Investigation on isobaric vapor–liquid equilibrium for acetic acid + water + methyl ethyl ketone + isopropyl acetate

Qiang Xie, Hui Wan, MingJuan Han, GuoFeng Guan*

College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China

ARTICLE INFO

ABSTRACT

Isobaric vapor–liquid equilibrium (VLE) data for acetic acid + water, acetic acid + methyl ethyl ketone (MEK), MEK + isopropyl acetate, acetic acid + MEK + water and acetic acid + MEK + isopropyl acetate + water are measured at 101.33 kPa using a modified Rose cell. The nonideal behavior in vapor phase of binary systems measured in this work is analyzed through calculating fugacity coefficients since mixture containing acetic acid deviates from ideal behavior seriously in vapor phase due to the associating effect of acetic acid. Combined with Hayden–O'Connell (HOC) equation, the VLE data of the measured binary systems for acetic acid + water, acetic acid + MEK and MEK + isopropyl acetate are correlated by the NRTL and UNIQUAC models. The NRTL model parameters obtained from correlating data of binary system are used to predict the VLE data of the ternary and quaternary systems, and the predicted values obtained in this way agree well with the experimental values.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

As an important derivative of cellulose, Cellulose Acetate (CA) is widely applied in membrane materials, cigarette filters, textile, plastic, food and pharmaceutical industries for its desirable properties. However, the manufacturing process of CA brings out a great deal of wastewater containing acetic acid, water, ketone and acetate [1], and the separation of these useful components from sewage discharged by CA factories attracts much attention for their significance in both economy and environment protection.

As a common separating process, distillation can be used in treating wastewater from CA production, and accurate vapor–liquid equilibrium (VLE) data are important for the design and simulation of distillation. Up to now, there is few VLE data for methyl ethyl ketone (MEK) + isopropyl acetate, MEK + acetic acid, MEK + acetic acid + water and MEK + acetic acid + water + isopropyl acetate available in literatures although the detailed study on VLE data for acetic acid + water [2], water + MEK [3], acetic acid + isopropyl acetate, and acetic acid + water + isopropyl acetate [4] have been reported.

Therefore, as an extension of the previous work carried out by our group [4], the investigations of the vapor–liquid phase equilibrium of MEK + isopropyl acetate, MEK + acetic acid, MEK + acetic acid + water and MEK + acetic acid + water + isopropyl acetate systems at 101.33 kPa, are performed. The aim of this paper is to investigate behavior of vapor–liquid phase equilibrium of these systems and to supply basic data for the simulation and design of the distillation process.

Considering the strong associating effect exists between molecules of acetic acid, the model developed by Prausnitz et al. [5] in 1980 on the basis of chemical theory [6], is applied to explain the associating effect of acetic acid under our investigations. Combined with chemical theory, for analyzing and correcting the nonideal behavior in vapor phase, the second virial coefficient and the fugacity coefficient are calculated by the Hayden–O'Connell (HOC) [7] equation. Meanwhile, the nonideal behavior in liquid phase is represented by activity coefficients using nonrandom two-liquids (NRTL) [8] model and the universal quasi-chemical (UNIQUAC) [9] model, separately.

In this paper, both of the NRTL and UNIQUAC models combined with HOC equation are used to correlate the vapor–liquid equilibrium of binary systems, then the obtained NRTL model parameters from binary data are used to predict ternary and quaternary VLE data.

2. Experimental

2.1. Materials

The chemicals used are acetic acid, water, MEK, isopropyl acetate. Acetic acid (≥99.5% mass%) and MEK (≥98% mass%) are purchased from Shanghai Lingfeng Chemical Reagents Co., Ltd. Deionized water (PA grade) is supplied by the Membrane Science Technology Research Laboratory of Nanjing University of Technology. Isopropyl acetate with a stated minimum purity of 98.5% is

---

Table 1
The properties of the experimental materials [5,10].

Properties	Acetic acid(1)	Water(2)	MEK(3)	Isopropyl acetate(4)
M.w./(g mol^{-1})	60.05	18.01	72.11	102.13
T_b/°C	117.93	100.00	79.61	89.12
T_c/°C	318.80	373.98	262.35	258.85
P_c/MPa	5.78	22.04	4.15	3.29
R_D/Å	2.610	0.615	3.135	3.679
μ/D	1.748	1.860	2.776	1.760
r	2.23	0.92	3.25	4.15
q	2.04	1.40	2.88	3.65
q'	2.04	1.00	2.88	3.65
$\eta_{solvation}$	4.50	1.70	0.90	0.53
$\eta_{association}$	(1)+(2) 2.5	(1)+(3) 1.8	(1)+(4) 2.0	(2)+(3) 1.0
$\eta_{association}$	(2)+(4) 1.3	(3)+(4) 1.1		
Antoine constants				
A	7.5596	8.0713	7.0636	7.3339
B	1644.05	170.63	1261.34	1436.50
C	39.63	39.72	51.18	39.49
Temperature range/K	290–391	274–373	316–361	313–393

Notes: Antoine equation: $(log(P_i^S/0.133) = A - B/(T + C),\ P_i^S/\text{kPa},\ T/\text{K})$.

bought from Sinopharm Chemical Reagent Co., Ltd. All of the solvents are further purified through distillation in a glass column so that no detectable impurity is observed in the gas chromatography (GC) analysis. The properties of the experimental materials are shown in Table 1 [5,10].

