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VAPOUR–LIQUID EQUILIBRIUM OF (METHANOL + A HEPTANONE) AT 323.15 K

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ABSTRACT

Vapour pressures for methanol + 2-heptanone, + 3-heptanone and + 4-heptanone at 323.15 K are reported. Liquid-phase values of G^E were determined from vapour pressures. Analysis using the maximum-likelihood principle enables evaluation of the variances of the calculated parameters, and the selection of the equation which provide a better representation of the results. A comparison with data at 298.15 K was made.

INTRODUCTION

Vapour–liquid equilibrium (VLE) data of binary systems containing methanol and one of the three heptanone isomers were required to study the thermodynamics of polymer solutions in these binary solvents. VLE data for these binary systems at 298.15 K have been published previously [1]. In order to know something about the temperature dependence of the excess Gibbs energies of these systems, the present work reports the VLE data at 323.15 K. As far as we know, there are no experimental VLE data for these systems in the literature.

EXPERIMENTAL

The vapour pressure measurements were carried out with an apparatus described previously [2]. The accuracy of the experimental measurements of pressure, p, temperature, T, and mole fraction of methanol, x, was 8 Pa, 0.01

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K and 1×10^{-4}, respectively. The temperature scale agrees with the IPTS-68 within experimental error [2].

All chemicals were tested and treated as described elsewhere [1].

RESULTS AND DISCUSSION

The vapour pressures of methanol + 2-heptanone, + 3-heptanone and + 4-heptanone were measured at 323.15 K. The second virial coefficient of methanol was taken from Dymond and Smith [3], heptanone virial coefficients were estimated using the method of Hayden and O'Connell [4]. Estimates for 2-heptanone, 3-heptanone and 4-heptanone are -3579 cm^3 mol^{-1}, -3662 cm^3 mol^{-1} and -3557 cm^3 mol^{-1}, respectively. As estimated previously [1], if we consider the uncertainty on the second virial coefficients of the heptanones to be of similar extent to the estimated second virial coefficient of methanol using the Hayden and O'Connell method, the estimated total uncertainty of calculated G^E must be smaller than 1 J mol^{-1}. This estimation includes the experimental uncertainties in pressure, temperature and composition.

Figure 1 shows the experimental vapour pressures vs. liquid-phase composition for the three systems considered here. Subscript 1 refers to methanol. Although 3-heptanone and 4-heptanone have the same volatility at 323.15 K, the binary mixtures exhibit different behaviour in the molar fraction range $0.2 < x_1 < 0.9$, indicating higher non-ideality of the mixture containing 4-heptanone. It was also observed [1] at 298.15 K that the most symmetrical molecule (4-heptanone) presents the most particular behaviour. Table 1 gives the experimental values of the total vapour pressure and the mole fraction of methanol for the three systems reported here.

Molar excess Gibbs energy values were calculated using a modified Barker's method, fitting G^E values to the equation [5]

$$G^E/RTx(1-x) = \sum_{i=0}^{m} A_i(2x-1)^i \Big/ \left\{1 + \sum_{j=1}^{n} B_j(2x-1)^j\right\} \quad (1)$$

where RT is the thermal energy, and A_i and B_j are the adjustable coefficients. Details of the regression method which is based on the maximum likelihood principle have been given previously [2,6]. Values of the assumed variances for temperature, pressure and mole fraction were: 0.01 K, 10 Pa and 1×10^{-4}, respectively, which are the experimental standard derivations of the variables. The influence of the assumed variances and other statistical discussions about the regression method are given elsewhere [7]. Following Abott and Van Ness [8], the vapour pressures of the pure components have been included in the regression as experimental quantities.

