Vapor-Liquid Equilibria for the Ternary System Acetonitrile + 1-Propanol + Dimethyl Sulfoxide and the Corresponding Binary Systems at 101.3 kPa

Quan-Yi Wang, Hong Zeng, Hang Song, Qi-Song Liu, and Shun Yao*

School of Chemical Engineering, Sichuan University, Chengdu 610065, China

Isobaric vapor-liquid equilibrium (VLE) data were measured at 101.3 kPa by using an improved Rose equilibrium still for three binary systems, acetonitrile (1) + 1-propanol (2), acetonitrile (1) + dimethyl sulfoxide (DMSO) (3), and 1-propanol (2) + DMSO (3), and for one ternary system, acetonitrile (1) + 1-propanol (2) + DMSO (3). The VLE data of the binary systems were examined by thermodynamic consistency tests and satisfactorily correlated by Wilson and NRTL models. The parameters of two models obtained from the binary data were used to predict the ternary VLE data. The prediction yielded reasonable results for the ternary system.

Introduction

Acetonitrile and 1-propanol have been used extensively as solvents or as important fine chemicals in the chemical and pharmaceutical production process^{1,2} as well as in chromatography separation.^{3,4} A large volume of acetonitrile and 1-propanol solution is generated continuously in the relative processes. A suitable and efficient method to recover the acetonitrile and 1-propanol is necessary. Separation of them with a conventional distillation process is very difficult due to the azeotropic system.⁵ Extractive distillation is a preferable way to improve the separation of azeotropic systems and approximate boiling point systems^{6,7} and was successfully used in the recovery of alcohol and 1,3-butadiene in related industries.^{8,9}

Dimethyl sulfoxide (DMSO), as the third component, was employed as the extractive solvent in the distillation to improve the separation of acetonitrile and 1-propanol in this work. To simulate and design the separation process, it is essential to determine the vapor-liquid equilibrium (VLE) data for the binary and ternary systems and to study their correlating models. The VLE data of the binary system acetonitrile (1) + 1-propanol (2) at atmospheric pressure were reported by Prasad et al.⁵ However, the VLE data for the binary systems acetonitrile (1) + DMSO (3) and 1-propanol (2) + DMSO (3) and the ternary system acetonitrile (1) + 1-propanol (2) + DMSO (3) at 101.3 kPa have not been available up to now.

This work was carried out to provide fundamental data for the separation of acetonitrile and 1-propanol by extractive distillation using DMSO as extractant. The isobaric VLE data for the binary and ternary systems at 101.3 kPa were measured in this work. Moreover, the VLE correlation for the binary systems and the prediction for the ternary with the Wilson and NRTL models were studied and discussed.

Experimental Section

Materials. Acetonitrile, 1-propanol, and DMSO (analytical grade, 99 % mass) were obtained commercially and were purified by redistillation. The purities of the reagents were checked by measuring their physical properties and further

* To whom correspondence should be addressed. E-mail: cusack@ scu.edu.cn.

confirmed by gas chromatography with more than 99.5 % mass. Good agreement of the properties was found between the measured values and literature ones as shown in Table 1. Refractive indices were measured by a WZS-I Abbe refractometer (Shanghai Optical Instruments Factory, China), with an uncertainty of \pm 0.0001. Densities were measured by a DMA-4100 densimeter (AntonPaar GmbH, Germany), with an uncertainty of \pm 0.0001 g·cm⁻³. Boiling temperatures were measured using a mercury-in-glass thermometer accurate to \pm 0.01 K.

Apparatus and Procedure. The modified Rose-type still and auxiliary equipment, the same as in the previous work,¹¹ were employed to measure isobaric VLE data at 101.3 kPa, and the favorable performance of the apparatus was verified in the previous measurement.

The experiments were accomplished under a dried inert atmosphere at a constant pressure of 101.3 kPa. The pressure was automatically adjusted to the desired value by an electric contact pressure adjuster (DYT01, Yangzhong Mechanical Instrument Factory, China) with an uncertainty of ± 1 mmHg. The inert air in the isobaric bottle would be heated to maintain the pressure adjuster. The liquid phase was kept boiling until the system reached constant temperature and pressure for 15 min or longer to ensure completed VLE. The temperature was recorded by a mercury-in-glass thermometer with an uncertainty of ± 0.01 K, and about 1.5 mL of the vapor and liquid samples was taken simultaneously with two syringes from the liquid outlet and the condensate outlet.

Sample Analysis. The equilibrium compositions of the liquid and vapor phases were analyzed by a gas chromatograph GC7890II with a flame ionization detector (FID), a capillary column (30 m by 0.25 mm i.d.) of the AT.FFAP stationary phase, and a chromatographic workstation N2000. High purity nitrogen was used as the carrier gas at a constant flow rate of 50 mL·min⁻¹. The injector, detectors, and oven temperature were kept at (483.15, 493.15, and 473.15) K, respectively. The gas chromatograph was calibrated with a set of mixtures of known compositions that were prepared gravimetrically by an electronic balance (uncertainty of \pm 0.0001 g). The reproducibility of concentration measurement was better than \pm 0.0003

Table 1. Thysical Tropernes of Tare Reagen	Table 1	. Physic	al Propertie	es of Pure	Reagen
--	---------	----------	--------------	------------	--------

		n _D		$\rho/g \cdot cm^{-3}$	$T_{\rm b}/{ m K}$		
substance	exptl	lit. ¹⁰	exptl	lit. ¹⁰	exptl	lit. ¹⁰	
acetonitrile	1.3449	1.3441 (293.15 K)	0.7831	0.7822 (293.15 K)	354.65	354.60	
1-propanol	1.3860	1.3856 (293.15 K)	0.8040	0.8036 (293.15 K)	370.24	370.20	
DMSO	1.4775	1.4773 (298.15 K)	1.0961	1.0958 (298.15 K)	462.06	462.15	

Table 2. Antoine Coefficients A, B, and C

		А	Antoine constants					
components	T range/K	A_i	B_i	C_i				
acetonitrile ^{12,a} 1-propanol ^{13,a} 1-propanol ^{14,a} 1-propanol ^{15,a} DMSO ^{16,b}	354 to 462 303 to 369 369 to 402 402 to 463 356 to 462	15.2851 ^c 16.0353 16.01787 14.6132 ^d 6.66676	3652.381 ^c 3415.56 3415.557 2587.343 ^d 1952.13	12.292 ^c 70.733 70.657 111.913 ^d 45.35				

^{*a*} ln(P_i^s) = $A_i - B_i/(T - C_i)$. Units: P_i^s/kPa , T/K. ^{*b*} log(P_i^s) = $A_i - B_i/(T - C_i)$. Units: P_i^{ss}/kPa , T/K. ^{*c*} Calculated from the vapor pressure in ref 12. ^{*d*} Calculated from the vapor pressure in ref 15.

Table 3. Intrinsic Properties of the Pure Liquids

	P _c	T _c	Vc		
compound	kPa	Κ	cm ³ •mol	ω	$Z_{\rm RA}$
acetonitrile 1-propanol	4830 ^a 5180 ^a	548.0 ^a 536.8 ^a	173.0 ^{<i>a</i>} 219.0 ^{<i>a</i>}	0.3270^{a} 0.6290^{a}	0.184^{a} 0.254^{a}
DMSO	5845 ^a	707.0 ^a	276.1 ^{<i>a</i>}	0.3627^{b}	0.274 ^{<i>a</i>}

^{*a*} Ref 19. ^{*b*} Calculated from our experimental data with the Lee-Kesler equation.¹⁹

mass fractions, and the maximum uncertainty for the measurements was \pm 0.0002.

Results and Discussion

Fundamental Equation. The activity coefficient γ_i of the component *i* in the mixtures was calculated from the following equation

$$\phi_i^{\rm v} y_i P = \gamma_i x_i \phi_i^{\rm s} P_i^{\rm s} \exp\left(\frac{\nu_i^{\rm L} (P - P_i^{\rm s})}{RT}\right) \tag{1}$$

where x_i and y_i are the mole fractions of the liquid and vapor phases in equilibrium, respectively; ϕ_i^{v} is the fugacity coefficient of vapor component *i*; ϕ_i^s is the fugacity coefficient of component *i* at saturation; R is the universal gas constant; T is the experimental temperature; P is total pressure of the system, 101.3 kPa, in this study; and P_i^s is the vapor pressure for the pure component calculated by an Antoine equation. The Antoine equation and its constants $(A_i, B_i, and C_i)$ are listed in Table 2, and the molar liquid volumes, $v_i^{\rm L}$, of pure compounds were estimated using the modified Rackett equation.¹⁷ The fugacity coefficients were calculated by using the virial equation of state truncated after the second term. The second virial coefficients were obtained from the Tsonopoulos¹⁸ empirical equation. All the required parameters are listed in Table 3. In this way, the liquid-phase activity coefficients can be calculated by experimental results through eq 1 as given in Table 4.

