Thermochimica Acta, 127 (1988) 337–346
Elsevier Science Publishers B V , Amsterdam – Printed in The Netherlands

LIQUID–LIQUID EQUILIBRIA FOR TERNARY MIXTURES CONTAINING TWO ALCOHOLS AND ONE SATURATED HYDROCARBON

ISAMU NAGATA

Department of Chemical Engineering, Kanazawa University, Kanazawa 920 (Japan)

(Received 11 August 1987)

ABSTRACT

Experimental tie-line data at 25°C are presented for the ternary systems methanol–(cyclohexane or n-heptane)–(1-propanol or 1-butanol or 2-butanol) The data were correlated by the extended UNIQUAC and UNIQUAC associated-solution models The UNIQUAC associated-solution model gives better calculated results than the extended UNIQUAC model

LIST OF SYMBOLS

A, B, C	alcohols and saturated hydrocarbon
a_{IJ}	binary interaction energy parameter
h_A	enthalpy of hydrogen-bond formation of alcohol
h_{AB}	enthalpy of hydrogen-bond formation between alcohols A and B
K_A, K_B	association constants of alcohols A and B
K_{AB}	solvation constant between alcohols A and B
P	total pressure
P_I^s	saturated vapour pressure of pure component I
q_I	molecular area parameter of pure component I
q_I'	molecular interaction area parameter of pure component I
R	universal gas constant
r_I	molecular volume parameter of pure component I
S_A, $\bar{S}_B$	sums as defined by eqns (8) and (9)
S_A, S_B	sums as defined by eqns (10) and (11)
T	absolute temperature
V	true molar volume of alcohol mixture given by eqn. (12)
$V_I^{\ominus}$	true molar volume of pure alcohol I given by eqn (14)
v_I^L	molar liquid-volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
Z	lattice coordination number equal to 10

0040-6031/88/$03 50

Greek letters

γ_I	activity coefficient of component I
θ_I	surface fraction of component I
τ_{IJ}	$\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
ϕ_I	vapour-phase fugacity coefficient of component I at T and P
ϕ_I^s	vapour-phase fugacity coefficient of pure component at T and P_I^s

Subscripts

A, B, C	alcohols and saturated hydrocarbon
A_1, B_1, C_1	monomers of components A, B and C
AB	binary complex between alcohols A and B
I, J, K	components
i, j, k, l	i, j, k and l-mers of alcohols

Superscripts

$\ominus$	pure-liquid reference state
α, β	conjugate liquid phases

INTRODUCTION

The number of papers on liquid–liquid equilibrium of ternary systems including two alcohols and one saturated hydrocarbon is small [1–4] The object of this work was to provide tie-line data at 25 °C for six ternary systems methanol–1-propanol–cyclohexane, methanol–1-butanol–cyclohexane, methanol–2-butanol–cyclohexane, methanol–1-propanol–n-heptane, methanol–1-butanol–n-heptane, methanol–2-butanol–*n*-heptane This paper presents the experimental results and their correlation by the extended UNIQUAC [5] and UNIQUAC associated-solution models [6] Vapour–liquid equilibrium data for the nine binary systems of the present ternary systems have already been published in the literature for methanol–1-propanol at 30 °C [7], for methanol–1-butanol at 25 °C [8], for methanol–2-butanol at 25 °C [8], for 1-propanol–cyclohexane at 25 °C [9], for 1-propanol–n-heptane at 25 °C [10], for 1-butanol–cyclohexane at 45 °C [11], for 1-butanol–n-heptane at 60 °C [12], for 2-butanol–cyclohexane at 45 °C [9], for 2-butanol–n-heptane at 65 °C [13] These binary vapour–liquid equilibrium data are used to evaluate the binary parameters of the models

EXPERIMENTAL

Chemicals

Cyclohexane, methanol, 1-propanol, 1-butanol, 2-butanol (Wako Pure Chemical Industries Ltd , guaranteed reagent-grade) and n-heptane (Kanto Chemical Co Inc , spectro-grade) were used without any further purification Densities and refractive indices of the chemicals at 25 ° C compared well with literature values (Table 1) These properties were measured by using an Anton Paar densimeter (DMA40) and a Shimadzu Pulfrich refractometer, respectively

