes. Ternary systems composed of hydrocarbons (saturated and unsaturated), water, and alkanols are of importance in the fuel industry where alkanol + gasoline blends are widely used to extend fuels. To understand the phase separation behavior in these mixtures Letcher and co-workers (1986; 1990; 1992; 1993; 1994) have studied experimentally liquid–liquid equilibria (tie lines and binodal curves) of a number of hydrocarbon + water + alkanol ternary mixtures. In these investigations the different hydrocarbons can be considered to be model compounds representing petrol.

Mixtures containing associating components are of interest in theoretical studies as well. They are appropriate for testing various molecular-statistical models. Apart from the activity coefficient models used in the correlation of LLE data in the systems under study, such as NRTL and UNIQUAC (Sørensen et al., 1979), and those used for the prediction of LLE data which use group-contribution methods like ASOG and UNIFAC (Fredenslund, 1977; Magnussen et al., 1980), there is an alternative way to describe fluid phase equilibria. This approach is based on a molecular-statistical theory which is applied to derive an equation of state (EOS). There are three basic types of EOS which are able to represent simultaneously LLE and VLE in systems with association (Economou and Donohue, 1991). They include the family of “chemical theory” equations, like the associated perturbed anisotropic chain theory (APACT), the statistical associating fluid theory (SAFT), and the lattice–fluid quasichemical EOS. An analysis of these approaches performed by Economou and Dono-

hue (1991) and more recently our study of local ordering effects in the quasichemical approximation for associating fluids (Prikhodko et al., 1995a) have shown similar results in the description of association equilibria. These results are in reasonable agreement with computer simulation data, in spite of the difference in the physical interaction terms of the EOS. The APACT (Ikonomou and Donohue, 1986; 1988; Economou and Donohue, 1992), the SAFT (Chapman et al., 1988; 1990; Huang and Radosz, 1990; 1991; Suresh and Elliott, 1992; Suresh and Beckman, 1994; Fu and Sandler, 1995), and the lattice quasichemical hole model (HM) (Smirnova and Victorov, 1987) appeared to be the most useful models for practical purposes. The HM, for example, has been thoroughly tested for binary and multicomponent mixtures containing different fluids such as hydrocarbons, alkanols, acetone, acetic acid, water, nitrogen, carbon dioxide, and hydrogen sulfide (Smirnova and Victorov, 1987; Victorov et al., 1989; Prikhodko et al., 1989a,b; Victorov and Fredenslund, 1991; Victorov et al., 1991; Abdulkadirova, 1992; Deak et al., 1995; Prikhodko et al., 1995a,b).

Although many results have been reported in the literature, the quantitative representation of LLE in associating mixtures still remains a major challenge. The objective of this paper is to extend the application of the HM and the APACT to ternary mixtures involving associating species and to compare the modeling of LLE data by the two different theoretical approaches. We present in this work results of LLE predictions with the aid of these EOS in ternary hydrocarbon + water + alkanol systems from binary data alone.

2. Theory

As both EOS and calculation procedures have been described in detail in the previous papers cited above, only a short outline of the models will be given here.

The associated perturbed anisotropic chain theory (APACT) is the result of superimposing an association model upon the PACT (Vimalchand and Donohue, 1985). The APACT is a closed-form EOS which takes into account hydrogen bonding and is given by

* To whom correspondence should be addressed at St. Petersburg State University. E-mail: prihodko@nonel.chem.lgu.spb.su.

[†] Presented at the 14th IUPAC Conference on Chemical Thermodynamics, Osaka, Japan, Aug 25–30, 1996.

[‡] University of Natal.

[§] Delft University of Technology.

Table 1. APACT Pure Component Parameters Determined in the Present Work and Description of Pure Fluid Properties (Liquid Volume and Vapor Pressure) with the Aid of the Model for the Temperature Range Shown

substance	T^* , K	v^* , cm ³ mol ⁻¹	c	μ^a (D)	α^a (Å ³)	% AAD v^{liq} (T, K)	% AAD P^{sat} (T, K)
heptene-1	337.98	79.86	1.951	0.63	13.53	0.6 (283–313)	0.3 (273–373)
heptyne-1	311.16	72.83	2.534	0.01	12.86	0.3 (293–333)	0.3 (293–403)

^a μ is the dipole moment in Debye and α is the average polarizability.

