Vapor–Liquid Equilibrium of *N*-Formylmorpholine with Toluene and Xylene at 101.33 kPa

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Isobaric vapor–liquid equilibrium (VLE) data for toluene + NFM, *o*-xylene + NFM, *m*-xylene + NFM, and *p*-xylene + NFM were measured at 101.33 kPa with a modified Rose−Williams still. Wilson and NRTL equations were used to correlate the VLE data through a nonlinear least-squares method.

Introduction

Equilibrium data are the basis for the design and computation of separating processes, such as distillation, absorption, extraction, and crystallization. An abundance of experimental data are needed for an accurate design of separation processes and facilities.

N-Formylmorpholine (NFM) is widely used in the recovery of aromatics as a solvent for its good selectivity and heat stability. To design or improve these processes, it is extremely important to determine the phase equilibrium data of systems containing NFM. However, only the vapor–liquid equilibrium (VLE) data for the benzene + NFM system at atmospheric pressure and the *m*-xylene + NFM system at 150 kPa were found in the literature.[1,2]

VLE data for toluene + NFM, *o*-xylene + NFM, *m*-xylene + NFM, and *p*-xylene + NFM at 101.33 kPa were measured. Binary interaction parameters (BIPs) adjusted on these four binary systems were obtained by correlating with the Wilson and NRTL equations, with which multicomponent-system VLE data can be predicted.

Experimental Section

Materials. All chemicals used in this study were supplied by Tianjin Reagent Co. except NFM, which was supplied by Shanghai Chemical Reagent Co. NFM was purified by distillation. Other liquids were subjected to no further purification. All chemicals were dried over 0.4 nm molecular sieves prior to their experimental use. The mole fraction purities tested by gas chromatography were as follows: NFM (> 0.995), benzene (> 0.995), toluene (> 0.995), *o*-xylene (> 0.995), *m*-xylene (> 0.995), *p*-xylene (> 0.999).

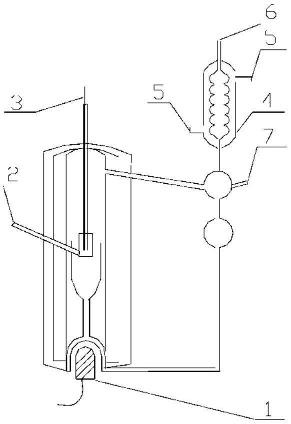

Figure 1. Rose−Williams VLE device. 1, heating column; 2, liquid sample connection; 3, a precise mercury thermometer; 4, condenser; 5, condensate; 6, contact with pressure-controlling devices; 7, vapor (cooled to liquid) sample connection.

Table 1. VLE Data and Calculation Data for the Benzene (1) + Toluene (2) System

no.	T/K	x_1	y_1	γ_1	γ_2	$\ln(\gamma_1/\gamma_2)$
1	355.25	0.9148	0.9658	0.9928	0.9736	0.0195
2	357.45	0.8149	0.9197	0.9932	0.9768	0.0167
3	359.45	0.7310	0.8749	0.9926	0.9796	0.0132
4	361.75	0.6391	0.8181	0.9924	0.9842	0.0083
5	364.35	0.5432	0.7486	0.9912	0.9882	0.0030
6	366.95	0.4553	0.6739	0.9888	0.9897	−0.0010
7	369.16	0.3841	0.6042	0.9878	0.9915	−0.0037
8	369.41	0.3763	0.5959	0.9875	0.9918	−0.0043
9	372.20	0.2935	0.5007	0.9854	0.9930	−0.0077
10	374.55	0.2290	0.4148	0.9816	0.9933	−0.0118
11	375.45	0.2047	0.3795	0.9808	0.9938	−0.0132
12	376.18	0.1850	0.3495	0.9803	0.9948	−0.0146
13	378.15	0.1347	0.2678	0.9789	0.9951	−0.0164
14	379.35	0.1061	0.2167	0.9750	0.9948	−0.0201
15	380.85	0.0703	0.1490	0.9735	0.9949	−0.0218
16	382.25	0.0374	0.0821	0.9733	0.9955	−0.0225

Apparatus and Procedures. The VLE data measurements were carried out in a modified Rose−Williams still, which is shown in Figure 1. In this still, both the vapor and the liquid phases are continuously recirculating to provide intimate contact of the phases and ensure that equilibrium can be established rapidly. In each experiment, equilibrium was assumed when constant vapor temperature has been obtained for more than 30 min.

