Isobaric (vapour + liquid) equilibria for the (1-pentanol + propionic acid) binary mixture at (53.3 and 91.3) kPa

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ABSTRACT

Isobaric (vapour + liquid) equilibrium measurements have been reported for the binary mixture of (1-pentanol + propionic acid) at (53.3 and 91.3) kPa. Liquid phase activity coefficients were calculated from the equilibrium data. The thermodynamic consistency of the experimental results was checked using the area test and direct test methods. According to these criteria, the measured (vapour + liquid) equilibrium results were found to be consistent thermodynamically. The obtained results showed a maximum boiling temperature azeotrope at both pressures studied. The measured equilibrium results were satisfactorily correlated by the models of Wilson, UNIQUAC, and NRTL activity coefficients. The results obtained indicate that the performance of the NRTL model is superior to the Wilson and UNIQUAC models for correlating the measured isobaric (vapour + liquid) equilibrium data.

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1. Introduction

(Vapour + liquid) equilibrium (VLE) data are very important in the design of separation and purification processes and pipeline systems especially in the field of pharmaceutical and petrochemical industries. Such information can be obtained experimentally or estimated by using the accurate solution theories and molecular thermodynamic models. Distillation is the most common process used in petroleum refineries, petrochemical, and chemical plants for the separation of a mixture into its component parts. The optimum design and operations of distillation columns for the mixture separations requires the availability of accurate and thermodynamically consistent VLE data [1]. The VLE data for multi-component mixtures can usually be predicted using the related binary and pure component values with fewer experimental measurements.

The short-chain aliphatic alcohols such as methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, may attract interest as a safe fuel and as a solvent in the pharmaceutical, paint, and cosmetic industries [2,3]. Mono-carboxylic acids such as acetic acid, propionic acid, and pentanoic acid may be used to produce numerous esters, salts, and other derivatives in the plastics, coatings, and perfume industries [4]. Mixtures of short-chain aliphatic alcohols with mono-carboxylic acids have been studied extensively for the chemical engineering applications in the synthesis, separation,

and purification processes [5]. In (alcohols + mono-carboxylic acids), the COOH self-association strength of mono-carboxylic acids is much more than that of the OH group of alcohols. Therefore, the association of (alcohols + mono-carboxylic acids) may be considered as two self-associations (COOH/COOH and OH/OH) and one cross-association (COOH/OH) which can be used to describe the non-ideality of these systems as azeotropic behaviour [6]. Considering the importance of non-ideal behaviour of (alcohol + mono-carboxylic acid) in design and operations of different steps of separation processes, especially in distillation, in this work isobaric VLE data for the binary mixture of (1-pentanol + propionic acid) were determined at (53.3 and 91.3) kPa. The VLE data for binary mixtures and the activity coefficients were found to be thermodynamically consistent. The experiment values were correlated using the local composition models such as Wilson [7], NRTL [8], and UNIQUAC [9] for the liquid phase activity coefficients. The measurements have been compared with those correlated by the activity-coefficient models. The correlated parameters of the models as well as the average absolute deviation in boiling temperatures and vapour-phase compositions were determined and are reported.

2. Experimental

2.1. Chemicals

The 1-pentanol and propionic acid were supplied by Merck Co. Inc., Germany. The purity of the chemicals was checked on the

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TABLE 1

Normal boiling temperature and refractive index of the chemicals.

	1-Pentanol	Propionic acid
$T_b^{lit\,a}/K$	411.13	414.30
T_b^{exp}/K	411.10	414.30
$n_D^{lit\,a}$	1.4101	1.3809
n_D^{exp}	1.4100	1.3810

[a] T_b and n_D values are taken from reference [10].

TABLE 2

Experimental refractive indices of the binary mixtures of {1-pentanol (1) + propionic acid (2)} at $T = 293.15$ K.

x_1	n_D
0.0000	1.3810
0.0985	1.3838
0.1745	1.3861
0.2541	1.3884
0.3256	1.3904
0.3974	1.3925
0.4321	1.3935
0.5000	1.3955
0.5732	1.3976
0.6528	1.3999
0.7243	1.4020
0.8001	1.4042
0.8759	1.4064
0.9324	1.4079
1.0000	1.4100

TABLE 3

Experimental vapour pressures at different temperatures.