Experimental Data. Experimental VLE data of the binary systems acetonitrile + 1-propanol, acetonitrile + DMSO, and 1-propanol + DMSO and the ternary system acetonitrile + 1-propanol + DMSO were measured at 101.3 kPa. The results are listed in Tables 4 and 6. The comparison between the measured VLE data of acetonitrile + 1-propanol with the literature⁵ is shown in Figure 1, with good agreement. The figure also suggests that the binary system acetonitrile and 1-propanol is an azeotropic

system with minimum azeotropic temperature (352.92 K), and the mole fractions of the liquid and vapor phases of azeotrope are 0.7792 and 0.7739, respectively. The unequal mole fractions in the two phases may be caused by experimental error.

The experimental binary VLE data were found to be thermodynamically consistent by means of the point-to-point test of Van Ness,²⁰ modified by Fredenslund et al.²¹ A Legendre polynomial was used for the excess Gibbs energy. According to this method, isobaric data would pass the consistency test if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, δy , was less than 0.01. The parameters of the Legendre polynomial and results of the tests for the binary systems are listed in Table 5. Each δy_1 of the three binary systems is less than 0.01. Therefore, all binary VLE data of this work could pass the thermodynamic consistency test.

Calculation of Binary Vapor–Liquid Equilibrium. The activity coefficients were correlated with the Wilson²² and NRTL²³ models in this work. The parameters of these models are given in Table 7, which were obtained by minimizing the following objective function (OF)



Figure 1. VLE relation for acetonitrile (1) + 1-propanol (2) at 101.3 kPa: \blacksquare , this work; \bigcirc , the literature data.⁵



Figure 2. Equilibrium diagram for the system acetonitrile (1) + 1-propanol (2) at 101.3 kPa: \blacksquare , experimental data; -, calculation based on the Wilson model; - -, calculation based on the NRTL model.

Table 4. Experimental VLE Data and Correlated Results of Binary Systems at 101.3 kPa

