ported in the present work were calculated to be as follows. The error in A_ϕ and A_γ varies from a minimum of ±0.10% at 25 °C and 1-atm pressure to a maximum of ±0.15% at 100 °C and 1000-atm pressure. The uncertainty in A_H ranges from ±3% at the minimum to a maximum of ±6.3%. The largest uncertainty is in A_J and ranges from about ±3% when component errors cancel each other to ±13.3% when the errors are additive. The uncertainty in A_V ranges from ±0.25% to ±0.5%. The uncertainty ranges for A_E and A_K are respectively 0.8–1.0% and 1.0–1.7%. In view of these uncertainties it is recommended that A_ϕ and A_V may be rounded off to four significant figures and the rest of the parameters to three significant figures for most practical work.

Registry No. Water, 7732-18-5.

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Isobaric Vapor–Liquid Equilibria of the 6-Methyl-5-hepten-2-one/Ethyl 3-Oxobutanoate and Methanol/1,6-Hexanediol Systems

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Isobaric vapor–liquid equilibria have been measured at 2.7 kPa for the 6-methyl-5-hepten-2-one/ethyl 3-oxobutanoate system and at 100.0 kPa for the methanol/1,6-hexanediol system. The experimental data have been obtained by using a new equilibrium still based on the flow method principle. Its main features, with respect to similar stills, are represented by the replacement of the Cottrell pump with a feed system that allows an independent control of overheating and of the liquid flow rate toward the equilibrium cell. The performance of the experimental apparatus has been checked by determining two literature systems.

It is generally agreed that equilibrium stills based on flow methods are the most valuable tools available at present for vapor–liquid determinations (*1*). Fast reaching of equilibrium conditions, precise temperature determinations, and applicability to partially miscible systems are the main advantages offered by this type of instrument. If one puts aside Cathala's dynamic ebulliometer because of several difficulties in its operation, the above-mentioned goals are perhaps realized in the most effective and simple way in an apparatus described by Vilim et al. (*2*). Such an apparatus is based on the assumption that equilibrium can be reached immediately, provided that the contact surface between the liquid and gas phases is large and the system is thermally insulated. These conditions are realized by means of an accurate control of overheating and of both the amount and the liquid/vapor ratio of the mixture fed to the equilibrium cell. Such a control can in turn be obtained by feeding the liquid phase to the Cottrell pump by means of hydraulic fall from a closed vessel through a float valve. In this way the amount of mixture fed to the equilibrium cell can be precisely replaced and the liquid level in the Cottrell pump kept constant. Fast attainment of equilibrium conditions is made possible through an adequate sizing of the equilibrium cell.

Despite the very good results obtained with this apparatus, the drawbacks caused by the Cottrell pump as a feeding element have not been eliminated, since the feed flow rate is always related to the overheating. Consequently, a separate

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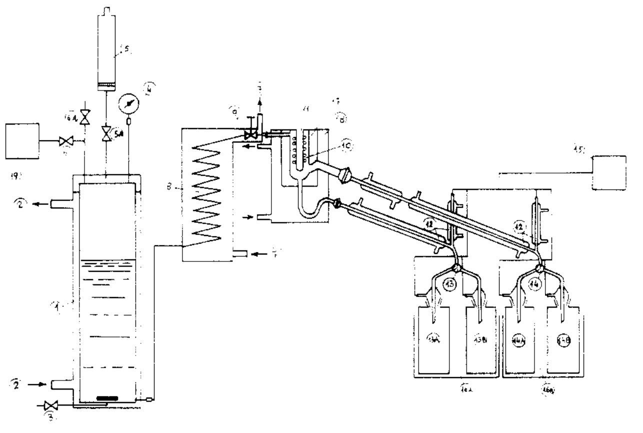

Figure 1. Described apparatus: (1) receiver for the pressurized liquid with thermostating jacket, (2, 7) thermostated lines, (3, 5A, 6, 6A, 9) valves, (4) manometer, (5) charge vessel, (8) overheating coil, (10) equilibrium cell, (11) thermowell, (12) vapor and liquid coolers, (13, 14) three-way cocks, (13A, 13B) liquid-phase samplers, (14A, 14B) vapor-phase samplers, (15) pressure regulator and indicator, (16A, 16B) cooling baths, (17) insulating jacket under high vacuum, (18) thermostated jacket, (19) helium cylinder.

