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NEW DOUBLE CIRCULATION APPARATUS FOR VLE DETERMINATION: ESTABLISHMENT AND APPLICATIONS IN THE DETERMINATION OF ISOBARS, ISOTHERMS, AND ISOPLETHES *

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ABSTRACT

A new double circulation VLE still and ebulliometer were established with the emphasis on improvements in the temperature stability, composition reliability, and rate of equilibration. Special techniques were employed to adjust the effective length of the Cottrell tube. Isobaric data for the system methanol–methyl methacrylate, and isothermal and isoplethic VLE data for the system ethanol–*n*-hexane were determined. Isothermal VLE, excess free enthalpy, and differential heat of vaporization were calculated from the isoplethic results.

INTRODUCTION

In the determination of vapor–liquid equilibrium (VLE), isothermal data and isoplethic data (data under constant liquid composition) are obtained mainly by the static method. Isothermal and isoplethic determinations by the double circulation method seem to be relatively rare [1–3]. Requiring no special equipment for determinations at high temperature and no complex degassing procedure, the double circulation method is comparatively more convenient than the static method.

In double circulation determinations the true equilibrium temperature (T_e) is measured indirectly from the temperature in the thermometer well (T_w) and can only be adjusted by varying the system pressure (P_e). Because of the recirculation, there is an inherent time lag of T_w to P_e and the fluctuation of T_e. As an open system, the liquid composition will not be constant if the measurement is not sufficiently rapid. Therefore the effectiveness of isothermal or isoplethic determinations relies strongly on the temperature stability and the rate of equilibration of the double circulation apparatus. Furthermore, a precise double circulation apparatus must be of

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high composition reliability, i.e. the composition in each receiver at equilibrium is stable and identical with the related equilibrium composition. One of the objectives of this investigation is to establish a VLE still which can be applied conveniently under both isobaric and isothermal conditions, and an ebulliometer which is suitable for rapid isoplethic determinations.

Calculations of isothermal VLE and differential heat of vaporization from isoplethic data are straightforward and possess acceptable accuracy [4,5]. Detailed data of the phase behaviour can be obtained by isoplethic determinations in a certain temperature range.

THE SG-I VLE APPARATUS

The VLE still and ebulliometer designed in this work were both termed the SG-I VLE apparatus. Their structures were shown in Fig. 1. Both were made of glass. The relationship between the features and the structures of the presented VLE apparatus is discussed in the following passages.

Temperature stability

For a double circulation apparatus having high temperature stability, the temperature in the thermometer well (T_w) must be stable and identical with the true equilibrium temperature. These usually require two conditions: (a) T_w is not influenced by the surroundings. This is ensured in the SG-I VLE apparatus by a dual vapour jacket outside the thermometer well which can perform effective thermal insulation. (b) The composition in the ebullator must be stable. It is considered that fluctuation of T_w is mainly caused by the fluctuation of the composition in the ebullator, which frequently arises from the fluctuation of liquid levels in the two reflux tubes of the mixer, and the reflux liquid levels will fluctuate in bumping occurs in the ebullator. Secondary vaporization of the condensed vapour occurs when the temperature at the joint point of vapour and liquid reflux is higher than the boiling point of the vapour condensate. In the SG-I VLE apparatus, a side-tube is added to the ebullator which can be heated to generate vaporization centres to promise stable ebullition in the ebullator. If necessary, liquid in the two reflux tubes can be cooled before being mixed, and thus secondary vaporization of the vapour condensate will be eliminated.

Composition reliability

The difference between the composition in each receiver at equilibrium and the related equilibrium composition is frequently caused by the partial condensation of vapour in the equilibrium chamber. The SG-I VLE apparatus possesses high composition reliability due to the fact that partial con-