Table 1 gives the values of the residuals, Δx and Δp, which are the

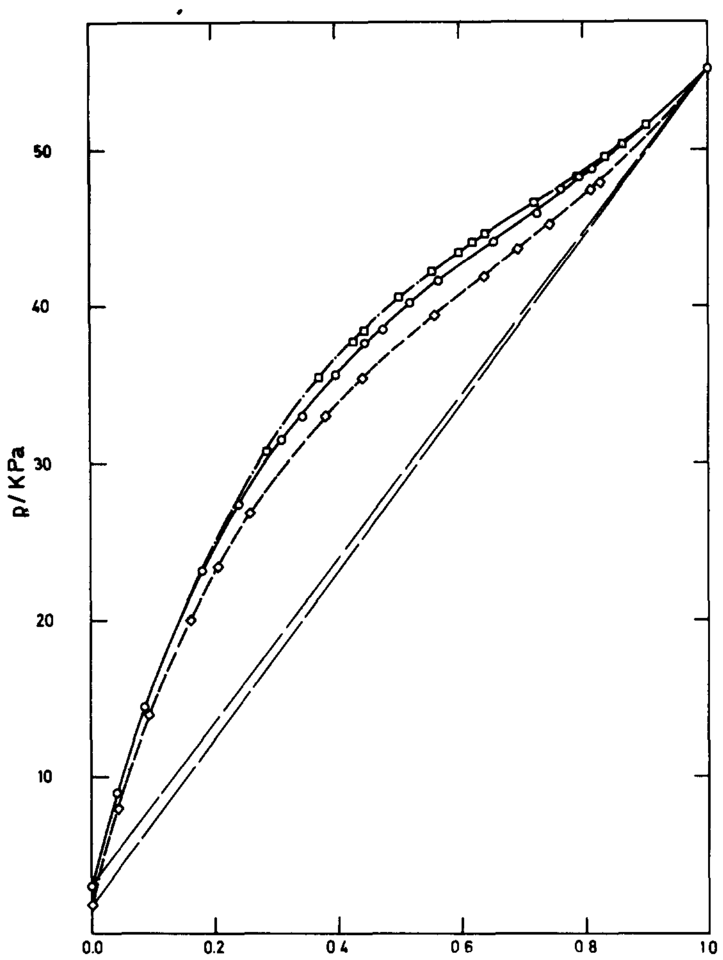

Fig. 1. Vapour pressures for $\{x\ CH_4O+(1-x)\ C_7H_{14}O\}$ systems at 323.15 K. ◇, 2-Heptanone; ○, 3-heptanone; □, 4-heptanone.

deviations between the experimental and the so-called true values of the variables [9], calculated during the regression. The temperature residuals are not reported because they are negligible ($<10^{-4}$ K). The thermodynamical consistency of the data has been checked applying Abbe's test to the deviations [10] and also, using the unconditional consistency criterion of Peneloux et al. [11].

Several Padé approximates [eqn. (1)] may be found which are able to represent the experimental data within the experimental uncertainties. Table 1 gives the values of the parameters of eqn. (1) and the standard deviation of the variables, s(p), and s(x), for the most appropriate approximant according to the systematic criteria discussed previously [6,7]. Table 1 also gives the values of G^E, the activity coefficients γ_1 of methanol and γ_2 of heptanone and the calculated mole fraction of methanol in the vapour phase, y_1. The uncertainties of G^E calculated from the variance–covariance matrix [12] are

TABLE 1

Experimental and calculated variables, their deviations from smoothed values, smoothing coefficients and standard deviations for $\{x\mathrm{CH_4O}+(1-x)\mathrm{C_7H_{14}O}\}$ at 323.15 K

x	$10^5\,\Delta x$	p (kPa)	Δp (Pa)	G^E (J mol^{-1})	γ_1	γ_2	y_1
Methanol (1) + 2-heptanone (2)							
0.0000	0	1.943	0	0	2.7903	1.0000	0.0000
0.0437	21	8.001	−38	116	2.5669	1.0019	0.7645
0.0965	9	14.021	−20	242	2.3329	1.0092	0.8716
0.1627	−14	20.069	38	379	2.0842	1.0262	0.9151
0.2082	7	23.554	22	460	1.9369	1.0435	0.9301
0.2598	4	26.942	−14	538	1.7904	1.0688	0.9411
0.3832	2	33.131	−13	668	1.5131	1.1577	0.9565
0.4428	−2	35.497	−10	701	1.4087	1.2174	0.9613
0.5624	−1	39.562	7	708	1.2443	1.3803	0.9689
0.6408	−1	42.001	9	669	1.1634	1.5279	0.9733
0.6956	1	43.708	−5	620	1.1175	1.6569	0.9764
0.7452	−1	45.263	5	560	1.0829	1.7968	0.9793
0.8134	1	47.541	−4	453	1.0453	2.0360	0.9836
0.8227	0	47.863	−3	436	1.0411	2.0738	0.9842
1.0000	0	55.182	0	0	1.0000	3.1840	1.0000