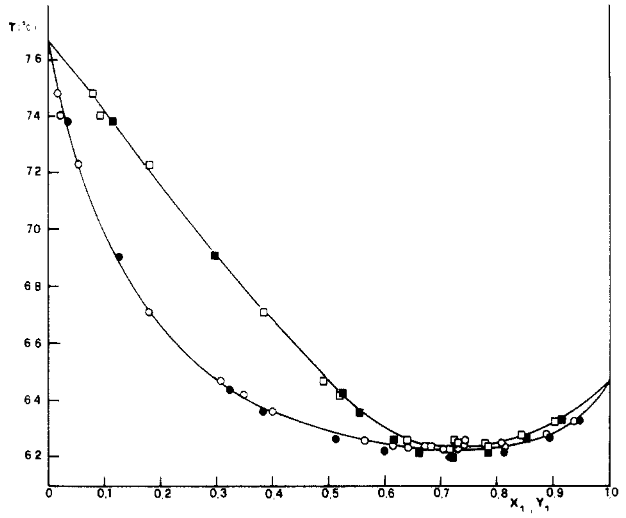

Figure 2. Methanol/ethyl acetate system at 101.3 kPa: mole fraction in the vapor phase, (□) literature data and (■) this work; mole fraction in the liquid phase, (○) literature data and (●) this work; (—) interpolating line.

control of the two variables is not allowed. Optimum conditions in terms of flow rate and amount of heat furnished to the liquid can only be reached by a trial-and-error procedure which results in lengthy experimentation and decreased accuracy. Furthermore, the Cottrell pump can hardly work satisfactorily under high-vacuum conditions or when mixtures of compounds having very different boiling points are processed. Finally, it should be noticed that small defects in the float valve can impair the correct performance of the whole apparatus.

It is the purpose of this work to show how the above-mentioned drawbacks can be eliminated by replacing the entire feed system of the Vilim apparatus with a new device (Figure 1). The liquid mixture is charged to a reservoir thermostated with a jacket and pressurized with an inert gas (e.g., helium). By careful opening of a valve equipped with an indicator, a fixed amount of the mixture is sent under pressure through a heating coil and then into the equilibrium cell. By means of this simple device the liquid flow rate can easily be modulated acting on two independent factors: the imposed inert gas pressure and the valve opening, both of which can be separately set at their optimum operating conditions. Furthermore, also the heating flow is split into two stages: a rough temperature regulation of all the mixture in the reservoir and a fine regulation of a small liquid amount in the heating coil submerged in a constant-temperature bath. The temperature gradient ΔT between the bath and the equilibrium cell is controlled as a function of the component boiling points and the charge composition. Typical values are within a range of about 10–30 °C. The ΔT value is not critical for a correct operation of the instrument and can be regulated, if necessary, on the basis of the collected amount of vapor.

The result of these double independent controls of the operating variables ensures an easy and quick optimization of the ratio of heat to liquid mixture flow rate and, ultimately, an almost instantaneous reaching of equilibrium conditions. Furthermore, temperature variations in the equilibrium cell are maintained within 0.1 °C.

The instrument thermal insulation has also been improved by surrounding the equilibrium cell with a double jacket; the first one is evacuated while a heating liquid, whose temperature is near the equilibrium value, is sent through the second one. By this modification it becomes possible to perform vapor–liquid equilibrium determinations also at very high temperatures (>200 °C). Condensation on the cell walls has also been reduced. Minor modifications concerning the condensing system prevent the loss of very volatile compounds.

Apparatus Operation

A correct apparatus operation is ensured by carefully observing the following points (see Figure 1):

(A) With valves 3, 9, and 6 closed, the previously and thoroughly homogenized mixture is charged through valve 5A, while valve 6A is open for venting.

(B) Valves 5A and 6A are closed and cylinder 1, containing the mixture, is pressurized at a fixed value by means of the pressure regulator.

(C) The pressure regulator and measuring device 15 is actuated.

(D) With the preheater 8 at the required temperature, valve 9 is opened, care being taken to ensure the proper functioning of cell 10.

(E) As soon as the temperature in cell 10 has reached a constant value, the equilibrium phases are collected in samplers 13A and 14A by simultaneously opening stopcocks 13 and 14.

(F) Once the desired amounts of the liquid and vapor phases have been collected, the liquid and vapor streams are sent into vessels 13B and 14B, respectively.

(G) Valve 9 is then closed, the contents of 13A and 14A are taken and analyzed, and the residual mixture is discharged through valve 3 while the heater contents are eliminated through 9.

