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Investigation on isobaric vapor liquid equilibrium for acetic acid + water + (*n*-propyl acetate or *iso*-butyl acetate)

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ABSTRACT

Isobaric vapor–liquid equilibrium (VLE) data for acetic acid + water, acetic acid + *n*-propyl acetate, acetic acid + *iso*-butyl acetate, acetic acid + water + *n*-propyl acetate, acetic acid + water + *iso*-butyl acetate are measured at 101.33 kPa with a modified Rose still. The nonideal behavior in vapor phase caused by the association of acetic acid are corrected by the chemical theory and Hayden–O'Connell method, and analyzed by calculating the second virial coefficients and apparent fugacity coefficients. The VLE data for acetic acid + water, acetic acid + *n*-propyl acetate, and acetic acid + *iso*-butyl acetate are correlated through the NRTL and UNIQUAC models using the nonlinear least square method. The obtained NRTL model parameters are used to predict the ternary VLE data. The ternary predicted values obtained in this way agree well with the experimental values.

1. Introduction

Acetic acid is a kind of fundamental organic chemical material. It can be used as a solvent or an additive for producing rubbers, paints, dyes, soft drink bottles, photographic film, synthetic fiber, and so on. Accordingly, there are many different commercial processes in chemical industry. The difficulty in purifying acetic acid from its aqueous solution is commonly encountered among these commercial processes. The main reason is that the relative volatility of acetic acid/water is close to 1 in the acetic acid-rich region. While, azeotropic distillation can solve this problem effectively, especially when the water content is low. In the azeotropic distillation process, water is mainly removed by forming a water-entrainer azeotrope. Several solvents, such as ethyl acetate [1], *n*-propyl acetate [2], *iso*-propyl acetate [3], *n*-butyl acetate [4,5], *iso*-butyl acetate [4,5] and *n*-pentyl acetate [3] have been investigated as entrainers for the separation of acetic acid. Unfortunately, there is not sufficient reported VLE data for the acetic acid + water + *n*-propyl acetate or *iso*-butyl acetate system. However, it is known that VLE data is vital to the simulation and design of the distillation process.

Therefore, as an extension of the previous work carried out by our group [3,6], the investigations of the vapor–liquid phase equilibrium of acetic acid + *n*-propyl acetate, acetic acid + *iso*-butyl acetate, acetic acid + water + *n*-propyl acetate and acetic acid + water + *iso*-butyl acetate systems are performed at 101.33 kPa. The aim of this article is to investigate behavior of vapor–liquid phase equilibrium of these systems and to supply basic data for the simulation and design of the azeotropic dehydration process.

As we know, the acetic acid molecules strongly self-associate to form dimers and trimers in both liquid and vapor phase due to the hydrogen bond [7]. In the present study, the model on the basis of chemical theory [8] developed by Prausnitz et al. [9] is adopted to handle the strong associating effect, which mainly exists between two molecules of acetic acid. For analyzing and correcting the nonideal behavior in vapor phase, the second virial coefficient and the fugacity coefficient are calculated using Hayden–O'Connell (HOC) equation [10]. Meanwhile, the nonideal behavior in liquid phase is corrected by activity coefficients using nonrandom two-liquids (NRTL) [11] model and the universal quasi-chemical (UNIQUAC) [12] model, separately.

In this work, both the NRTL and UNIQUAC models combined with the HOC equation are used to correlate the measured binary VLE data, and then the NRTL model parameters obtained from binary data are used to predict VLE data of the ternary systems containing the associating component acetic acid.

2. Experimental

2.1. Materials

The chemical reagents used are acetic acid, water, *n*-propyl acetate, *iso*-butyl acetate. Acetic acid (≥99.5% mass%) is purchased from Shanghai Shenbo Chemical Co. Ltd. Deionized water (PA grade) is supplied by the Membrane Science Technology Research

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Table 1
The physical properties of the experimental materials [13,14].

Properties	Acetic acid (1)	Water (2)	*n*-Propyl acetate (3)	*Iso*-butyl acetate (4)
M (g mol^{-1})	60.05	18.01	102.13	116.16
T_b (K)	391.05	373.15	374.65	389.80
T_c (K)	591.95	647.13	549.73	560.80
P_c (MPa)	5.78	22.06	3.36	3.01
R_D (Å)	2.610	0.615	3.969	4.276
μ (D)	1.739	1.850	1.789	1.871
r	2.195	0.920	4.153	4.827
q	2.072	1.400	3.656	4.192
q'	2.072	1.00	3.656	4.192
$\eta_{\text{association}}$	4.50	1.70	0.53	0.53
$\eta_{\text{solvation}}$	(1) + (2) 2.5	(1) + (3) 2.0	(1) + (4) 2.0	(2) + (3) 1.3
$\eta_{\text{solvation}}$	(2) + (4) 1.3	(3) + (4) 0.53		
Antoine parameters[a]				
A	16.8080	18.3036	16.2291	15.9987
B	3405.57	3816.44	2980.47	3127.60
C	−56.34	−46.13	−64.15	−60.15
Temperature range (K)	290–430	284–441	280–410	288–432

[a] Antoine equation: $(\ln (P^S{}_i\ (\text{mmHg}))) = A - B/(T\ (\text{K}) + C)$, $P^S{}_i$ (mmHg), T (K)).