_

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$							ca	lculated by W	ilson	ca	lculated by N	RTL
Accelorative (1) 1+Proposed (2) 1 361.19 0.1121 0.2100 2.3324 1.0883 0.73 0.0078 0.038 0.038 0.0025 0.0143 3 359.00 0.2398 0.527 1.8571 1.0445 0.57 0.0052 0.0111 0.0021 0.0131 0.88 0.0041 0.0023 5 356.44 0.3486 0.0447 1.4009 1.0333 0.0131 0.0114 0.033 0.0031 0.0134 0.0134 0.0134 0.0134 0.0134 0.0134 0.0134 0.0134 0.0134 0.0178 0.353.46 0.5707 0.6629 1.3173 1.3166 0.176 0.0061 0.0010 0.0121 0.0016 0.0001 0.0131 0.0036 0.0016 0.0016 0.0016 0.0016 0.0016 0.0016 0.0016 0.0016 0.0016 0.0016 0.0016 0.0016 0.0164 0.0016 0.0176 0.0662 0.0164 0.0165 0.0178 0.0354 0.0164 0.01	no.	T/K	x_1	y_1	γ_1	γ_2	ΔT^a	$\Delta y_1^{\ b}$	Δy_2^b	ΔT^a	$\Delta y_1^{\ b}$	$\Delta y_2^{\ b}$
1 361.38 0.1121 0.3210 2.3342 1.0683 0.22 0.0038 0.038 0.0032 0.0034 3 390.05 0.2586 0.4712 1.9748 1.0269 0.57 0.0014 0.0105 0.441 0.0105 0.401 0.0023 0.0114 4 355.55 0.4115 0.627 1.3517 1.10475 0.161 0.0022 0.0024 0.0024 0.0024 0.0024 0.0024 0.0037 7 354.75 0.4615 0.0522 1.0031 0.0114 0.0404 0.0031 0.0114 0.0402 0.0071 12 352.42 0.6490 0.7722 1.1131 1.6723 0.114 0.0011 0.0001 0.0001 0.0001 0.0001 0.0001 0.0001 0.0001 0.0001 0.0001 0.0001 0.0001 0.0001 0.0001 0.0001 0.0114 0.0114 0.0114 0.0114 0.0114 0.0114 0.0114 0.0114 0.0114 0.0114 0.0114					Ac	etonitrile (1) +	- 1-Propano	l (2)				
2 360.19 0.1519 0.3716 2.1780 1.0518 0.22 0.00643 0.0163 0.436 0.0025 0.0151 4 358.30 0.2339 0.577 1.8571 1.0743 0.0371 0.0031 0.0041 0.0021 0.0021 5 355.56 0.4115 0.6337 1.4733 1.1377 0.466 0.0034 0.0004 0.0014 0.0034 8 354.15 0.6423 1.4733 1.1376 0.0166 0.0004 0.0014 0.0034 0.0004 0.0014 0.0034 0.0004 0.0014 0.0031 0.00331 0.0031 0.0031 <	1	361.38	0.1121	0.3210	2.3342	1.0683	0.73	0.0078	0.0358	0.88	0.0032	0.0348
3 359.06 0.2486 0.4712 1.9748 1.0264 0.30 0.0415 0.438 0.0414 0.0153 4 358.56 0.3158 0.315 0.315 0.315 0.036 0.030 0.037 0.033 0.037 9 353.68 0.5707 0.642 1.138 0.041 0.040 0.0064 0.011 0.0065 0.0011 0.033 0.037 0.033 0.037 0.033 0.036 0.0364 0.0118 0.021 0.066 0.0015 0.035 0.035 0.035 0.035 0.035 0.035 0.035 0.035 0.035 0.035 0.035 0.	2	360.19	0.1519	0.3916	2.1780	1.0518	0.22	0.0060	0.0163	0.36	0.0025	0.0154
4 338.50 0.25.99 0.247 1.3071 1.0045 0.87 0.0012 0.0311 0.88 0.00141 0.0121 6 335.64 0.3471 1.0301 1.0378 0.241 0.0121 0.038 0.003 0.0034 0.0031 0.0031 0.0035 0.0001 0.0035 0.0010 0.0035 0.0010 0.0035 0.0010 0.0034 0.0044 0.0040 0.0035 0.0010 0.0044 0.0046 0.0035 0.0010 0.0044 0.0035 0.0010 0.0044 0.0035 0.0016 0.0044 0.00	3	359.06	0.2086	0.4712	1.9748	1.0260	0.50	0.0044	0.0105	0.40	0.0025	0.0115
2 336.4 0.2173 0.232 0.0012 0.0038 0.034 0.0142 0.0242 7 354.75 0.4561 0.4541 1.333 1.225 0.356 0.0011 0.0014 0.0034 0.0017 8 354.15 0.5132 0.6452 1.3137 1.4150 0.09 0.0014 0.0103 0.0031 0.0031 0.0031 0.0031 0.0037 10 353.46 0.5300 0.7724 1.1103 1.6972 0.18 0.0059 0.0044 0.11 0.0033 0.0019 11 352.92 0.7722 0.7730 1.0442 1.5410 0.0165 0.0188 0.033 0.0114 0.040 0.00053 13 352.92 0.7720 0.7739 1.0498 0.0142 0.153 0.033 0.0118 0.0208 0.0114 0.040 0.0125 0.0155 0.0152 0.0226 0.037 0.0105 0.0152 0.0226 0.037 0.0105 0.0125 0.028 0.0114	4	358.30	0.2539	0.527	1.8571	1.0045	0.87	0.0032	0.0311	0.80	0.0041	0.0321
7 332.73 0.1461 0.0624 1.2380 1.2218 0.38 0.0034 0.0044 0.00744 0.00744 8 354.15 0.4132 0.6629 1.1377 1.3056 0.017 0.0044 0.0034 0.0034 0.0034 0.0049 0.0114 0.023 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0035 0.0001 0.0010 0.0010 0.0010 0.0019 0.0024 0.0114 0.025 0.0135 0.033 0.0106 0.0125 13 31.31 0.0324 0.0310 0.03285 3.4671 0.958 0.0184 0.0125 0.018 0.0184 0.0126 0.0168 0.0168 0.0168 0.0168 0.0168 0.0168 0.0168 0.0168 0.0168 0.0168 0.0175 0.0269 0.077 0.0168 0.0175 0.0269 0.0160	5	350.04	0.3498	0.5945	1.6000	1.058/	0.93	0.0015	0.0308	0.88	0.0014	0.0323
8 354.15 0.05132 0.0639 1.3137 1.3556 0.17 0.0044 0.0144 0.0043 0.031 0.00431 0.00431 0.00431 0.00431 0.00431 0.00431 0.00431 0.00431 0.00431 0.00441 0.0161 0.0044 0.0111 0.0035 0.00441 0.0114 0.00464 0.0114 0.00464 0.0114 0.00464 0.0114 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.00461 0.0153 0.00461 0.0154 0.01641 0.01251 0.0154 0.01641 0.01251 0.0154 0.01641 0.0224 0.0184 0.0124 0.0184 0.0124 0.0184 0.0124 0.0184 0.0124 0.0184 0.0124 0.0124 0.0124 0.0233 0.0141 0.0243 0.0141 0.0243 0.0141 0.0243 0.0124 0.0233	7	354.73	0.4115	0.6257	1.4755	1.1337	0.04	0.0022	0.0200	0.39	0.0022	0.0223
9 353.68 0.5707 0.0842 1.2473 1.4150 0.09 0.0016 0.0003 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0031 0.0033 0.0016 0.0016 0.0111 0.0033 0.0018 0.0016 0.0114 0.0033 0.0108 0.0116 13 352.92 0.7792 0.7792 0.7792 0.7792 0.7792 0.7792 0.07976 0.0380 0.0165 0.0153 0.03 0.0184 0.0208 14 352.92 0.9776 0.9398 0.9801 5.0842 0.158 0.0122 0.033 0.0184 0.0226 0.37 0.0184 0.0226 14 352.92 0.9976 0.9398 0.9801 1.0778 0.47 0.0026 0.37 0.0152 0.0262 14 350.90 0.9990 1.0778 0.47 0.0028	8	354.15	0.5132	0.6629	1 3137	1 3056	0.30	0.0034	0.0049	0.11	0.0042	0.0078
10 353.40 0.6300 0.7722 1.1695 0.12 0.0019 0.0021 0.0066 0.0001 0.0016 11 353.22 0.6907 0.7334 1.103 1.6972 0.18 0.0076 0.0044 0.11 0.0036 0.00061 12 353.13 0.7235 0.7779 1.0498 2.0448 0.04 0.0125 0.0114 0.044 0.0066 0.0075 14 352.97 0.8283 0.8014 1.0211 2.2934 0.041 0.0185 0.033 0.0164 0.0165 15 353.18 0.8451 0.9901 5.0482 0.15 0.0184 0.0254 0.18 0.0184 0.0254 0.18 0.0190 0.224 0.0269 0.242 0.0003 0.0190 0.241 0.0003 0.0213 0.0437 0.70 0.0003 0.0213 0.0433 0.0114 0.043 0.0213 0.0424 0.0044 0.0138 0.0144 0.0053 0.0224 0.0044 0.0138 <t< td=""><td>9</td><td>353.68</td><td>0.5707</td><td>0.6842</td><td>1.2373</td><td>1.4150</td><td>0.09</td><td>0.0016</td><td>0.0003</td><td>0.03</td><td>0.0031</td><td>0.0037</td></t<>	9	353.68	0.5707	0.6842	1.2373	1.4150	0.09	0.0016	0.0003	0.03	0.0031	0.0037
11 353.22 0.6907 0.7324 1.103 1.6972 0.18 0.0069 0.00462 0.11 0.0035 0.0019 13 352.92 0.7792 0.7792 1.0494 2.0348 0.041 0.0162 0.0114 0.0066 0.0075 14 352.97 0.8283 0.8014 1.0111 2.2394 0.04 0.0125 0.03 0.0184 0.0126 15 353.18 0.8824 0.8399 0.9970 2.6752 0.04 0.0125 0.08 0.0184 0.0268 18 354.22 0.9953 0.6941 1.53838 0.36 0.0125 0.0269 0.37 0.0125 0.0269 2 421.43 0.0003 0.0008 2.0400 1.0778 0.47 0.0098 0.0370 0.0111 0.016 3 409.64 0.0911 0.118 0.0214 0.0014 0.0017 0.111 0.018 4 410.03 0.1215 0.6662 2.0184 1.0	10	353.40	0.6300	0.7072	1.1688	1.5405	0.12	0.0019	0.0021	0.06	0.0001	0.0019
12 353.13 0.7735 0.7740 1.0498 2.0348 0.044 0.0075 0.0075 0.0075 0.0075 0.0075 0.0075 0.0075 0.0114 0.014 0.004 0.0075 14 352.97 0.8283 0.8014 1.0211 2.2934 0.04 0.0125 0.0138 0.03 0.0104 0.0166 15 355.18 0.8384 0.8399 0.99979 2.6752 0.04 0.0125 0.0284 0.0184 0.0124 0.018 0.0124 0.0184 0.0124 0.0182 0.0278 18 354.22 0.9950 0.9656 2.0828 1.0112 0.211 0.0003 0.0192 0.0004 0.0152 0.0224 0.0005 0.00253 2 421.43 0.06050 0.7708 2.0400 1.0778 0.47 0.0098 0.0370 0.70 0.0031 0.0110 0.0015 0.0041 4 400.63 0.2125 0.9391 1.81810 0.944 0.022 <td< td=""><td>11</td><td>353.22</td><td>0.6907</td><td>0.7324</td><td>1.1103</td><td>1.6972</td><td>0.18</td><td>0.0059</td><td>0.0044</td><td>0.11</td><td>0.0036</td><td>0.0001</td></td<>	11	353.22	0.6907	0.7324	1.1103	1.6972	0.18	0.0059	0.0044	0.11	0.0036	0.0001