The temperature was measured with a precise mercury thermometer whose uncertainty is ± 0.1 K. The pressure of the system was determined by a U-shaped differential mano-

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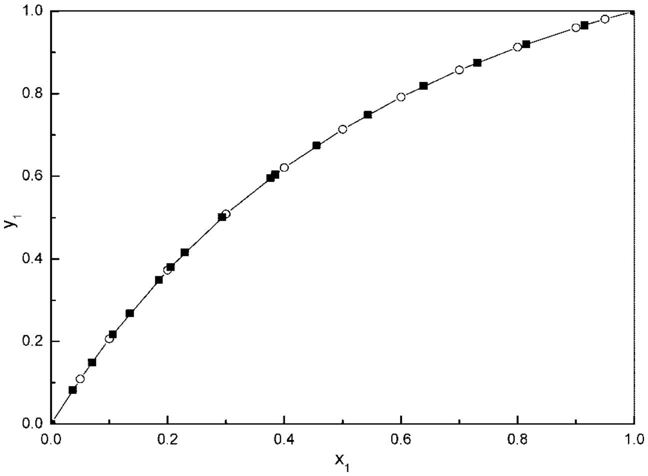

Figure 2. $x-y$ phase equilibrium for the benzene (1) + toluene (2) system at 101.33 kPa: ○, literature data;[4] ■, experimental data.

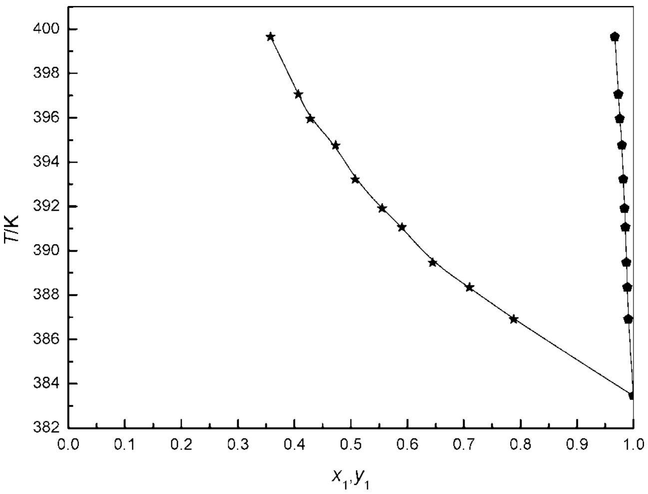

Figure 3. $T-x-y$ phase equilibrium for the toluene (1) + NFM (2) system at 101.33 kPa: ★, $x-T$ experimental data; solid pentagon, $y-T$ experimental data.

Table 2. VLE Data for the Four Binary Systems at 101.33 kPa

no.	T/K	x_1	y_1	no.	T/K	x_1	y_1
			Toluene (1) + NFM (2) System				
1	386.90	0.7882	0.9909	6	393.22	0.5074	0.9819
2	388.34	0.7098	0.9892	7	394.75	0.4732	0.9797
3	389.46	0.6448	0.9873	8	395.95	0.4281	0.9757
4	391.05	0.5903	0.9857	9	397.06	0.4071	0.9733
5	391.90	0.5553	0.9839	10	399.65	0.3580	0.9668
			o-Xylene (1) + NFM (2) System				
1	417.95	0.9291	0.9866	6	427.55	0.6712	0.9471
2	421.45	0.8203	0.9705	7	429.35	0.6320	0.9411
3	423.60	0.7644	0.9601	8	431.05	0.5850	0.9306
4	424.65	0.7374	0.9549	9	433.15	0.5428	0.9196
5	426.80	0.6900	0.9491	10	435.40	0.5109	0.9148
			m-Xylene (1) + NFM (2) System				
1	413.25	0.9361	0.9880	6	421.85	0.6663	0.9624
2	416.05	0.8406	0.9799	7	425.85	0.5911	0.9513
3	417.45	0.7984	0.9749	8	427.35	0.5602	0.9450
4	419.05	0.7441	0.9677	9	429.50	0.5231	0.9367
5	420.62	0.6975	0.9652				
			p-Xylene (1) + NFM (2) System				
1	414.25	0.8811	0.9824	6	425.75	0.5788	0.9494
2	416.05	0.8062	0.9722	7	428.75	0.5336	0.9434
3	417.26	0.7766	0.9705	8	432.62	0.4805	0.9377
4	419.75	0.7062	0.9630	9	436.20	0.4303	0.9248
5	422.35	0.6407	0.9553				

meter whose fluctuation was held within 0.03 kPa with a two-step automatic control system.

