Experimental isobaric (vapor + liquid) equilibrium data for the binary system *N*, *N*-dimethyl formamide + dimethyl sulfoxide and the quaternary system *sec*-butyl alcohol + *sec*-butyl acetate + *N*, *N*-dimethyl formamide + dimethyl sulfoxide at 101.3 kPa

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ABSTRACT

Isobaric vapor−liquid equilibrium (VLE) data for the quaternary system *sec*-butyl alcohol + *sec*-butyl acetate + *N*, *N*-dimethyl formamide (DMF) + dimethyl sulfoxide (DMSO) and the constituent binary system DMF + DMSO were determined at 101.3 kPa with a modified Othmer still. The measured experimental data of binary and quaternary systems were certified to be thermodynamically consistent according to the Van Ness method. And the experimental binary data were correlated by Wilson, NRTL and UNIQUAC activity coefficient models. The rest of binary interaction parameters have been obtained in our previous work. Then, the binary and quaternary vapor−liquid equilibrium were predicted by the models with the correlated parameters. The results show that the three models yield a good prediction for the binary and quaternary systems. But NRTL model performed better than the other two models in predicting VLE of the quaternary system.

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1. Introduction

sec-Butyl alcohol is widely used in industry, such as pharmaceutical intermediates, spices, dyes, flotation agents, polymerization additives, rubber additives, the solubilizers of nitrocellulose lacquer and nitrocellulose lacquer thinner and so on. But by now, it is mainly used to produce methyl ethyl ketone [1,2]. The traditional methods of producing *sec*-butyl alcohol are indirect and direct hydration of butylene. The method of indirect hydration of butylene has two serious drawbacks: first, serious corrosion to equipment because of sulfuric acid as catalyst; second, low selectivity. Although the process of direct hydration of butylenes has overcome the drawback of corrosion, it requires high purity of raw material and has low conversion ratio [3,4]. Recently, a novel method of producing *sec*-butyl alcohol by transesterifying *sec*- butyl acetate with alcohols was exploited

by some researchers, which is superior to traditional method by the hydration of butylenes. In this new process, *sec*-butyl alcohol and *sec*-butyl acetate form a "pseudo-azeotrope", in which the vapor and liquid composition is so close that it should be ignored nearly [5]. Extractive distillation as a special distillation is suitable to separate this type of systems. And Extractive agent selection is important aspect for a process of extractive distillation.

In our previous work, DMF (3) and DMSO (4) were certified to be effective extractive solvents for separation of *sec*-butyl alcohol (1) and *sec*-butyl acetate (2) and DMSO performed better than DMF [5,6]. But the boiling point of DMSO is so high that it is likely to decompose when recovering extractive agent by distillation at 1 atm and even can cause explosion. If DMSO and DMF are mixed as extractive agent, the temperature of tower bottom can be reduced. At same time, DMF can inhibit the dissociation of DMSO at high temperature [7]. Consequently, the mixed solvent as extractive agent to separate *sec*-Butyl alcohol (1) and *sec*-Butyl acetate (2) is better than a single agent such as DMF (3) or DMSO (4) in industrial applications. So, it is necessary to measure isobaric VLE data for the

quaternary system sec-Butyl alcohol (1) + sec-Butyl acetate (2) + DMF (3) + DMSO (4) and the constituent binary systems. The binary interactive parameters of the five systems: sec-butyl alcohol (1) + sec- butyl acetate (2) [8], sec-butyl alcohol (1) + DMF (3) [5], sec-butyl alcohol (1) + DMSO (4) [6], sec-butyl acetate (2) + DMF (3) [5], sec-butyl acetate (2) + DMSO (4) [6] have been obtained in our previous work. Guo L. et al. measured vapor pressure of the binary system of DMF (3) + DMSO (4) at various temperature and concentrations by using a quasi-static ebulliometer method [7]. But there is no isobaric VLE data for DMF (3) + DMSO (4) system and sec-butyl alcohol (1) + sec-butyl acetate (2) + DMF (3) + DMSO (4) system in open literatures. Thus, the absent isobaric VLE data for the two systems were explored experimentally in this work to supply basic data for the separation of sec-butyl alcohol (1) + sec-butyl acetate (2) by extractive distillation using the mixed solvent of DMF (3) and DMSO (4) as extractive agent.

