Thermochimica Acta, 128 (1988) 93–98
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

VAPOUR–LIQUID EQUILIBRIUM AND SOLID–LIQUID EQUILIBRIUM IN THE SYSTEM FORMED BY 1-OCTANOL AND n-OCTANE

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(Received 20 August 1987)

ABSTRACT

The total vapour pressures of the binary system containing 1-octanol and n-octane were measured at 373.15 K and 383.15 K using the ebulliometric method. The solid–liquid equilibrium data were determined by the Rossini method. The experimental data were correlated by means of Redlich–Kister, NRTL and modified NRTL equations.

INTRODUCTION

The purpose of this study was to provide reliable and accurate binary vapour–liquid equilibrium (VLE) and solid–liquid equilibrium (SLE) data for the system formed by 1-octanol and n-octane. This is part of a systematic investigation on binary mixtures containing 1-alcohol and n-alkane, 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. The vapour–liquid equilibrium data presented here, extend the range of temperatures and pressures in comparison with those previously reported for this system.

In this paper binary VLE and SLE data are reported and, in addition, a method for correlating the data is proposed.

EXPERIMENTAL

All reagents were pure standard substances supplied by Chemipan, Warsaw with a guaranteed purity of better than 99.95% determined by GLC analysis. The remaining moisture was removed by sorption on molecular sieves (A3, Wolfen Zeosorb). To prevent further contamination, each sample was distilled into the ebulliometer directly from the distillation column just prior to measurement.

0040-6031/88/$03.50

As mentioned above, 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 a temperature meter type S1220 (0.001 K resolution) were used for pressure and temperature measurements, respectively.

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

For the determination of equilibrium temperature the "micro-Rossini" kinetic method was used. This consists of measuring the temperature T of the sample as a function of time Z during the melting and freezing process under controlled heat exchange conditions between the surroundings and the sample. A Pyrex glass cell about 1 ml in volume, held in a vacuum (0.1–1 Pa) jacket was filled with a 1-octanol–n-octane mixture of a known composition. The vessel with the sample was immersed in a cooling bath (225 K) until the mixture completely solidified. Then it was transferred into a heating bath in which a temperature T_B was maintained, higher than the equilibrium temperature T^L. 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 and 0.02 K, respectively.

Figure 1 shows the method of determination of the freezing and melting temperatures T_f. A temperature T close to T_f can be ascertained by extrapolating the LF part of the equilibrium freezing curve to the intersection with the cooling curve of the liquid (AC). This temperature is very close to T_f when the substance is pure and easily crystallized. In the case of subcooling,

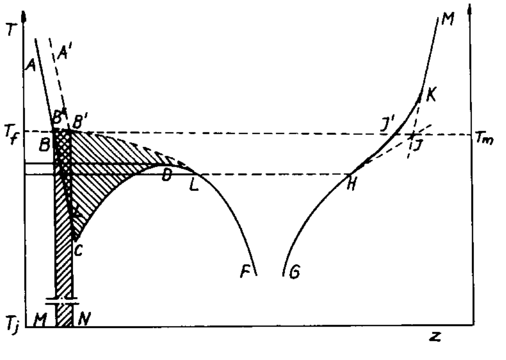

Fig. 1. The method of determination of freezing and melting temperatures (T_f).

the introduction of an extra term is necessary because the subcooling reduces the temperature difference $T - T_j$ and gives a longer crystallization time. When subcooling does not appear (it appeared in the system investigated) the substance should change its temperature according to A′B′LF and then $T_{B'} = T_f$. The freezing point can be determined from the melting curve by extrapolation of the equilibrium part of the GH curve to the intersection with the heating curve (melting curve)—point J.

The eutectic temperature T^E was ascertained numerically by extrapolating the straight-line equilibrium part of the melting curve down to the intersection with the extrapolated heating curve of the solid approximated by the equation [2]

$$T = T^{\ominus} - \Delta T^{\ominus} \exp(-kZ) \qquad (1)$$

where $T^{\ominus}$ is the temperature of the surroundings, $\Delta T^{\ominus} = T_0 - T$ at $Z = 0$ and k is a constant.

RESULTS

Total vapour pressures for the 1-octanol–n-octane system were measured at two constant temperatures of 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, which enabled an accurate thermodynamic interpretation of the results to be made.