13 352.92 0.7792 0.7792 0.7792 0.2739 0.044 0.0022 0.01133 0.013 0.013 0.0113 0.0113 0.0113 0.0113 0.0113 0.0113 0.0113 0.0113 0.0113 0.0113 0.0113 0.0114 0.01154 0.01154 0.01154 0.01154 0.01154 0.01154 0.01154 0.01154 0.01154 0.01154 0.01154 0.0120 18 354.22 0.9953 0.9954 0.38383 0.36 0.0152 0.0026 0.0120 0.0120 0.0124 0.0026 0.0055 2 421.43 0.06963 0.7008 2.0480 1.0718 0.0178 0.0170 0.0101 0.0138 0.0043 0.0123 3 409.44 0.0911 0.8156 2.0481 1.0111 0.18 0.0010 0.0018 0.0018 0.0041 0.0038 0.0041 0.0038 0.0041 0.0038 0.0041 0.0038 0.0041 0.0038 0.0041 0.0038 0.0041 <td>12</td> <td>353.13</td> <td>0.7235</td> <td>0.7470</td> <td>1.0842</td> <td>1.8019</td> <td>0.18</td> <td>0.0076</td> <td>0.0062</td> <td>0.11</td> <td>0.0053</td> <td>0.0019</td>	12	353.13	0.7235	0.7470	1.0842	1.8019	0.18	0.0076	0.0062	0.11	0.0053	0.0019
14 352.97 0.8283 0.0014 1.0211 2.2934 0.04 0.0125 0.0138 0.03 0.0108 0.0108 15 353.18 0.8384 0.8390 0.9979 2.6752 0.04 0.0165 0.0184 0.0215 0.0184 0.0128 0.0184 0.0152 0.0184 0.0152 0.0184 0.0152 0.0253 18 354.22 0.9953 0.9656 2.0824 0.18 0.0152 0.0005 0.0052 0.0005 0.00152 2 421.43 0.0603 0.7098 2.0400 1.0778 0.47 0.0098 0.0370 0.044 0.0005 0.0014 4 400.63 0.1215 0.8662 2.0186 1.0379 0.073 0.0188 0.71 0.0111 0.0014 0.0004 0.0114 0.0014 0.0004 0.0114 0.0014 0.0014 0.0014 0.0014 0.0014 0.0014 0.0014 0.0014 0.0014 0.0014 0.0014 0.0014 0.0014	13	352.92	0.7792	0.7739	1.0498	2.0348	0.04	0.0082	0.0114	0.04	0.0060	0.0075
15 353.18 0.8824 0.8990 0.9979 2.6752 0.04 0.0165 0.0165 0.0181 0.01154 0.01081 17 354.07 0.9776 0.9998 0.9841 5.0842 0.15 0.0194 0.0225 0.018 0.0194 0.0226 0.37 0.0152 0.0269 0.37 0.0152 0.0269 0.37 0.0152 0.0269 0.37 0.0152 0.0269 0.37 0.0152 0.0269 0.0055 0.0055 0.0269 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0055 0.0041 0.0016 0.0041 0.0018 0.0041 0.0018 0.0041 0.0018 0.0041 0.0018 0.0042 0.0035 0.0042 0.0042 0.0042 0.0042 0.0042 0.0035 0.0041 0.0032 0.228 0.0040 0.0077 0.40 0.0041 0.0035 0.0011 0.0018	14	352.97	0.8283	0.8014	1.0211	2.2934	0.04	0.0125	0.0153	0.03	0.0108	0.0120
16 353.69 0.9451 0.9010 0.9886 3.4671 0.98 0.0184 0.0215 0.08 0.0181 0.0208 18 354.22 0.9953 0.9654 0.9843 15.8823 0.36 0.0152 0.0254 0.0152 0.0254 0.0152 0.0254 2 421.43 0.0603 0.0190 0.24 0.0005 0.0005 2 421.43 0.0603 0.0295 0.5056 2.0828 1.0112 0.21 0.0003 0.0190 0.24 0.0005 0.0015 2 421.43 0.0603 0.1215 0.8662 2.0400 1.0778 0.0730 0.0180 0.0111 0.0163 4 400.64 0.0911 0.8156 2.0481 1.0111 0.18 0.00136 0.20 0.005 0.0055 0.0111 0.0118 0.01018 0.0014 0.0079 0.082 0.28 0.0044 0.0035 389 372.81 0.3314 0.9755 1.7380 0.9704	15	353.18	0.8824	0.8399	0.9979	2.6752	0.04	0.0165	0.0188	0.03	0.0154	0.0166
17 354.07 0.97/6 0.9398 0.9841 3.0842 0.15 0.0134 0.0124 0.0184 0.01254 Acctoninte(1)+ DMSO (3) Calconinte(1)+ DMSO (3)	16	353.69	0.9451	0.9010	0.9836	3.4671	0.98	0.0184	0.0215	0.08	0.0181	0.0208
18 534.22 0.9935 0.9934 0.9835 0.536 0.0152 0.0129 0.0152 0.0125 1 439.01 0.0295 0.5056 2.0828 1.0112 0.21 0.0003 0.0190 0.24 0.0005 0.0025 2 421.43 0.0610 0.7008 2.0400 1.0778 0.47 0.0098 0.0370 0.0113 0.0015 4 400.63 0.1215 0.366 2.0481 1.0111 0.18 0.0035 0.0118 0.0113 0.0016 6 364.55 0.2123 0.3398 1.8810 0.9484 0.22 0.0009 0.0081 0.010 0.0005 6 364.56 0.2123 0.331 1.8810 0.9484 0.26 0.00029 0.0082 0.28 0.0044 0.0033 9 372.81 0.3314 0.9675 1.7580 0.9704 0.17 0.0014 0.0077 0.40 0.0028 0.28 0.0060 0.0115 0.0028 <t< td=""><td>17</td><td>354.07</td><td>0.9776</td><td>0.9398</td><td>0.9801</td><td>5.0842</td><td>0.15</td><td>0.0194</td><td>0.0254</td><td>0.18</td><td>0.0194</td><td>0.0253</td></t<>	17	354.07	0.9776	0.9398	0.9801	5.0842	0.15	0.0194	0.0254	0.18	0.0194	0.0253
Acteminite (1) + DMSO (3) 1 439.01 0.0295 0.5055 2.0828 1.0112 0.0003 0.0170 0.0043 0.0015 2 421.43 0.0663 0.7008 2.0400 1.0778 0.47 0.0003 0.0170 0.0138 0.0111 0.0163 4 400.63 0.1215 0.8662 2.0186 1.0379 0.37 0.0053 0.010 0.0004 0.0138 0.21 0.0035 0.0005 0.0005 6 384.56 0.2123 0.9398 1.8148 0.9594 0.26 0.0009 0.0088 0.010 0.0018 0.010 0.0018 0.0042 0.0035 9 372.81 0.3314 0.9675 1.7080 0.020 0.0024 0.0079 0.39 0.0084 0.0038 10 370.01 0.3727 0.9772 1.6520 0.9960 0.0024 0.0075 0.28 0.0065 0.0012 11 367.53 0.4237 0.9764 1.5758	18	354.22	0.9953	0.9654	0.9843	13.8383	0.36	0.0152	0.0269	0.37	0.0152	0.0269
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		120.01	0.0005	0.505.5	A	cetonitrile (1)	+ DMSO ((3)	0.0100		0.0007	0.0055
2 421.43 0.0603 0.7008 2.0440 1.0718 0.0478 0.01370 0.70 0.0043 0.01171 4 400.63 0.1215 0.8662 2.0186 1.0379 0.37 0.0053 0.0118 0.71 0.0138 0.71 0.0138 0.0045 5 384.56 0.2123 0.9398 1.8148 0.9484 0.22 0.0009 0.0081 0.10 0.0018 0.0044 0.0035 7 379.48 0.2536 0.9531 1.8148 0.9570 0.18 0.0010 0.0079 0.28 0.0042 0.0035 9 372.81 0.3314 0.9675 1.7880 0.02104 0.0077 0.42 0.0084 0.0021 11 367.35 0.4237 0.9766 1.5758 1.0231 0.17 0.0024 0.0077 0.52 0.0129 0.0131 12 363.87 0.5032 0.9816 1.4765 1.8758 1.0231 0.0775 0.28 0.0066	1	439.01	0.0295	0.5056	2.0828	1.0112	0.21	0.0003	0.0190	0.24	0.0005	0.0055
3 400.64 0.0911 0.0110 0.0131 0.0111 0.0131 0.0111 0.0131 0.0111 0.0131 0.0113 5 389.11 0.1801 0.9198 1.9277 1.0186 0.011 0.00033 0.0188 0.071 0.0015 6 384.56 0.2123 0.9398 1.8810 0.9484 0.220 0.0002 0.28 0.0044 0.0033 9 372.81 0.3314 0.9675 1.7080 0.9704 0.17 0.0010 0.0077 0.40 0.0084 0.0021 10 370.10 0.3727 0.9722 1.6520 0.9660 0.004 0.0077 0.40 0.0084 0.0021 11 367.35 0.4237 0.9766 1.5758 1.0231 0.17 0.0027 0.0077 0.22 0.0015 0.0015 13 362.92 0.5319 0.9829 1.4387 1.1183 0.01 0.0077 0.28 0.0066 0.0014 14 3	2	421.43	0.0603	0.7008	2.0400	1.0778	0.47	0.0098	0.0370	0.70	0.0043	0.0213
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	409.64	0.0911	0.8156	2.0481	1.0111	0.18	0.0031	0.0170	0.51	0.0111	0.0016
3 357.11 0.1801 0.9198 1.2271 1.0180 0.011 0.0019 0.01031 0.023 0.0001 0.00031 0.110 0.0013 0.00031 0.00041 0.0077 0.42 0.00071 0.023 0.00051 0.0011 13 362.92 0.5319 0.9829 1.4387 1.1183 0.01 0.0023 0.0075 0.25 0.0055 0.0014 14 361.58 0.5800 0.9848 1.2131 1.4766 0.0017 0.0072 0.014 0.00033 0.0160 0.0014 </td <td>4</td> <td>400.05</td> <td>0.1215</td> <td>0.8002</td> <td>2.0180</td> <td>1.0379</td> <td>0.57</td> <td>0.0055</td> <td>0.0188</td> <td>0.71</td> <td>0.0138</td> <td>0.0043</td>	4	400.05	0.1215	0.8002	2.0180	1.0379	0.57	0.0055	0.0188	0.71	0.0138	0.0043
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5	384.56	0.1801	0.9198	1.9277	0.0484	0.01	0.0004	0.0130	0.20	0.003	0.0003
1 17749 0.2003 0.2004 0.2005 0.2007 0.2003 0.2004 0.00033 9 372.81 0.3314 0.9675 1.7080 0.9704 0.17 0.0014 0.00079 0.23 0.0042 0.00033 10 370.01 0.3727 0.9722 1.6520 0.9960 0.004 0.00079 0.39 0.0087 0.0021 11 367.35 0.4237 0.9722 1.6520 0.9960 0.0004 0.00075 0.28 0.0066 0.0015 12 363.87 0.5320 0.9816 1.4765 1.0870 0.02 0.00077 0.25 0.0056 0.0014 13 362.92 0.531 0.9853 1.1744 0.03 0.0003 0.0073 0.18 0.0006 0.0014 15 360.32 0.6331 0.9865 1.3113 1.2660 0.04 0.0007 0.22 0.0084 0.0014 16 358.62 0.7222 0.9888 1.2131 <	7	379.48	0.2125	0.9598	1.8810	0.9464	0.22	0.0009	0.0081	0.10	0.0018	0.0044