2. Experimental

2.1. Chemicals

In this work, Analytical reagents (AR), sec-butyl alcohol, sec-butyl acetate and DMF and DMSO were used. The molecular formula, CASRN, source, grade and mass fraction are listed in Table 1. The physical properties of the pure components are listed in Table 2, which are used to calculate fugacity coefficients. Purity of all these chemicals were checked by a gas chromatography (GC) equipped with a flame ionization detector (FID) and no appreciable peak of impurity was detected. And the water contents were detected by Karl Fischer titration and no appreciable water was detected. In additional, the boiling points of the pure components were measured with the modified Othmer still at 101.30 kPa with an uncertainty of ±0.01 K, which are shown in Table 3, together with the corresponding literature values. The measured normal boiling points are basically consistent with literature values. Therefore, all of the chemicals were used without further purification.

2.2. Apparatus and procedures

In this work, a modified Othmer still was used to measure VLE data. A detailed description of the apparatus has been previously reported [16]. The experimental method and the test of the instrument reliability were reported by our previous work [17]. In each experiment, the solution with a certain concentration prepared in advance was measured. The equilibrium state was assumed to be established when the fluctuation in equilibrium temperature was within 0.1 K in an about 0.5 h and the vapor and liquid samples were withdrawn simultaneously with syringes.

A Fisher M101 pressure control system was used to measure and control the pressure. The pressure in the still was maintained at 101.3 ± 0.1 kPa during the measurement process. And the equilibrium temperature was measured with a PT-1000 connected to a

Table 2
Physical properties of the components.[a]

Component	sec-Butyl alcohol	sec-Butyl acetate	DMF	DMSO
$M/\text{g mol}^{-1}$	74.1228	116.1601	73.0947	78.1350
T_c/K	535.90	561.00	649.60	729.00
P_c/kPa	4188.50	3170.00	4420.00	5650.00
ω	0.5808	0.3954	0.3177	0.2806
Z_c	0.2540	0.2640	0.2140	0.2120
$V_c/\text{m}^3\ \text{kmol}^{-1}$	0.2700	0.3890	0.2620	0.2270

[a] Taken from Aspen Plus V7.2 physical properties databanks.

Table 3
Comparison of the boiling points (T_b) at 101.3 kPa of the pure components with literature data.

Component	T_b/K	
	This work	Literature
sec-Butyl alcohol	372.61	372.55 [9]
		372.604 [10]
		372.66 [11]
		372.90[a]
sec-Butyl acetate	385.31	385.35 [12]
		385.15[a]
DMF	425.10	425.65 [13]
		425.15 [14]
		425.15[a]
DMSO	463.99	463.15 [15]
		464[a]

[a] Taken from Aspen Plus V7.2 physical properties databanks.

digital temperature meter (AMETEK DTI-1000) with an uncertainty of ±0.01 K [18].

2.3. Sample analysis

All the samples were analyzed with a gas chromatograph (GC) (SP-2100, supplied by Beijing Beifen Ruili Analysis Instrument Ltd.). The instrument was equipped with a flame ionization detector (FID) and a silica capillary column (0.25 mm (i.d.) × 30 m × 0.25 μm) packed with PEG-20M. Nitrogen was used as the carrier gas at a constant flow of 30 mL/min. The temperatures of vaporizer and detector were set at 473.15 K and 493.15 K, respectively. The column temperature was programmed at 363.15 K for 5 min, then increased to 463.15 K at 20 K min^{-1}, finally was maintained at 463.15 K for 5 min.

3. Results and discussion

3.1. Experimental data

The experimental VLE data of the binary system of DMF (3) + DMSO (4) and the quaternary system of sec-butyl alcohol (1) + sec-butyl acetate (2) + DMF (3) + DMSO (4) were measured with a modified Othmer still mentioned above at 101.3 kPa. The experimental data are listed in Tables 4 and 5.

Table 1
Experimental chemicals.

Component	sec-Butyl alcohol	sec-Butyl acetate	DMF	DMSO
Molecular formula	$C_4H_{10}O$	$C_6H_{12}O_2$	C_3H_7NO	C_2H_6OS
CASRN	78-92-2	105-46-4	68-12-2	67-68-5
Source	YuanLi,china	YuanLi,china	YuanLi,china	YuanLi,china
Purity grade	AR	AR	AR	AR
w[a](mass fraction)	0.999	0.999	0.999	0.999

[a] Uncertainties: $u(w) = 0.001$.