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THERMODYNAMICS OF COMPLEX FORMATION IN TERNARY LIQUID MIXTURES CONTAINING ACETONITRILE

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ABSTRACT

Vapor—liquid and liquid—liquid equilibria and excess enthalpies for ternary mixtures formed from acetonitrile, benzene, *n*-heptane, toluene, and carbon tetrachloride are successfully correlated with a modified version of the associated solution theory proposed by Lorimer and Jones in 1977, which assumes two types of self-association for acetonitrile and binary complexes between acetonitrile and unsaturated hydrocarbons and does not include any ternary parameters.

NOTATION

C_i, D_i	constants of eqn. (24)
G_{ji}	$\exp(-\alpha_{ji}\tau_{ji})$
g_{ji}	binary interaction parameter
g^E	excess Gibbs free energy
h_2	standard enthalpy of head-to-head dimer formation of acetonitrile
h_A	standard enthalpy of chain polymer formation of acetonitrile
h_{AB}	standard enthalpy of complex formation between acetonitrile and unsaturated hydrocarbon
h^E	excess enthalpy
K_2	equilibrium constant of head-to-head dimer formation of acetonitrile
K_A	equilibrium constant of chain polymer formation of acetonitrile
K_{AB}	equilibrium constant of complex formation between acetonitrile and unsaturated hydrocarbon
n	number of moles of a particular species
P	total pressure
P_i^s	saturated vapor pressure of pure component i
R	gas constant
S	stoichiometric sum given by eqn. (8)
T	abosolute temperature
v_i^L	molar liquid volume of pure component i
x_i	liquid phase mole fraction of component i
y_i	vapor phase mole fraction of component i
Greek symbols	
α_{ji}	nonrandomness parameter
γ_i	activity coefficient of component i

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τ_{ji}	$(g_{ji} - g_{ii})/RT$
ϕ_i	vapor phase fugacity coefficient of component i
ϕ_i^s	vapor phase fugacity coefficient of pure component i at system temperature T and pressure P_i^s

Superscripts

L	liquid
0	pure acetonitrile
s	saturation
I, II	phases
$'$	head-to-head dimer

Subscripts

A	acetonitrile, component 1
A_1, A_i	acetonitrile monomer and i-mer, respectively
AB	complex formation between acetonitrile and unsaturated hydrocarbon (=component B)
A_iB	acetonitrile i-mer—unsaturated hydrocarbon complex
B, C	unassociated components 2 and 3, respectively
chem	chemical
f	complex formation
i, j, k	components
phys	physical

INTRODUCTION

Lorimer and Jones [1] have derived equations for the excess Gibbs energy, excess enthalpy, and volume of mixing from thermodynamic association theory for complex binary liquid mixtures containing self-associating species and binary complexes. The equations were used to correlated experimental data for the three thermodynamic properties for the three binary systems formed from acetonitrile, carbon tetrachloride, and chloroform. However, a good fit to the excess enthalpy data of acetonitrile—carbon tetrachloride was not obtained. Furthermore, the association theory could not represent correctly mutual solubility data for acetonitrile—n-heptane mixtures. This may be because nonspecific interactions among the various species present are not well described through general nonspecific interactions of the simple mixtures.

The theory has not been extended to ternary mixtures. Experimental data are available for three ternary systems formed from acetonitrile, benzene, n-heptane, toluene, and carbon tetrachloride. Palmer and Smith [2] presented data on isothermal vapor—liquid and liquid—liquid equilibria for the acetonitrile—benzene—n-heptane system at 45° C, and Werner and Schuberth [3] also measured liquid—liquid equilibria for the same system at 20°C. Heinrich and Dojcansky [4] investigated liquid—liquid equilibria for the acetonitrile—toluene—n-heptane system at 40°C. Missen and co-workers [5,6] obtained excess Gibbs free energies and excess enthalpies for the acetonitrile— benzene—carbon tetrachloride system at 45° C

In this work, we present a modification of the association theory of Lorimer and Jones to represent the thermodynamic properties of binary and ternary liquid mixtures containing acetonitrile.