9 372.81 0.3314 0.9675 1.7080 0.9704 0.17 0.0014 0.0077 0.40 0.0084 0.0028 10 370.01 0.3727 0.9722 1.6520 0.9960 0.08 0.0004 0.0077 0.39 0.0087 0.0021 11 367.35 0.4237 0.9766 1.578 1.0231 0.17 0.0024 0.0075 0.22 0.0055 0.0014 13 362.92 0.5310 0.9848 1.3783 1.1183 0.01 0.0023 0.0075 0.22 0.0084 0.0014 15 363.22 0.6331 0.9863 1.313 1.2660 0.040 0.0072 0.04 0.0006 0.0014 16 358.99 0.7000 0.9883 1.2369 1.4256 0.00 0.017 0.0072 0.44 0.0046 0.0014 17 358.62 0.7222 0.9883 1.2369 1.4256 0.00 0.0017 0.0226 0.0067 0.44	8	376.98	0.2803	0.959	1.7827	0.9570	0.18	0.0010	0.0079	0.28	0.0042	0.0033
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9	372.81	0.3314	0.9675	1.7080	0.9704	0.17	0.0014	0.0077	0.40	0.0084	0.0028
11 367.35 0.4237 0.9766 1.5758 1.0231 0.17 0.0024 0.0077 0.52 0.0129 0.0015 12 363.87 0.5032 0.9816 1.4785 1.0870 0.02 0.0075 0.28 0.0066 0.0015 13 362.92 0.5319 0.9829 1.4387 1.1183 0.01 0.0027 0.0075 0.28 0.0055 0.0014 14 361.58 0.5800 0.9848 1.3758 1.1764 0.03 0.0004 0.0070 0.22 0.0084 0.0014 16 358.99 0.7000 0.9883 1.21369 1.4296 0.01 0.0018 0.0069 0.30 0.0166 0.0014 18 357.61 0.7918 0.9903 1.1429 1.8144 0.04 0.0029 0.0055 0.44 0.0153 0.0010 21 356.01 0.9204 0.9935 1.0361 3.4248 0.09 0.0036 0.0033 0.16 0.0047	10	370.01	0.3727	0.9722	1.6520	0.9960	0.08	0.0004	0.0079	0.39	0.0087	0.0021
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11	367.35	0.4237	0.9766	1.5758	1.0231	0.17	0.0024	0.0077	0.52	0.0129	0.0019
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12	363.87	0.5032	0.9816	1.4765	1.0870	0.02	0.0027	0.0075	0.28	0.0066	0.0015
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	13	362.92	0.5319	0.9829	1.4387	1.1183	0.01	0.0023	0.0075	0.25	0.0055	0.0014
	14	361.58	0.5800	0.9848	1.3758	1.1764	0.03	0.0008	0.0073	0.18	0.0038	0.0014
16 358.99 0.7000 0.9883 1.2369 1.4256 0.00 0.0017 0.0070 0.22 0.0084 0.0014 17 358.62 0.7222 0.9888 1.2131 1.4989 0.01 0.0018 0.0067 0.49 0.0163 0.0014 18 357.61 0.7918 0.9903 1.1429 1.8144 0.04 0.0024 0.0067 0.49 0.0163 0.0014 19 357.61 0.8876 0.9925 1.0588 2.7418 0.05 0.0027 0.0059 0.47 0.0133 0.0006 21 356.01 0.9204 0.9935 1.0361 3.4248 0.09 0.0036 0.0053 0.40 0.0133 0.0006 22 355.29 0.9700 0.9962 1.0081 5.4941 0.05 0.0021 0.0033 0.15 0.0047 0.0025 2 449.78 0.0611 0.3394 0.5367 1.0305 0.68 0.0393 0.0079 0.05 0.0205 0.0226 0.0226 3 439.47 0.1136 0.5456 </td <td>15</td> <td>360.32</td> <td>0.6331</td> <td>0.9865</td> <td>1.3113</td> <td>1.2660</td> <td>0.04</td> <td>0.0004</td> <td>0.0072</td> <td>0.04</td> <td>0.0006</td> <td>0.0014</td>	15	360.32	0.6331	0.9865	1.3113	1.2660	0.04	0.0004	0.0072	0.04	0.0006	0.0014
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	16	358.99	0.7000	0.9883	1.2369	1.4256	0.00	0.0017	0.0070	0.22	0.0084	0.0014
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	17	358.62	0.7222	0.9888	1.2131	1.4989	0.01	0.0018	0.0069	0.30	0.0106	0.0014
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	18	357.61	0.7918	0.9903	1.1429	1.8144	0.04	0.0024	0.0067	0.49	0.0163	0.0014
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	19	357.11	0.8309	0.9911	1.1008	2.0975	0.06	0.0029	0.0065	0.54	0.0179	0.0013
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20	356.01	0.8870	0.9923	1.0360	2.7410	0.03	0.0027	0.0059	0.47	0.0138	0.0010
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	21	355 29	0.9204	0.9962	1.0081	5 4941	0.09	0.0021	0.0033	0.40	0.0133	0.0000
1 458.68 0.0198 0.1267 0.5079 1.0271 0.26 0.0166 0.0178 0.61 0.0075 0.0236 2 449.78 0.0611 0.3394 0.5367 1.0305 0.68 0.0393 0.0079 0.05 0.0205 0.0220 3 439.47 0.1136 0.5456 0.5905 1.0041 1.14 0.0373 0.0117 0.37 0.0176 0.0076 4 433.86 0.1448 0.6373 0.6209 0.9794 1.16 0.0301 0.0207 0.48 0.0133 0.0001 5 425.94 0.1927 0.7435 0.6666 0.9335 0.92 0.0152 0.0295 0.49 0.0053 0.0087 6 422.43 0.2157 0.7864 0.6914 0.8931 0.75 0.0326 0.04 0.0124 0.0133 8 410.51 0.3013 0.8722 0.777 0.8724 0.15 0.0235 0.0203 0.0633 0.0203 0.0	22	555.27	0.9700	0.7702	1.0001	December 21 (2)		2)	0.0000	0.15	0.0017	0.0002
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	159 69	0.0108	0 1267	0.5070	-Propanol (2)	+ DMSU (3) 0.0166	0.0178	0.61	0.0075	0.0226
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	438.08	0.0198	0.1207	0.5367	1.0271	0.20	0.0100	0.0178	0.01	0.0075	0.0230
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	439.47	0.1136	0.5456	0.5905	1.0041	1 14	0.0373	0.0077	0.03	0.0205	0.0220
5 425.94 0.1927 0.7435 0.6666 0.9335 0.92 0.0152 0.0295 0.49 0.0053 0.0087 6 422.43 0.2157 0.7864 0.6914 0.8931 0.75 0.0039 0.0356 0.44 0.0024 0.0152 7 416.98 0.2519 0.8329 0.7277 0.8724 0.15 0.0117 0.0326 0.04 0.0124 0.0133 8 410.51 0.3013 0.8782 0.7708 0.8436 0.39 0.0257 0.0284 0.27 0.0195 0.0110 9 402.97 0.3709 0.9196 0.8207 0.8017 0.26 0.0335 0.0230 0.36 0.0199 0.0083 10 398.33 0.4200 0.9378 0.8414 0.7936 0.53 0.0243 0.0177 0.0051 11 394.01 0.4715 0.9532 0.8756 0.7673 0.74 0.0299 0.0111 0.21 0.0101 0.0028	4	433.86	0.1448	0.6373	0.6209	0.9794	1.14	0.0301	0.0207	0.48	0.0133	0.0001
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	425.94	0.1927	0.7435	0.6666	0.9335	0.92	0.0152	0.0295	0.49	0.0053	0.0087
7 416.98 0.2519 0.8329 0.7277 0.8724 0.15 0.0117 0.0326 0.04 0.0124 0.0133 8 410.51 0.3013 0.8782 0.7708 0.8436 0.39 0.0257 0.0284 0.27 0.0195 0.0110 9 402.97 0.3709 0.9196 0.8207 0.8017 0.26 0.0335 0.0230 0.36 0.0199 0.0083 10 398.33 0.4200 0.9378 0.8414 0.7936 0.53 0.0243 0.0177 0.06 0.0073 0.0051 11 394.01 0.4715 0.9532 0.8756 0.7673 0.74 0.0299 0.0111 0.21 0.0101 0.0028 12 388.94 0.5439 0.9685 0.9126 0.7238 0.73 0.029 0.0111 0.21 0.0101 0.0028 13 385.99 0.5908 0.9752 0.9353 0.7114 0.78 0.0295 0.0086 0.29 0.0119 0.0018 14 383.79 0.6337 0.9803 0.9458 <td>6</td> <td>422.43</td> <td>0.2157</td> <td>0.7864</td> <td>0.6914</td> <td>0.8931</td> <td>0.75</td> <td>0.0039</td> <td>0.0356</td> <td>0.44</td> <td>0.0024</td> <td>0.0152</td>	6	422.43	0.2157	0.7864	0.6914	0.8931	0.75	0.0039	0.0356	0.44	0.0024	0.0152
8 410.51 0.3013 0.8782 0.7708 0.8436 0.39 0.0257 0.0284 0.27 0.0195 0.0110 9 402.97 0.3709 0.9196 0.8207 0.8017 0.26 0.0335 0.0230 0.36 0.0199 0.0083 10 398.33 0.4200 0.9378 0.8414 0.7936 0.53 0.0243 0.0177 0.06 0.0073 0.0051 11 394.01 0.4715 0.9532 0.8756 0.7673 0.74 0.0299 0.0145 0.21 0.0111 0.0038 12 388.94 0.5439 0.9685 0.9126 0.7238 0.73 0.0295 0.0086 0.29 0.0119 0.0018 13 385.99 0.5908 0.9752 0.9353 0.7114 0.78 0.0295 0.0086 0.29 0.0119 0.0018 14 383.79 0.6337 0.9803 0.9458 0.6632 0.46 0.0182 0.0057 0.09 <td< td=""><td>7</td><td>416.98</td><td>0.2519</td><td>0.8329</td><td>0.7277</td><td>0.8724</td><td>0.15</td><td>0.0117</td><td>0.0326</td><td>0.04</td><td>0.0124</td><td>0.0133</td></td<>	7	416.98	0.2519	0.8329	0.7277	0.8724	0.15	0.0117	0.0326	0.04	0.0124	0.0133
9 402.97 0.3709 0.9196 0.8207 0.8017 0.26 0.0335 0.0230 0.36 0.0199 0.0083 10 398.33 0.4200 0.9378 0.8414 0.7936 0.53 0.0243 0.0177 0.06 0.0073 0.0051 11 394.01 0.4715 0.9532 0.8756 0.7673 0.74 0.0299 0.0145 0.21 0.0111 0.0038 12 388.94 0.5439 0.9685 0.9126 0.7238 0.73 0.029 0.0111 0.21 0.0101 0.0028 13 385.99 0.5908 0.9752 0.9353 0.7114 0.78 0.0295 0.0086 0.29 0.0119 0.0018 14 383.79 0.6337 0.9803 0.9458 0.6632 0.46 0.0182 0.0057 0.09 0.0046 0.0011 16 378.89 0.7417 0.9895 0.9701 0.6319 0.18 0.0079 0.0042 0.09 <td< td=""><td>8</td><td>410.51</td><td>0.3013</td><td>0.8782</td><td>0.7708</td><td>0.8436</td><td>0.39</td><td>0.0257</td><td>0.0284</td><td>0.27</td><td>0.0195</td><td>0.0110</td></td<>	8	410.51	0.3013	0.8782	0.7708	0.8436	0.39	0.0257	0.0284	0.27	0.0195	0.0110
