



Liquid–liquid equilibrium data for (n-hexane + ethyl acetate + acetonitrile) ternary system at (298.15, 308.15, and 318.15) K



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ABSTRACT

Liquid–liquid equilibrium (LLE) data for ternary system (n-hexane + ethyl acetate + acetonitrile) have been measured at 298.15, 308.15 and 318.15 K under atmosphere pressure. NRTL and UNIQUAC models were used to correlate the LLE data and their model parameters were obtained. The fitting root-mean-square deviations (RMSD) of NRTL and UNIQUAC models were both below 0.17%, which demonstrated the successful correlations for the ternary LLE experimental data. Moreover, NRTL model gave slightly better predict results than UNIQUAC. Simultaneously, distribution coefficient (K) and separation factor (S) were calculated from the LLE data. Results showed that the extraction of ethyl acetate from n-hexane with acetonitrile as solvent was feasible.

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1. Introduction

Since Tu Youyou won the Nobel Prize in medicine for the year 2015 in terms of her extracting successfully artemisinin from *Artemisia annua* with ethyl ether, the method of using solvent to extract effective drug from plants attracted people's attention. Besides ethyl ether, n-hexane and ethyl acetate are also usually used to achieve this aim, such as extracting d-limonene from polygodium [1], extracting phenolic compound from *rhodiola rosea* [2] etc. After effective drugs, i.e. d-limonene or phenolic compound, were separated from the extraction solution, the rest discard solution was mainly composed of n-hexane and ethyl acetate. Thus it is essential to separate n-hexane and ethyl acetate mixture for recycling.

N-hexane and ethyl acetate form azeotrope at atmospheric pressure and cannot be separated by ordinary distillation. Some methods have been presented to separate n-hexane-ethyl acetate system. Batch azeotropic distillation was used to separate n-hexane-ethyl acetate system with acetone [3,4] or acetonitrile [5] as

light entrainer. Extractive distillation has been used to separate n-hexane-ethyl acetate system with N-methyl-2-pyrrolidone (NMP) [6] or N, N-dimethylformamide (DMF) [7] as heavy entrainer. Furthermore, solvent extraction is a desirable separation method due to its smaller energy consumption and is used to separate n-hexane-ethyl acetate system with acetonitrile as candidate solvent in our project.

Solvent selection and subsequent process design of solvent extraction need liquid–liquid equilibrium (LLE) data between solvents and material compositions. For the measurement of LLE data for related components, H. Sugi and T. KATAYAMA have measured ternary liquid–liquid equilibria data for n-hexane-ethanol-acetonitrile at 40 °C and water-acetonitrile-ethyl acetate at 60 °C [8].

In this paper, isothermal ternary LLE data for n-hexane-ethyl acetate-acetonitrile system have been measured at (298.15, 308.15 and 318.15) K under atmosphere pressure. The thermodynamic models of NRTL (non-random two liquid) [9] and UNIQUAC (universal quasi-chemical) [10] were then used to correlate the LLE data with Aspen Plus physical parameter regression system. Distribution coefficient (K) and separation factor (S) were finally calculated to evaluate the availability of acetonitrile as solvent to extract ethyl acetate from n-hexane.

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2. Experimental

2.1. Materials

The analytical grade chemicals n-hexane, ethyl acetate and acetonitrile were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. For all reagents, the purities checked by gas chromatograph were listed Table 1. All reagents were used directly in the experiment without further purification. The densities and refractive index for all reagents were also measured by a digital vibrating-tube densimeter (DMA 4500, Anton Paar, Austria) at 298.15 K with an uncertainty of $\pm 0.00005 \text{ g cm}^{-3}$ and a full automatic refract-meter (Hanon A610, Hanon Instrument, China) with an uncertainty of ± 0.0001 , respectively. The densities and refractive index were also listed in Table 1 and compared with the literature values [11–13], with the good agreement in general.

2.2. Apparatus and procedures

The measurement methods and procedures of LLE experiments data were similar to those described in the literature [14–16]. Firstly, a 100 mL glass container was filled up by the mixtures of known overall composition as much as possible to avoid perhaps appearance of additional vapor phase. Then the glass container was stirred intensely by ultrasonic at least 1 h to make the sample mix completely and was sealed with a glass tap. The glass container was then placed in a cryogenic thermostatic (THD-2006, Ningbo Tianheng Instrument Factory, China) at constant temperatures under atmospheric pressure. The maximum temperature fluctuations were within 0.05 K. After almost 20 h, syringes were used to take the samples from both phases. To cover the entire two-phase region as far as possible, the volume for one component was usually fixed and those for the other two were altered with one increased and the other decreased. The change step of volume for each component was 7–8 mL each time.

With a gas chromatograph (GC-2010 Plus from Shimadzu Co. Ltd., Japan) with a flame ionization detector (FID), all samples for the equilibrium phases were analyzed. The GC column is a Rtx-5 low polarity capillary column (30 m \times 0.25 mm \times 0.25 μm , Restek Corporation, USA). The carrier gas is nitrogen with a purity of 99.999%, with a flowrate of 30 $\text{cm}^3 \text{ min}^{-1}$ and a pressure of 0.3 MPa. For each sample, the response of gas chromatography analysis was calibrated with several standard mixtures of known composition prepared gravimetrically over the entire composition range. The final composition was determined from the average of three replications. The uncertainty of the equilibrium mixture composition is estimated to within ± 0.001 in mole fraction.