THEORY

Excess Gibbs energy

We use a mole fraction model to describe a ternary associated solution where acetonitrile molecules (A) self-associate and interact with two other nonassociated components (B and C). A physical interaction term for nonpolar interaction is assumed to be given by the NRTL of Renon and Prausnitz [7], which is more flexible than a general nonspecific interaction used by Lorimer and Jones [1] in data reduction.

The model is summarized as follows. We assume two association reactions for acetonitrile: dimerization corresponding to antiparallel association of acetonitrile dipoles, and chain association corresponding to head-to-tail association of acetonitrile dipoles.

$$A_1 + A_1 = A'_2 \qquad K_2 = x'_{A_2}/x^2_{A_1} \tag{1}$$

$$A_1 + A_i = A_{i+1} \qquad K_A = x_{A_{i+1}}/x_{A_i}x_{A_1} \qquad i \geqslant 1 \tag{2}$$

Acetonitrile and benzene (or toluene) molecules are assumed to form complexes [8].

$$A_i + B = A_iB \qquad K_{AB} = x_{A_iB}/x_{A_i}x_{B_1} \qquad i \geqslant 1 \tag{3}$$

Component C is inert and does not form any complex with acetonitrile. x_{A_i} and x'_{A_2} refer to i-mer and head-to-head dimer, respectively. K_2, K_A, and K_{AB} are mole fraction equilibrium constants. The species mole fractions are interrelated with the following equations

$$\sum_{i=1}^{\infty} x_{A_i} + x'_{A_2} + \sum_{i=1}^{\infty} x_{A_iB} + x_{B_1} + x_{C_1} = \frac{x_{A_1}}{1 - K_A x_{A_1}} + K_2 x^2_{A_1} + \frac{K_{AB} x_{A_1} x_{B_1}}{1 - K_A x_{A_1}} + x_{B_1} + x_{C_1} = 1 \tag{4}$$

$$\sum_{i=1}^{\infty} i x_{A_i} + 2x'_{A_2} + \sum_{i=1}^{\infty} i x_{A_iB} = \frac{x_{A_1}}{(1 - K_A x_{A_1})^2} + 2K_2 x^2_{A_1} + \frac{K_{AB} x_{A_1} x_{B_1}}{(1 - K_A x_{A_1})^2} = x_1 S \tag{5}$$

$$\sum_{i=1}^{\infty} x_{A_iB} + x_{B_1} = \frac{K_{AB} x_{A_1} x_{B_1}}{1 - K_A x_{A_1}} + x_{B_1} = x_2 S \tag{6}$$

$$x_{C_1} = x_3 S \tag{7}$$

The stoichiometric sum, S, is given by

$$S = \sum_{i=1}^{\infty} i x_{A_i} + 2x'_{A_2} + \sum_{i=1}^{\infty} i x_{A_iB} + \sum_{i=1}^{\infty} x_{A_iB} + x_{B_1} + x_{C_1}$$
$$= \frac{x_{A_1}}{(1 - K_A x_{A_1})^2} + 2K_2 x^2_{A_1} + \frac{K_{AB} x_{A_1} x_{B_1}}{(1 - K_A x_{A_1})^2} + \frac{K_{AB} x_{A_1} x_{B_1}}{(1 - K_A x_{A_1})} + x_{B_1} + x_{C_1} \tag{8}$$

where x_1, x_2, and x_3 are the nominal mole fractions of components. The monomer mole fractions x_{A_1}, x_{B_1}, and x_{C_1} are obtained by solving eqns. (4)—(8) by iteration if the equilibrium constants are known. The assumption of AB complex formation leads to similar equations, which will not be described here.

The excess Gibbs energy is given by the sum of g^E_{chem} and g^E_{phys}.

$$g^E = g^E_{\text{chem}} + g^E_{\text{phys}} \tag{9}$$

$$\frac{g^E_{\text{chem}}}{RT} = x_1 \ln \frac{x_{A_1}}{x_1 x^0_{A_1}} + x_2 \ln \frac{x_{B_1}}{x_2} + x_3 \ln \frac{x_{C_1}}{x_3} \tag{10}$$

$$\frac{g^E_{\text{phys}}}{RT} = \sum_{i=1}^{m} x_i \frac{\sum\limits_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum\limits_{k=1}^{m} G_{ki} x_k} \tag{11}$$

where

$$\tau_{ji} = (g_{ji} - g_{ii})/RT \tag{12}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{13}$$

The nonrandomness parameter α_{ji} $(=\alpha_{ij})$ was assumed to be equal to 0.3 for all binaries studied in this work, as recommended by Renon and Prausnitz [7], and each binary system has two adjustable parameters ($g_{21} - g_{11}$ and $g_{12} - g_{22}$). $x^0_{A_1}$ is the value of x_{A_1} at pure acetonitrile state.