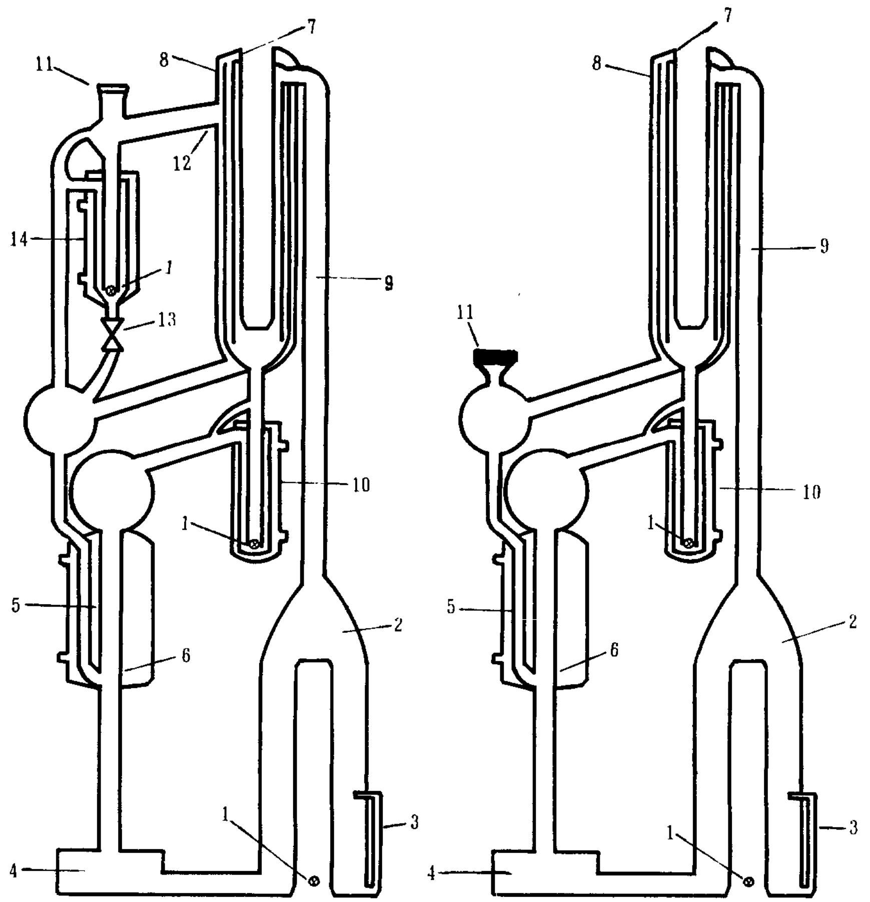

Fig. 1. The SG-I VLE still and ebulliometer. 1, Withdrawal port; 2, ebullator; 3, side tube; 4, magnetic stirrer functioning as a centrifugal pump; 5, mixer with cooler; 6, joint point of vapour and liquid reflux; 7, thermometer well; 8, equilibrium chamber; 9, Cottrell tube; 10, liquid receiver; 11, to manostat via cooler; 12, vapour outlet; 13, valve; 14, vapour receiver.

densation in the outer jacket of the equilibrium chamber does not change the composition in the liquid receiver, and that the composition in the vapour receiver will also be unaffected if the condensation occurs under the vapour outlet.

Rate of equilibration

The rate of equilibration is related to heating power. As far as the structure of the apparatus is concerned, it is mainly decided by three factors.

(a) The quantity of vapour hold-up in the reflux tubes and in the vapour receiver. The volume of the vapour receiver of the SG-I VLE still is approximately 2.5 ml, which is sufficient for composition analysis by density, reflective index, gas chromatography, or some methods of chemical analysis. Excluding the vapour receiver, the SG-I ebulliometer has a negligible amount of vapour hold-up when the liquid level in the mixer is lowered to the joint point by using the magnetic stirrer (which functions as a centrifugal pump).

(b) The thermal lag of the equilibrium chamber. The equilibrium chamber of the SG-I apparatus has a small radius of 17.5 mm with a thermometer well which is 9 mm in diameter. The dual vapour jacket provides a large surface for contact between the equilibrium chamber and the vapour which is at the equilibrium temperature, and therefore the thermal lag is considerably decreased.

(c) The dynamic characteristics of the composition circulation in the apparatus. It is considered that equilibration of the whole apparatus is dominated by the composition circulation. In the SG-I VLE apparatus a valve is added under the vapour receiver, the moderate opening of which can ensure a non-overcorrection composition equilibration process for effectively accelerating the equilibration in the whole apparatus.

Adjustment of the effective length of the Cottrell tube

While eliminating over-heating of the vapour–liquid mixture, the application of the Cottrell tube requires extra vaporization in the ebullator and thus may cause problems to stable ebullition. In determinations under elevated pressure, the vapour–liquid mixture may be unable to spurt through the Cottrell tube into the equilibrium chamber. As a result it is, in practice, valuable for the VLE apparatus to have different effective lengths of the Cottrell tube for various systems under various conditions. In the SG-I VLE apparatus the effective length of the Cottrell tube can be adjusted by heating outside the Cottrell tube (below the liquid level in it), together with the use of a magnetic stirrer to raise the liquid level in the Cottrell tube. The higher the power of the magnetic stirrer, the higher the liquid level in the Cottrell tube, and the shorter the effective length of the Cottrell tube. This is particularly convenient in various types of determination.