Tie-line measurements

A two-liquid-phase mixture was intensely stirred in an equilibrium cell thermostated in a water bath and was left for 2 h at 25 ± 0 01° C Sample solutions were obtained from two phases by using Hamilton syringes and analysed with a Shimadzu gas chromatograph (GC-4C) and a Shimadzu chromatopac (C-R3A) The accuracy of the mole fraction measurements was ± 0 002

RESULTS AND DISCUSSION

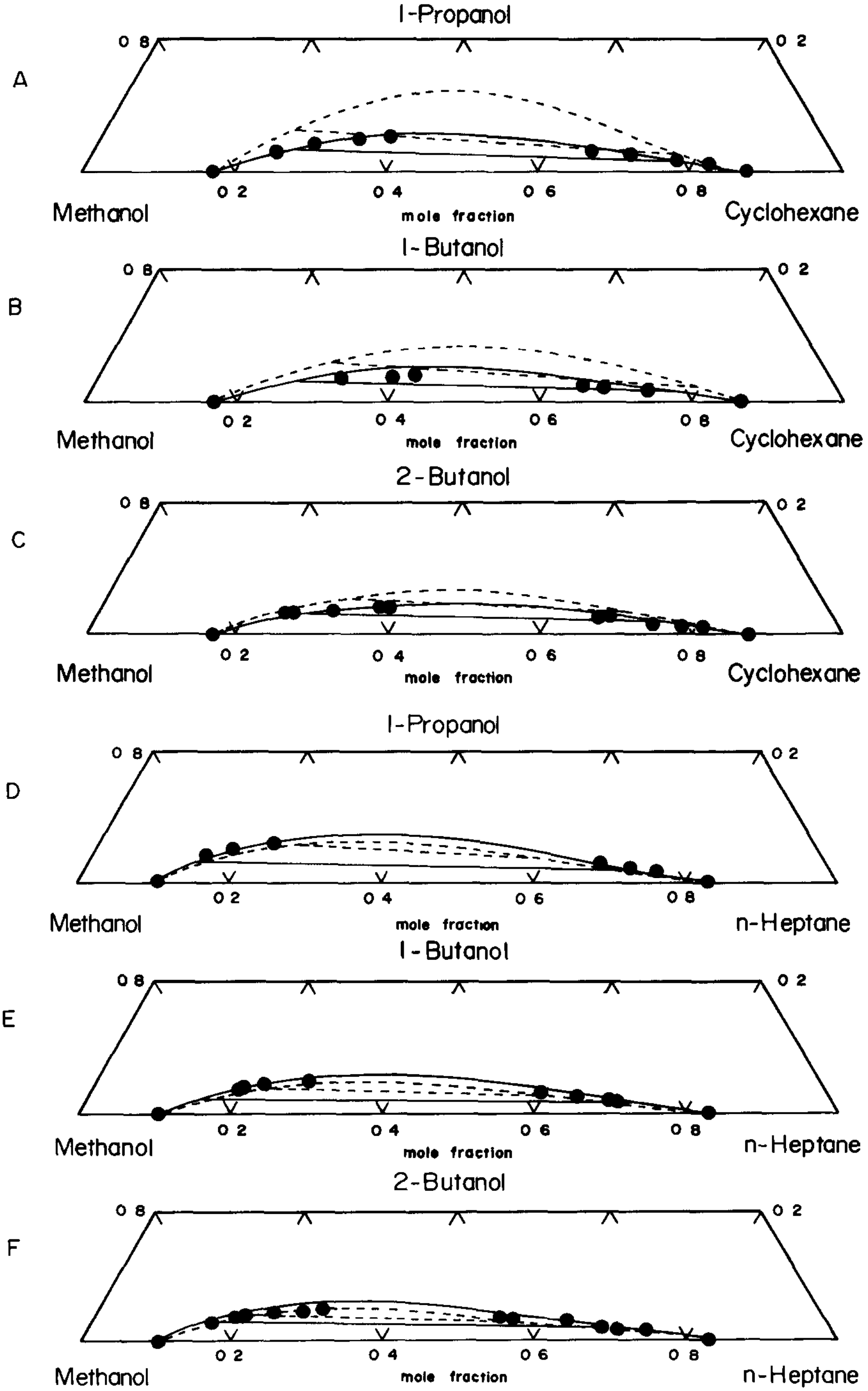
Table 2 shows the tie-line data for the six ternary systems The experimental data are compared with those calculated by the extended UNIQUAC [5] and UNIQUAC associated-solution models [6] in Fig 1

