VAPOUR–LIQUID EQUILIBRIUM AND SOLID–SOLID EQUILIBRIUM IN THE SYSTEM FORMED BY OCTAN-1-OL AND n-DECANE: MEASUREMENT AND CALCULATION

ZOFIA PLESNAR, PAWEŁ GIERYCZ, JACEK GREGOROWICZ
and ANDRZEJ BYLICKI

Instytut Chemii Fizycznej P.A.N., Kasprzaka 44/52, Warszawa (Poland)

(Received 25 January 1989)

ABSTRACT

The total vapour pressures of the binary system containing octan-1-ol and n-decane were measured at 373.15 K and 383.15 K using the ebulliometric method. The solid–liquid equilibrium (SLE) data were determined by the Rossini method. The experimental data were correlated using the Redlich–Kister, NRTL and modified NRTL equations. The prediction of SLE data from vapour–liquid equilibrium (VLE) and excess enthalpy H^E data is proposed and discussed.

INTRODUCTION

The aims of this work were to check the methods of prediction of solid–liquid equilibrium (SLE) data from binary vapour–liquid equilibrium (VLE) and excess enthalpy (H^E) data and to provide reliable and accurate binary VLE and SLE data for the octan-1-ol–n-decane system. This is part of a systematic investigation on binary mixtures containing 1-alcohols and n-alkanes which has been undertaken at the Institute of Physical Chemistry, Polish Academy of Sciences.

The solid–liquid equilibrium data in this system have not been reported in the literature. In this paper measurements of the binary SLE data are reported and a method of correlation and prediction of the data is proposed.

EXPERIMENTAL

All reagents used were pure standard substances supplied by Chemipan (Warsaw) with a guaranteed purity of better than 99.95% as determined by gas–liquid chromatography. Moreover, the purities of the materials were determined by cryometric measurements and were found to be 99.80% for octan-1-ol and 99.98% for n-decane.

The vapour pressures were measured using the ebulliometric method. The apparatus and experimental procedure have been reported previously [1]. A Texas Instruments precision pressure gauge (type 144-01) with a quartz Bourdon capsule (0.5 Pa resolution) and temperature meter (type S1220; 0.001 K resolution) were used for pressure and temperature measurement respectively.

The overall accuracy of the measurements was checked by determination of the saturation pressure of water. The analysis of this measurement gave accuracies of 0.01 K for the temperature and 3 Pa for the pressure.

To determine the solid–liquid equilibrium and eutectic temperatures the "micro-Rossini" kinetic method [2,3] was used; in this method the temperature of the sample is measured as a function of time during the melting and freezing processes under controlled heat exchange conditions between the surroundings and the sample. A Pyrex glass cell (volume, ≈ 1 ml) held in a vacuum (0.1–1 Pa) jacket [3] was filled with an octan-1-ol–n-decane mixture of a well-known composition. The vessel and sample were immersed in a cooling bath (225 K) until the mixture had completely solidified. The vessel and sample were then transferred into a heating bath in which a constant temperature was maintained, higher than the equilibrium temperature. The temperature of the sample was measured with a platinum resistance thermometer (PT 100) operated in conjunction with a UNIPAN 654 current source, a standard resistance and a DC-01 V digital voltmeter connected to a printer. Voltage values were recorded every 20 s. The accuracies of the temperature increments and absolute values measured were 0.01 K and 0.02 K respectively.

RESULTS

The total vapour pressures for the octan-1-ol–n-decane system were measured at two constant temperatures: 373.15 and 383.15 K. The results of VLE measurements are given in Table 1. In all cases the same experimental procedure and apparatus were used.

The corrected compositions (x_i) of the liquid phase were calculated by the iterative procedure reported previously [1], using the equation

$$G^E = RTx_1x_2 \sum_{j=0}^{m} A_j(x_1 - x_2)^j \tag{1}$$

where $m + 1$ is the number of adjustable constants A, R is the gas constant, T is the temperature (K) and G^E is the excess Gibbs energy of one mole of mixture. The difference between the measured and calculated pressure was chosen as an objective function.

