



Isobaric vapor–liquid equilibrium for binary system of *N, N*-dimethyl formamide + *N, N*-dimethyl acetamide and quaternary system of *sec*-butyl alcohol + *sec*-butyl acetate + *N, N*-dimethyl formamide + *N, N*-dimethyl acetamide at 101.3 kPa



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ABSTRACT

Isobaric vapor–liquid equilibrium (VLE) for the binary system *N, N*-dimethyl formamide (DMF) + *N, N*-dimethyl acetamide (DMAC) and the quaternary system *sec*-butyl alcohol (SBA) + *sec*-butyl acetate (SBAC) + DMF + DMAC were determined at 101.3 kPa using a vapor–liquid equilibrium still. The thermodynamic consistency test for the experimental data was checked by Van Ness point test. The binary VLE data were correlated with the NRTL, UNIQUAC and Wilson activity coefficient models respectively. And the VLE data of the quaternary system predicted by the correlated binary interaction parameters agree well with the experimental data. And the mixture of DMF (3) and DMAC (4) can eliminate the pseudo-azeotrope of *sec*-butyl alcohol (1) + *sec*-butyl acetate (2). Thus, the mixture of DMF and DMAC is appropriate for separation of the pseudo-azotrope of SBA and SBAC by extractive distillation.

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1. Introduction

sec-Butyl alcohol (SBA) is an important intermediate for production of methyl ethyl ketone. It is also used as pesticides mineral-dressing agent, emulsifiers, plasticizers and the co-solvent of methanol for improving the octane number of gasoline [1–3]. SBA is traditionally produced by hydration of *n*-butene with water. The indirect hydration process uses sulfuric acid as catalyst and causes serious equipment corrosion and low selectivity [4,5]. Direct hydration process avoids the drawback of corrosion to equipment by replacing sulfuric acid with acidic catalyst, such as heteropolyacid, resin and molecular sieve. But it requires high reaction temperature and pressure, more energy consumption and high purity of *n*-butene and has low conversion of *n*-butene [5,6]. To develop an efficient, stable, environment-friendly process for SBA, the transesterification of *sec*-butyl acetate (SBAC) with alcohols was presented by researchers [7], which has high conversion, low energy-consumption and no corrosion to equipment.

In the process of transesterification of SBAC with alcohols, SBA and SBAC can form a pseudo-azotrope [8]. Extractive distillation is effective in separation of close-boiling, azeotropic and pseudo-azeotropic systems, in which solvent selection is essential. Berg indicated that the mixture of *N, N*-dimethyl formamide (DMF) and *N, N*-dimethyl acetamide (DMAC) is effective in separation SBA from SBAC [9]. However, the VLE data of DMF (3) + DMAC (4) and SBA (1) + SBAC (2) + DMF (3) + DMAC (4) have not been found in the opened literature so far. The VLE data is very important for the simulation and design of the extractive distillation column [10]. Thus, isobaric VLE data at 101.3 kPa of the two systems were measured in this work to provide fundamental data for the separation of SBA and SBAC by extractive distillation.

2. Experimental

2.1. Chemicals

Analytical reagents (AR), SBA, SBAC, DMF and DMAC were used in this work, whose information is listed in Table 1. Purity of all these chemicals were checked by a gas chromatograph (GC) equipped with a flame ionization detector (FID), and no appreciable

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Table 1
Experimental reagents list.

Reagent ^a	SBA	SBAC	DMF	DMAC
Molecular formula	C ₄ H ₁₀ O	C ₆ H ₁₂ O ₂	C ₃ H ₇ NO	C ₄ H ₉ NO
CASRN	78-92-2	105-46-4	68-12-2	127-19-5
Source	Jiangtian, China	Jiangtian, China	Jiangtian, China	Jiangtian, China
Purity (mass fraction)	0.999	0.997	0.998	0.999

^a SBA-*sec*-butyl alcohol, SBAC- *sec*-butyl acetate, DMF- *N,N*-dimethyl formamide, DMAC- *N,N*-dimethyl acetamide.

peak of impurity was detected. The water contents determined by Karl Fischer titration were less than 0.003 (mass fraction). Therefore, all of the chemicals were used without further purification.

2.2. Apparatus and procedure

The VLE data were determined in a circulation vapor–liquid equilibrium still (a modified Othmer still) at 101.3 kPa. Its reliability for VLE measurements was verified in our previous work [11]. It includes a liquid-phase sampling port, a vapor-phase sampling port, an equilibrium chamber, a heating bar and a condenser. The internal volume of the still is about 60 cm³, of which about 45 cm³ is occupied by the liquid. During the experimental process, both the vapor and the liquid phase continuously circulate to ensure that the equilibrium could be established. In each experiment, equilibrium between the vapor and the liquid phase was assumed when the temperature remained constant for 60 min. Three liquid samples and three vapor samples were taken respectively under each composition in order to reduce errors. To decrease the influence of sample amount to the equilibrium of the system, the sample amount was determined as 0.1–0.2 mL which is negligible compared with the volume of the liquid. More details about the apparatus were reported in our previous work [11,12].