(H) A new equilibrium point can now be measured on a new charge by repeating the operation described above.

Results

The new equilibrium still can be applied to the determination of vapor–liquid equilibria in a wide range of temperature from subatmospheric pressure up to 101.3 kPa. Its ability to furnish meaningful results under different pressure conditions has been tested by studying the following systems: (a) methanol/ethyl acetate, 101.3 kPa; (b) 2-propanol/water, 25.3 kPa; (c) 6-methyl-5-hepten-2-one/ethyl 3-oxobutanoate, 2.7 kPa; (d) methanol/1,6-hexanediol, 100.0 kPa.

The last two systems have not been previously investigated, while the first two are known from the literature (*3*,*4*). Satisfactory agreement with respect to the previously published data has been found for the literature system (see Figures 2 and 3), whose thermodynamic consistency has already been verified by Hala et al. (*1*). The new experimental data are reported in Tables I and II and plotted in Figures 4 and 7. The thermo-

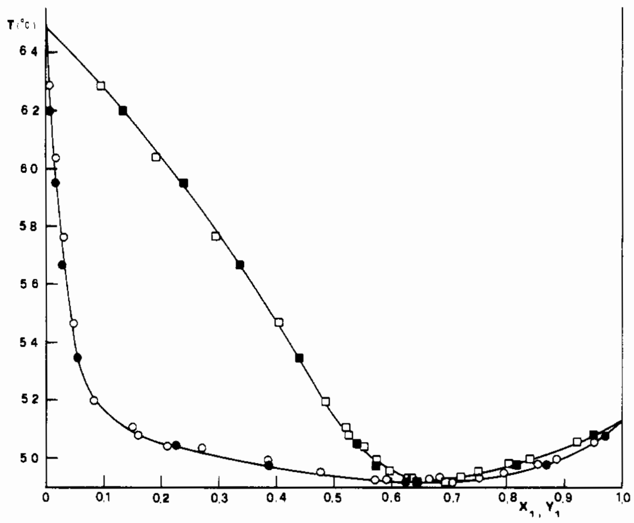

Figure 3. 2-Propanol/water system at 25.3 kPa: mole fraction in the vapor phase, (□) literature data and (■) this work; mole fraction in the liquid phase, (○) literature data and (●) this work; (—) interpolating line.

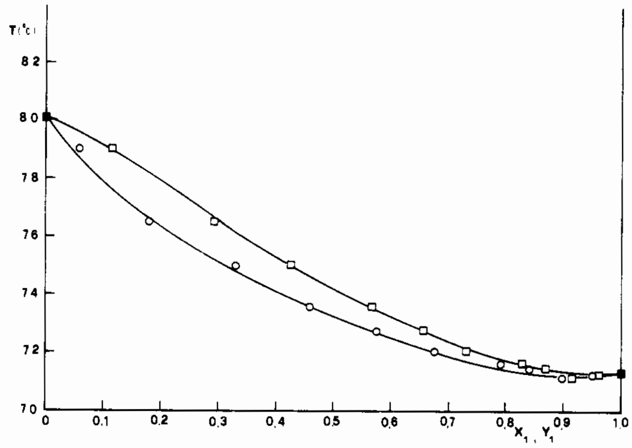

Figure 4. 6-Methyl-5-hepten-2-one/ethyl 3-oxobutanoate system at 2.7 kPa: (□) mole fraction in the vapor phase, (○) mole fraction in the liquid phase; (—) interpolating line.