These two models give the following forms for the activity coefficient of component I in the present ternary systems

TABLE 1

Densities and refractive indices of chemicals at 25 ° C

Compound	Density ($\mathrm{g\ cm^{-3}}$)		Refractive index	
	Exptl	Lit [14]	Exptl	Lit [14]
Cyclohexane	0 8838	0 77389	1 42324	1 42354
n-Heptane	0 6794	0 67951	1 38487	1 38511
1-Butanol	0 8059	0 8060	1 39730	1 3973
2-Butanol	0 8027	0 8026	1 39501	1 3950
Methanol	0 7866	0 78664	1 32655	1 32652
1-Propanol	0 7998	0 7997	1 38374	1 38370



The legend to Fig 1 appears on page 341

TABLE 2
Experimental tie-line data for six ternary systems at 25 °C

Phase I			Phase II		
x_1	x_2	x_3	x_1	x_2	x_3
Methanol(1)–1-propanol(2)–cyclohexane(3)					
0 8758	0	0 1242	0 1716	0	0 8284
0 7281	0 0318	0 2401	0 1724	0 0097	0 8179
0 6731	0 0413	0 2856	0 2086	0 0163	0 7751
0 6073	0 0515	0 3412	0 2651	0 0262	0 7087
0 5673	0 0520	0 3807	0 3123	0 0315	0 6562
Methanol(1)–1-butanol(2)–cyclohexane(3)					
0 8758	0	0 1242	0 1716	0	0 8284
0 6466	0 0339	0 3195	0 2475	0 0172	0 7353
0 5757	0 0354	0 3889	0 3075	0 0228	0 6697
0 5439	0 0382	0 4179	0 3289	0 0239	0 6472
Methanol(1)–2-butanol(2)–cyclohexane(3)					
0 8758	0	0 1242	0 1716	0	0 8284
0 7193	0 0296	0 2511	0 1781	0 0110	0 8109
0 7046	0 0323	0 2631	0 2055	0 0140	0 7805
0 6556	0 0335	0 3109	0 2415	0 0169	0 7416
0 5903	0 0400	0 3697	0 2958	0 0236	0 6806
0 5777	0 0404	0 3819	0 3095	0 0260	0 6645
Methanol(1)–1-propanol(2)–n-heptane(3)					
0 8949	0	0 1051	0 1695	0	0 8305
0 8095	0 0395	0 1508	0 2300	0 0147	0 7553
0 7738	0 0525	0 1737	0 2608	0 0219	0 7173
0 7137	0 0639	0 2224	0 2944	0 0325	0 6731
Methanol(1)–1-butanol(2)–n-heptane(3)					
0 8949	0	0 1051	0 1695	0	0 8305
0 7723	0 0372	0 1905	0 2797	0 0181	0 7022
0 7652	0 0384	0 1964	0 2890	0 0196	0 6914
0 7333	0 0426	0 2241	0 3290	0 0241	0 6469
0 6688	0 0484	0 2828	0 3763	0 0319	0 5918
Methanol(1)–2-butanol(2)–n-heptane(3)					
0 8949	0	0 1051	0 1695	0	0 8305
0 8091	0 0305	0 1604	0 2448	0 0140	0 7412
0 7761	0 0376	0 1863	0 2824	0 0191	0 6985
0 7615	0 0399	0 1986	0 3011	0 0221	0 6768
0 7227	0 0459	0 2314	0 3424	0 0326	0 6250
0 6788	0 0465	0 2747	0 4078	0 0345	0 5577
0 6540	0 0504	0 2956	0 4256	0 0359	0 5385