Table 2. Results of VLE and LLE Correlations for Binary Systems with the Aid of APACT Using Anderko's Approximation

system	type of equilibrium	conditions		k_{ij}	% AAD in P	Δx_i^a %	data source ^b
		T , K	P , bar				
H ₂ O + CH ₃ OH	VLE	298	0.036–0.146	0.015	3.0		1
H ₂ O + C ₂ H ₅ OH	VLE	303	0.058–0.105	–0.041	3.6		2
H ₂ O + C ₃ H ₇ OH	VLE	298, 323	0.033–0.187	–0.024	5.2		1
H ₂ O + C ₄ H ₉ OH	LLE	293, 298	1.0	–0.014		12.0	3, 4
H ₂ O + C ₅ H ₉ OH	LLE	273–323	1.0	–0.082		3.0	5
H ₂ O + C ₆ H ₁₁ OH	LLE	273–323	1.0	–0.085		2.0	5
H ₂ O + C ₇ H ₁₅	LLE	298, 313	1.0	0.0		0.1	6, 7
H ₂ O + C ₇ H ₁₄	LLE	298, 318	0.1, 0.277	0.0		0.02	6
H ₂ O + C ₇ H ₁₂	LLE	298	1.0	0.080		0.1	6
H ₂ O + C ₆ H ₆	LLE	313–473	0.45–30.5	0.055		0.4	8, 9
H ₂ O + C ₇ H ₈	LLE	373–473	1.5–23.6	0.060		0.2	9
CH ₃ OH + C ₇ H ₁₆	VLE	332–333	1.0	–0.015	1.8		1
CH ₃ OH + C ₇ H ₁₄	VLE	332–343	1.0	–0.018	1.8		10
CH ₃ OH + C ₆ H ₆	VLE	313	0.328–0.487	–0.018	2.7		11
CH ₃ OH + C ₇ H ₈	VLE	313	0.088–0.372	–0.015	3.4		11
C ₂ H ₅ OH + C ₇ H ₁₆	VLE	303	0.135–0.162	0.016	1.2		12
C ₂ H ₅ OH + C ₇ H ₁₄	VLE	344–347	1.0	0.016	1.1		13
C ₂ H ₅ OH + C ₆ H ₆	VLE	313	0.215–0.334	–0.004	1.8		11
C ₂ H ₅ OH + C ₇ H ₈	VLE	313	0.088–0.203	–0.001	5.8		11
C ₃ H ₇ OH + C ₇ H ₁₆	VLE	303	0.072–0.102	0.019	1.7		14
C ₃ H ₇ OH + C ₇ H ₁₄	VLE	298, 318	0.132–0.233	0.010	2.3		15
C ₃ H ₇ OH + C ₆ H ₆	VLE	313	0.116–0.260	–0.002	2.4		11
C ₃ H ₇ OH + C ₇ H ₈	VLE	313	0.086–0.113	–0.001	3.1		11
C ₄ H ₉ OH + C ₇ H ₁₆	VLE	367–383	1.0	0.021	0.8		1
C ₄ H ₉ OH + C ₆ H ₆	VLE	313	0.063–0.243	–0.001	2.3		11
C ₄ H ₉ OH + C ₇ H ₈	VLE	313	0.038–0.085	–0.001	2.0		11