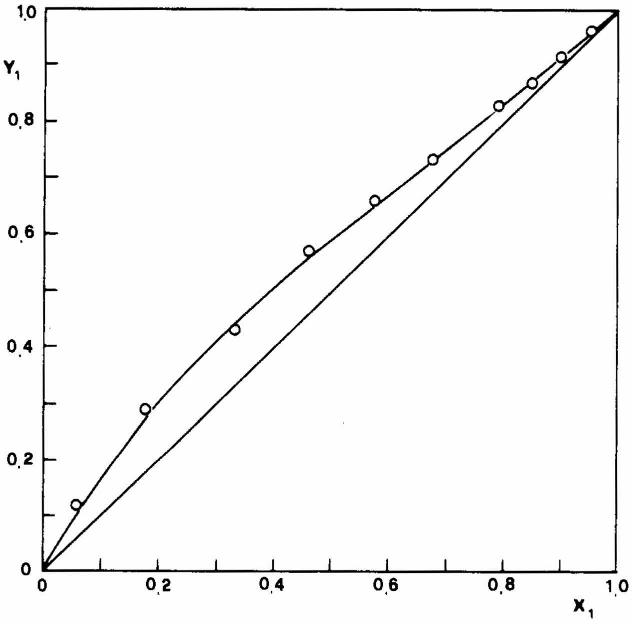

Figure 5. 6-Methyl-5-hepten-2-one/ethyl 3-oxobutanoate system at 2.7 kPa, X–Y curves: (○) experimental data, (—) values obtained by means of the Redlich–Kister equation.

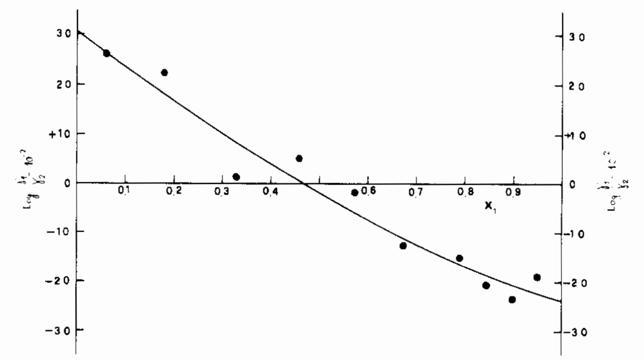

Figure 6. 6-Methyl-5-hepten-2-one/ethyl 3-oxobutanoate system at 2.7 kPa, thermodynamic consistency plot: (●) experimental data, (—) calculated line.

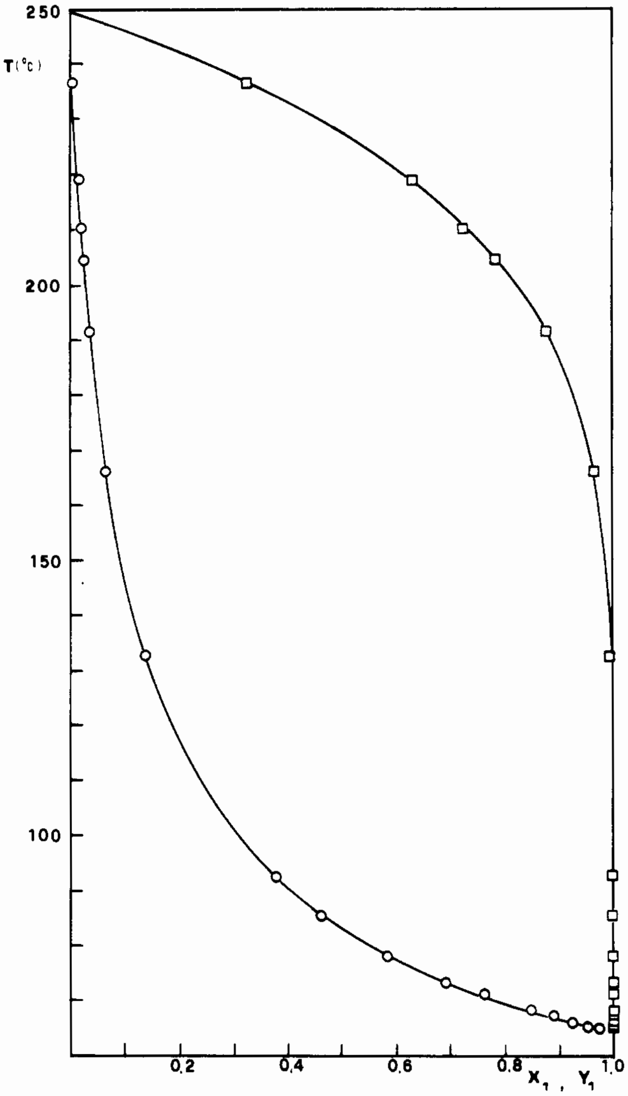

Figure 7. Methanol/1,6-hexanediol system at 100.0 kPa: (□) mole fraction in the vapor phase, (○) mole fraction in the liquid phase; (—) interpolating line.

dynamic consistency of the methylheptenone/ethyl 3-oxobutanoate system has been checked by applying both the Redlich–Kister method and the Redlich–Kister equation, as shown in Figures 5 and 6. This system has been studied at low pressure in order to avoid the partial decomposition of ethyl 3-oxobutanoate. The suitability of the new still for high-temperature studies has been tested through the methanol/1,6-hexanediol system at atmospheric pressure and in a temperature range of 65–236 °C, as shown in Table II. However, the