The activity coefficient of component i is expressed by the sum of chemical and physical contributions.

$$\ln \gamma_i = \ln(\gamma_i)_{\text{chem}} + \ln(\gamma_i)_{\text{phys}} \tag{14}$$

$$\ln(\gamma_1)_{\text{chem}} = \ln(x_{A_1}/x_1 x^0_{A_1}) \tag{15}$$

$$\ln(\gamma_2)_{\text{chem}} = \ln(x_{B_1}/x_2) \tag{16}$$

$$\ln(\gamma_3)_{\text{chem}} = \ln(x_{C_1}/x_3) \tag{17}$$

$$\ln(\gamma_i)_{\text{phys}} = \frac{\sum\limits_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum\limits_{k=1}^{m} G_{ki} x_k} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum\limits_{k=1}^{m} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum\limits_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum\limits_{k=1}^{m} G_{kj} x_k} \right) \tag{18}$$

Excess enthalpy

The excess enthalpy is also given as the sum of chemical and physical contributions.

$$h^E = h^E_{\text{chem}} + h^E_{\text{phys}} \tag{19}$$

The enthalpy of complex formation is expressed by

$$h_f = h_2 n'_{A_2} + h_A \sum_{i=1}^{\infty} (i-1)(n_{A_i} + n_{A_iB}) + h_{AB} \sum_{i=1}^{\infty} n_{A_iB} \tag{20}$$

The definition of the excess enthalpy gives

$$h^E_{chem} = h_f - x_1 h_f^0 \tag{21}$$

where h_f^0 is the value of h_f for pure acetonitrile.

$$\begin{aligned} h^E_{chem} = & \left\{ h_2 K_2 x^2_{A_1} + \frac{h_A K_A x^2_{A_1}}{(1 - K_A x_{A_1})^2} (1 + K_{AB} x_{B_1}) + \frac{h_{AB} K_{AB} x_{A_1} x_{B_1}}{1 - K_A x_{A_1}} \right\} \Big/ S \\ & - x_1 \left\{ h_2 K_2 x^{02}_{A_1} + \frac{h_A K_A x^{02}_{A_1}}{(1 - K_A x^0_{A_1})^2} \right\} \Big/ \left\{ \frac{x^0_{A_1}}{(1 - K_A x^0_{A_1})^2} + 2 K_2 x^{02}_{A_1} \right\} \end{aligned} \tag{22}$$

h^E_{phys} is given by differentiation of (g^E_{phys}/T) with temperature.

$$h^E_{phys} = \frac{\partial (g^E_{phys}/T)}{\partial (1/T)} = R \sum_{i=1}^{m} x_i \left[\frac{\sum_{j=1}^{m} x_j \frac{\partial (\tau_{ji} G_{ji})}{\partial (1/T)}}{\sum_{k=1}^{m} G_{ki} x_k} - \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j \sum_{k=1}^{m} x_k \frac{\partial (G_{ki})}{\partial (1/T)}}{\left(\sum_{k=1}^{m} G_{ki} x_k \right)^2} \right] \tag{23}$$

We assume that the energy parameters change linearly with temperature.

$$g_{ji} - g_{ii} = C_i + D_i (T - 273.15) \tag{24}$$

CALCULATED RESULTS

Reproduction of binary data

The equilibrium constants and the standard enthalpy changes for acetonitrile association are the same as those given by Lorimer and Jones [1]: $K_2 = 8.35$ and $K_A = 2.1$ at 45°C, $h_2 = -8.9$ kJ mole^{-1} and $h_A = -6.7$ kJ mole^{-1}. We used $K_{AB} = 0.2$ at 45°C and $h_{AB} = -5.2$ kJ mole^{-1} for complex formation between acetonitrile and benzene (or toluene). The temperature dependence of the equilibrium constant is fixed by the van't Hoff equation. Tables 1 and 2 list the results of binary data fit.