Fig 1 Experimental tie-lines and calculated binodal curves at 25 °C A, methanol–1-propanol–cyclohexane, B, methanol–1-butanol–cyclohexane, C, methanol–2-butanol–cyclohexane, D, methanol–1-propanol–n-heptane, E, methanol–1-butanol–n-heptane, F, methanol–2-butanol–*n*-heptane (●) Experimental Calculated - - - - - -, extended UNIQUAC model, ———, UNIQUAC associated-solution model

Extended UNIQUAC model

$$\ln \gamma_I = \ln\frac{\Phi_I}{x_I} + 1 - \frac{\Phi_I}{x_I} - \left(\frac{Z}{2}\right)q_I\left(\ln\frac{\Phi_I}{\theta_I} + 1 - \frac{\Phi_I}{\theta_I}\right)$$
$$- q_I' \ln\left(\sum_J \theta_J \tau_{JI}\right) + q_I \sum_J \left(\frac{q_J'}{q_J}\right)\theta_J - q_I \sum_J \frac{(q_J'/q_J)\theta_J \tau_{IJ}}{\sum_K \theta_K \tau_{KJ}} \qquad (1)$$

where the coordination number Z is taken as 10 and the segment fraction Φ, the surface fraction θ and the adjustable binary parameter τ are expressed by

$$\Phi_I = x_I r_I / \sum_J x_J r_J \qquad (2)$$

$$\theta_I = x_I q_I / \sum_J x_J q_J \qquad (3)$$

$$\tau_{IJ} = \exp(-a_{IJ}/T) \qquad (4)$$

r, q and q' are pure-component structural constants and a_{IJ} is the binary interaction energy parameter for the I–J pair

UNIQUAC associated-solution model

According to the model assumptions the two alcohols (A, B) self-associate and solvate each other linearly to form A_i, B_i, $(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$, $B_i(A_jB_k)_l$, where the subindices i, j, k and l can go from unity to infinity

$$\ln \gamma_I = \ln\frac{\Phi_{I_1}}{\Phi_{I_1}^{\ominus} x_I} + \frac{r_I}{V_I^{\ominus}} - \frac{r_I}{V} - \left(\frac{Z}{2}\right)q_I\left(\ln\frac{\Phi_I}{\theta_I} + 1 - \frac{\Phi_I}{\theta_I}\right)$$
$$+ q_I\left[1 - \ln\left(\sum_J \theta_I \tau_{JI}\right) - \sum_J \frac{\theta_J \tau_{IJ}}{\sum_K \theta_K \tau_{KJ}}\right] \qquad (5)$$

The monomer segment fractions of the two alcohols are solved from the following mass-balance equations

$$\Phi_A = \overline{S}_A + \frac{r_A K_{AB} \overline{S}_A S_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)^2}$$
$$\times\left[2 + r_B K_{AB} S_A \left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_A K_{AB} S_B\right] \qquad (6)$$

$$\Phi_B = \overline{S}_B + \frac{r_B K_{AB} S_A \overline{S}_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)^2}$$
$$\times\left[2 + r_A K_{AB} S_B \left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_B K_{AB} S_A\right] \qquad (7)$$

where the sums $\overline{S}_A$, $\overline{S}_B$, S_A and S_B are given by

$$\overline{S}_A = \Phi_{A_1}/(1 - K_A\Phi_{A_1})^2 \tag{8}$$

$$\overline{S}_B = \Phi_{B_1}/(1 - K_B\Phi_{B_1})^2 \tag{9}$$

$$S_A = \Phi_{A_1}/(1 - K_A\Phi_{A_1}) \tag{10}$$

$$S_B = \Phi_{B_1}/(1 - K_B\Phi_{B_1}) \tag{11}$$

The true molar volume of the ternary mixture is expressed by

$$\frac{1}{V} = \frac{S_A}{r_A} + \left(\frac{2}{r_A r_B K_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B}\right)\frac{r_A r_B K_{AB}^2 S_A S_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)} + \frac{S_B}{r_B} + \frac{\Phi_{C_1}}{r_C} \tag{12}$$

At pure alcohol state $\Phi_{I_1}^{\ominus}$ and $V_I^{\ominus}$ are given by

$$\Phi_{I_1}^{\ominus} = \frac{2K_I + 1 - (1 + 4K_I)^{0.5}}{2K_I^2} \tag{13}$$

$$\frac{1}{V_I^{\ominus}} = \frac{1 - K_I\Phi_{I_1}^{\ominus}}{r_I} \tag{14}$$

For the saturated hydrocarbon (C) $K_C = 0$, $\Phi_C = \Phi_{C_1}$ and $\Phi_{C_1}^{\ominus} = 1$.