DIRECT DETERMINATIONS OF ISOBARS, ISOTHERMS, AND ISOPLETHES

Reagent purification

Ethanol, methanol, and *n*-hexane of G.R. grade were subjected to fractional distillation; C.P. methyl methacrylate (MMA) was distilled under a pressure of less than 13 kPa. Gas chromatographic analysis did not detect any appreciable impurities in the purified chemicals. Table 1 shows the densities and the refractive indices of the compounds, together with their literature values [6].

TABLE 1

Densities and refractive indices of compounds at 293.15 K

	Density (g ml^{-1})		Refractive index	
	This work	Ref. 6	This work	Ref. 6
Methanol	0.7912	0.7914	1.3287	1.3288
Ethanol	0.7897	0.7893	1.3611	1.3611
n-Hexane	0.6595	0.6606	1.3750	1.37506
Methyl methacrylate	0.9433	0.9440	1.4144	1.4142

Measurement and control of temperature and pressure

A microcomputer-aided real-time control system for temperature and pressure (which will be presented in detail elsewhere) was employed. The system was designed to perform on-line measurement and real-time control of temperature and pressure by adjusting the pressure in the double circulation apparatus. The measuring and controlling accuracy was 0.01 K for temperature and 0.1% for pressure.

Composition analysis

An Anton Paar DMA-45 digital densimeter was employed for composition analysis. Densities (in g ml^{-1}) at 293.15 K were measured for the systems, and correlated to the composition (in mole fraction). The correlated equations and the accuracies for the correlations are

methanol(1)–MMA(2)

$$D_4^{20} = -0.162912X_1^5 + 0.294257X_1^4 - 0.260938X_1^3 + 0.0424854X_1^2 - 0.0654298X_1 + 0.9438 \quad (1)$$

$$DX_{\mathrm{ave}} = 0.0004$$

$$DX_{\mathrm{max}} = 0.0015$$

ethanol(1)-n-hexane(2)

$$D_4^{20} = 0.0341109X_1^5 + 0.00496871X_1^4 - 0.0258255X_1^3 + 0.0753070X_1^2 + 0.0419717X_1 + 0.6592 \quad (2)$$

$$DX_{\mathrm{ave}} = 0.0006$$

$$DX_{\mathrm{max}} = 0.0020$$

For the system ethanol–*n*-hexane, the density is not sensitive to composition when the mole fraction of ethanol is between 0 and 0.1. In this region the composition is analyzed by gas chromatography with an accuracy of 1.5%.

Determinations of isobaric VLE

Employing the SG-I VLE still, isobaric data were determined for the system methanol–MMA at 13.33 and 26.66 kPa. The experimental results are compared with the literature data [7] at 26.66 kPa in Fig. 2.

In sub-atmospheric determinations, withdrawal of samples is often difficult especially when the pressure is very low. In this work the problem was solved by interrupting the circulation in the still by quickly increasing the system pressure to atmospheric before sampling. Because of the side-tube

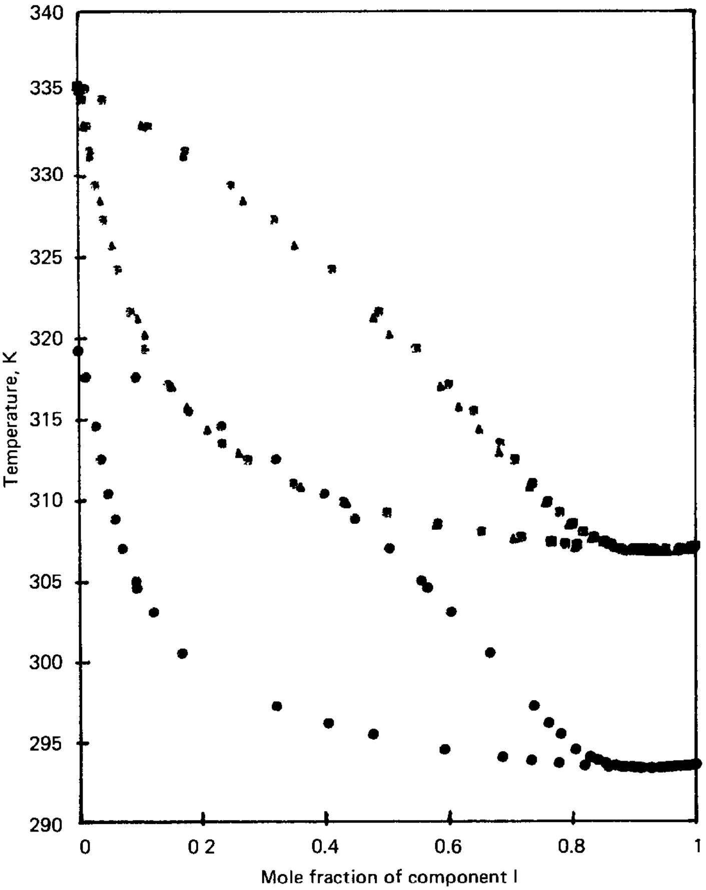

Fig. 2. Vapour–liquid equilibria for the system methanol(1)–methyl methacrylate(2) at 13.33 and 26.66 kPa. ●, Data at 13.33 kPa, this work; ▲, data at 26.66 kPa [7]; ■, data at 26.66 kPa, this work.

beside the ebullator, stable ebullition could be regained after the system pressure was restored to determine the next data point.