Vapor—liquid equilibrium calculations were performed using the following equation [16]

$$\phi_i y_i P = \gamma_i x_i \phi_i^s P_i^s \exp[v_i^L (P - P_i^s)/RT] \tag{25}$$

The fugacity coefficient ϕ is obtained from the volume explicit virial equation truncated after the second term and the pure component and cross-virial coefficients are estimated by the generalized method of Hayden and O'Connell [17]. Antoine constants are used to calculate the pure component vapor pressure P^s. The simplex method [18] was used to determine energy parame-

TABLE 1

Correlation of binary vapor—liquid and liquid—liquid equilibria

System (1—2)	Temp. (°C)	No of data points	Type *	Parameters			Absolute arith. mean dev.			Ref.
				$g_{21}-g_{11}$ (J mole^{-1})	$g_{12}-g_{22}$ (J mole^{-1})	α_{12}	Vapor mole fraction (X1000)	Pressure (mm Hg)	δ ** (J mole^{-1})	
Acetonitrile—carbon tetrachloride	45	13		1988.32	1135.48	0.3	4 8	1 7		9
Acetonitrile—*n*-heptane	45	9		2268.07	5265.13	0.3	9 2	4.9		2
Acetonitrile—benzene	45	11	1	−1869.81	3655.57	0.3	2 5	1 2		2
			2	−1561.17	3067.38	0.3	2.9	1.2		
	20	45	1	−1261.96	2630.74	0 3	6 6	1 1		3
			2	−1260.01	2595.60	0 3	6.1	1 0		
Acetonitrile—toluene	45	9	1	−1804.74	4135.34	0.3			5.9	10
			2	−1774.63	4213.74	0.3			6 0	
Benzene—*n*-heptane	45	15		−1455.45	3708.27	0.3	2.9	1 6		2
	20	22		−674.29	2593.72	0.3	2 6	0.3		3
Toluene—*n*-heptane	40	9		−1289 22	2537.52	0.3			0.4	11
Benzene—carbon tetrachloride	70	8		−6.52	312.80	0.3	0.3	0.7		12
	40	8		−255 68	588.35	0.3	0 7	0.1		
Acetonitrile—*n*-heptane	45	S ***		1997.28	5123.12	0.3				2
	40	S		1917.65	5350.11	0.3				13
	20	S		2594.72	5340 19	0 3				3

* Type 1 = A_iB complexes were assumed for acetonitrile (A)—unsaturated hydrocarbon (B) mixtures and type 2 = AB complex was assumed.

** δ = deviation from smoothed experimental g^E data, which were obtained at equally spaced mole fractions from the Redlich-Kister equations whose constants were described in reference.

*** S = solubility data.

TABLE 2

Correlation of binary excess enthalpies

System (1—2)	Temp. (°C)	No. of data points	Type *	Parameters					Absolute arith. mean dev. (J mole^{-1})	Ref.
				C_1 (J mole^{-1})	C_2 (J mole^{-1})	D_1 (J mole^{-1} K^{-1})	D_2 (J mole^{-1} K^{-1})	α_{12}		
Acetonitrile—carbon tetrachloride	45	9 **		4526.95	8287.08	0.5440	23.3628	0.3	3.2	14
Acetonitrile—*n*-heptane	45	14		3135.73	3368.88	−11.5674	−13.2662	0.3	20.0	2
Acetonitrile—benzene	45	16	1	1879.84	648.39	17.8015	−8.9477	0.3	2.3	2
			2	3519.78	785.04	19.3932	−3.8768	0.3	1.6	
Acetonitrile—toluene	41.2	14	1	596.00	2615.91	2.8352	1.6051	0.3	4.8	15
			2	−2125.15	2954.76	−9.8726	7.8091	0.3	5.1	
Benzene—carbon tetrachloride	45	5		400.00	179.22	−0.1862	0.3240	0.3	4.6	6

* Type 1 = A,B complexes were assumed for acetonitrile (A)—unsaturated hydrocarbon (B) mixtures and type 2 = AB complex was assumed.