For computation of the vapour phase non-ideality the Hayden–O'Connell correlation [4] was applied.

TABLE 1

Experimental isothermal VLE data for the n-decane(1)–octan-1-ol(2) system

n	Temperature			
	373.15 K		383.15 K	
	x_1	P (mmHg)	x_1	P (mmHg)
1	1.0000	71.85	1.0000	105.43
2	0.9502	72.39	0.9503	106.34
3	0.8544	71.80	0.8549	105.88
4	0.7479	70.35	0.7487	103.91
5	0.6396	68.27	0.6408	100.91
6	0.5378	65.53	0.5392	97.09
7	0.4372	61.88	0.4387	92.14
8	0.4410	61.93	0.4425	92.19
9	0.3834	58.98	0.3850	88.44
10	0.3281	55.74	0.3298	83.91
11	0.2324	48.34	0.2343	73.60
12	0.1299	36.75	0.1316	58.54
13	0.0387	25.11	0.0396	41.57
14	0.0000	19.21	0.0000	32.71

For correlation of the results obtained the NRTL and NRTLMK [5] equations were used. The correlation results are summarized in Table 2. The deviations $D(P)$ between the observed P^{exp} and calculated P^{cal} total pressure values for n experimental points and $m+1$ adjustable constants were calculated according to the formula

$$D(P) = \left[\frac{\sum_{i=1}^{n} \left(P_i^{exp} - P_i^{cal} \right)^2}{n - m - 1} \right]^{1/2} \tag{2}$$
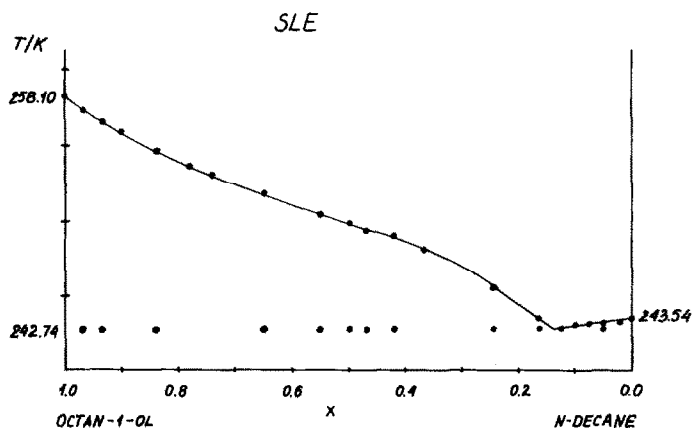

Fig. 1. Solid–liquid equilibrium for the octan-1-ol–n-decane system: ●, experimental point.

TABLE 2

Results of the correlation using the NRTL and NRTLMK equations for the n-decane(1)–octan-1-ol(2) system

n	373.15 K			383.15 K		
	x_1	NRTL	NRTLMK	x_1	NRTL	NRTLMK
		P (mmHg)	P (mmHg)		P (mmHg)	P (mmHg)
1	1.0000	0.000	0.000	1.0000	0.000	0.000
2	0.9502	−0.075	−0.050	0.9503	−0.165	−0.141
3	0.8544	−0.020	0.016	0.8549	−0.051	−0.015
4	0.7479	0.043	0.083	0.7487	0.079	0.116
5	0.6396	−0.046	−0.021	0.6408	−0.030	−0.005
6	0.5378	−0.137	−0.139	0.5392	−0.145	−0.145
7	0.4372	0.084	0.058	0.4387	0.121	0.098
8	0.4410	−0.041	−0.066	0.4425	−0.063	−0.085
9	0.3834	−0.056	−0.086	0.3850	0.090	−0.061
10	0.3281	0.143	0.117	0.3298	0.129	0.102
11	0.2324	0.348	0.353	0.2343	0.006	0.006
12	0.1299	−0.461	−0.410	0.1316	−0.226	−0.179
13	0.0387	0.011	0.054	0.0396	0.110	0.153
14	0.0000	0.000	0.000	0.0000	0.000	0.000
RMSD	D (P)	0.168	0.159	D (P)	0.108	0.100

RMSD, root mean square deviation.