Determinations of isothermal VLE

Using the SG-I VLE still, direct isothermal determinations were performed at 323.15 and 328.15 K for the system ethanol–*n*-hexane. The Wilson equation was used for correlations. The vapour fugacity was calculated by the virial equation in which the second virial coefficient was obtained by the method of Tsonopoulos[8]. The results are shown in Figs. 3 and 4 and are compared with literature results [9] at 328.15 K.

Over the full composition range of the determinations, the SG-I still showed a temperature fluctuation of less than 0.01 K. The time for the

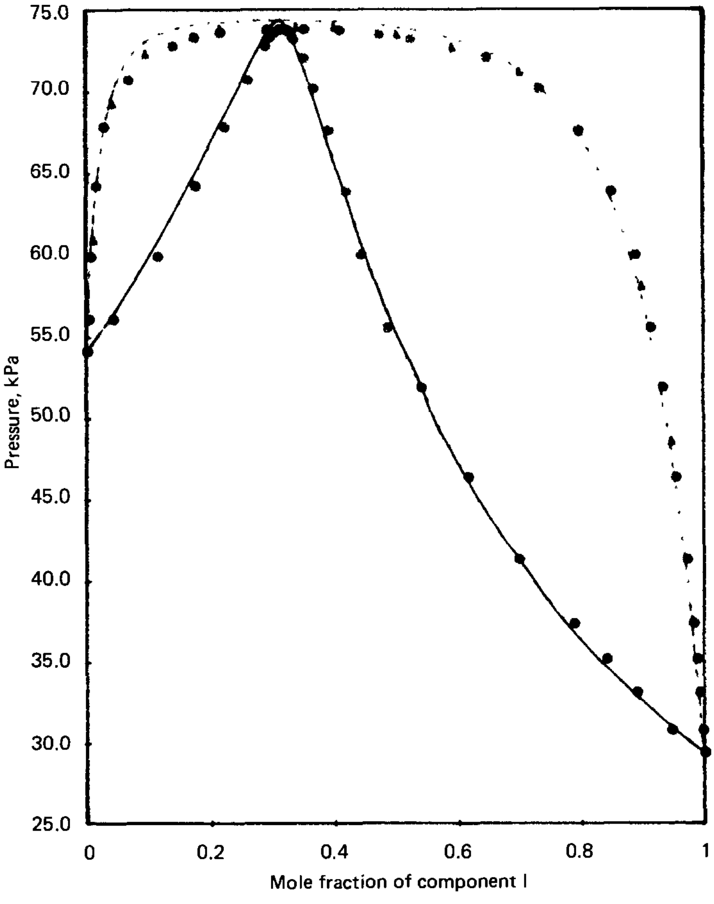

Fig. 3. Vapour–liquid equilibria for the system ethanol(1)–*n*-hexane at 323.15 K. ———, Wilson equation; ●, direct isothermal results from this work; ▲, vapour pressure from isoplethic results.