A Pt-1000 sensor was employed to measure the equilibrium temperatures. The probe was connected to a digital temperature meter (AMETEK DTI-1000) with standard uncertainty of ±0.01 K according to the calibration certificate (ITS-905). The pressure of the VLE apparatus was measured and controlled by a Fischer M101 system and the pressure of the still was controlled at 101.3 ± 0.1 kPa.

2.3. Sample analysis

The equilibrium of the liquid and vapor samples were analyzed by the gas chromatograph (GC) SP-2100 (Beijing Beifeng Ruili Analysis Instrument Ltd) that was equipped with a flame ionization detector (FID) and a silica capillary column (0.25 mm (i.d.) × 30 m) packed with PEG – 20 M. High purity nitrogen was used as the carrier gas at a constant flow rate of 30 mL/min. The flow rates of hydrogen and air were kept at 30 and 300 mL/min, respectively. The temperatures of detector and vaporizer were 468.15 K and 458.15 K, respectively. The details of the column temperature program were as follows: First, it kept at 343.15 K for 4 min. Then, it rose to 423.15 K with the increment of 20 °C/min. Finally, it stayed at 423.15 K for 2.5 min.

The injection volume of each sample into the GC was 0.4 μL, the final composition was determined from the average of three replications. The standard uncertainty of compositions was 0.002 in mole fraction of the three repeated measurements.

3. Results and discussion

3.1. Experimental data

In this work, the isobaric VLE data of the binary system DMF

(3) + DMAC (4) and the quaternary system SBA (1) + SBAC (2) + DMF (3) + DMAC (4) were measured by the modified Othmer still at 101.3 kPa. The experimental data are listed in Table 2 and Table 3, respectively.

3.2. Vapor–liquid equilibrium model

The activity coefficient can be calculated by the following equation [13].

$$y_i = \left[\widehat{\phi}_i^v y_i P / (x_i \phi_i^v P_i^s) \right] \exp \left[(P - P_i^s) V_i^L / RT \right], \quad (i = 1, 2, \dots, N) \quad (1)$$

where y_i and x_i are the mole fractions of component i in the vapor and liquid phases, respectively; P and T are the pressure and the temperature of the equilibrium system; P_i^s is the saturated vapor pressure of pure component i , which was calculated by the Antoine equation at system temperature T . And the Antoine constants for each component are listed in Table 4; $\widehat{\phi}_i^v$ is the fugacity coefficient of component i in the vapor phase. ϕ_i^v is the fugacity coefficient of pure i at the temperature T and the saturation pressure P_i^s . They were calculated by the Soave-Redlich-Kwong (SRK) equation; R is the gas constant; V_i^L is the liquid molar volume of pure component i . The Poynting factor $\exp[(P - P_i^s)V_i^L/RT]$ is approximately equal to 1 at low pressure. So Eq. (1) can be simplified as the follows:

$$y_i = \widehat{\phi}_i^v y_i P / (x_i \phi_i^v P_i^s) \quad (2)$$

The saturated vapor pressure P_i^s of the chemicals is calculated by the following extended Antoine equation [14].

Table 2
Isobaric VLE data and activity coefficients for the binary system of DMF (3) + DMAC (4) at 101.3 kPa^a

T/K	x ₁	y ₁	γ ₁	γ ₂
438.93	0.000	0.000	–	1.000
437.59	0.010	0.020	1.457	1.132
436.34	0.051	0.094	1.409	1.131
435.82	0.070	0.126	1.402	1.130
435.25	0.093	0.165	1.389	1.127
434.64	0.119	0.202	1.361	1.127
433.98	0.151	0.248	1.346	1.124
433.12	0.194	0.305	1.318	1.123
432.17	0.249	0.373	1.293	1.117
431.32	0.303	0.431	1.257	1.121
430.32	0.374	0.495	1.207	1.140
429.63	0.427	0.545	1.189	1.145
428.76	0.499	0.599	1.148	1.186
428.19	0.550	0.644	1.143	1.188
427.43	0.621	0.692	1.114	1.248
426.24	0.739	0.782	1.100	1.324
425.09	0.861	0.883	1.107	1.372
424.39	0.938	0.946	1.113	1.442
424.02	0.979	0.981	1.119	1.507
423.91	1.000	1.000	1.000	–

^a Uncertainties: $u(x_1) = 0.002$, $u(y_1) = 0.002$, $u(T) = 0.01$ K, $u(P) = 0.1$ kPa.

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