10398.330.42000.93780.84140.79360.530.02430.01770.060.00730.005111394.010.47150.95320.87560.76730.740.02990.01450.210.01110.003812388.940.54390.96850.91260.72380.730.0290.01110.210.01010.002813385.990.59080.97520.93530.71140.780.02950.00860.290.01190.001814383.790.63370.98030.94580.66780.550.02150.00720.110.00560.001515381.450.68060.98490.96050.66320.460.01820.00570.090.00460.001116378.890.74170.98950.97010.63190.180.00780.00330.040.00050.000517377.590.77220.99130.97830.62580.190.00430.00250.060.00160.000419374.650.83360.99530.98960.59360.040.00180.00180.00180.00180.00120.00320373.350.89250.99680.99470.58100.030.00140.00120.030.00040.000121372.280.93090.99880.99350.62330.140.00540.00020.160.00570.0001	9	402.97	0.3709	0.9196	0.8207	0.8017	0.26	0.0335	0.0230	0.36	0.0199	0.0083
11394.010.47150.95320.87560.76730.740.02990.01450.210.01110.003812388.940.54390.96850.91260.72380.730.0290.01110.210.01010.002813385.990.59080.97520.93530.71140.780.02950.00860.290.01190.001814383.790.63370.98030.94580.66780.550.02150.00720.110.00560.001515381.450.68060.98490.96050.66320.460.01820.00570.090.00460.001116378.890.74170.98950.97010.63190.180.00790.00420.090.00220.000817377.590.77220.99130.97830.62580.190.00780.00330.040.00050.000518376.050.81340.99350.98460.60790.100.00430.00250.060.00160.000419374.650.85360.99530.98960.59360.040.00180.00180.00180.00120.0030.000120373.350.89250.99680.99470.58100.030.00140.00120.030.000421372.280.93090.99880.59080.090.00330.00060.120.00420.000022371.510.95940.9988 <t< td=""><td>10</td><td>398.33</td><td>0.4200</td><td>0.9378</td><td>0.8414</td><td>0.7936</td><td>0.53</td><td>0.0243</td><td>0.0177</td><td>0.06</td><td>0.0073</td><td>0.0051</td></t<>	10	398.33	0.4200	0.9378	0.8414	0.7936	0.53	0.0243	0.0177	0.06	0.0073	0.0051
12388.940.54390.96850.91260.72380.730.0290.01110.210.01010.002813385.990.59080.97520.93530.71140.780.02950.00860.290.01190.001814383.790.63370.98030.94580.68780.550.02150.00720.110.00560.001515381.450.68060.98490.96050.66320.460.01820.00570.090.00460.001116378.890.74170.98950.97010.63190.180.00790.00420.090.00220.000817377.590.77220.99130.97830.62580.190.00430.00250.060.001518376.050.81340.99350.98460.60790.100.00430.00250.060.00160.000419374.650.85360.99530.98960.59360.040.00180.0180.0180.00120.0030.000120373.350.89250.99680.99470.58100.030.00140.00120.030.00020.00420.000021372.280.93090.99800.99380.59080.090.00330.00060.120.00420.000022371.510.95940.99880.99350.62330.140.00540.00020.160.00570.0001	11	394.01	0.4715	0.9532	0.8756	0.7673	0.74	0.0299	0.0145	0.21	0.0111	0.0038
13 385.99 0.5908 0.9752 0.9353 0.7114 0.78 0.0295 0.0086 0.29 0.0119 0.0018 14 383.79 0.6337 0.9803 0.9458 0.6878 0.55 0.0215 0.0072 0.11 0.0056 0.0015 15 381.45 0.6806 0.9849 0.9605 0.6632 0.46 0.0182 0.0057 0.09 0.0046 0.0011 16 378.89 0.7417 0.9895 0.9701 0.6319 0.18 0.0079 0.0042 0.09 0.0022 0.0008 17 377.59 0.7722 0.9913 0.9783 0.6258 0.19 0.0043 0.0025 0.06 0.0005 18 376.05 0.8134 0.9935 0.9846 0.6079 0.10 0.0043 0.0025 0.06 0.0014 0.0018 0.0018 0.0018 0.001 0.0012 0.003 0.0014 0.0012 0.03 0.0001 0.0003 0.0011 0.0013	12	388.94	0.5439	0.9685	0.9126	0.7238	0.73	0.029	0.0111	0.21	0.0101	0.0028
14 383./9 0.633/ 0.9803 0.9458 0.6878 0.55 0.0215 0.0072 0.11 0.0056 0.0015 15 381.45 0.6806 0.9849 0.9605 0.6632 0.46 0.0182 0.0057 0.09 0.0046 0.0011 16 378.89 0.7417 0.9895 0.9701 0.6319 0.18 0.0079 0.0042 0.09 0.0022 0.0008 17 377.59 0.7722 0.9913 0.9783 0.6258 0.19 0.0043 0.0025 0.06 0.0016 0.0004 18 376.05 0.8134 0.9935 0.9846 0.6079 0.10 0.0043 0.0025 0.06 0.0016 0.0004 19 374.65 0.8536 0.9953 0.9896 0.5936 0.04 0.0018 0.0018 0.07 0.0021 0.0003 20 373.35 0.8925 0.9968 0.9947 0.5810 0.03 0.0014 0.0012 0.03 0.0004 0.0012 21 372.28 0.9309 0.9988 0.5908	13	385.99	0.5908	0.9752	0.9353	0.7114	0.78	0.0295	0.0086	0.29	0.0119	0.0018
15 581.45 0.6806 0.9849 0.9605 0.0632 0.46 0.0182 0.0057 0.09 0.0046 0.0011 16 378.89 0.7417 0.9895 0.9701 0.6319 0.18 0.0079 0.0042 0.09 0.0022 0.0008 17 377.59 0.7722 0.9913 0.9783 0.6258 0.19 0.0043 0.0025 0.06 0.0016 0.0005 18 376.05 0.8134 0.9935 0.9846 0.6079 0.10 0.0043 0.0025 0.06 0.0016 0.0004 19 374.65 0.8536 0.9953 0.9896 0.5936 0.04 0.0018 0.0018 0.07 0.0021 0.0003 20 373.35 0.8925 0.9968 0.9947 0.5810 0.03 0.0014 0.0012 0.03 0.0004 0.0002 21 372.28 0.9309 0.9988 0.5938 0.09 0.0033 0.0006 0.12 0.0042 <	14	383.79	0.6337	0.9803	0.9458	0.6878	0.55	0.0215	0.0072	0.11	0.0056	0.0015
10 578.89 0.7417 0.9895 0.9701 0.6319 0.18 0.0079 0.0042 0.09 0.0022 0.0008 17 377.59 0.7722 0.9913 0.9783 0.6258 0.19 0.0078 0.0033 0.04 0.0005 0.0005 18 376.05 0.8134 0.9935 0.9846 0.6079 0.10 0.0043 0.0025 0.06 0.0016 0.0004 19 374.65 0.8536 0.9953 0.9896 0.5936 0.04 0.0018 0.0018 0.07 0.0021 0.0003 20 373.35 0.8925 0.9968 0.9947 0.5810 0.03 0.0014 0.0012 0.03 0.0008 0.00001 21 372.28 0.9309 0.9988 0.5936 0.09 0.0033 0.0006 0.12 0.0042 0.0000 22 371.51 0.9594 0.9988 0.9935 0.6233 0.14 0.0022 0.16 0.0057 0.0001 <td>15</td> <td>381.45</td> <td>0.6806</td> <td>0.9849</td> <td>0.9605</td> <td>0.6632</td> <td>0.46</td> <td>0.0182</td> <td>0.0057</td> <td>0.09</td> <td>0.0046</td> <td>0.0011</td>	15	381.45	0.6806	0.9849	0.9605	0.6632	0.46	0.0182	0.0057	0.09	0.0046	0.0011
17 377.37 0.7722 0.9913 0.9763 0.6236 0.19 0.0078 0.0035 0.04 0.0005 0.0005 18 376.05 0.8134 0.9935 0.9846 0.6079 0.10 0.0043 0.0025 0.06 0.0016 0.0004 19 374.65 0.8536 0.9953 0.9896 0.5936 0.04 0.0018 0.0018 0.007 0.0021 0.0003 20 373.35 0.8925 0.9968 0.9947 0.5810 0.03 0.0014 0.0012 0.03 0.0004 0.0042 0.0003 21 372.28 0.9309 0.9988 0.5908 0.09 0.0033 0.0006 0.12 0.0042 0.0000 22 371.51 0.9594 0.9988 0.9935 0.6233 0.14 0.0054 0.0002 0.16 0.0057 0.0001	10	3/8.89	0.7417	0.9895	0.9701	0.0319	0.18	0.0079	0.0042	0.09	0.0022	0.0008
19 374.65 0.8536 0.9953 0.9896 0.5936 0.04 0.0043 0.0023 0.00 0.0016 0.0004 19 374.65 0.8536 0.9953 0.9896 0.5936 0.04 0.0018 0.0018 0.002 0.002 0.0021 0.0004 20 373.35 0.8925 0.9968 0.9947 0.5810 0.03 0.0014 0.0012 0.03 0.00012 0.03 0.0004 0.0012 0.03 0.0004 0.0012 0.03 0.0004 0.0012 0.03 0.0004 0.0012 0.03 0.0004 0.0012 0.03 0.0004 0.0012 0.042 0.0000 21 372.28 0.9309 0.9988 0.9935 0.6233 0.14 0.0054 0.0002 0.16 0.0057 0.0001 22 371.51 0.9594 0.9988 0.9935 0.6233 0.14 0.0054 0.0002 0.16 0.0057 0.0001	17	376.05	0.7722	0.9915	0.9763	0.0238	0.19	0.0078	0.0055	0.04	0.0005	0.0003
20 373.35 0.8925 0.9968 0.9947 0.5810 0.03 0.0016 0.0016 0.0021 0.0003 21 372.28 0.9309 0.9980 0.9938 0.5908 0.09 0.0033 0.0006 0.12 0.0042 0.0001 22 371.51 0.9594 0.9988 0.9935 0.6233 0.14 0.0054 0.0002 0.16 0.0057 0.0001	19	374.65	0.8536	0.9953	0.9896	0.5936	0.10	0.0043	0.0023	0.00	0.0021	0.0004
21 372.28 0.9309 0.9980 0.9938 0.5908 0.09 0.0033 0.0006 0.12 0.0042 0.0001 22 371.51 0.9594 0.9988 0.9935 0.6233 0.14 0.0054 0.0002 0.16 0.0057 0.0001	20	373.35	0.8925	0.9968	0.9947	0.5810	0.03	0.0014	0.0012	0.03	0.0008	0.0001
22 371.51 0.9594 0.9988 0.9935 0.6233 0.14 0.0054 0.0002 0.16 0.0057 0.0001	21	372.28	0.9309	0.9980	0.9938	0.5908	0.09	0.0033	0.0006	0.12	0.0042	0.0000
	22	371.51	0.9594	0.9988	0.9935	0.6233	0.14	0.0054	0.0002	0.16	0.0057	0.0001