** Smoothed experimental data, which were obtained at equally spaced mole fractions from the Redlich-Kister equation whose constants were described in reference.

ters from vapor—liquid equilibrium data by minimizing the sum of squares of deviations in $\ln(\gamma_1/\gamma_2)$ for all data points. The energy parameters for the carbon tetrachloride—benzene system at 45° C were obtained by linear interpolation.

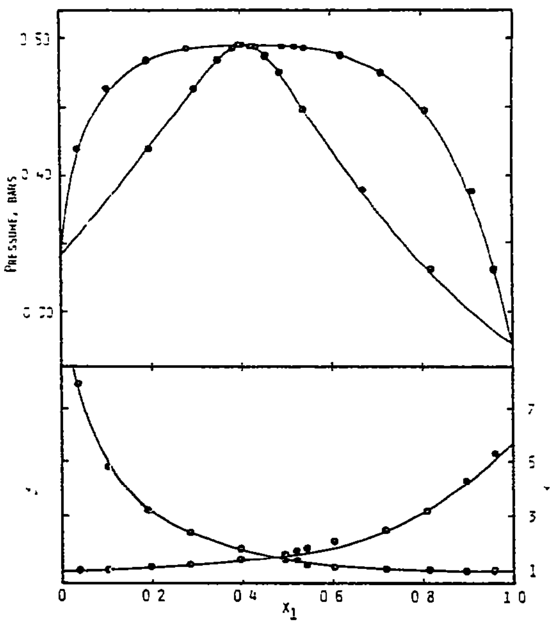
Liquid—liquid equilibria provide one set of equations for each component to calculate the compositions of two liquid phases in mutual equilibrium.

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \qquad (26)$$

Figures 1—5 compare calculated values with experimental data. Agreement with experiment seems to be acceptable. When the energy parameters for the partially miscible binary (acetonitrile—*n*-heptane) were obtained from solubility data, the reproduction of binary vapor—liquid equilibria is remarkably good, as shown in Fig. 2. This suggests that these energy parameters could be used for ternary prediction.

Ternary prediction

The accuracy of the ternary prediction of vapor—liquid equilibrium and excess enthalpy data for two systems is given in Table 3. The RMSD of the predicted ternary g^E values based on the NRTL equation was 107.5 J mole^{-1}



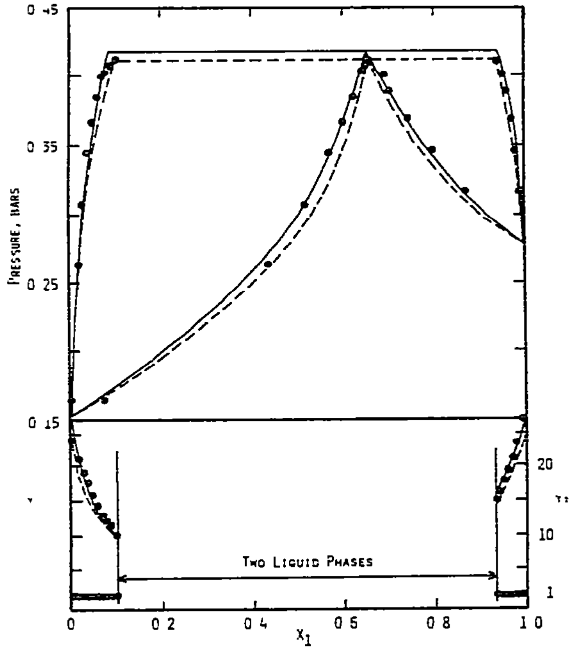
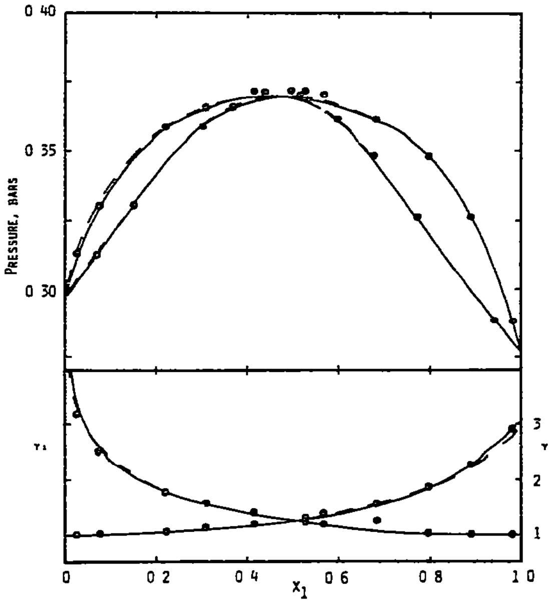