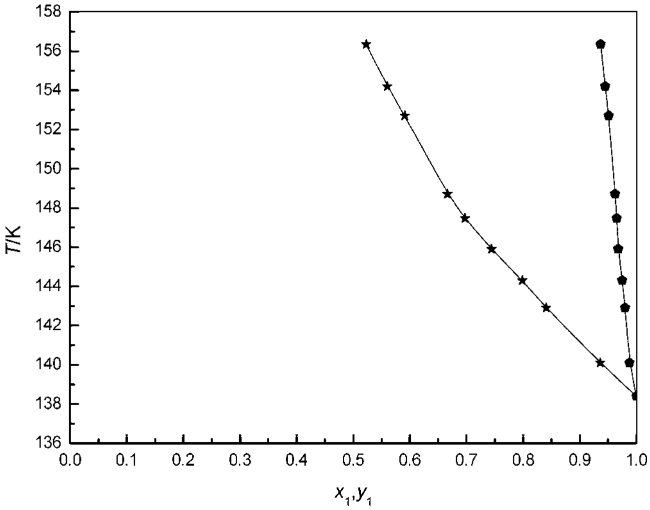

Figure 4. $T-x-y$ phase equilibrium for the *o*-xylene (1) + NFM (2) system at 101.33 kPa: ★, $x-T$ experimental data; solid pentagon, $y-T$ experimental data.

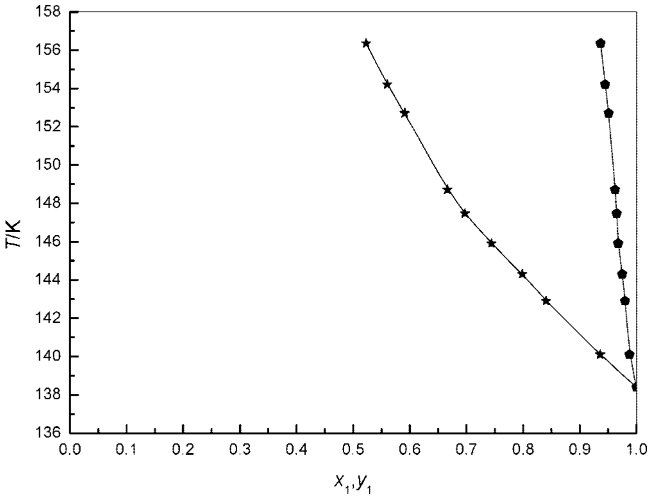

Figure 5. $T-x-y$ phase equilibrium for the *m*-xylene (1) + NFM (2) system at 101.33 kPa: ★, $x-T$ experimental data; solid pentagon, $y-T$ experimental data.

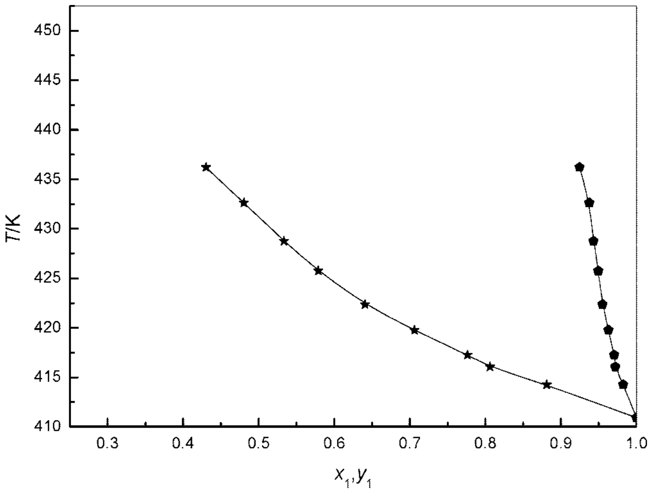

Figure 6. $T-x-y$ phase equilibrium for the *p*-xylene (1) + NFM (2) system at 101.33 kPa: ★, $x-T$ experimental data; solid pentagon, $y-T$ experimental data.