^a $\Delta x = (100/4M) \sum_k \sum_i \sum_j |x_{ijk}^{exp} - x_{ijk}^{calc}|$ where x^{exp} is experimental mole fraction, x^{calc} is calculated mole fraction, $i = 1, 2$ (components), $j = 1, 2$ (phases), and $k = 1, 2, \dots, M$ (tie lines). ^b (1) Kogan, V. B.; Fridman, V. M.; Kafarov, V. V. *Equilibrium between Liquid and Vapor*. Nauka: Moscow, Leningrad, 1966 (in Russian). (2) Pemberton, R. C.; Mash, C. J. *J. Chem. Thermodyn.* **1978**, *10*, 867. (3) Letcher, T. M.; Siswana, P. M. *Fluid Phase Equilib.* **1992**, *74*, 203. (4) Fischer, K.; Gmehling, J. *J. Chem. Eng. Data.* **1994**, *39*, 309. (5) Stephenson, R.; Stuart, J.; Tabak, M. *J. Chem. Eng. Data* **1984**, *29*, 287. (6) McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267. (7) Budantseva, L. S.; Lesteva, T. M.; Nemtsov, M. S. *Dep. VINITI.* **1976**, N437–76 (in Russian). (8) Tsonopoulos, C.; Wilson, G. M. *AIChE J.* **1983**, *29*, 990. (9) Anderson, F. E.; Prausnitz, J. M. *Fluid Phase Equilib.* **1986**, *32*, 63. (10) Budantseva, L. S.; Lesteva, T. M.; Nemtsov, M. S. *Russ. J. Phys. Chem.* **1975**, *49*, 1844. (11) Oracz, P.; Kolasinska, G. *Fluid Phase Equilib.* **1987**, *35*, 253. (12) Ronc, M.; Ratcliff, G. R. *Can. J. Chem. Eng.* **1976**, *54*, 326. (13) Toome, M. Yu.; Kudryavtseva, L. S. *Proceedings of Tallin Polytechnical Institute*, **1981**, Ser. 509, 27 (in Russian). (14) Sipowska, J. T.; Wieczorek, S. A. *J. Chem. Thermodyn.* **1980**, *12*, 459. (15) Pukinsky, I. B.; Chernik, G. G.; Chistyakova, G. O.; Smirnova, N. A. *Chemistry and Thermodynamics of Solutions*. Leningrad, Issue 5, **1982**, 157 (in Russian).

$$Z = \frac{n_t}{n_0} + c(Z_{rep}^{CS} + Z_{att}^J + Z_{polar})$$

where Z is the compressibility factor and n_t/n_0 is the extent of association. The repulsive term is obtained from the Carnahan–Starling expression, the attractive term accounts for the isotropic interactions between Lennard-Jones molecules, Z_{polar} is the sum of the contributions due to polar forces such as dipoles and quadrupoles, and c is one-third of the total number of external degrees of freedom. The final expression for n_t/n_0 in the model is written as follows

$$\frac{n_t}{n_0} = \frac{2}{1 + \sqrt{1 + KRT/v}}$$

Here, K is the equilibrium constant for the association equilibria; it is related to the enthalpy and entropy of association through

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

Table 3. HM Parameters Estimated in the Present Work

type of groups s and t	w_{st}	h_{st}	c_{st}
C=C–H ₂ O	Alkenes + Water		
	0.052 65	0.052 65	0
MeOH–C=C	Methanol + Alkenes		
	0.004 44	0.130 96	0
OH–C=C	Alkanols + Alkenes		
	0.048 05	–0.225 09	0

The APACT model contains three pure-component molecular parameters: T^* , the characteristic segmental energy, v^* , the characteristic molecular size, and c (see above). For associating molecules two additional parameters are needed to quantify the association equilibria: ΔH^0 and ΔS^0 . These parameters are unique for each pure component and must be obtained by fitting experimental data. In the following, these parameters are used in calculations to predict phase equilibria of binary and multicomponent mixtures.

The hole quasichemical model (HM) is a generalization of the well-known Barker lattice theory (Barker, 1952) in its group-contribution formulation by allowing vacant lattice sites. The HM EOS incor-

1 hole	1
2 CH ₂	2
3 CH ₃	3
4 S (H ₂ S)	4
5 2H (H ₂ S)	5
6 C (CO ₂)	6
7 2O (CO ₂)	7
8 N ₂	8
9 C ₁	9
10 C ₂	10
11 C ₃	11
12 O (H ₂ O)	12
13 2H (H ₂ O)	13
14 O (alkanol)	14
15 H (alkanol)	15
16 CH ₃ COO	16
17 H (CH ₃ COOH)	17
18 ACH (aromatic)	18
19 CH ₂ =CH-	19
20 -C≡C-	20
21 ACCOO	21
22 H (ACCOOH)	22
23 CH ₃ CH ₃ CH-	23
24 =CH-	24
25 C ₃ H ₆ (acetone)	25
26 O= (acetone)	26
27 N (NH ₃)	27
28 3H (NH ₃)	28
29 CH ₃ O (MeOH)	29
30 H (MeOH)	30
31 CCH ₃ (toluene)	31
32 C ₂ H ₅ (EtOH)	32
33 C ₃ H ₇ (i-PrOH)	33
34 -OCH ₂ CH ₂ -	34
35 -N- (pyridine)	35