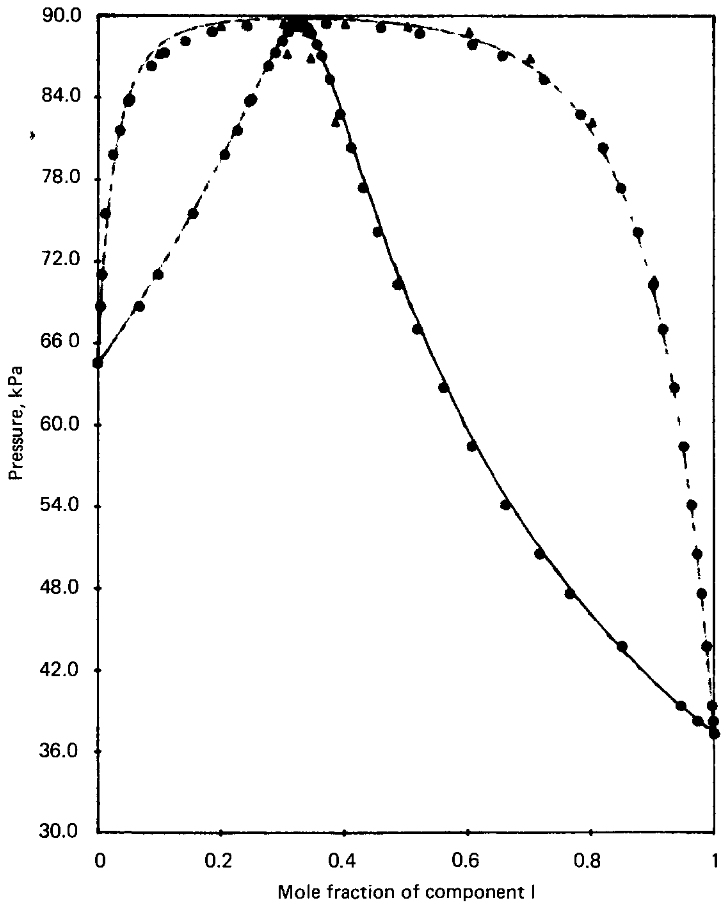

Fig. 4. Vapour–liquid equilibria for the system ethanol(1)–*n*-hexane(2) at 328.15 K. ———, Wilson equation; ●, direct isothermal results from this work; ▲, results from ref. 9.

determination of each point was about 5 min. The thermodynamic consistency test by the area method showed a variation of less than 1.0% for each set of data in this work, which verified the composition reliability of the new apparatus.

Determinations of isoplethic VLE

By using the SG-I ebulliometer, isoplethic VLE data for the system ethanol–*n*-hexane were determined at 15 different compositions in the temperature range from 298 to 331 K. In the determinations some measurements were taken to stablize the liquid composition.

(a) Cryogenic alcohol at −30 °C (at least 50 °C below the equilibrium temperature in the apparatus) was used as a cooling substance in the cooler through which the ebulliometer was connected to a manostat.

(b) The determination was arranged from low pressure to high pressure to prevent the escape of vapour by vacuating.

(c) The power used heating the ebulliometer was carefully adjusted to ensure a stable and small amount of vapour reflux (approximately 10 drops per minute).

In the determinations, the liquid composition may change due to the escape of vapour or changes in the vapour hold-up. The stability of the liquid composition and the influence of change in the liquid composition at the equilibrium temperature were tested at 298 K under the aforesaid conditions. In two hours, which is sufficient for determinations of isoplethic data at one concentration, the shift of equilibrium temperature was found to be 0.04 K for mole fractions of ethanol of 0.02–0.98, and 0.08 K in the two dilute regions. At the beginning and at the end of each determination the liquid densities were measured; the change was less than 0.0003 g ml^{-1}, which is in the range of the accuracy of sampling and measurement.

The isoplethic results were correlated by the Antoine equation

$$\ln P = A - \frac{B}{T+C} \tag{3}$$

where P is in kPa and T in K. The Antoine constants and the absolute mean deviations for pressure are listed in Table 2.

TABLE 2

Antoine constants for the system ethanol(1)–n-hexane(2) in the temperature range from 298 to 331 K

No.	X_1	A	B	C	D_p (%)
1	0.0000	13.8260	2695.38	−49.10	0.05
2	0.0101	12.1275	1861.16	−91.06	0.15
3	0.0407	13.4138	2281.77	−74.52	0.08
4	0.0947	14.8687	2941.70	−45.35	0.05
5	0.2144	15.9175	3484.42	−23.21	0.04
6	0.3379	15.9797	3496.14	−23.76	0.04
7	0.3986	15.9353	3471.61	−24.74	0.05
8	0.5006	16.1297	3582.15	−20.45	0.07
9	0.5898	16.2933	3689.96	−15.87	0.05
10	0.6986	15.9677	3505.57	−23.63	0.04
11	0.7978	16.0951	3596.66	−20.51	0.09
12	0.8970	16.7296	3987.54	−08.42	0.08
13	0.9452	16.1637	3646.33	−26.30	0.13
14	0.9796	17.3801	4236.64	−15.21	0.15
15	1.0000	17.6122	4199.39	−28.06	0.07

[a] D_p is the absolute mean deviation of pressure.

APPLICATIONS OF THE ISOPLETHIC DATA

Calculation of isothermal VLE and excess free enthalpy

In the temperature range of the isoplethic determinations, vapour pressure can be calculated from the corresponding Antoine equations. Isothermal VLE, excess free enthalpy, and the vapour compressibility factor (Z^v) can be obtained from correlations of the vapour pressure data employing the Barker's method with the Wilson equation as a model of excess free enthalpy.

