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Phase equilibria involved in extractive distillation of dipropyl ether + 1-propyl alcohol using 2-ethoxyethanol as entrainer

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Abstract

Consistent vapour–liquid equilibrium data at 101.3 kPa have been determined for the ternary system dipropyl ether + 1-propyl alcohol + 2-ethoxyethanol and two constituent binary systems: dipropyl ether + 2-ethoxyethanol and 1-propyl alcohol + 2-ethoxyethanol. The dipropyl ether + 2-ethoxyethanol system shows positive deviations from ideal behaviour and 1-propyl alcohol + 2-ethoxyethanol system exhibits no deviation from ideal behaviour. The activity coefficients and the boiling points were correlated with their compositions by the Wilson, NRTL and UNIQUAC equations. It is shown that the models allow a very good prediction of the phase equilibria of the ternary system using the pertinent parameters of the binary systems. The parameters obtained from binary data were utilized to predict the phase behaviour of the ternary system. The results showed a good agreement with the experimental values. Moreover, the entrainer capabilities of 2-ethoxyethanol were compared with 1-pentanol, butyl propionate and *N*,*N*-dimethylformamide, concluding that *N*,*N*-dimethylformamide is the best entrainer.

Keywords: Vapour–liquid equilibria; Dipropyl ether; 1-Propyl alcohol; 2-Ethoxyethanol; Activity coefficient models

1. Introduction

This work was undertaken as a part of a thermodynamic study on the separation of mixtures formed by alcohols and ethers using different entrainers. The purpose for screening solvents for extractive distillation is to determine whether this is a promising separation technique, and if so to select which of several solvents appears to be the most selective. Because selectivity is but one property that a good solvent must possess, these solvents will also be evaluated from the standpoint of such factors as cost, stability, viscosity and toxicity. Consideration of these factors will undoubtedly reduce the number of potential solvents and hence the experimental data necessary for a more complete evaluation.

The present work required a previous selection of possible solvents, which has been done by Sheibels criterion [1], and by means of the calculation of the separation factor. We chose 1-pentanol [2], butyl propionate [3] and *N*,*N*-dimethylformamide [4] which have been used previously in some former work and in the present research we show the results obtained by using 2-ethoxyethanol (widely known by its trade name, cellosolve) which is a common solvent in laboratory practice and in the chemical industry.

The data collections of phase equilibria for ternary or higher complexity are scarce because the experimental procedure to obtain a complete description of every mixture of industrial interest has a high economical and time cost. In this work, to improve the knowledge of the phase behaviour of the original mixture dipropyl ether (1) + 1-propyl alcohol (2) with 2-ethoxyethanol (3) as entrainer, we measured isobaric vapour-liquid equilibria (VLE) data for the ternary system dipropyl ether (1) + 1-propyl alcohol (2) + 2-ethoxyethanol (3) and the constituent binary systems dipropyl ether (1) + 2-ethoxyethanol (3) and 1-propyl alcohol (2) + 2-ethoxyethanol (3) at 101.3 kPa, for which only isothermal data have been published [5,6]. In a previous paper, we reported the VLE data for the binary system dipropyl ether (1) + 1-propyl alcohol (2) at 101.3 kPa [7].

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

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2. Experimental

2.1. Chemicals

1-Propyl alcohol (>99.5 mass%, *analytical grade*) was purchased from Panreac, dipropyl ether (90 mass%, *for synthesis*) and 2-ethoxyethanol (>99.0 mass%, *puriss. p.a.* (*GC*)) were supplied by Merck. Dipropyl ether and 2-ethoxyethanol were purified to >99.5 mass% by batch distillation in a Fischer SPALTROHR-column HMS-500, controlled by a Fischer system D301-C. 1-Propyl alcohol was 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 degasified and subsequently dried over molecular sieves (Union Carbide, type 4 Å, 1/16 in. pellets). The refractive indexes of the pure components were measured at 298.15 K using an Abbe refractometer Atago 3T, and the densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to ±0.01 K with a thermostated bath. The uncertainly in refractive index and density measurements are ±0.0002 and ±0.01 kg m^{-3}, 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 system used to measure VLE data was a dynamic recirculation apparatus described in a previous paper [2]. The accuracy of the temperature and the pressure are estimated to be ±0.01 K and ±0.1 kPa, respectively.

In each experiment, the pressure was fixed and the heating and stirring 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 both liquid and vapour phases were taken at low temperature to prevent evaporation leakage. Precautions were taken in order to minimize evaporation losses during storage and manipulation of the phase samples. A more detailed description of the experimental procedure may be collected from earlier works [2,3].

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 & Scientific). The GC response peaks were treated with Chrom-Card for Windows. Column, injector and detector temperatures were 333, 473, and 498 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 vapour composition. The standard deviation in the mole fraction was usually less than 0.001.

3. Results and discussion

3.1. Pure component vapour pressures

The pure component vapour pressure for 2-ethoxyethanol, P_i^{o}, was determined experimentally as a function of the temperature using the same equipment as that was used to obtain the VLE data. The pertinent results appear in Table 2. The measured vapour pressures were correlated using the Antoine equation:

$$\ln P_i^{\mathrm{o}}\,(\mathrm{kPa}) = A_i - \frac{B_i}{T(\mathrm{K}) + C_i} \qquad (1)$$

whose parameters A_i, B_i and C_i are reported in Table 3 together with some literature values. The deviations, $\Delta P_i^{\mathrm{o}} = P_{i,\mathrm{lit}}^{\mathrm{o}} - P_{i,\mathrm{exptl}}^{\mathrm{o}}$, calculated by means of the Antoine equation using the constant values from Table 3 have been graphically represented in Fig. 1. In this figure, it can be observed that the mean error was less than 1.2% with respect to the values reported by Chylinski et al. [11] and Daubert and Danner [9] and less than 0.5% with respect to the data reported by Chiavone-Filho et al. [12].

The pure component vapour pressures for dipropyl ether (1) and 1-propyl alcohol (2) were determined experimentally and reported in previous papers [7,13]. However, we measured the vapour pressures of dipropyl ether (1) and 1-propyl alcohol (2) up to about the normal boiling point of the respective pure components, which are lower than the 2-ethoxyethanol (3) boiling point. So, to avoid excessive extrapolations of the Antoine equation for the two more volatile components (dipropyl ether and

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	Experimental	Literature	Experimental	Literature
Dipropyl ether (1)	741.81	742.00[a]	1.3784	1.3780[a]	363.16	362.79[b]
1-Propyl Alcohol (2)	799.62	799.51[a]	1.3836	1.3837[a]	369.75	370.35[b]
2-Ethoxyethanol (3)	925.38	925.20[c]	1.4062	1.4057[b]	407.95	408.15[b]

[a] Taken from TRC tables [8].

[b] Taken from Daubert and Danner [9].

[c] Taken from Marsh [10].