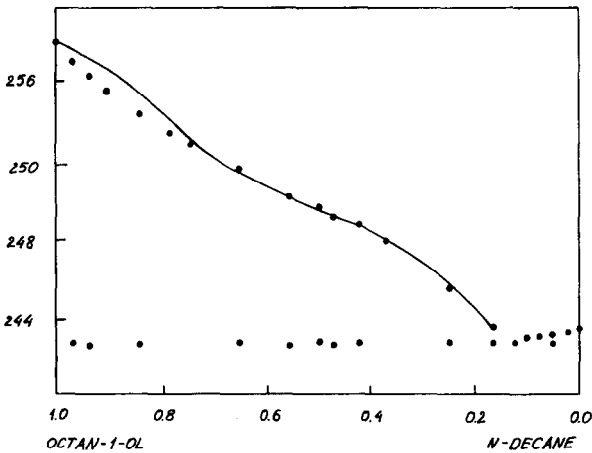$P = P^{exp} - P^{cal}$; P^{cal} is the total vapour pressure from the NRTL or NRTLMK equation.

Fig. 2. Comparison of experimental and calculated solid–liquid equilibrium for the octan-1-ol–n-decane system: ●, experimental point; ———, calculated from the Redlich–Kister equation.

TABLE 3

Solubility data and calculated activity coefficients for the octan-1-ol–*n*-decane system

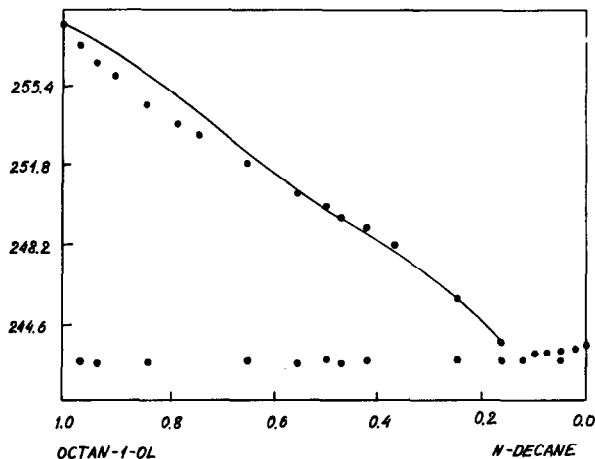| n	T (K)	x_{exp}	γ1 (eqn. (3))	γ1 (RK(3))	γ1 (NRTL)	γ1 (NRTLMK)	Deviation (%) (RK(3))	Deviation (%) (NRTL)	Deviation (%) (NRTLMK)
1	258.10	1.0000	1.00	1.00	1.00	1.00	0.00	0.00	0.00
2	257.28	0.9684	0.95	0.99	0.99	0.96	4.74	5.01	0.59
3	256.53	0.9366	0.93	0.98	0.99	0.93	6.35	7.31	0.08
4	255.86	0.9023	0.91	0.97	0.99	0.91	6.38	8.41	0.54
5	254.62	0.8404	0.89	0.94	0.98	0.89	5.87	10.09	0.17
6	253.67	0.7821	0.88	0.92	0.97	0.89	3.42	9.29	0.31
7	253.15	0.7424	0.90	0.91	0.97	0.90	0.99	7.49	0.19
8	251.88	0.6503	0.93	0.90	0.96	0.93	2.35	3.79	0.15
9	250.46	0.5528	0.97	0.95	0.98	0.98	2.10	1.02	0.95
10	249.92	0.4976	1.03	1.01	1.01	1.03	2.72	2.21	0.60
11	249.36	0.4697	1.05	1.04	1.03	1.06	0.48	1.38	0.91
12	248.94	0.4196	1.13	1.12	1.08	1.12	0.99	4.32	1.34
13	248.09	0.3675	1.20	1.22	1.16	1.20	1.59	3.82	0.66
14	245.65	0.2463	1.47	1.54	1.48	1.49	5.20	0.75	1.53
15	243.59	0.1645	1.84	1.79	1.89	1.83	2.95	2.50	0.60
16	243.06	0.0999							
17	243.11	0.0766							
18	243.17	0.0508							
19	243.32	0.0229							
20	243.54	0.0000							