Figure 1. Matrix of the hole group-contribution model available (■) parameters.

porates two terms:

$$Z = \frac{P_{\text{rep}} v^*}{RT} + \frac{P_{\text{res}} v^*}{RT}$$

where

$$\frac{P_{\text{rep}} v^*}{RT} = -\ln(1 - \eta) + \eta \frac{l}{r} + \frac{z}{2} \ln \left[1 - \eta \left(1 - \frac{q}{r} \right) \right]$$

$$\frac{P_{\text{res}} v^*}{RT} = -z \ln X_0$$

Here, z is the coordination number, v^* is the molar volume per lattice site, η is the reduced density, r and q are the geometrical parameters characterizing molecular size and surface area, and l is the bulkiness factor. The repulsion part of the EOS takes into account the effects of molecular size and shape. The residual part is defined by the quantity X_0 calculated in quasichemical approximation. It depends on the surface fractions of different functional groups and on their interaction parameters (w , h , c). The HM has the same form for mixtures in which case $r = \sum x_i r_i$, $q = \sum x_i q_i$, $l = \sum x_i l_i$, where x_i is the mole fraction of component i . Thus, to carry out calculations of phase equilibria in pure and mixed molecular fluids using the HM, it is necessary to have values for the geometrical (r_s and q_s) and energetic (w_{st} , h_{st} , c_{st}) model parameters.

The formulation of the HM EOS is quite general and does not depend on the particular type of association in the system. The specific and nonspecific interactions between groups are considered in exactly the same way, differing only in the value of the interaction parameters.

3. Results of Modeling

The HM and APACT parameters which are necessary to perform calculations were taken from earlier publications (Smirnova and Victorov, 1987; Victorov et al., 1989; Victorov and Fredenslund, 1991; Victorov et al., 1991; Abdulkadirova, 1992; Deak et al., 1995; Prikhodko et al., 1995a,b), and unavailable ones were obtained in the present work. New APACT parameters together with results of VLE description for pure components are shown in Table 1. The optimal values of APACT binary interaction parameters k_{ij} were determined by fitting experimental data individually to each constituent binary system (Table 2). Because of the lack of necessary VLE experimental information to estimate k_{ij} for the heptyne + alkanol mixtures, the corresponding k_{ij} s were set equal to zero. In this work we applied APACT with the infinite equilibria model, which is recommended in modeling hydrogen bonding of alkanol and water molecules that form linear association species. Also, in this study a two-site model for these molecules was used since it was proved to be adequate and computationally efficient to describe thermodynamic properties and phase equilibria in pure and mixed fluids with hydrogen bonding (Ikonomou and Donohue, 1986; 1988; Economou and Donohue, 1992; Suresh and Elliott, 1992; Suresh and Beckman, 1994). According to the assumption by Ikonomou and Donohue (1988) for two associating species, $K_{12} \approx (K_1 K_2)^{1/2}$, where K_1 , K_2 , and K_{12} are the equilibrium constants of the association reactions of a particular type $A_1 + iA_1 = A_{i+1}$ and the solvation (cross-association) reaction $A_i + B_j = A_i B_j$ ($i, j = 1, 2, \dots, \infty$), respectively. This allows one to avoid introducing an additional adjustable parameter K_{12} . Extensions of the expression for n_t/n_0 to systems containing any number of associating and inert components are given by Ikonomou and Donohue (1988) and