Fig. 1. Representation of vapor—liquid equilibria and activity coefficients for the acetonitrile (1)—carbon tetrachloride(2) system at 45°C. Experimental data of Brown and Smith [9], ●; calculated, ———.

Fig. 2. Representation of vapor—liquid equilibria and activity coefficients for the acetonitrile(1)—*n*-heptane(2) system at 45°C. Experimental data of Palmer and Smith [2], ●; calculated, ——— (vapor—liquid equilibria), - - - - - - (solubility data only).



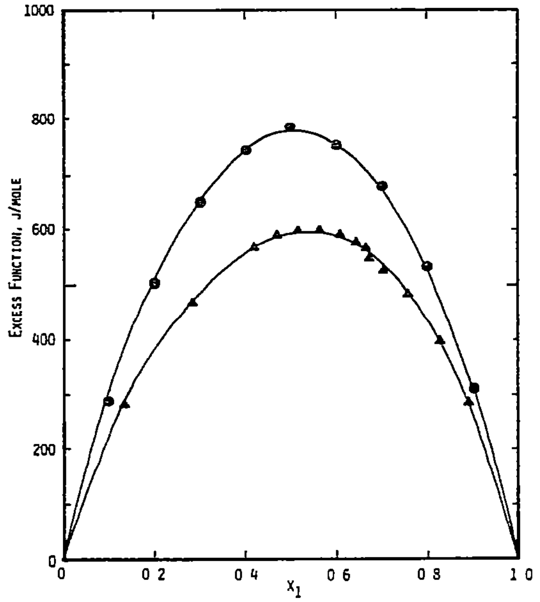


Fig. 3. Representation of vapor—liquid equilibria and activity coefficients for the acetonitrile(1)—benzene(2) system at 45°C. Experimental data of Palmer and Smith [2], ●; calculated, ——— (A_iB complex), - - - - - - (AB complex).

Fig. 4. Representation of excess functions for the acetonitrile (1)—toluene(2) system. Experimental: g^E data of Orye and Prausnitz [10] at 45°C, ●; h^E data of Sergio et al. [15] at 41.2°C, ▲; calculated, ———.

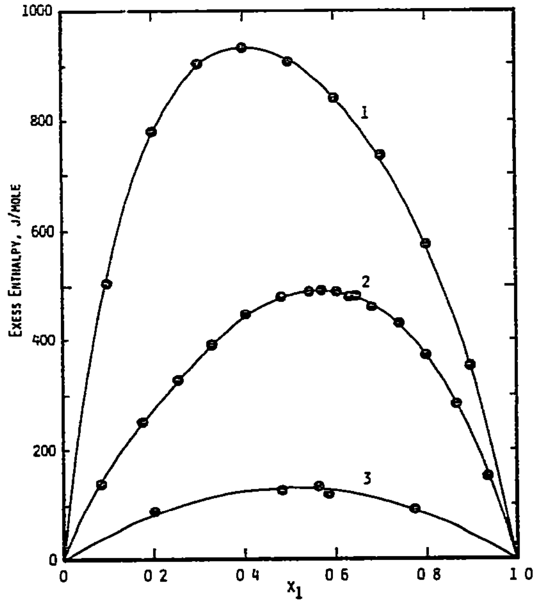


Fig. 5. Representation of excess enthalpies for three binary systems at 45°C. Experimental, ●: 1, data of Brown and Fock [14] for acetonitrile(1)—carbon tetrachloride (2); 2, data of Palmer and Smith [2] for acetonitrile(1)—benzene(2); 3, data of Lien and Missen [6] for benzene(1)—carbon tetrachloride(2). Calculated, ———.

