Liquid−liquid equilibria for the ternary system containing 1-Butanol + methoxy(methoxymethoxy)methane + water at temperatures of 303.15, 323.15 and 343.15 K

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ABSTRACT

Liquid−liquid equilibria data for the ternary mixture of 1-Butanol + methoxy(methoxymethoxy) methane + water were measured at atmospheric pressure and temperatures of 303.15, 323.15 and 343.15 K. The ternary system forms a type II phase diagram with two partially miscible region. The distribution coefficient (K) and separation factor (S) were calculated according to the measured tie-line data. The root-mean-square deviation (RMSD) values of NRTL and UNIQUAC models were below 0.91%, demonstrating the two activity coefficient models were successfully applied to correlate the experimental data of the ternary system.

1. Introduction

Being promising diesel additive, the synthesis of polyoxymethylene methyl butyl ether and methoxy(methoxymethoxy) methane (DMM2) have attracted a great deal of attention due to their extraordinary properties, such as high cetane number and high oxygen content [1,2]. When the additive was blended into diesel fuel, the emission of pollutants PM can be decreased due to the significant increase of the oxidation rate [3,4]. However, the existing of dimethoxymethane (DMM) and raw materials such as 1-Butanol and methanol have a negative effect on the physicochemical properties of the diesel additive [5]. Unfortunately, the research on the separation of these products is paid less attention, which is an important issue to be solved.

At present, our group has investigated the VLE data for 1-Butanol + DMM2 mixture, providing a reference for distillation process [6]. However, considering the close boiling point of DMM2 and 1-Butanol, the extraction is a possible technique to separate the mixture especially when trace amounts of 1-Butanol exists. When 1-Butanol and formaldehyde are used as reactants, water exists as a by-product in the synthesis process. It is worthy to investigate the

feasibility of water as a solvent to extract DMM2 from the mixture with 1-Butanol. Therefore, in this work, the LLE data for the ternary mixture of 1-Butanol + DMM2 + water were measured at atmospheric pressure and different temperatures of 303.15, 323.15 and 343.15 K. The distribution coefficient (K) and separation factor (S) are defined as the standard to assess the separation efficiency. The definition equations are given in Part 3.1. They are calculated from the LLE data and used to evaluate the feasibility of water as a solvent. The experimental data were correlated by the Non-Random Two Liquids (NRTL) [7] and Universal Quasi-Chemical (UNIQUAC) [8] activity coefficient models and the binary interaction parameters of the two models were simultaneously obtained.

2. Experimental

2.1. Materials

The chemicals used were 1-Butanol, DMM2 (molecular structure is shown in Fig. 1) and water. The details about the chemicals are presented in Table 1. 1-Butanol is purchased from Sinopharm Chemical Reagent. DMM2 was synthesized from formaldehyde and methanol over acid catalyst [3] and purified by distillation. Deionized water was prepared in our laboratory. All these materials were tested by gas chromatography and no appreciable peaks of

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List of symbols

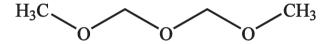|	
a, b	interaction parameters
K	the distribution coefficient
M	number of tie lines
n_D	refractive index
OF	objective function
q	area parameter in UNIQUAC equation or randomly varying quantity described by a probability distribution
$\bar{q}$	arithmetic mean of n independent repeated observations q_k of randomly-varying quantity q
q_k	kth independent repeated observation of randomly-varying quantity q
r	volume parameter in UNIQUAC equation
RMSD	root mean square deviation
$s(\bar{q})$	experimental standard deviation of the mean q, equal to the positive square root of $s^2(\bar{q})$
$s(q_k)$	experimental standard deviation, equal to the positive square root of $s^2(q_k)$
$s(\bar{X}_i)$	experimental standard deviation of input mean X_i, equal to the positive square root of $s^2(\bar{X}_i)$
S	the separation factor
$u(x_i)$	standard uncertainty of input estimate xi that estimates input quantity X_i
x_i	mass fraction composition of liquid phase or estimate of input quantity X_i
X_i	i th input quantity on which the measure and depends
$\bar{X}_i$	estimate of the value of input quantity X_i
$X_{i,k}$	kth independent repeated observation of X_i

Greek letter

α	non-randomness factor in NRTL equation
ρ	density

Superscripts

^	calculated

Subscript

i, j	component identification1, 2, 3
k	number of the tie line

Fig. 1. The molecular structure of methoxy(methoxymethoxy)methane.

Table 1
Materials description.

Component	CAS	Source	GC purity (mass%)	Purification method
1-Butanol	71-63-3	Sinopharm	99.85	None
DMM2	628-90-0	Homemade	99.98	Dehydration by K_2CO_3
Water	7732-18-5	Homemade	99.99	None

impurities were found.

Furthermore, the density (ρ) and refractive index (n_D) of pure components were measured at 298.15 K by the pycnometer method and an Abbe refractometer. The experimental values of these properties are listed in Table 2 as well as those given in the literature [9–11]. It can be seen that the measured density and refractive index were essentially consistent with literature ones. Besides, structural parameters r and q of pure components for the UNIQUAC model [10] are also given in Table 2.

Table 2
The density (ρ)[a], refractive index (n_D)[a] and UNIQUAC parameters of pure components at atmosphere pressure[a].

Component	ρ (298.15 K) (g/cm³)		n_D (298.15 K)		r	q
	Exp.	Lit.	Exp.	Lit.		
1-Butanol	0.8052	0.8058 [9]	1.3967	1.3971 [9]	3.45 [10]	3.05 [10]
DMM2	0.9578	0.960 [11]	1.3789	1.3970 [11]	3.88[b]	3.50[b]
Water	0.9970	0.9971 [9]	1.3325	1.3325 [9]	0.92 [10]	1.40 [10]

[a] Standard uncertainties u are u(ρ) = 0.0001 g/cm3, u(nD) = 0.0001, u(p) = 0.3 kPa.
[b] obtained from Property Estimation by Aspen plus 7.2 software.

2.2. Apparatus and procedure

LLE data for the studied ternary system were measured at 303.15, 323.15 and 343.15 K under atmospheric pressure. The set of experimental equipment was schematically shown in Fig. 2. The 100 mL glass equilibrium still, whose temperature was controlled by a thermostatic bath with an accuracy of 0.01 K, was employed for each measurement. The contrast tests have been carried out at different agitation and settling time, which indicated the equilibria could be attained in 1 h. So, this mixture was agitated vigorously for at least 1 h and left to settle for 1 h to reach phase equilibrium. Then the mixture separated into two clear liquid phases with a well-defined interface. The evaporated compounds were completely condensed by the condenser.

When the liquid−liquid equilibria was formed, the samples were taken from the two liquid phases by syringes and then analyzed by Agilent GC6820 gas chromatograph. The type of chromatographic column is Porapak N produced by Hangzhou Kexiao Chemical Instrument Company. The carrier gas was hydrogen with a flow rate of 60 mL/min. The temperature of injector and detector was 433.15 K. The oven was operated at a programmed temperature that ranged from 413.15 to 473.15 K. The area normalization method was used to obtain quantitative results in the analysis. Each sample was analyzed at least three times and the average values were used as the sample compositions. The liquid phase compositions were obtained with a standard uncertainty of 0.001. A series of LLE data were obtained by changing the