Isobaric vapour–liquid equilibria for binary systems of 2-butanone with ethanol, 1-propanol, and 2-propanol at 20 and 101.3 kPa

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ABSTRACT

Consistent isobaric vapour–liquid equilibrium data have been measured for 2-butanone + ethanol, 2-butanone + 1-propanol, and 2-butanone + 2-propanol at 20 and 101.3 kPa. The binary systems 2-butanone + ethanol and 2-butanone + 2-propanol present a minimum boiling azeotrope at both pressures, and show that the azeotropic compositions is strongly dependent on pressure. The equilibrium data were correlated using the Wilson, NRTL, and UNIQUAC models for which the parameters are reported.

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1. Introduction

Traditionally, 2-butanone has been used as a solvent in paints and resin adhesives [1]. A mixture of different alcohols with this ketone that form azeotropes is a very common product. Therefore, the purification of the ketone and recovery of the alcohol for recycling are usually impracticable by distillation. The separation can be improved by adding an agent that alters the relative volatility of the components [2] (extractive distillation) or by making a simple change in pressure, provided that the azeotropic composition is sensitive to pressure [3] (pressure-swing distillation).

In the previous work VLE of the binary systems 2-butanone (1) + ethanol (2), 2-butanone (1) + 1-propanol (3), and 2-butanone (1) + 2-propanol (4) were studied at isobaric conditions. The present work was undertaken to measure the VLE data for the three systems mentioned at 20 and 101.3 kPa, with the purpose of studying the influence of the pressure on the composition of the azeotropic mixture, which is interesting in order to investigate the possibility of separation by pressure-swing distillation (PSD). This effect can be exploited to separate a binary mixture containing a minimum boiling azeotrope provided that the azeotropic mixture significantly changes composition over a moderate pressure range.

For the three binary systems, VLE data at 101.3 kPa can be found in the literature: 2-butanone + ethanol [4–6]; 2-butanone + 1-propanol [7]; 2-butanone + 2-propanol [8,9]. No isobaric VLE data at 20 kPa are available for these three binary systems.

The experimental VLE data of the binary systems investigated were found to be thermodynamically consistent. Data reduction was carried out using the Wilson, NRTL, and UNIQUAC equations to relate activity coefficients with compositions.

2. Experimental

2.1. Chemicals

2-Butanone ($\geq$99.7 mass%, *assay GC*) and 2-propanol (99.9 mass%, *assay GC*) were purchased from Aldrich Ltd., ethanol ($\geq$99.5 mass%, *analytical grade*) and 1-propanol ($\geq$99.9 mass%, *assay GC*) were purchased from Acros. The reagents were used without further purification after chromatography failed to show any significant impurities. The water content, determined using a Karl Fischer volumetric automatic titrator (Metrohm, 701 KF Titrino), was small in all chemicals (<0.05 mass%). Before measurements, the liquids were degassed and subsequently dried over molecular sieves (Aldrich, type 4 Å, 1.6 mm pellets). The refractive indexes of the pure components were measured at 298.15 K using an Anton Paar refractometer Abbemat-HP, and the densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to $\pm$0.01 K with a thermostated bath. The accuracy in refractive index, and density measurements are $\pm$0.00002 and $\pm$0.01 kg m^{-3}, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with

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Table 1
Density d, refractive index n_D, and normal boiling point T_b of pure components

Component	d (kg m^{-3}) (298.15 K)		n_D (298.15 K)		T_b (K)	
	Experimental	Literature[a]	Experimental	Literature[a]	Experimental	Literature[b]
2-Butanone (1)	799.62	800.02	1.37614	1.3764	352.68	352.79
Ethanol (2)	786.47	785.01	1.35939	1.3594	351.46	351.44
1-Propanol (3)	799.44	799.51	1.38305	1.3837	370.21	370.35
2-Propanol (4)	780.75	781.25	1.37497	1.3752	355.40	355.41

[a] Taken from TRC tables [10].
[b] Taken from Ref. [11].

those given in the literature. Appropriate precautions were taken when handling the reagents in order to avoid hydration.

2.2. Apparatus and procedure

The equilibrium vessel used in the measurements (Labodest VLE 602/D) was an all-glass dynamic-recirculating still equipped with a Cottrell circulation pump, manufactured by Fischer Labor und Verfahrenstechnik (Germany). The Cottrell pump ensures that both liquid and vapour phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Hart Scientific thermometer model 1502A and a Pt 100 probe Hart Scientific, model 5622 calibrated at the ENAC-accredited Spanish *Instituto Nacional de Técnica Aeroespacial*. The accuracy is estimated to be ±0.01 K. The temperature probe was checked against the ice and steam points of distilled water. A Fisher M101 pressure control system was used to measure and control the pressure and the heating power. The pressure accuracy is ±0.1 kPa. The manometer was calibrated using the vapour pressure of ultrapure water.

In each experiment, the pressure was fixed and the heating and stirring system of the liquid mixture was turned on. The still was operated at constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 30 min or longer. Then, samples of liquid and condensate were taken for analysis. The sampling was carried out with special syringes that allowed withdrawal of small volume samples.

2.3. Analysis

The composition of the sampled liquid and condensed vapour phase were determined using a CE Instruments GC 8000 Top gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m, 0.454 mm i.d., capillary column (DB-MTBE, J &

Table 2
Experimental vapour pressure (P_i^0) of 2-butanone

T (K)	P (kPa)
362.08	135.91
361.22	132.46
360.32	128.72
359.12	124.08
357.91	119.51
356.39	114.07
355.29	110.24
354.04	105.95
352.68	101.32
351.40	97.29
350.49	94.41
349.95	92.74
348.59	88.73
347.19	84.73
345.74	80.72
344.29	76.74
342.70	72.72
341.07	68.73
339.37	64.72
337.53	60.73
335.64	56.74
333.61	52.73
331.49	48.73
329.31	44.73
326.86	40.72
324.08	36.72
321.20	32.71
319.63	30.72
318.16	28.71
316.39	26.73
313.80	24.01
312.56	22.74
310.48	20.76
308.22	18.73

W Scientific). The GC response peaks were treated with Chrom-Card for Windows. Column, injector, and detector temperatures were 373, 473, and 498 K, respectively, for all systems. Very good peak separation was achieved under these conditions, and calibration

Table 3
Vapour pressure parameters

Compound	Equation[a]	A_i	B_i	C_i	D_i	E_i	Reference
2-Butanone (1)	(1)	14.1154	2803.41	−57.475			This work
	(2)	7.054	1226.52	214.050			b
	(3)	114.740	−7130.00	−15.1840	1.7234×10^{-2}	1	c
	(1)	14.133	2843.87	−53.875			d
Ethanol (2)	(3)	67.5672	−7164.30	−7.3270	3.1340×10^{-6}	2	c
1-Propanol (3)	(1)	16.0353	3415.56	−70.733			e
2-Propanol (4)	(1)	16.4089	3439.60	−63.417			e

[a] Vapour pressure equations: (1) $\ln P^0$ (kPa) $= A - B/[(T(\text{K})+C]$; (2) $\log P^0$ (mmHg) $= A - B/[(T(^\circ\text{C})+C]$; (3) $\ln P^0$ (Pa) $= A + B/T(\text{K}) + C\ln T(\text{K}) + D(T(\text{K}))^E$.
[b] Parameters taken from Dortmund Data Bank [13].
[c] Parameters taken from Ref. [11].
[d] Parameters taken from Ref. [14].
[e] Parameters taken from Ref. [12].