1-Pentanol		Propionic acid	
P/kPa	T/K	P/kPa	T/K
113.3	414.65	112.7	417.65
101.9	411.35	105.3	415.45
94.5	409.00	93.5	411.65
81.3	404.60	82.5	407.75
69.3	400.05	61.2	403.95
56.9	394.70	72.9	399.05
49.2	390.75	61.8	393.75
40.0	385.65	51.4	391.90
35.3	382.40	43.5	389.10
31.3	379.35	38.3	385.60
		34.5	382.45
		30.8	379.65

TABLE 4

The parameters of Antoine equation, (1).

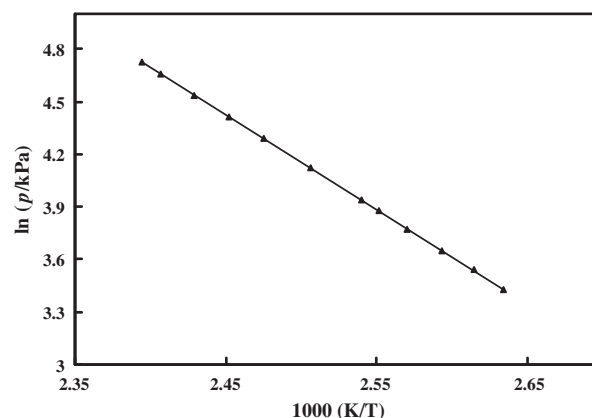| Components	A	B	C
1-Pentanol	4.39646	1336.010	166.320
Propionic acid	4.75466	1662.582	209.046

FIGURE 1. Plot of experimental vapour pressure against reciprocal temperature for propionic acid, ▲, Solid line calculated from the Antoine equation.

basis of its refractive index at $T = 293.15$ K. The refractive index was measured using thermostatically controlled Abbe Refractometer (Atago 1T/4T) equipped with a digital thermometer with an uncertainty of ±0.05 °C with an accuracy of ±0.0001n_D. The measured physical properties of 1-pentanol and propionic acid are listed in table 1 along with values from the literature [10]. Boiling temperature measurements were obtained by using a Fischer boiling point measurement. The estimated uncertainty in the boiling temperature measurements was ±0.05 K. The materials used directly without further purification.

2.2. Experimental procedure

In this work, vapour pressures of the pure components and the isobaric VLE results were obtained using a dynamic equilibrium still. The apparatus and procedure were described in the previous work [11]. At least three analyses were made for each sample. The measured refractive indices of the binary mixtures of (1-pentanol + propionic acid) at $T = 293.15$ K are reported in table 2. The maximum deviations from the average value were less than 0.15%. The uncertainties of the pressure and equilibrium composition measurements were ±0.1 kPa and ±0.0005 mole fraction, respectively.

3. Results and discussion

3.1. Vapour pressure

Table 3 shows the experimental vapour pressure of the binary mixture of (1-pentanol + propionic acid). The vapour pressure values were compared with those obtained by Antoine equation [12]. Table 4 shows the Antoine constant parameters of the chemicals from the literature [12]. Our measured vapour pressures and those predicted by the Antoine equation are presented in figure 1. According to this figure, the vapour pressure results are well matched with the Antoine equation.

3.2. Isobaric VLE

The VLE data have been measured at (53.3 and 91.3) kPa for the binary mixtures of (1-pentanol + propionic acid). Table 5 indicates the results obtained including vapour and liquid-phase compositions, temperature, and liquid phase activity coefficients. The thermodynamic consistency of the experimental values was checked by means of the area test and direct test methods [13–15]. According to these test criteria, the measured VLE results are of acceptable quality. The formation of ester has been checked by the method of the area percentage in the chromatographic analysis using Perkin–Elmer model 8500 gas chromatograph (GC). The results obtained verify that the amount of ester formed is not significant, and it can be ignored in this investigation. To obtain the experimental liquid phase activity coefficient of component i, it can be safely assumed as an ideal gas at the low experimental pressures $(Pr < 0.02)$. Therefore, the experimental liquid phase activity coefficient of component i was evaluated by the following equation:

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}}, \tag{1}$$

where y_i, x_i, P, and P_i^{sat} are respectively the gas phase mole fraction, the liquid phase mole fraction, the total pressure, and the saturated pressure of component i. The Wilson, NRTL, and UNIQUAC activity-coefficient models were used for VLE calculations of the studied binary mixture by a bubble temperature calculation procedure [16]. The binary interaction parameters of the models were determined by minimization of the following objective function (OF) [17]: