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Phase equilibria in the systems isobutyl alcohol + *N*,*N*-dimethylformamide, isobutyl acetate + *N*,*N*-dimethylformamide and isobutyl alcohol + isobutyl acetate + *N*,*N*-dimethylformamide at 101.3 kPa

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Abstract

Consistent vapor–liquid equilibria (VLE) were determined for the ternary system isobutyl alcohol (IBA) + isobutyl acetate (IBAc) + *N*,*N*-dimethylformamide (DMF) and two constituent binary systems at 101.3 kPa. The IBA + DMF system exhibits negative deviation from ideal behaviour and IBAc + DMF system deviates positively from ideal behaviour. The activity coefficients of the solutions were correlated with its composition by the Wilson, NRTL and UNIQUAC models. The ternary system is well predicted from binary interaction parameters.

Keywords: Vapor–liquid equilibria; Isobutyl alcohol; Isobutyl acetate; *N*,*N*-Dimethylformamide; Activity coefficient models

1. Introduction

The separation of alcohol–acetate mixtures can be carried out by extractive distillation, which requires the addition of a solvent (entrainer) that modifies the relative volatility of the different components in the mixture. This work was undertaken as a part of our thermodynamic research on the separation of mixtures formed by alcohols and acetates using different entrainers. The mixture under study is formed by isobutyl alcohol (IBA), isobutyl acetate (IBAc) and *N*,*N*-dimethylformamide (DMF). We choose DMF as entrainer because it is a promising effective solvent for the separation of these alcohol–acetate mixtures by extractive distillation [1]. Moreover, DMF is a polar compound which does not form any azeotropes with the original components in the mixture, its boiling temperature is higher than the IBA and IBAc boiling temperatures and it is completely miscible with them in all proportions [2].

In this work, to improve the knowledge of the phase behaviour of the original mixture IBA + IBAc with DMF as entrainer, we measured isobaric vapor–liquid equilibrium (VLE) data for the ternary system IBA (1) + IBAc (2) + DMF (3) and the constituent binary systems IBA (1) + DMF (3) and IBAc (2) + DMF (3) at 101.3 kPa, for which no isobaric data have been published. In a previous work, we reported the VLE data for the binary system IBA (1) + IBAc (2) at 101.3 kPa [3].

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

2. Experimental section

2.1. Chemicals

IBA (99.5 mass%, *HPLC grade*), IBAc (>99 mass%, *analytical grade*) and DMF (>99.9 mass%, *HPLC grade*) were

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Table 1
Densities d, refractive index n_D and normal boiling points T_b of pure components

Component	d (kg m^{-3}) (298.15 K)		n_D (298.15 K)		T_b (K)	
	Experimental	Literature	Experimental	Literature	Experimental	Literature
IBA (1)	797.83	797.80[a]	1.3937	1.3938[a]	381.09	380.81[a]
IBAc (2)	866.12	867.70[a]	1.3876	1.3880[a]	389.90	389.75[a]
DMF (3)	948.72	948.69[b]	1.4265	1.4269[b]	425.63	425.15[b]

[a] Taken from TRC Tables [4].
[b] Taken from Daubert and Danner [5].

purchased from *Aldrich Ltd*. The reagents were used without further purification after chromatography failed to show any significant impurities. The water content was small in all chemicals (<0.05 mass%). Before measurements, the liquids were dried over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets). The refractive indexes of pure liquids were measured at 298.15 K using an Abbe refractometer Atago 3T, and the densities were measured at 298.15 K (IBA) and 293.15 K (IBAc and DMF) using an Anton Paar DMA 55 densimeter. Temperature was controlled to ±0.01 K with a thermostated batch. The accuracy in density and refractive index measurements are ±0.01 kg m^{-3} and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with 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 apparatus is capable of handling pressures from 0.25 to 400 kPa, and temperature up to 523.15 K. The Cottrell pump ensures that both liquid and vapor 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 Spanish *Instituto Nacional de Técnica Aeroespacial*. The accuracy is estimated to be ±0.02 K. The temperature probe was calibrated against the ice and steam points of distilled water. A Fisher M101 phase equilibrium control system was used for measure and control of the pressure and the heating power. The measured pressure in the still was 101.3 ± 0.1 kPa. The manometer was calibrated using the vapor pressure of ultrapure water.

In each experiment, the pressure was fixed and the heating and shaking system of the liquid mixture was turned on. The still was operated under 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 sample extractions were carried out with special syringes that allowed withdrawal of small volume samples.

2.3. Analysis

Composition of the sampled liquid and condensed vapor 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 & Scientific). The GC response peaks were treated with Chrom-Card for Windows. Column, injector and detector temperatures were 363, 473 and 503 K, respectively, for all systems. Very good peak separation was achieved under these conditions and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. At least two analyses were made of each liquid and vapor composition. The standard deviation in the mole fraction was usually less than 0.001.

Table 2
Experimental vapor pressures (P_i^0) for *N*,*N*-dimethylformamide (DMF)

T (K)	P (kPa)
345.45	6.30
350.38	7.81
354.51	9.27
359.05	11.16
362.74	12.93
366.70	15.07
370.69	17.53
374.89	20.48
379.24	23.95
382.97	27.32
386.75	31.10
390.07	34.78
393.20	38.56
396.61	43.04
399.91	47.82
403.10	52.73
405.94	57.53
408.79	62.66
411.23	67.37
413.35	71.68
415.66	76.65
417.84	81.58
419.86	86.33
421.87	91.37
423.70	96.06
425.60	101.20