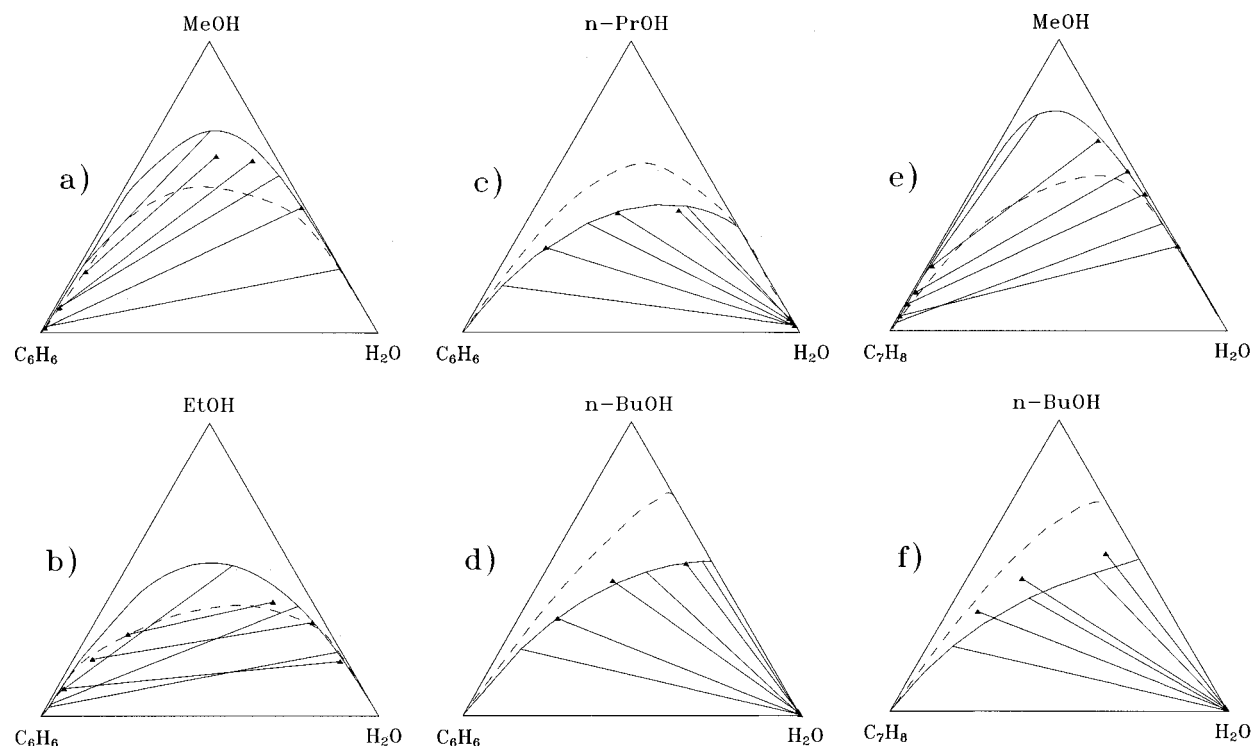


Figure 2. LLE predictions with the aid of HM (solid lines) and AFACT model (dashed lines) in the ternary aromatic hydrocarbon + water + alkanol systems. Experimental tie lines (points, straight lines) by Letcher et al, 1990; 1992. (a) benzene + water + methanol; (b) benzene + water + ethanol; (c) benzene + water + *n*-propanol; (d) benzene + water + *n*-butanol; (e) toluene + water + methanol; (f) toluene + water + *n*-butanol.

Table 4. List of Ternary Hydrocarbon + Water + *n*-Alkanol Systems Examined in This Work

system	conditions	type	ref
<i>n</i> -heptane + water + MeOH	298 K, 0.1 MPa	LLE	Letcher et al., 1986
<i>n</i> -heptane + water + EtOH			
<i>n</i> -heptane + water + PrOH			
<i>n</i> -heptane + water + BuOH			
<i>n</i> -heptane + water + pentanol			
<i>n</i> -heptane + water + hexanol			
benzene + water + MeOH	298 K, 0.1 MPa	LLE	Letcher et al., 1990
benzene + water + EtOH			
benzene + water + PrOH			
benzene + water + BuOH			
toluene + water + MeOH	298 K, 0.1 MPa	LLE	Letcher et al., 1992
toluene + water + EtOH			
toluene + water + PrOH			
toluene + water + BuOH			
heptyne-1 + water + MeOH	298 K, 0.1 MPa	LLE	Letcher et al., 1993
heptyne-1 + water + EtOH			
heptyne-1 + water + PrOH			
heptyne-1 + water + BuOH			
heptene-1 + water + MeOH	298 K, 0.1 MPa	LLE	Letcher et al., 1994
heptene-1 + water + EtOH			
heptene-1 + water + PrOH			
heptene-1 + water + BuOH			

by Anderko (1989). Suresh and Elliott (1991) have evaluated and compared both methods. They have demonstrated that the use of these approximations has led to similar results for VLE of binary mixtures containing associating fluids. As can be seen from Table 2, good agreement with experimental data is found for each system using small k_{ij} values. The application of Anderko's method leads to a better representation of LLE for water + alkanol mixtures than was found by using Ikonomou's approximation. However, for the water + *n*-butanol binary, calculated tie lines are longer in comparison with experimental ones. In contrast to experiment, the AFACT model as well as the HM predicts liquid phase splitting for the water + propanol system. In this work the AFACT model together with

Anderko's approximation was used to compute the LLE concentrations for the ternary systems.

Some additional HM group interaction parameters, necessary to carry out ternary calculations (Table 3), have been estimated for binary mixtures containing long-chain hydrocarbons and also containing alkanols with a carbon number greater than one. New interaction parameters for water + alkene have been found from mutual solubility data (McAuliffe, 1966). The methanol + alkene parameters were adjusted by using low pressure VLE data for MeOH + pentene (Kogan et al., 1966) and MeOH + octene (Budantseva et al., 1975), δP being 2.9% and 2.1%, respectively (δP denotes the average absolute deviation between calculated and experimental bubble pressures). Unfortunately, the HM

with this set of parameters predicts limited miscibility of methanol with heptene at low temperatures. The parameters for alkanol (higher than methanol) + alkene were determined from VLE at 298–318 K (Pukinsky et al., 1982) for two systems *n*-PrOH + hexene and *n*-PrOH + heptene ($\delta P = 0.9\%$ and 1.6%).

Figure 1 illustrates the availability of group parameters for the HM and details of the specifications of functional groups. The parameters listed in Table 3 together with those determined previously are sufficient to predict LLE in the ternary mixtures under consideration (Table 4).

Low pressure LLE predictions using a *p,T*-flash routine for a number of ternary hydrocarbon + water + alkanol systems are presented in Figure 2. It is seen that the models reflect correctly the change in the slope of the tie lines from hydrocarbon-rich phase to water-rich phase going from lower to higher alkanols and describe the binodal curves with reasonable accuracy. Unfortunately, the models show significant deviations between experimental and calculated mole fractions of components in the hydrocarbon-rich phase for the hydrocarbon + water + methanol or ethanol ternary mixtures. Typical average differences between the experimental composition value and those calculated by using the HM are no less than 4%. The corresponding difference using the APACT model is somewhat larger. Both EOS predict an erroneous type of phase behavior for the hydrocarbon + water + propanol systems. The HM also gives an incorrect type of phase diagram for the heptene + water + methanol ternary system. This is a result from the description of the binary water + PrOH and MeOH + heptene subsystems, as was mentioned above. However, for these ternaries the slope of the tie lines remains correct. In several cases large discrepancies between experimental and calculated compositions of conjugate phases are observed in the vicinity of the plait points, which is to be expected since classical EOS are not able to reproduce the critical region accurately, even though a few methods have been proposed to overcome this shortcoming (De Pablo and Prausnitz, 1989; 1990).

4. Conclusions

The application of the Associated Perturbed Anisotropic Chain Theory (APACT) and the hole quasilattice group-contribution model (HM) has been extended to the hydrocarbon + water + alkanol ternary systems. The models are shown to provide a reasonable representation of liquid–liquid equilibria for the mixtures investigated. The HM proved to be superior in predicting the binodal curves. Both equations of state used appear to reproduce the slopes of the tie lines correctly but the APACT model gives a heterogeneous region which is, as a rule, somewhat different from the experimental one. In most cases, however, the models predict the correct type of phase diagram. The results demonstrate that the HM is a good predictive tool in *a priori* estimates for chemical engineering applications.