The pure-component structural constants for the extended UNIQUAC model were mainly taken from a previous paper [5] except for $q' = 1.00$ for methanol [15] and those for the UNIQUAC associated-solution model were estimated by the method of Vera et al. [16]. Table 3 shows the values of the pure-component structural constants of the two models.

In the correlation of the binary vapour–liquid equilibrium data, the optimal binary parameters of the two models were obtained by using a computer program similar to that developed by Prausnitz et al. [17], based

TABLE 3

Pure component structural parameters for two models

Component	Extended UNIQUAC model			UNIQUAC associated-solution model	
	r	q	q'	r	q
Cyclohexane	3.97	3.01	$q^{0.5}$	3.18	2.55
n-Heptane	5.17	4.40	$q^{0.5}$	4.15	3.52
1-Butanol	3.45	3.05	0.88	2.77	2.42
2-Butanol	3.45	3.05	0.88	2.77	2.42
Methanol	1.43	1.43	1.00	1.15	1.12
1-Propanol	2.78	2.51	0.89	2.23	1.98

on the maximum likelihood principle, and eqns (15) and (16)

$$P\phi_I y_I = x_I \gamma_I P_I^s \phi_I^s \exp\left[v_I^L (P - P_I^s)/RT\right] \tag{15}$$

$$\ln \phi_I = \left(2\sum_I y_I B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ}\right)\frac{P}{RT} \tag{16}$$

where P is the total pressure, ϕ is the fugacity coefficient, y is the vapour-phase mole fraction, P^s is the pure-component vapour pressure taken from original references of vapour–liquid equilibrium data or calculated from the Antoine equation [14], v^L is the molar pure-liquid volume calculated by using the modified Rackett equation [18] and B is the second virial coefficient estimated from the correlation of Hayden and O'Connell [19].

The standard deviations for the measured variables were 1 torr for pressure, 0.05 K for temperature, 0.001 for liquid-phase mole fraction and 0.003 for vapour-phase mole fraction.

The binary parameters of the models to correlate mutual solubility data were derived by solving eqn [17] for each component

$$(x_I \gamma_I)^{\alpha} = (x_I \gamma_I)^{\beta} \tag{17}$$

where the superscripts, α and β, denote equilibrium two liquid-phases.

The association constant of the alcohol at 50 °C is available from Brandani [20]. A value of $h_A = -23.2$ kJ mol^{-1} [21] was selected to express the enthalpy of hydrogen-bond formation between like and unlike alcohol molecules. Table 4 gives the equilibrium constants and their temperature-dependences. The results of phase equilibrium data reduction are reported in Table 5. Figure 1 illustrates that the UNIQUAC associated-solution model gives smaller solubility envelopes than the extended UNIQUAC model for the three systems involving cyclohexane, and both models provide comparable results, close to the experimental results of the three n-heptane-contain-

TABLE 4

Association and solvation equilibrium constants and their temperature-dependences

A	B	K_{AB} at 50 °C	$-h_{AB}$(kJ mol^{-1})
Methanol	Methanol	173.9	23.2
1-Propanol	1-Propanol	87.0	23.2
1-Butanol	1-Butanol	69.5	23.2
2-Butanol	2-Butanol	31.1	23.2
Methanol	1-Propanol	100	23.2
Methanol	1-Butanol	85	23.2
Methanol	2-Butanol	60	23.2