Fig. 3. Comparison of experimental and calculated solid–liquid equilibrium for the octan-1-ol–*n*-decane system: ●, experimental point; ———, calculated from the NRTL equation.

The results of the measurement of the SLE data are presented in Table 3 and Fig. 1. Table 3 also shows the results of the calculation of the activity coefficients using the equation

$$\gamma_i = \frac{1}{x_i} \exp\left[\frac{H_i^m}{R} \left(\frac{1}{T^m} - \frac{1}{T} \right) \right] \tag{3}$$

The SLE data presented were also correlated using the Redlich–Kister equation with three constants, the NRTL equation with $\alpha = 0.3$ and the NRTLMK equation. The calculated "γ" values and percentage deviations are given in Table 3 and are shown in Figs. 2–4.
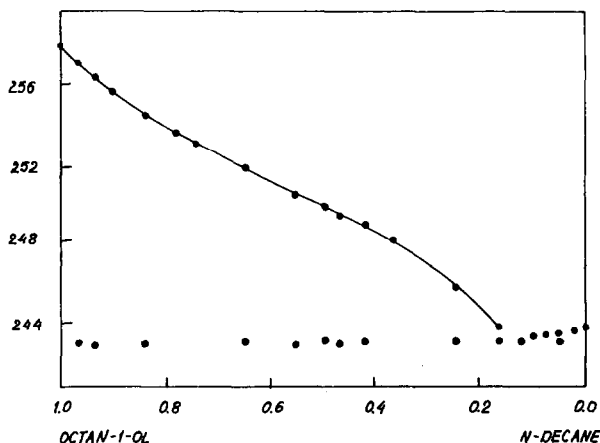

Fig. 4. Comparison of experimental and calculated solid–liquid equilibrium for the octan-1-ol–*n*-decane system: ●, experimental point; ———, calculated from the NRTLMK equation.

It can be seen that only the NRTLMK equation can reasonably describe the SLE data for this system. This means that for systems containing strong associating compounds only models which take association into consideration should be used to obtain a good description. The results of the correlation of the VLE data for this system (Table 2) show that the description using the NRTLMK equation is only slightly better than that using the NRTL equation. This is because the association is much weaker at higher temperatures. This is in agreement with the results of correlation for other systems formed by alcohols and hydrocarbons [6].

PREDICTION

We have attempted to predict SLE data for this system from VLE data assuming a linear temperature dependence for the activity coefficients. We obtained very poor results (Table 4). There are two reasons for these results. The first main reason is that the temperature dependence of the activity coefficients cannot be treated as linear (see Fig. 5) over such a large temperature range. The second reason is that the values of the activity coefficients calculated from the VLE data are not suitable for the prediction of the activity coefficients for liquid–liquid equilibrium (LLE), SLE or excess enthalpy (H^E) in systems with strong molecular interaction because they are dependent on the calculation of the vapour phase in the