2.3. Uncertainty measurement

For each variable determined experimentally, including density

(ρ), refractive index (n_D), temperature (T), composition (x) and pressure (p), their uncertainties were determined according to the JCGM guidance document [17] and were shown in the respective table footnote.

3. Results and discussion

3.1. LLE experimental data

The ternary LLE tie-line data at (298.15, 308.15, 318.15) K were listed in Table 2 shown as mole fraction, and triangle phase diagrams were plotted and shown in Fig. 1 separately. According to Treybal [18], these are Type I ternary diagrams. In other words, n-hexane-acetonitrile system is partial miscible, while n-hexane-ethyl acetate and ethyl acetate-acetonitrile systems both are completely miscible with each other in the temperature range investigated. The immiscible area in the triangle diagrams decrease with the temperature rising from 298.15 K to 318.15 K. The positive slope of tie-line in triangle phase graph manifests the positive

Table 2

The experimental tie-line data (mole fraction) for n-hexane (1) + ethyl acetate (2) + acetonitrile (3) at T=(298.15, 308.15 and 318.15) K under atmospheric pressure.^a

Feed		n-hexane rich phase (I)		Acetonitrile rich phase (II)		K ₁	K ₂	S
x ₁	x ₂	x ₁	x ₂	x ₁	x ₂			
298.15 K								
0.4708	0.0491	0.8601	0.0298	0.0798	0.0703	0.0928	2.359	25.43
0.4143	0.0992	0.8202	0.0696	0.1103	0.1295	0.1345	1.861	13.84
0.3797	0.1525	0.7611	0.1191	0.1305	0.1894	0.1715	1.590	9.27
0.3718	0.1842	0.7213	0.1488	0.1507	0.2189	0.2089	1.471	7.04
0.3407	0.2253	0.6614	0.1888	0.1908	0.2594	0.2885	1.374	4.76
0.3250	0.2617	0.6004	0.2291	0.2310	0.2887	0.3847	1.260	3.28
0.3055	0.2905	0.5313	0.2584	0.2724	0.3187	0.5127	1.233	2.41
0.2941	0.3103	0.4722	0.2877	0.3316	0.3189	0.7022	1.108	1.58
308.15 K								
0.4958	0.0355	0.8601	0.0295	0.0904	0.0395	0.1051	1.339	12.74
0.4606	0.0690	0.8410	0.0488	0.0996	0.0901	0.1184	1.846	15.59
0.4205	0.1128	0.7900	0.0898	0.1198	0.1396	0.1516	1.555	10.25
0.3923	0.1584	0.7305	0.1293	0.1498	0.1899	0.2051	1.469	7.16
0.3675	0.1948	0.6806	0.1591	0.1818	0.2288	0.2671	1.438	5.38
0.3416	0.2312	0.6215	0.1999	0.2224	0.2589	0.3578	1.295	3.62
0.3169	0.2647	0.5404	0.2389	0.2703	0.2895	0.5002	1.212	2.42
0.3006	0.2813	0.4914	0.2685	0.3207	0.2989	0.6526	1.113	1.71
318.15 K								
0.5065	0.0403	0.8498	0.0301	0.0999	0.0499	0.1176	1.658	14.10
0.4676	0.0811	0.8108	0.0594	0.1212	0.0989	0.1495	1.665	11.14
0.4448	0.1267	0.7607	0.0991	0.1406	0.1493	0.1848	1.507	8.15
0.3993	0.1572	0.7115	0.1288	0.1701	0.1797	0.2391	1.395	5.84
0.3789	0.1904	0.6607	0.1598	0.1907	0.2194	0.2886	1.373	4.76
0.3550	0.2223	0.6012	0.1989	0.2307	0.2492	0.3837	1.253	3.27
0.3392	0.2437	0.5616	0.2195	0.2601	0.2698	0.4631	1.229	2.65
0.3215	0.2632	0.4926	0.2488	0.3210	0.2791	0.6516	1.122	1.72

^a Standard uncertainties u are $u(x) = 0.0010$, $u(T) = 0.05 \text{ K}$.

Table 1

Experimental and literature values of density ρ and refractive index n_D , van der Waals molecular structural parameters of pure component for UNIQUAC, and mass fraction purity w.

Chemical name	$\rho^{a,b}/(\text{g cm}^{-3})$		$n_D^{a,b}$		r^c	q^c	w^d
	Experimental	Literature	Experimental	Literature	Volume	Surface area	Mass fraction purity
n-hexane	0.65512	0.65507 [11]	1.3725	1.3720 [11]	4.4998	3.8560	0.9974
Ethyl acetate	0.89461	0.89460 [12]	1.3701	1.3699 [12]	3.4786	3.1160	0.9982
Acetonitrile	0.77655	0.77664 [13]	1.3413	1.3411 [13]	1.8701	1.7240	0.9978

^a The experimental values of density and refractive index are reported at 298.15 K and atmospheric pressure.

^b Standard uncertainties: $u(\rho) = \pm 0.00007 \text{ g cm}^{-3}$; $u(n_D) = \pm 0.0001$ and $u(p) = \pm 0.3 \text{ kPa}$, all with 0.95 level of confidence.

^c Taken from Aspen property databank.

^d Determined by Gas Chromatography.

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