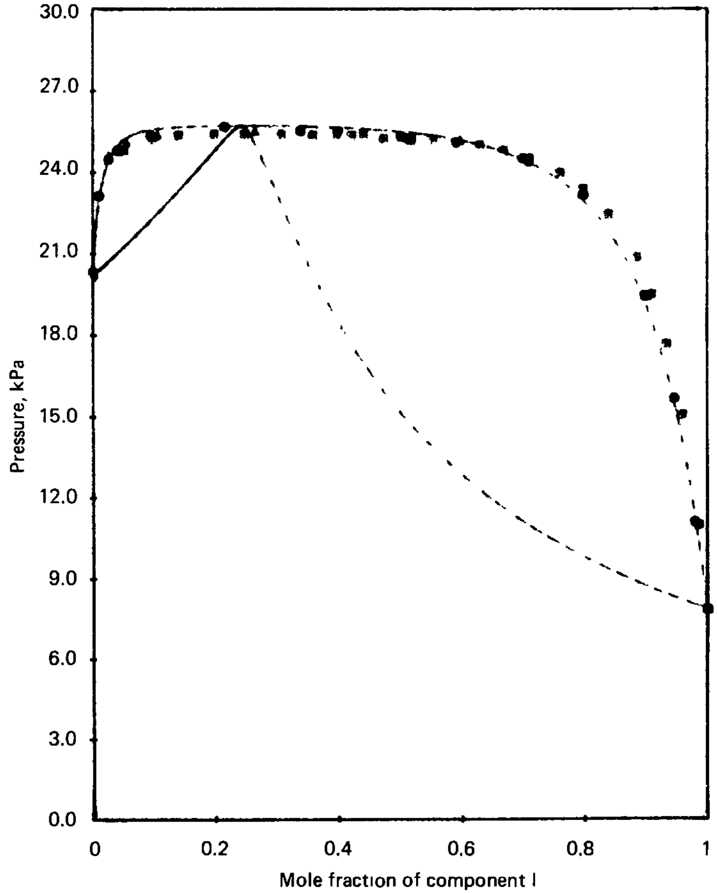

Fig. 5. Vapour–liquid equilibria for the system ethanol(1)–*n*-hexane(2) at 298.15 K. ———, Barker's method; ●, vapour pressure from isoplethic results; ■, vapour pressure by the static method [12]; ▲, vapour pressure by the static method [13].

TABLE 3

Isothermal VLE and excess free enthalpy for the system ethanol(1)–*n*-hexane(2)

X_1	298.15 K						328.15 K					
	Isoplethic results of this work			Ref. 12			Isoplethic results, this work			Isothermal results, this work		
	P(kPa)	Y_1	G^E(kJ)	P(kPa)	Y_1	G^E(kJ)	P(kPa)	Y_1	G^E(kJ)	P(kPa)	Y_1	G^E(kJ)
0.1	25.56	0.232	0.667	25.17	0.226	0.627	87.66	0.291	0.668	87.77	0.292	0.669
0.2	25.68	0.240	1.044	25.36	0.242	1.002	89.32	0.314	1.072	89.47	0.316	1.075
0.3	25.68	0.245	1.267	25.36	0.258	1.238	89.61	0.324	1.317	89.76	0.325	1.321
0.4	25.62	0.249	1.376	25.34	0.259	1.364	89.54	0.331	1.440	89.70	0.332	1.446
0.5	25.47	0.254	1.388	25.25	0.262	1.391	89.14	0.339	1.457	89.32	0.340	1.464
0.6	25.14	0.262	1.308	25.04	0.268	1.323	88.17	0.351	1.376	88.39	0.352	1.384
0.7	24.44	0.277	1.137	24.54	0.278	1.161	86.01	0.370	1.198	86.30	0.370	1.206
0.8	22.89	0.306	0.872	23.28	0.301	0.899	81.16	0.407	0.918	81.58	0.406	0.926
0.9	19.09	0.384	0.500	19.87	0.368	0.522	69.52	0.500	0.526	70.05	0.497	0.531

Calculation of differential heat of vaporization

The differential heat of vaporization can be calculated from P–T relationships [10] or the Antoine constants in the temperature range of the isoplethic determinations

$$L_v = (Z^v - Z^l)R\left[\frac{\partial(\ln P)}{\partial(1/T)}\right]_x \tag{4}$$

$$L_v = -(Z^v - Z^l)RT^2\frac{B}{(T+C)^2} \tag{5}$$

where the liquid compressibility factor (Z^l) can be calculated by the assumption of ideal mixing from the liquid molar volume data of pure substances, which is available for ethanol and *n*-hexane in the literature [11].