TABLE 1

Experimental isothermal VLE data for n-octane(1)–1-octanol(2)

n	Temperature			
	100 °C		110 °C	
	x_1	*P* (mmHg)	x_1	*P* (mmHg)
1	0.0000	19.34	0.0000	32.54
2	0.0143	26.75	0.0172	48.54
3	0.0828	77.48	0.0800	113.85
4	0.1884	146.78	0.1888	206.33
5	0.2863	195.47	0.2916	269.11
6	0.3992	236.99	0.4027	324.32
7	0.4625	255.14	0.4597	347.23
8	0.4165	243.75	0.4563	345.76
9	0.5099	267.09	0.6030	395.96
10	0.6186	288.83	0.7333	417.09
11	0.7360	308.65	0.8279	436.08
12	0.8535	323.81	0.9470	464.25
13	0.9471	339.24	1.0000	480.79
14	1.0000	351.37		

TABLE 2

Results of the correlation using the NRTL and NRTLMK equations for the system n-octane(1)–1-octanol(2)

n	100 °C			110 °C		
	x_1	NRTL ΔP (mmHg) [a]	NRTLMK ΔP (mmHg) [a]	x_1	NRTL ΔP (mmHg) [a]	NRTLMK ΔP (mmHg) [a]
1	0.0000	0.00	0.00	0.0000	0.00	0.00
2	0.0143	3.83	−1.25	0.0172	2.46	−1.49
3	0.0828	3.06	−1.37	0.0800	−0.55	0.64
4	0.1884	−1.22	−0.50	0.1888	−2.70	0.35
5	0.2863	−1.57	0.92	0.2916	1.42	−0.54
6	0.3992	−0.09	0.47	0.4027	1.44	−0.28
7	0.4625	0.80	−0.50	0.4597	1.00	−0.23
8	0.4165	−1.27	−0.12	0.4563	1.22	−1.53
9	0.5099	0.92	0.14	0.6030	−4.84	1.73
10	0.6186	1.20	−0.01	0.7333	1.43	−0.74
11	0.7360	−0.94	0.39	0.8279	0.65	−0.36
12	0.8535	0.00	0.11	0.9470	0.24	−0.55
13	0.9471	0.44	−0.57	1.0000	0.00	0.00
14	1.0000	0.00	0.00			
RMSD	$D(P)$	1.67	0.74	$D(P)$	2.05	0.97

[a] $\Delta P = P^{\mathrm{exp}} - P^{\mathrm{cal}}$. P^{cal} is the total vapour pressure from the NRTL or the NRTLMK equations.

The corrected compositions x_i of the liquid phase were calculated by the iterative procedure reported previously [1] with the use of eqn. (2). The difference between the measured and calculated pressure was chosen as an objective function

$$G^{\mathrm{E}} = RTx_1x_2 \sum_{j=0}^{m} A_j(x_1 - x_2)^j \tag{2}$$

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.

For computation of the vapour phase non-ideality the Hayden–O'Connell correlation [3] was applied.

For correlation of the obtained results the NRTL and NRTLMK [4] 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

$$D(P) = \left[\frac{\sum_{i=1}^{n} \left(P_i^{\mathrm{exp}} - P_i^{\mathrm{cal}} \right)^2}{n - m - 1} \right]^{1/2} \tag{3}$$

Results of measurements of SLE are presented in Table 3 and Fig. 2. The eutectic temperature $T^E = 216.3$ K was ascertained numerically and is shown in Fig. 2. Table 3 also shows results of the calculation of activity coefficients γ_i from eqn. (4).

$$\gamma_i = \frac{1}{x_i} \exp\left[\frac{\Delta H_i^m}{R}\left(\frac{1}{T^m} - \frac{1}{T}\right)\right] \tag{4}$$

The SLE data presented were also correlated by the Redlich–Kister (RK) equation with three constants, the NRTL equation with $\alpha = 0.3$ and the NRTLMK equation [4]. The calculated γ values and percentage deviation are given in Table 3.

It is seen that only the NRTLMK equation can reasonably describe the SLE data for this system. This means that for systems with strong associating compounds only those models which take the association into account should be used for good description. The NRTLMK equation describes the

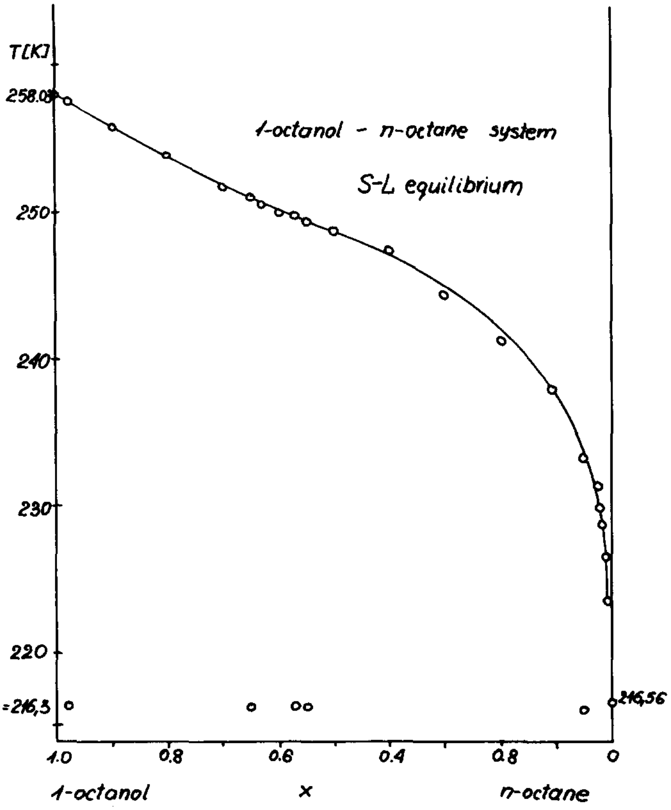

Fig. 2. Solid–liquid equilibrium for the 1-octanol–n-octane system: ○, experimental point; ———, calculated from the NRTLMK equation.

TABLE 3

Solubility data and calculated activity coefficients for the 1-octanol–n-octane system

n	T (K)	x_{exp}	γ_1 (eqn. (4))	γ_1 RK(3)	γ_1 NRTL	γ_1 NRTLMK	% dev. RK(3)	% dev. NRTL	% dev. NRTLMK
1	223.53	0.0097	4.91	4.78	6.06	5.12	2.66	23.38	4.26
2	226.48	0.0104	6.16	4.74	5.04	5.92	22.98	18.16	3.27
3	228.45	0.0172	4.52	4.43	4.35	4.48	2.06	3.74	0.86
4	229.82	0.0202	4.40	4.30	3.98	4.30	2.24	9.57	2.30
5	231.20	0.0259	3.91	4.06	3.60	3.83	3.88	8.04	2.13
6	233.28	0.0486	2.54	3.30	2.95	2.69	30.14	16.36	5.85
7	237.89	0.1078	1.75	2.11	1.97	1.86	20.87	12.99	6.72
8	241.94	0.1977	1.36	1.33	1.38	1.37	2.24	1.16	1.02
9	244.29	0.2979	1.11	1.01	1.11	1.11	8.88	0.02	0.04
10	247.40	0.4017	1.07	0.90	0.95	0.95	15.50	10.50	9.14
11	248.59	0.5002	0.95	0.89	0.91	0.91	5.57	3.77	4.55
12	249.36	0.5485	0.92	0.90	0.90	0.90	1.45	1.89	2.41
13	249.81	0.5710	0.92	0.91	0.90	0.90	0.26	1.75	2.41
14	249.89	0.5986	0.89	0.92	0.90	0.90	4.32	1.84	1.23
15	250.63	0.6328	0.88	0.94	0.90	0.90	6.20	2.47	2.53
16	250.91	0.6506	0.88	0.94	0.91	0.91	7.57	3.34	3.79
17	251.79	0.7015	0.87	0.96	0.92	0.93	10.33	5.16	5.41
18	253.87	0.8011	0.90	0.99	0.95	0.95	9.86	5.34	6.00
19	255.81	0.8995	0.94	1.00	0.98	0.98	6.91	5.08	4.43
20	257.69	0.9790	0.99	1.00	1.00	1.00	0.50	0.40	0.41
21	258.03	1.0000	1.00	1.00	1.00	1.00	0.00	0.00	0.00

VLE data for this system quite well, whereas the NRTL equation gives poor results (Table 2).

ACKNOWLEDGEMENT

This work was carried out within the Polish Academy of Sciences Research Project wpr/9-III.

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