$A_0=1.0653\pm0.0008$; $A_1=-0.3787\pm0.0281$; $B_1=-0.4071\pm0.0255$
$s(p)/\mathrm{Pa}=17$; $s(x)=7\times10^{-5}$; $\sigma(T)/\mathrm{K}<1\times10^{-4}$

Methanol (1) + 3-heptanone (2)							
0.0000	0	2.972	0	0	2.8574	1.0000	0.0000
0.0420	−6	8.850	11	114	2.6426	1.0017	0.6756
0.0886	7	14.457	−14	230	2.4309	1.0075	0.8083
0.1821	1	23.178	−3	428	2.0803	1.0326	0.8889
0.2404	2	27.380	−7	529	1.9018	1.0576	0.9101
0.3115	−4	31.524	18	627	1.7181	1.0993	0.9261
0.3453	−6	33.210	29	665	1.6419	1.1239	0.9316
0.3983	3	35.632	−18	711	1.5348	1.1698	0.9388
0.4462	3	37.527	−17	740	1.4499	1.2194	0.9441
0.4741	−1	38.518	9	751	1.4051	1.2525	0.9469
0.5194	1	40.082	−7	759	1.3388	1.3137	0.9510
0.5664	2	41.584	−14	755	1.2778	1.3885	0.9548
0.6548	−1	44.180	7	711	1.1819	1.5697	0.9616
0.7228	−2	46.106	15	645	1.1227	1.7593	0.9668
0.7632	1	47.279	−6	590	1.0928	1.9020	0.9701
0.7924	0	48.119	−3	544	1.0736	2.0238	0.9725
0.8152	0	48.782	3	503	1.0600	2.1324	0.9746
1.0000	0	55.182	0	0	1.0000	4.0423	1.0000

$A_0=1.1277\pm0.0005$; $A_1=-0.5013\pm0.0065$; $B_1=-0.5516\pm0.0054$
$s(p)/\mathrm{Pa}=12$; $s(x)=3\times10^{-5}$; $s(T)/\mathrm{K}<1\times10^{-4}$

Methanol (1) + 4-heptanone (2)							
0.0000	−1	3.078	−26	0	2.6829	1.0000	0.0000
0.2870	2	30.798	−8	589	1.8114	1.0709	0.9217
0.3745	−1	35.510	5	693	1.6245	1.1303	0.9368

TABLE 1 (continued)

x	$10^5 \Delta x$	p (kPa)	Δp (Pa)	G^E (J mol^{-1})	γ_1	γ_2	y_1
0.4270	−1	37.820	6	737	1.5262	1.1785	0.9431
0.4444	−1	38.511	9	748	1.4958	1.1970	0.9450
0.5016	0	40.582	2	773	1.4027	1.2681	0.9502
0.5550	2	42.280	−13	779	1.3250	1.2988	0.9544
0.5979	0	43.482	4	771	1.2688	1.4340	0.9575
0.6209	0	44.105	0	762	1.2409	1.4847	0.9590
0.6398	2	44.613	−15	751	1.2190	1.5304	0.9603
0.7208	0	46.625	0	678	1.1366	1.7772	0.9657
0.7894	0	48.345	1	578	1.0809	2.0756	0.9708
0.8360	−1	49.580	9	487	1.0507	2.3477	0.9749
0.8657	−1	50.430	7	418	1.0348	2.5612	0.9779
0.9015	−1	51.530	7	325	1.0193	2.8725	0.9822
1.0000	1	55.182	−2	0	1.0000	4.2028	1.0000

$A_0 = 1.1519 \pm 0.0007$; $A_1 = -0.0965 \pm 0.0047$; $B_1 = -0.2649 \pm 0.0035$
$s(p)/\text{Pa} = 10$; $s(x) = 1 \times 10^{-5}$; $s(T)/\text{K} < 1 \times 10^{-4}$

always smaller than 0.9 J mol^{-1}. Then we may assume that the maximum uncertainty in G^E is 1 J mol^{-1}, as was calculated from the experimental errors.