^{*a*} $\Delta T = |T^{\text{exptl}} - T^{\text{calcd}}|$. ^{*b*} $\Delta y_i = |y_i^{\text{exptl}} - y_i^{\text{calcd}}|$.

The calculated values from Wilson and NRTL models and the comparison between the experimental and the calculated values for the three binary systems are shown in Table 4 and Figures 2 to 4. It could be seen that in the acetonitrile + DMSO system

the composition variations of the vapor and liquid phases with temperature were not obvious when the mole fraction of acetonitrile in the liquid phase was greater than 0.4 as shown in Figure 3, and a similar trend was found when the mole

5274 Journal of Chemical & Engineering Data, Vol. 55, No. 11, 2010

Table 5. Results of the Thermodynamic Consistency Test

system	$A_0{}^a$	A_1^a	A_2^a	A_3^a	$A_4^{\ a}$	$\delta y_1{}^b$	$\delta P^c/\mathrm{kPa}$
acetonitrile $(1) + 1$ -propanol (2)	1.1109	0.0035	0.0004	0.0221	0.0111	0.0056	1.17
acetonitrile $(1) + DMSO(3)$	1.2218	0.6413	0.2836	0.1399	0.0519	0.0075	0.81
1-propanol (2) + DMSO (3)	-0.5740	0.1429	0.0307	0.0189	0.0329	0.0046	0.91

^a The parameters of the Legendre polynomial. ^b Average absolute deviation in vapor-phase composition. ^c Average absolute deviation in pressure.

Table 6. Experimental VLE Data and Correlated Results of the Ternary System at 101.3 kPa

	acetonitri	le $(1) + 1-p$	ropanol (2)	+ DMSO (3)		calculated	d by Wilson	L	calculated by NRTL			
no.	T/K	x_1	<i>x</i> ₂	<i>y</i> 1	<i>y</i> ₂	ΔT^a	$\Delta y_1{}^b$	$\Delta y_2{}^b$	$\Delta y_3{}^b$	ΔT^a	$\Delta y_1{}^b$	Δy_2^{b}	$\Delta y_3{}^b$
1	355.26	0.8148	0.1003	0.9108	0.0817	0.15	0.0050	0.0082	0.0032	0.22	0.0022	0.0031	0.0009
2	356.72	0.5042	0.3924	0.7186	0.2764	0.76	0.0006	0.0033	0.0027	0.49	0.0029	0.0067	0.0038
3	358.84	0.2827	0.6513	0.5605	0.4381	0.80	0.0034	0.0039	0.0005	0.43	0.0117	0.0132	0.0015
4	360.97	0.3160	0.5063	0.6342	0.3636	1.15	0.0011	0.0027	0.0016	0.31	0.0135	0.0156	0.0021
5	366.40	0.2348	0.4565	0.6133	0.3845	0.90	0.0086	0.0155	0.0069	0.77	0.0143	0.0163	0.0020
6	367.92	0.1069	0.7230	0.3554	0.6433	1.14	0.0026	0.0053	0.0027	0.33	0.0220	0.0233	0.0013
7	373.45	0.1285	0.5214	0.4391	0.5423	1.40	0.0304	0.0249	0.0055	0.40	0.0049	0.0235	0.0186
8	379.68	0.2301	0.1526	0.8460	0.1192	2.87	0.0160	0.0146	0.0014	0.72	0.0098	0.0100	0.0002
9	382.32	0.0441	0.5427	0.2027	0.7756	0.56	0.0294	0.0315	0.0021	0.76	0.0010	0.0206	0.0216
10	385.15	0.1021	0.3715	0.4667	0.5205	2.97	0.0268	0.0481	0.0213	0.17	0.0006	0.0122	0.0128
11	388.31	0.1298	0.2631	0.6234	0.3530	4.33	0.0060	0.0273	0.0213	0.11	0.0071	0.0160	0.0231
12	390.87	0.0907	0.3204	0.4735	0.5021	3.97	0.0230	0.0458	0.0228	0.14	0.0062	0.0182	0.0244
13	399.68	0.1219	0.0683	0.8121	0.0767	2.92	0.0161	0.0239	0.0078	1.49	0.0215	0.0142	0.0073
14	404.78	0.1023	0.0345	0.7970	0.0402	0.94	0.0005	0.0201	0.0206	1.57	0.0325	0.0097	0.0228
15	408.10	0.0923	0.0592	0.7648	0.0873	3.27	0.0199	0.0235	0.0036	1.54	0.0195	0.0151	0.0044

^{*a*} $\Delta T = |T^{\text{exptl}} - T^{\text{calcd}}|$. ^{*b*} $\Delta y_i = |y_i^{\text{exptl}} - y_i^{\text{calcd}}|$.