Laboratory of Nanjing University of Technology. *n*-propyl acetate (≥98.5%, mass%) and *iso*-butyl acetate (≥98.0%, mass%) are purchased from Sinopharm Chemical Reagent Co. Ltd. All of the solvents are further purified through precise distillation in a column. The physical properties of the experimental materials are shown in Table 1 [13,14].

2.2. Apparatus and procedure

The modified Rose recirculation still used for VLE experiments in this study is similar to that in our previous report [15] and also shown in Fig. 1. A volume of the mixed material to be studied is charged to the still and heated. Boiled liquid and vapor are raised up to the vapor–liquid separator through the vapor–liquid riser. At the vapor–liquid separator, the vapor and the liquid depart from each other. The separated vapor moves on and is condensed by circulated cooling water to shape droplets and collected in the vapor-phase sample reservoir. Meanwhile, the separated liquid droplets drop into the liquid-phase sample reservoir. Part of the liquid phase in the liquid-phase sample reservoir and part of the liquid derived from the vapor-phase sample reservoir mix with each other in the mixing chamber, and then return to the boiler to be heated once more. Under the circumstances, both the vapor and liquid phases are sufficiently contacted to reach equilibrium. Generally, it takes about 2–3 h to establish the vapor–liquid equilibrium when equilibrium temperature is kept invariable, then the samples are taken out and analyzed by GC. Material is then added to the still to change the composition to get another VLE point.

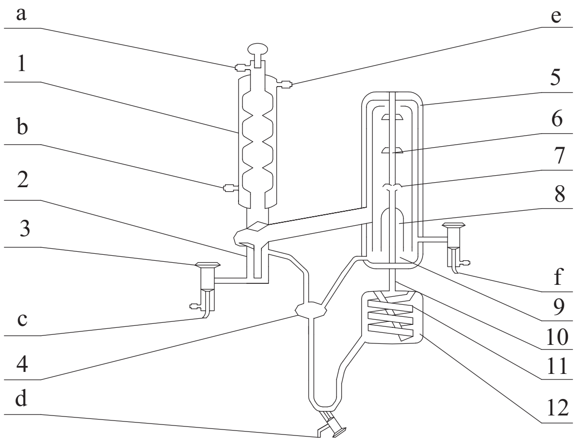

Fig. 1. Modified Rose recirculation still (a) to pressure controlling devices, (b) cooling water inlet, (c) vapor sample connection, (d) liquid discharging outlet, (e) cooling water outlet, (f) liquid sample connection; (1) vapor condenser, (2) vapor phase sample reservoir, (3) teflon cock, (4) vapor liquid mixing chamber, (5) vacuum thermal insulating jacket, (6) thermometer casing, (7) vapor liquid separator, (8) gas chamber, (9) liquid phase sample reservoir, (10) vapor liquid riser, (11) inner heater, (12) boiler.

The equilibrium temperature is measured by a standard mercury thermometer, and the standard uncertainty of temperature measurements is 0.1 K. The pressure is obtained and kept at 101.33(±0.04) kPa with the help of a pressure control system, which is consisted of one electromagnetic relay, one vacuum pump, two manometers, two reservoirs and three triple valves. The principle of the pressure control system is reported in our previous work [6].

2.3. Sample analysis

The compositions of samples containing water are analyzed with an SP6800A gas chromatograph with a thermal conductivity detector (TCD). The GC column is a stainless steel tube packed with Porapak Q (50–80 mesh) of 3 m-length, 3 mm-diameter. The carrier gas is hydrogen (purity ≥ 99.999%) with a flow rate of 50 cm^3 min^{-1}. Accordingly, the compositions of samples without water are also analyzed by an SP6800A gas chromatograph, but with a flame ionization detector (FID) and a capillary column (OV-1701, 30 m × 0.32 mm × 1 μm). The carrier gas is nitrogen (purity ≥ 99.999%) with a flow rate of 50 cm^3 min^{-1}. Both of the TCD and FID responses are treated with a Zhejiang Zhida chromatography station.

For the systems without water, acetic acid + *n*-propyl acetate, acetic acid + *iso*-butyl acetate, the temperatures of the column, injector and detector of GC are kept at 393, 423 and 433 K. For the systems containing water, acetic acid + water, acetic acid + water + *n*-propyl acetate and acetic acid + water + *iso*-butyl acetate, the detector current is 150 mA, the temperatures of the column, injector and detector of GC are kept at 413, 423 and 433 K.

The GC is calibrated with gravimetrically prepared standard solutions. A single analysis of the vapor or liquid composition by gas chromatography is frequently imprecise. At least two analyses are made of each liquid and each vapor composition. Consequently, with repeated measurements, the standard uncertainty of liquid composition x_i and vapor composition y_i analysis is 0.001.