Acknowledgment

Financial support of this work by the International Science Foundation (Grant R5K300) is gratefully appreciated. We thank Prof. Marc D. Donohue (Johns Hopkins University) for supplying APACT software.

Literature Cited

- Abdulkadirova, H. S. Phase Equilibrium Modeling for Systems Alkanol + Water on the Basis of the Hole Quasichemical Model. *Russ. J. Phys. Chem.* **1992**, *66*, 2133.
- Anderko, A. A Simple Equation of State Incorporating Association. *Fluid Phase Equilib.* **1989a**, *45*, 39.
- Anderko, A. Extension of the AEOS Equation of State to Systems Containing Any Number of Associating and Inert Components. *Fluid Phase Equilib.* **1989b**, *50*, 21.
- Barker, J. A. Cooperative Orientation Effects in Solutions. *J. Chem. Phys.* **1952**, *20*, 1526.
- Chapman, W. G.; Jackson, G.; Gubbins, K. E. Phase Equilibria of Associating Fluids: Chain Molecules with Multiple Sites. *Molec. Phys.* **1988**, *65*, 1057.
- Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New Reference Equation of State for Associating Liquids. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709.
- Deak, A.; Victorov, A. I.; de Loos, Th.W. High Pressure VLE in Alkanol-Alkane Mixtures. Experimental Results and Predictions by Three Equation of State Methods. *Fluid Phase Equilib.* **1995**, *107*, 277.
- De Pablo, J. J.; Prausnitz, J. M. Liquid–Liquid Equilibrium for Binary and Ternary Systems Including the Critical Region. Transformation to Non-Classical Coordinates. *Fluid Phase Equilib.* **1989**, *50*, 101.
- De Pablo, J. J.; Prausnitz, J. M. Thermodynamics of Liquid-Liquid Equilibria Including the Critical Region. Transformation to Non-Classical Coordinates Using Revised Scaling. *Fluid Phase Equilib.* **1990**, *59*, 1.
- Economou, I. G.; Donohue, M. D. Chemical, Quasichemical and Perturbation Theories for Associating Fluids. *AIChE J.* **1991**, *37*, 1875.
- Economou, I. G.; Donohue, M. D. Equation of State with Multiple Associating Sites for Water and Water-Hydrocarbon Mixtures. *Ind. Eng. Chem. Res.* **1992**, *31*, 2388.
- Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapour-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
- Fu, Y.-H.; Sandler, S. I. A Simplified SAFT Equation of State for Associating Compounds and Mixtures. *Ind. Eng. Chem. Res.* **1995**, *34*, 1897.
- Huang, S. H.; Radosz, M. Equation of State for Small, Large, Polydisperse, and Associating Molecules. *Ind. Eng. Chem. Res.* **1990**, *29*, 2284.
- Huang, S. H.; Radosz, M. Equation of State for Small, Large, Polydisperse, and Associating Molecules: Extension to Fluid Mixtures. *Ind. Eng. Chem. Res.* **1991**, *30*, 1994.
- Ikononou, G. H.; Donohue, M. D. Thermodynamics of Hydrogen Bonded Molecules: the Associated-Perturbed-Anisotropic-Chain-Theory. *AIChE J.* **1986**, *32*, 1716.
- Ikononou, G. H.; Donohue, M. D. Extension of the APACT to Mixtures with More than One Associating Component. *Fluid Phase Equilib.* **1988**, *39*, 129.
- Letcher, T. M.; Wooten, S.; Shuttelworth, B.; Heward, C. Phase Equilibria for (*n*-Heptane + Water + an Alkanol) at 298.2 K. *J. Chem. Thermodyn.* **1986**, *18*, 1037.
- Letcher, T. M.; Sewry, J. D.; Radloff, S. E. (Liquid-Liquid) Equilibria of Benzene-Water-an Alcohol at 298.15 K. *S. Afr. J. Chem.* **1990**, *43*, 56.
- Letcher, T. M.; Siswana, P. M. Liquid-Liquid Equilibria for Mixtures of an Alkanol + Water + a Methyl Substituted Benzene at 25 °C. *Fluid Phase Equilib.* **1992**, *74*, 203.
- Letcher, T. M.; Bricknell, M. B.; Sewry, J. D. Phase Equilibria for (an Alkanol + Hept-1-yne + Water) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1993**, *25*, 1183.
- Letcher, T. M.; Bricknell, M. B.; Sewry, J. D.; Radloff, S. E. Liquid-Liquid Equilibria for Mixtures of an Alkanol + Hept-1-ene + Water at 25 °C. *J. Chem. Eng. Data* **1994**, *39*, 320.
- Magnussen, T.; Sørensen, J. M.; Rasmussen, P.; Fredenslund, Aa. Liquid-Liquid Equilibrium Data: Their Retrieval, Correlation and Prediction. Part III: Prediction. *Fluid Phase Equilib.* **1980**, *4*, 151.
- Prikhodko, I. V.; Victorov, A. I.; Smirnova, N. A. Calculations of Thermodynamic Properties of Petroleum Light Components by the Hole Quasichemical Model. *Russ. J. Appl. Chem.* **1989a**, *62*, 2734.
- Prikhodko, I. V.; Schmelzer, J.; Victorov, A. I.; Smirnova, N. A. Phase Equilibria Modeling for the Mixtures of Oil/Gas Compounds with the Aid of Group-Contribution Equations of State. *Russ. J. Appl. Chem.* **1989b**, *62*, 2738.