TABLE 4

Prediction of SLE data for the octan-1-ol–n-decane system from VLE data and H^E data

| n	T (K)	x_{exp}	$\gamma 1$ (eqn. (3))	γ_1	
				VLE	H^E
1	258.10	1.0000	1.00	1.00	1.00
2	257.28	0.9684	0.95	1.00	0.97
3	256.53	0.9366	0.93	0.99	0.94
4	255.86	0.9023	0.91	0.98	0.93
5	254.62	0.8404	0.89	0.98	0.91
6	253.67	0.7821	0.88	0.97	0.90
7	253.15	0.7424	0.90	0.97	0.93
8	251.88	0.6503	0.93	0.98	0.96
9	250.46	0.5528	0.97	1.02	1.00
10	249.92	0.4976	1.03	1.07	1.04
11	249.36	0.4697	1.05	1.11	1.06
12	248.94	0.4196	1.13	1.22	1.17
13	248.09	0.3675	1.20	1.41	1.31
14	245.65	0.2463	1.47	2.34	1.62
15	243.59	0.1645	1.84	3.88	2.01
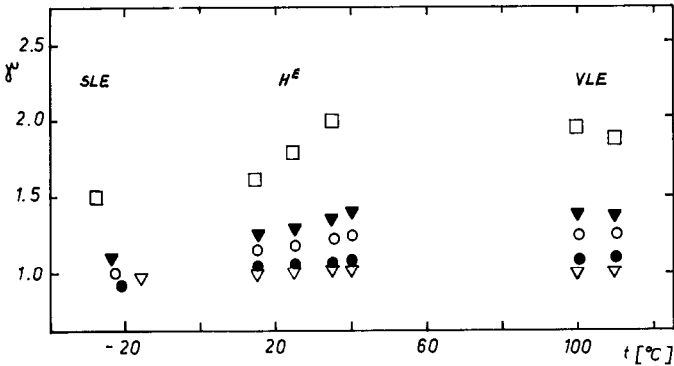
Fig. 5. Calculated activity coefficients for the octan-1-ol(1)–n-decane(2) system from VLE, H^E and SLE data: ▽, $x_1 = 0.9684$; ●, $x_1 = 0.6503$; ○, $x_1 = 0.4976$; ▼, $x_1 = 0.4196$; □, $x_1 = 0.2463$.

vapour–liquid equilibrium (usually virial coefficients are used for this purpose and in most cases their accuracy is about 20%–30%).

Therefore the activity coefficients calculated from the excess enthalpy were used to predict the solid–liquid equilibrium data. Calculations using the NRTLMK equation were performed for all the available H^E data [7–9] for this system. They covered the temperature range 293.15–313.15 K. The results of the prediction are given in Table 4 and Fig. 5.

It can be seen that in this case the prediction is much better. It should be noted that reasonable (but poorer) results were also obtained using the correlation equations based on a local composition concept. Therefore this method can be proposed for the prediction of SLE data. The prediction can be improved if C_p^E data are available and if SLE data are predicted from both H^E and C_p^E data.

It can be concluded that for the prediction of SLE data in systems containing n-alkanes and 1-alcohols H^E and C_p^E data should be used instead of VLE data. This is because of the temperature range (closer to solid–liquid equilibrium) in which the data are available and the poor accuracy of the calculation of the activity coefficients from VLE data.

REFERENCES

1 M. Rogalski and S. Malanowski, Fluid Phase Equilibria, 1 (1977) 137.
2 Z. Plesnar, P. Gierycz and A. Bylicki, Thermochim. Acta, 128 (1988) 93.

3 Z. Bugajewski and A. Bylicki, J. Chem. Thermodyn., 20 (1988) 1191.
4 J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem., Process Des. Dev., 14 (1975) 209.
5 P. Gierycz, Thermochim. Acta, 108 (1986) 229.
6 P. Gierycz, Thermochim. Acta, 116 (1987) 267.
7 T.H. Nguyen and G.A. Racliff, J. Chem. Eng. Data, 20 (1975) 252.
8 J.D.B. Featherstone and N.A. Dickinson, J. Chem. Thermodyn., 9 (1977) 75.
9 J.J. Christensen, R.M. Izatt, B.D. Still and R.W. Hanks, J. Chem. Thermodyn., 11 (1979) 262.