We have found that a three-parameter approximant of degree (1/1) is the most adequate for all three systems reported in this work. The correlation matrices of the parameters indicate that, in general, the coefficients A_1 and B_1 are correlated in these fits. In principle, it is possible to substitute the correlated parameters by a linear combination of them [13]. Nevertheless, the substitution of the (1/1) approximant into a (1/0) approximant introduces larger standard deviations in all variables as well as a certain degree of thermodynamical inconsistency. This situation has been found previously [1,14] for similar and dissimilar systems. In this case, it is easy to understand that the approximant would not fit the data because eqn. (1) becomes a parabola when $m = 1$ and $n = 0$ and subsequently, a two-parameters curve may have difficulties to bend itself to the recalculated values of $G^E/RTx(1-x)$.

Figure 2 shows the G^E curves for the three systems vs. composition, and also the curve tops of the same function for the same systems at 298.15 K [1]. It may be observed that the G^E values of systems with 2-heptanone and 3-heptanone decrease when temperature goes from 298.15 to 323.15 K. On the other hand, the G^E of the methanol + 4-heptanone system exhibits the opposite behaviour, thus indicating a different change of entropy.

Although the three systems have its maxima of the G^E curve, near the equimolar mixture, it may be observed, in Fig. 2, that the system with

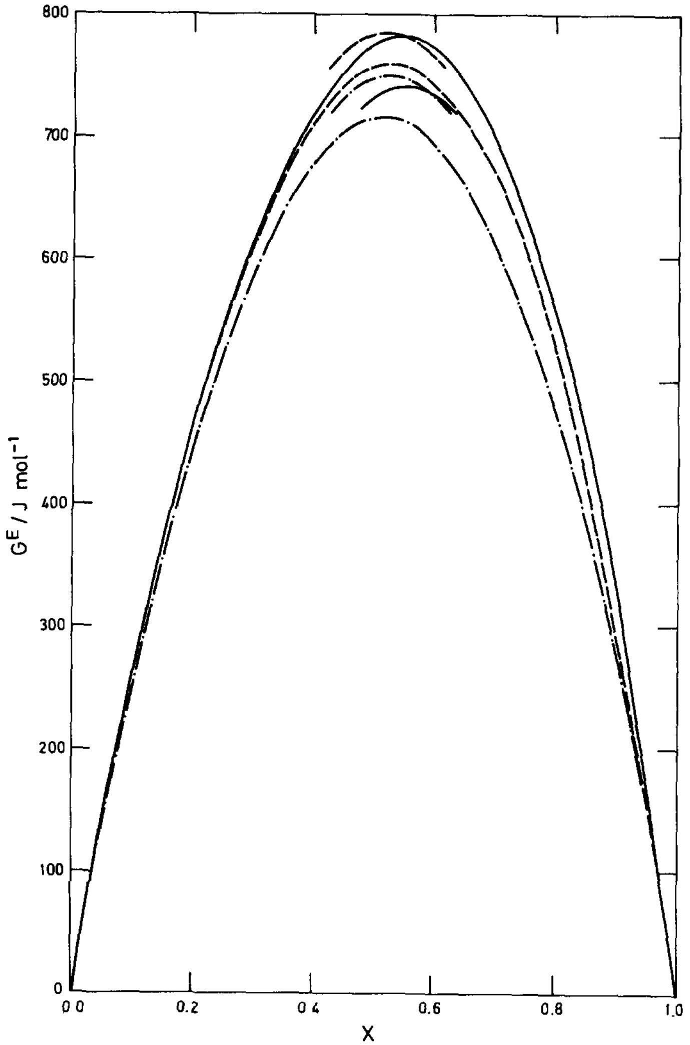

Fig. 2. Molar excess Gibbs energy for $\{x\ CH_4O+(1-x)\ C_7H_{14}O\}$ systems at 323.15 K. (————), Methanol + 4-heptanone system; (- - - - - -), 3-heptanone system; (– · – · –), 2-heptanone system. The curve tops of the same magnitude and systems at 298.15 K are also plotted.

4-heptanone is the one which presents a higher asymmetry, both at 298.15 and 323.15 K. This may indicate that the association equilibria in the methanol + 4-heptanone system are of different strength than in the other systems.

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