2.2. Apparatus and procedure

In this work, the recirculating still of modified Rose type [11,12] is used to measure VLE data. Fig. 1 shows the diagram for this still. Mixture is heated in the boiler to boil, and some boiled liquid taking with some gas spills up to the vapor–liquid separator through the vapor–liquid riser. In the vapor–liquid separator, the gas and the liquid separates with each other. The separated liquid droplets drop into the liquid-phase sample reservoir, while the gas goes into the vapor-phase condenser, where the gas is condensed by circulation of cooling water to shape droplets which are collected in the vapor-phase sample reservoir. Part of liquid coming from the condensed gas phase and part of the liquid phase in the liquid-phase sample reservoir mix with each other in the vapor–liquid phases mixing chamber, then this mixture flows back into the boiler to be heated continuously. In this process, both the vapor and the liquid phases are continuously recirculating to provide intimate contact of the two phases and ensure that equilibrium can be established.
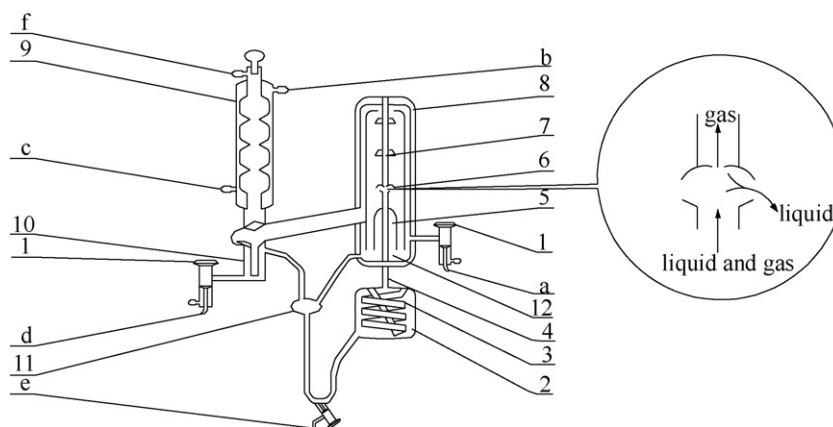
It takes approximately 2 h for the circulation in Rose cell to achieve equilibrium between vapor and liquid phases when equilibrium temperature is kept constant, and the sample are taken out and analyzed.

The equilibrium temperature is gauged with a standard mercury thermometer, and the measurement error of temperature is less than 0.1 K. The uncertainty of the measured vapor-phase mole fractions is 0.001. The pressure is obtained and kept at 101.33 kPa with the help of a pressure control system, which is consisted of one water manometer, one mercury manometer, three triple valves, one vacuum pump, two reservoirs, and one electromagnetic-type relay.

2.3. Sample analysis

To determine the compositions of the equilibrium phases, a SP6800A gas chromatograph with a thermal conductivity detector is used, and the response is treated with a Zhejing Zhida chromatography station. The GC is calibrated with solutions of known compositions for each mixture which are prepared gravimetrically, and the relationship between the peak area and the composition is determined for each mixture [13]. The GC column is made of a 3 m length stainless steel tube with 3 mm diameter and packed with Porapak Q (80–100 mesh). The carrier gas is hydrogen with a purity of 99.9% and a flow rate of 50 cm^3 min^{-1}.

For the binary systems, acetic acid + water, acetic acid + MEK and MEK + isopropyl acetate, the temperatures of the column, injector and detector of GC are kept at 408, 423 and 418 K, respectively, and the detector current is 150 mA.

For ternary and quaternary systems, acetic acid + water + MEK and acetic acid + water + MEK + isopropyl acetate, the flow rate of the carrier gas is adjusted to be 30 cm^3 min^{-1} and the column temperature is turned down a little to be 403 K. We should point out that except for the two elements of carrier gas flow rate and the column temperature, other conditions of GC analysis for ternary and quaternary systems are kept the same with those of binary systems.

3. Results and discussion

3.1. Experimental data

Vapor–liquid equilibrium data for the binary systems such as acetic acid + water, acetic acid + MEK and MEK + isopropyl acetate are obtained at 101.33 kPa, just as shown in Table 2. The vapor–liquid equilibrium data for the acetic acid + water + MEK ternary system and acetic acid + water + MEK + isopropyl acetate

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