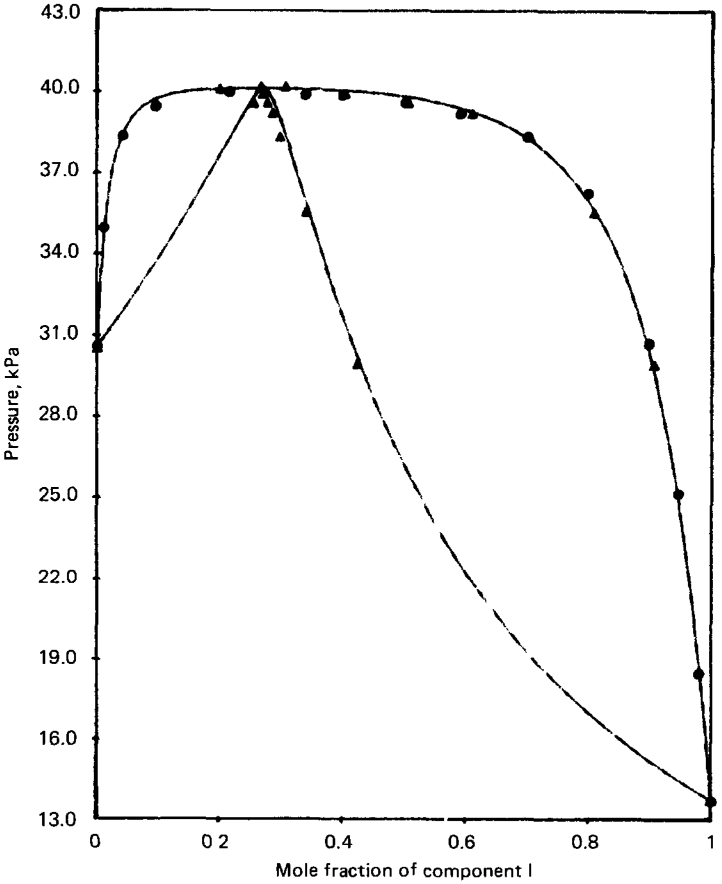

Fig. 6. Vapour–liquid equilibria for the system ethanol(1)–*n*-hexane(2) at 308.15 K. ———, Barker's method; ●, vapour pressure from isoplethic results; ▲, literature results [9].

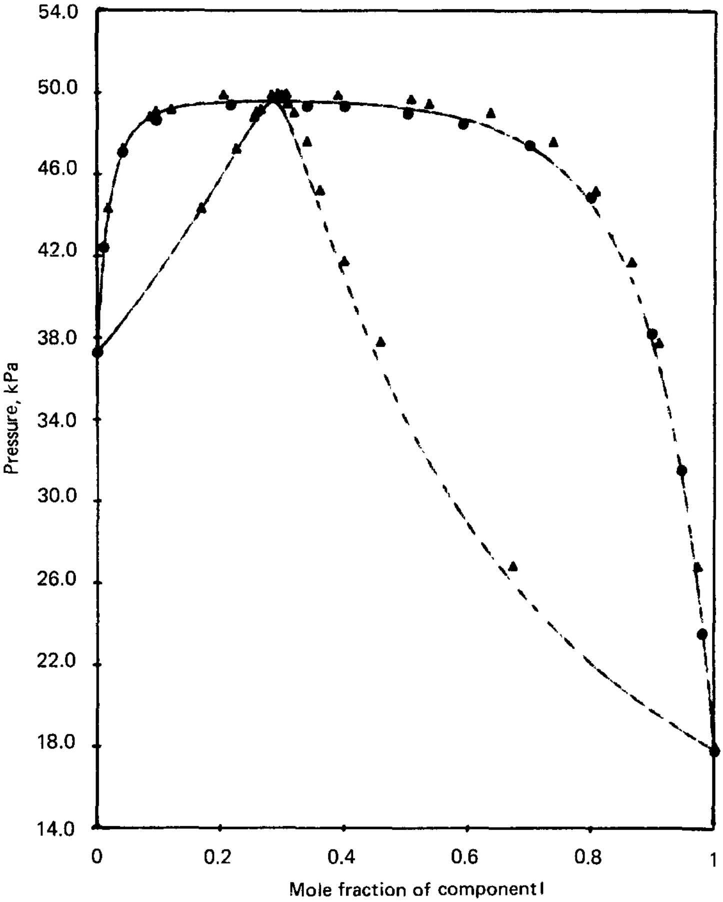

Fig. 7. Vapour–liquid equilibria for the system ethanol(1)–*n*-hexane(2) at 313.15 K. ———, Barker's method; ▲, vapour pressure from isoplethic results; ▲, direct isothermal results from the literature [11].