TABLE 3

Predicted results for ternary vapor—liquid equilibria and excess enthalpies

System	Temp. (°C)	No. of data points	Absolute arithmetic mean dev.								Root-mean square dev.				Ref.
			Vapor mole fraction (X1000)		Pressure (mm Hg)		g^E (J mole^{-1})		h^E (J mole^{-1})		g^E (J mole^{-1})		h^E (J mole^{-1})		
			1 *	2 *	1	2	1	2	1	2	1	2	1	2	
Acetonitrile(1)— benzene(2)— *n*-heptane(3)	45	51	13.4 10.2 12.3	12.9 9.0 9.6	6.6	6.2	34.0	28.1			43.9	36.9			2
Acetonitrile(1) **— benzene(2)— *n*-heptane(3)	45	51	11.6 9.4 7.3	10.9 8.2 6.9	7.3	5.8	49.5	41.4			57.5	48.3			2
Acetonitrile(1)— benzene(2)— carbon tetrachloride(3)	45	62 (g^E) 26 (h^E)	9.4 6.0 7.0	7.8 5.5 6.0	5.2	4.1	33.3	28.3	17.5	21.9	39.2	33.8	20.8	25.8	5,6

* 1 = A_iB complexes were assumed for the acetonitrile(A)—benzene(B) system, 2 = AB complex was assumed.

** The energy parameters for the acetonitrile—*n*-heptane system were obtained from solubility data.

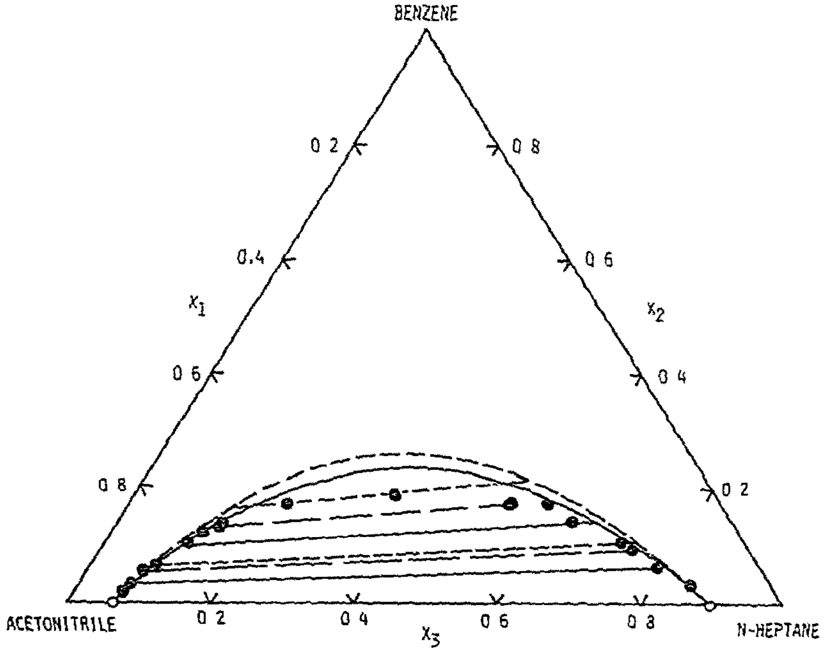


Fig. 6. Representation of ternary liquid—liquid equilibria for the acetonitrile(1)—benzene(2)—n-heptane(3) system at 45°C. Experimental data of Palmer and Smith [2], ●— · — · —●; calculated, ——— AB complex was assumed for acetonitrile—benzene, - - - - - -A_iB complexes were assumed.