Table I. 6-Methyl-5-hepten-2-one (1)/Ethyl 3-Oxobutanoate (2) System at 2.7 kPa

X_1	Y_1	temp, °C	X_1	Y_1	temp, °C
1.0000	1.0000	71.5	0.5755	0.6550	72.8
0.9500	0.9585	71.3	0.4610	0.5660	73.6
0.8990	0.9130	71.2	0.3325	0.4255	75.0
0.8435	0.8670	71.5	0.1820	0.2890	76.5
0.7910	0.8265	71.7	0.0620	0.1155	79.0
0.6760	0.7293	72.1	0.0000	0.0000	80.2

Table II. Methanol (1)/1,6-Hexanediol (2) System at 100.0 kPa

X_1	Y_1	temp, °C	X_1	Y_1	temp, °C
1.0000	1.0000	64.3	0.3800	0.9996	92.7
0.9715	1.0000	64.9	0.1370	0.9935	132.5
0.9555	0.9999	65.1	0.0665	0.9640	166.3
0.9260	0.9999	66.1	0.0390	0.8775	191.5
0.8925	0.9999	67.3	0.0275	0.7860	204.5
0.7670	0.9999	71.0	0.0230	0.7240	210.2
0.6915	0.9999	73.4	0.0170	0.6335	218.8
0.5860	0.9999	78.2	0.0060	0.3255	236.5
0.4655	0.9998	85.5	0.0000	0.0000	248.5

Redlich and Kister equation cannot be applied to these data, due to the large temperature difference between the two farthest experimental points. An analogous check with the isobaric Gibbs–Duhem equation is also impossible since the enthalpic data for 1,6-hexanediol are not reported in the literature. The obtained results, however, appear to be coherent on the basis of their graphical representation (Figure 7). All the products used in this work were of 99+ mol% purity.

Concluding Remarks

A flow apparatus represents the most versatile approach presently available for the vapor–liquid determinations at low pressure. The favorable features of flow systems in terms of fast equilibrium attainment and accurate results can be fully exploited by replacing the Cottrell pump with the device proposed in the paper.

The following main advantages of the new apparatus can be stressed: simplified operations under vacuum and at moderate pressures; wide application field for both low- and high-boiling substances and their mixtures; temperature determinations of outstanding accuracy; reduced overheating time, which enables vapor–liquid determinations with temperature-sensitive compounds; applicability to systems showing miscibility gaps.

Finally, high-pressure work can be carried out with the proposed apparatus by simply replacing the glass parts with similar metallic ones, as is currently performed in our laboratories.

Registry No. 6-Methyl-5-hepten-2-one, 110-93-0; ethyl 3-oxobutanoic acid, 141-97-9; methanol, 67-56-1; 1,6-hexanediol, 629-11-8.

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Vapor–Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 5. Binary Mixtures of 1,3-Dioxolane with Cyclohexanone and Cyclohexanol

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This paper presents vapor–liquid equilibrium (VLE) data at 300, 500, and 740 mmHg for the binary systems of 1,3-dioxolane (1)–cyclohexanone and –cyclohexanol. The activity coefficients in the liquid phase are correlated from experimental *t*,*x* data by using the Redlich–Kister equation with temperature-dependent parameters. Both systems show deviation from ideality with activity coefficients up to 2.5.

Introduction

As a continuation of earlier works (*1–5*) on isobaric VLE data of binary mixtures containing 1,3-dioxolane (1,3-$C_3H_6O_2$) as a common component, new data for the two systems containing cyclohexanone ($C_6H_{10}O$) and cyclohexanol ($C_6H_{12}O$) as noncommon components are reported.

Measurements are taken in order to detect the effect of a six-membered cyclic ketone and alcohol on a five-membered cyclic ether.

Materials Used

The source and the treatment of 1,3-dioxolane have been given previously (*1*). Cyclohexanone and cyclohexanol (from Carlo Erba, Milan; purity > 99 wt %) were used without further purification. Major impurities were water (0.1 wt %) and cyclohexanol (0.5 wt %) in cyclohexanone and water (0.2 wt %) in cyclohexanol.

Experimental Section

The experimental apparatus was the same as that previously employed (*1–5*). The pressures were measured with an ac-