The vapor (cooled to liquid) and liquid compositions were analyzed by a gas chromatograph (GC112A) with a flame ionization detector (FID), after calibration with solutions prepared by gravimetrical standard. They were all produced by

Table 3. Parameters for the Four Binary Systems Using the Wilson and NRTL Equations

	Wilson		NRTL		
system	$(\lambda_{12} - \lambda_{11})$ J·mol^{-1}	$(\lambda_{21} - \lambda_{22})$ J·mol^{-1}	$g_{12} - g_{22}$	$g_{21} - g_{11}$	α
toluene (1) + NFM (2)	621.013	8203.357	6157.229	−231.922	0.3346
o-xylene (1) + NFM (2)	1194.390	2240.666	1602.558	397.044	2.2066
m-xylene (1) + NFM (2)	2378.960	2873.394	3834.253	−55.631	1.4946
p-xylene (1) + NFM (2)	2588.320	2760.085	3928.278	−40.602	1.5825

Table 4. Deviations between the Calculated and Experimental Vapor-Phase Mole Fraction Δy_1 and Temperature Change ΔT of the Four Binary Systems Using the Wilson and NRTL Equations [a]

		Wilson		NRTL	
system		Δy_1	ΔT/K	Δy_1	ΔT/K
toluene (1) + NFM (2)	ave	0.0057	0.17	0.0081	0.30
	max	0.0108	0.41	0.0283	1.04
o-xylene (1) + NFM (2)	ave	0.0047	0.20	0.0054	0.22
	max	0.0109	0.43	0.0140	0.55
m-xylene (1) + NFM (2)	ave	0.0037	0.15	0.0048	0.19
	max	0.0109	0.45	0.0119	0.45
p-xylene (1) + NFM (2)	ave	0.0034	0.14	0.0027	0.11
	max	0.0081	0.34	0.0074	0.31

[a] Note: ave, the average value; max, the maximum value.

Table 5. VLE Data for the Benzene (1) + Toluene (2) + NFM (3) System at 101.33 kPa

no.	T/K	x_1	x_2	x_3	y_1	y_2	y_3
1	364.55	0.5517	0.4483	0.0000	0.7015	0.2985	0.0000
2	369.35	0.5032	0.4096	0.0872	0.6794	0.3206	0.0000
3	370.55	0.4714	0.3752	0.1534	0.6737	0.3263	0.0000
4	372.20	0.4419	0.3617	0.1964	0.6906	0.3094	0.0000
5	375.60	0.3911	0.3204	0.2885	0.6650	0.3350	0.0000
6	375.73	0.3954	0.3333	0.2713	0.6806	0.3192	0.0002
7	379.46	0.3259	0.2878	0.3863	0.6660	0.3337	0.0003
8	381.75	0.3331	0.2711	0.3958	0.6507	0.3477	0.0016
9	383.80	0.3022	0.2678	0.4300	0.5715	0.3532	0.0753
10	384.25	0.2909	0.1968	0.5123	0.6633	0.3104	0.0263
11	390.15	0.2390	0.2086	0.5524	0.6161	0.3725	0.0114
12	392.85	0.2352	0.2219	0.5429	0.6060	0.3842	0.0098
13	402.00	0.1502	0.2228	0.6270	0.4957	0.4873	0.0170
14	404.83	0.1596	0.1446	0.6958	0.5915	0.3890	0.0195
15	404.90	0.1297	0.1424	0.7279	0.5618	0.4178	0.0204
16	411.20	0.0843	0.1886	0.7271	0.4234	0.5356	0.0410
17	418.75	0.1015	0.0745	0.8240	0.5847	0.3388	0.0765
18	421.45	0.0940	0.0918	0.8142	0.5395	0.3950	0.0655
19	430.45	0.0781	0.0918	0.8301	0.5050	0.4207	0.0743
20	440.65	0.0584	0.0633	0.8783	0.4761	0.3835	0.1404

Shanghai Precision & Scientific Instrument Co., Ltd. The GC column was an OV-17 capillary column (50 m × φ0.32 mm × 0.1 μm). High-purity nitrogen (99.999 %) was used as the carrier gas. The detector was connected to an N2000 chromatograph work station. Each sample was analyzed at least three times to ensure the accuracy. The uncertainty of mole fraction was within ± 0.001.