Table 7. Parameters and Correlation Deviations of Wilson and NRTL Models

	$(\lambda_{12} - \lambda_{11})/R^a$	$(\lambda_{21} - \lambda_{22})/R^a$					$AADT^{c}$				
systems	K	K	α	$AADy_1^b$	$AADy_2^b$	$AADy_3^b$	K				
Acetonitrile $(1) + 1$ -Propanol (2)											
Wilson	357.56	117.84	-	0.0077	0.0163	-	0.38				
NRTL	230.43	203.32	0.3	0.0067	0.0159	-	0.30				
	Acetonitrile $(1) + DMSO(3)$										
Wilson	94.87	696.16	-	0.0023	0.0102	-	0.12				
NRTL	827.84	-140.11	0.3	0.0081	0.0029	-	0.35				
		1-Pr	opanol (2) +	DMSO (3)							
Wilson	-75.60	-153.11	-	0.0181	0.0130	-	0.47				
NRTL	-490.59	374.33	0.3	0.0085	0.0058	-	0.21				
Acetonitrile $(1) + 1$ -Propanol $(2) + DMSO(3)$											
Wilson	-	-	-	0.0126	0.0199	0.0083	1.88				
NRTL	-	-	0.3	0.0113	0.0145	0.0098	0.63				

 ${}^{a}(\lambda_{12} - \lambda_{11})/R$ and $(\lambda_{21} - \lambda_{22})/R$ are the parameters adjusted by using experimental VLE data. ${}^{b}AADy = (1/N)\sum_{i=1}^{N}|y^{exptl} - y^{calcd}|$. ${}^{c}AADT = (1/N)\sum_{i=1}^{N}|T^{exptl} - T^{calcd}|$; N = number of data points.

$$OF = \sum_{k} \sum_{i} (y_i^{exptl} - y_i^{calcd})_k^2$$
(2)

fraction of 1-propanol in the liquid phase was greater than 0.6 in Figure 4. The average absolute deviations (AAD) in temperature and vapor mole fraction are listed in Table 7. It could be found from the above tables and figures that values correlated by the Wilson and NRTL models agree well with the experimental ones.

Predication of Ternary Vapor–Liquid Equilibria. In this study, the Wilson and NRTL models were used to predict the VLE data of the ternary system. The VLE data and the deviations in temperatures and vapor mole fraction are listed in Tables 6 and 7. The azeotrope and tie-lines of the ternary system are shown in Figure 5. These results suggest that the Wilson and NRTL models could give a good representation of the experimental data, and the NRTL model could be comparatively better in this work.

Conclusions

The VLE data of the ternary system acetonitrile + 1-propanol + DMSO and the corresponding binary systems, acetonitrile



Figure 3. Equilibrium diagram for the system acetonitrile (1) + DMSO (3) at 101.3 kPa: \blacksquare , experimental data; -, calculation based on the Wilson model; - -, calculation based on the NRTL model.

+ 1-propanol, acetonitrile + DMSO, and 1-propanol + DMSO, were measured, respectively, at 101.3 kPa by using an improved Rose equilibrium still. The thermodynamic consistency test was



Figure 4. Equilibrium diagram for the system 1-propanol (2) + DMSO(3) at 101.3 kPa: \blacksquare , experimental data; —, calculation based on the Wilson model; - -, calculation based on the NRTL model.



Figure 5. Tie-lines for the ternary system acetonitrile (1) + 1-propanol (2) + DMSO (3) at 101.3 kPa: \bigcirc , liquid-phase mole fraction; \triangle , vapor-phase mole fraction; \bullet , azeotrope.

passed using the point-to-point method. The parameters of Wilson and NRTL models were obtained from the binary systems. Then, the VLE data of the ternary system were predicted with Wilson and NRTL models and agreed well with the experimental data. The Wilson and NRTL models could be adopted to correlate VLE of the present binary systems, and the NRTL model yielded more reasonable predictions for the ternary system.

Literature Cited

- Rahmathullah, S. M.; Hall, J. E.; Bender, B. C.; et al. Prodrugs for amidines: synthesis and anti-pneumocystis carinii activity of carbamates of 2,5-Bis (4-amidinophenyl) furan. *J. Med. Chem.* **1999**, *42*, 3994–4000.
- (2) Colosio, C.; Ariano, E.; Carcano, M.; et al. Preparation and validation of exposure and risk profiles for pesticide use in greenhouse. *Toxicol. Lett.* 2008, 180, 26–33.

- (3) Aberham, A.; Schwaiger, S.; Stuppner, H.; et al. Quantitative analysis of iridoids, secoiridoids, xanthones and xanthone glycosides in Gentiana lutea L. roots by RP-HPLC and LC-MS. J. Pharmaceut. Biomed. 2007, 45, 437–442.
- (4) Xie, Z. Y.; Zhong, D. F.; Li, Y. The separation of enantiomers by acid glycoprotein chiral stationary phase. Chinese. J. Anal. Chem. 2006, 34, 223–226.
- (5) Prasad, A. R.; Rao, K. V. Vapor-liquid equilibria of acetonitrile-1propanol mixtures. *Can. J. Chem. Eng.* **1986**, *64*, 813–819.
- (6) Lelkes, Z.; Lang, P.; Benadda, B.; Moszkowicz, P. Feasibility of extractive distillation in a batch rectifier. *AIChE J.* **1998**, *44*, 810– 822.
- (7) Lelkes, Z.; Lang, P.; Moszkowicz, P.; Benadda, B.; Otterbein, M. Batch extractive distillation: the process and the operational policies. *Chem. Eng. Sci.* **1998**, *53*, 1331–1348.
- (8) Perry, R. H.; Green, D. W. Perry's Chemical Engineers' Handbook, 7th ed.; New York: McGraw Hill, 1997.
- (9) Wen, H. W. Process intensification and application of extractive distillation. Doctor thesis. Tianjin University: 19 Tianjin, China, 2006.
- (10) Chen, N. L. Solvent Handbook; Chemical Industry Press: Beijing, 2008.
- (11) Song, H.; Liu, L. M.; Zhang, Y. K.; Fu, C. Isobaric Vapor-liquid equilibria for the ternary system of 2-methyl-1-butanol, 3-methyl-1butanol, and ethylene glycol at 101.3 kPa. *J. Chem. Eng. Data* 2004, 49, 1535–1538.
- (12) Ewing, M. B.; Sanchez Ochoa, J. C. Vapor pressures of acetonitrile determined by comparative ebulliometry. J. Chem. Eng. Data 2004, 49, 486–491.
- (13) Dejoz, A.; Gonzalez-Alfaro, V.; Llopis, F. J.; et al. Isobaric vaporliquid equilibrium of binary mixtures of 1-propanol + chlorobenzene and 2-propanol + chlorobenzene. *Fluid Phase Equilib.* **1997**, *134*, 151– 161.
- (14) Dejoz, A.; Gonzalez-Alfaro, V.; Llopis, F. J.; et al. Phase equilibria and variation of the azeotropic composition with pressure for binary mixtures of 1-propanol + chlorobenzene and 1-butanol + chlorobenzene. *Fluid Phase Equilib.* **1998**, *145*, 287–299.
- (15) Deák, A.; Victorov, A. I.; de Loos, T. W. High pressure VLE in alkanol + alkane mixtures. Experimental results for n-butane + ethanol, + 1-propanol, + 1-butanol systems and calculations with three EOS methods. *Fluid Phase Equilib.* **1995**, *107*, 277–301.
- (16) Tochigi, K.; Akimoto, K.; Ochi, K.; et al. Isothermal vapor-liquid equilibria for water + 2-aminoethanol +dimethyl sulfoxide and its constituent three binary systems. J. Chem. Eng. Data 1999, 44, 588– 590.
- (17) Spencer, C. F.; Danner, R. P. Improved equation for prediction of saturated liquid density. J. Chem. Eng. Data 1972, 17, 236–241.
- (18) Tsonopoulos, C. Empirical Correlation of Second Virial Coefficients. *AIChE J.* **1974**, 20, 263–272.
- (19) Zhang, Y. Y.; Zhang, K. W. Handbook of molecular thermodynamic properties: Calculation and the latest experimental data; Chemical Industry Press: Beijing, 2009.
- (20) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor-liquid Equilibrium.I: An Appraisal of Data Reduction Methods. *AIChE J.* **1973**, *19*, 238– 244.
- (21) Fredenslund, A.; Gmehling, J.; Rasmussen, P. Vapor-Liquid Equilibria Using UNIFAC. A Group Contribution Method; Elsevier: Amsterdam, 1977
- (22) Kirss, H.; Kuus, M.; Siimer, E. Isobaric Vapor-Liquid Equilibria of the Ternary System Toluene +Ethylbenzene + Amyl Acetate. J. Chem. Eng. Data 2004, 49, 465–467.
- (23) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J. 1968, 14, 135–144.

Received for review January 11, 2010. Accepted September 3, 2010. This project was supported by the Youth Science Foundation (No.JS20090719506921) of Sichuan University.

JE100033S