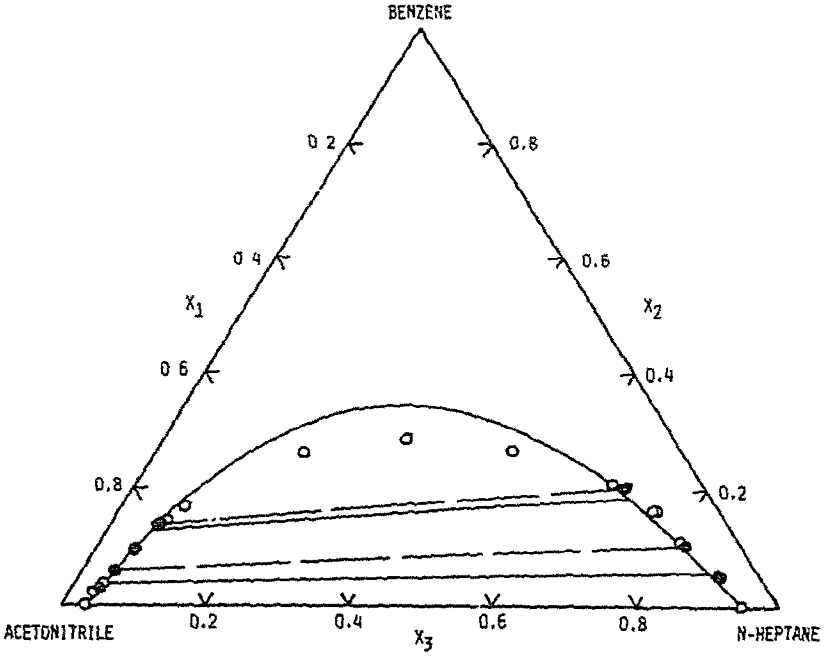


Fig. 7. Representation of ternary liquid—liquid equilibria for the acetonitrile(1)—benzene(2)—n-heptane(3) system at 20°C. Experimental data of Werner and Schuberth [3], ○ (solubility), ●— · — · —● (tie line). Calculated, ———.

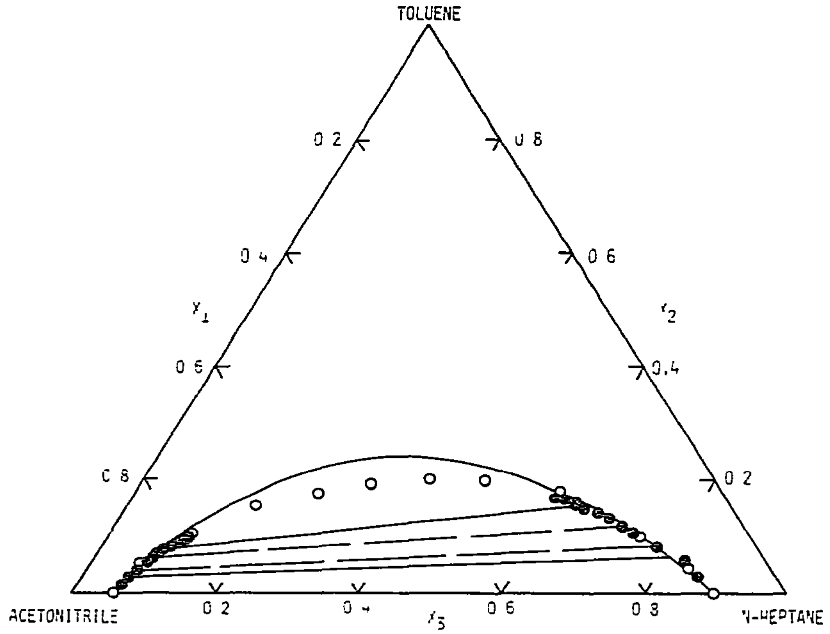


Fig 8. Representation of ternary liquid—liquid equilibria for the acetonitrile (1)—toluene (2)—*n*-heptane (3) system at 40°C. Experimental data of Heinrich and Dojcansky [4], ○ (solubility), ●— · — · —● (tie line). Calculated, ———

for the acetonitrile—benzene—*n*-heptane system [19]. This was not as accurate as the values obtained with the present associated solution equations.

The ternary solubility envelope and tie lines can be predicted with the activity coefficient equations and the method of Null [20]. Figures 6—8 show observed and calculated liquid—liquid equilibria for the two systems: acetonitrile—benzene—*n*-heptane and acetonitrile—toluene—*n*-heptane. The predicted results based on the binary data alone agree well with the experimental data except in the region of the plait point where successful prediction is often difficult. Both models of A_2B and AB for complex formation between acetonitrile and unsaturated hydrocarbons give similar results in ternaries as well as binaries.

In conclusion, the modified version of the associated solution model of Lorimer and Jones is able to predict well the excess thermodynamic properties of ternary liquid mixtures containing acetonitrile with only binary parameters.

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