Calculated results

For the ethanol–*n*-hexane system concerned in this investigation, the temperature for the calculations was selected in the 298.15–328.15 K range. Vapour pressure data are shown in Figs. 4–8. Calculated isothermal VLE are shown in Figs. 6–8 and are listed in Table 3. Excess free enthalpy figures are also listed in Table 3. Results from the literature [9,12–14] or from direct isothermal determinations in this work were presented together. Good agreement was observed between the data from isothermal determinations and those from isoplethic determinations. Comparisons with the literature data were satisfactory. Data for the differential heat of vaporization are presented in Table 4 together with vapour and liquid compressibility factors.

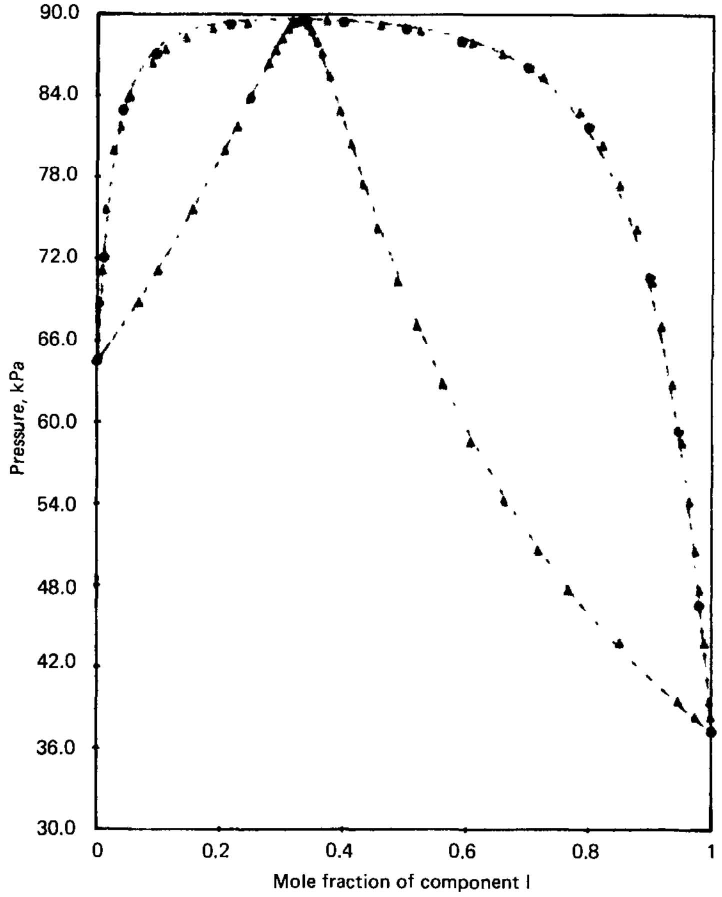

Fig. 8. Vapour–liquid equilibria for the system ethanol(1)–*n*-hexane(2) at 328.15 K. ———, Barker's method; ●, vapour pressure from isoplethic results; ▲, direct isothermal results from this work.

TABLE 4

Differential heat of vaporization for the system ethanol(1)–*n*-hexane(2)

No.	X_1	298.15 K			328.15 K		
		$Z^{v\ a}$	$Z^{l\ b}$	L_v ^{c} (kJ)	$Z^{v\ a}$	$Z^{l\ b}$	L_v ^{c} (kJ)
1	0.0000	0.960	0.001	−30.80	0.929	0.003	−28.70
2	0.0101	0.952	0.001	−30.50	0.916	0.004	−27.03
3	0.0407	0.947	0.001	−31.90	0.900	0.004	−28.45
4	0.0947	0.945	0.001	−32.11	0.893	0.004	−29.27
5	0.2144	0.945	0.001	−32.16	0.890	0.004	−29.72
6	0.3379	0.945	0.001	−32.40	0.889	0.004	−29.90
7	0.3986	0.945	0.001	−32.40	0.889	0.004	−29.88
8	0.5006	0.945	0.001	−32.41	0.890	0.003	−30.04
9	0.5898	0.946	0.001	−32.34	0.890	0.003	−30.05
10	0.6986	0.947	0.001	−32.52	0.893	0.003	−30.12
11	0.7978	0.950	0.001	−32.73	0.898	0.002	−30.48
12	0.8970	0.957	0.000	−33.60	0.911	0.002	−31.74
13	0.9452	0.965	0.000	−35.19	0.926	0.001	−33.14
14	0.9796	0.977	0.000	−38.21	0.944	0.001	−36.52
15	1.0000	0.984	0.000	−41.86	0.959	0.001	−39.99

[a] Vapour compressibility factor.
[b] Liquid compressibility factor.
[c] Differential heat of vaporization.

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