- Prikhodko, I. V.; de Loos, Th. W.; Victorov, A. I. Prediction of Multiphase Equilibria in Associating Fluids by a Contact-Site Quasichemical Equation of State. *Int. J. Thermophys.* **1995a**, *16*, 1287.
- Prikhodko, I. V.; Victorov, A. I.; Smirnova, N. A.; de Loos, Th. W. Phase Equilibria Modeling by the Quasilattice Equation of State for Binary and Ternary Systems Composed of Carbon Dioxide, Water and Some Organic Components. *Fluid Phase Equilib.* **1995b**, *110*, 17.
- Smirnova, N. A.; Victorov, A. I. Thermodynamic Properties of Pure Fluids and Solutions from the Hole Group-Contribution Model. *Fluid Phase Equilibria* **1987**, *34*, 235.
- Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. Liquid-Liquid Equilibrium Data: Their Retrieval, Correlation and Prediction. Part II: Correlation. *Fluid Phase Equilib.* **1979**, *3*, 47.
- Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1980**, *4*, 47.
- Suresh, J.; Beckman, E. J. Prediction of Liquid-Liquid Equilibria in Ternary Mixtures from Binary Data. *Fluid Phase Equilibria* **1994**, *99*, 219.
- Suresh, S. J.; Elliott, J. R., Jr. Application of a Generalized Equation of State for Associating Mixtures. *Ind. Eng. Chem. Res.* **1991**, *30*, 524.
- Suresh, S. J.; Elliott, J. R., Jr. Multiphase Equilibrium Analysis via a Generalized Equation of State for Associating Mixtures. *Ind. Eng. Chem. Res.* **1992**, *31*, 2783.
- Victorov, A.; Kudryavtseva, L.; Kuus, M. Application of the Hole Group-Contribution Model to the Systems with Unsaturated Hydrocarbons. *Proceedings of the Academy of Sciences of the Estonian SSR. Chemistry.* **1989**, *38*, 178.
- Victorov, A. I.; Fredenslund, Aa. Application of the Hole Quasi-Chemical Group-Contribution Equation of State for Phase Equilibrium Calculation in Systems with Association. *Fluid Phase Equilib.* **1991**, *66*, 77.
- Victorov, A. I.; Fredenslund, Aa.; Smirnova, N. A. Fluid Phase Equilibria in Water + Natural Gas Component Mixtures and Their Description by the Hole Group-Contribution Equation of State. *Fluid Phase Equilib.* **1991**, *66*, 187.
- Vimalchand, P.; Donohue, M. D. Thermodynamics of Quadrupolar Molecules: the Perturbed-Anisotropic-Chain Theory. *Ind. Eng. Chem. Fundam.* **1985**, *24*, 246.

Received for review January 6, 1997
Revised manuscript received July 2, 1997
Accepted July 2, 1997*

IE970007Y

* Abstract published in *Advance ACS Abstracts*, September 1, 1997.