TABLE 5

Binary parameters and root-mean-square deviations

System	Temp (° C)	No of data points	Model [a]	Root-mean-square deviations				Parameters (K)	
				δP (torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}
Methanol(A)– 1-propanol(B)	30	9	I	0 30	0 00	0 0		276 65	−17 62
			II	0 48	0 00	0 1		37 90	119 33
Methanol(A)– 1-butanol(B)	25	21	I	0 48	0 00	0 1	1 0	−46 03	135 51
			II	0 44	0 00	0 1	3 4	−83 50	297 28
Methanol(A)– 2-butanol(B)	25	15	I	1 16	0 01	0 2	3 0	330 45	−28 68
			II	1 27	0 01	0 2	2 9	−50 32	214 05
1-Propanol(A)– cyclohexane(B)	25	27	I	1 05	0 01	0 2		171 31	914 39
			II	0 72	0 00	0 1		250 39	−130 94
1-Propanol(A)– n-heptane(B)	25	11	I	0 19	0 00	0 0		174 15	1671 54
			II	0 23	0 00	0 0		50 98	−3 38
1-Butanol(A)– cyclohexane(B)	45	43	I	0 42	0 01	0 1		106 84	958 48
			II	0 72	0 02	0 2		147 25	−85 11
1-Butanol(A)– n-heptane(B)	60	19	I	0 39	0 01	0 3	3 2	139 97	955 44
			II	0 27	0 01	0 4	3 6	103 75	−52 00
2-Butanol(A)– cyclohexane(B)	45	42	I	0 90	0 02	0 3		86 44	749 15
			II	0 91	0 02	0 4		200 01	−124 81
2-Butanol(A)– n-heptane(B)	65	18	I	1 97	0 00	1 0	8 9	106 58	743 16
			II	2 76	0 00	1 0	12 1	100 90	−61 77
Methanol(A)– cyclohexane(B)	25	MS[b]	I					280 63	1123 40
			II					7 42	86 62
Methanol(A)– n-heptane(B)	25	MS	I					412 41	1329 40
			II					17 94	72 04

[a] I, extended UNIQUAC model, II, UNIQUAC associated-solution model

[b] MS, mutual solubilities

ing systems The UNIQUAC associated-solution model was considered suitable to calculate the ternary liquid–liquid equilibrium of the systems studied in this work

REFERENCES

1 J M Sørensen and W Arlt, Liquid–Liquid Equilibrium Data Collection, Vol V, Part 2, DECAEMA, Frankfurt am Main, 1980

2 I Nagata and T Ohta, J Chem Eng Data, 28 (1983) 256

3 I Nagata, J Chem Thermodyn , 16 (1984) 737

4 I Nagata, Fluid Phase Equilibria, 18 (1984) 83

5 I Nagata, Thermochim Acta, 56 (1982) 43

6 I Nagata and K Ohtsubo, Thermochim Acta, 102 (1986) 185

7 G C Schmidt, Z Phys Chem , 121 (1926) 221

8 J Polák, S Murakami, V T Lam, H D Pflug and G C Benson, Can J Chem , 48 (1970) 2457

9 S -C Hwang and R L Robinson, Jr, J Chem Eng Data, 22 (1977) 319

10 S G Sayeh, J H Vera and G A Ratcliff, Can J Chem Eng , 57 (1979) 513

11 H T French, J Solution Chem , 12 (1983) 869

12 C Berro and A Peneloux, J Chem Eng Data, 29 (1984) 206

12 A Kumar and S S Katti, Indian J Technol , 18 (1980) 60

14 J A Riddick and W B Bunger, Organic Solvents, 3rd edn , Wiley-Intersience, New York, 1970, pp 77, 86, 145, 148, 151

15 I Nagata, K Miyamoto, P Alessi and I Kikic, Thermochim Acta, 120 (1987) 63

16 J H Vera, S G Sayeh and G A Ratcliff, Fluid Phase Equilibria, 1 (1977) 113

17 J M Prausnitz, T F Anderson, E A Grens, C A Eckert, R Hsieh and J P O'Connell, Computer Calculations for Multicomponent Vapor–Liquid Equilibria, Prentice-Hall, Englewood Cliffs, 1980, Chapts 3, 4, 6 and Appendices C, D

18 C F Spencer and R P Danner, J Chem Eng Data, 17 (1972) 236

19 J G Hayden and J P O'Connell, Ind Eng Chem Process Des Dev , 14 (1975) 209

20 V Brandani, Fluid Phase Equilibria, 12 (1983) 87

21 R H Stokes and C Burfitt, J Chem Thermodyn , 5 (1973) 236