Experimental Reliability Test. To verify the performance of the modified Rose still, the VLE data for benzene−toluene were measured and compared with the values in the literature.[4] The results are shown in Table 1 and Figure 2. Then the boiling point of analytical grade ethanol was measured at 101.33 kPa, and the experimental value was 351.56 K which is close to the values (351.44 K and 351.56 K) in the literature.[5,6] All of these indicate that the performance of the still is favorable.

Experimental Results. The four experimentally determined binary VLE data are shown in Table 2 and Figures 3 to 6.

Thermodynamic Consistency Test. The semiempirical method of the thermodynamics consistency test for isobaric binary VLE data suggested by Herington[7] was adopted to verify the quality of the experimental data. Herington suggested that if $(D–J) < 10$, then the experimental points are considered to be thermodynamically consistent.

$$D = \left|\frac{(\text{area}+) - (\text{area}-)}{(\text{area}+) + (\text{area}-)}\right| \cdot 100 \qquad (1)$$

where the values of "area +" and "area −" are from the $\ln(\gamma_1/\gamma_2) - x_1$ diagram.

$$J = 150 \cdot \frac{T_{\max} - T_{\min}}{T_{\min}} \qquad (2)$$

where $T_{\max}$ and $T_{\min}$ are the maximum and minimum temperatures of the system, respectively.

In this study, VLE data of the whole concentrations of the four systems were difficult to obtain, so that VLE data of the benzene−toluene system were measured to test thermodynamics consistency.

The calculated data are: $D = 3.85$; $J = 12.74$; $(D - J) = -8.89$.

The result indicates that the experimental data conform to testing criterion and the experimental device is reliable.

Correlations for Binary Data. The experimental data of the four binary systems have been correlated by using Wilson[8] and NRTL[9] equations. The objective function F for the calculation is

$$F = \frac{1}{n}\sum_{i=1}^{n}\left[\left|\frac{y_{\text{calcd}} - y_{\text{exptl}}}{y_{\text{exptl}}}\right|_i + \left|\frac{T_{\text{calcd}} - T_{\text{exptl}}}{T_{\text{exptl}}}\right|_i\right] \qquad (3)$$

where y is the mole fraction of the vapor phase; T is the equilibrium temperature, K; n is the number of experimental points; and the subscripts "calcd" and "exptl" represent calculated and experimental values, respectively. Parameters for toluene−NFM, *o*-xylene−NFM, *m*-xylene−NFM, and *p*-xylene−NFM systems using the Wilson and NRTL equations are listed in Table 3.

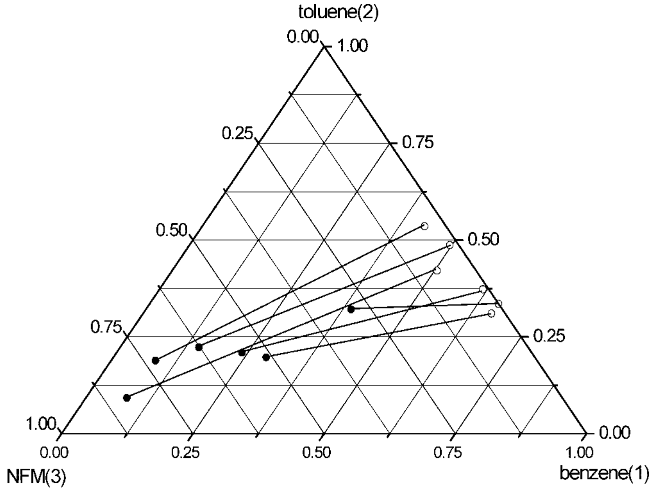

Figure 7. VLE data for the benzene (1) + toluene (2) + NFM (3) system at 101.33 kPa: ●, liquid phase; ○, vapor phase.

Table 6. Predicted Results for the Benzene (1) + Toluene (2) + NFM (3) System Using the Wilson Equation at 101.3k Pa

no.	T/K	Λ_{12}	Λ_{21}	Λ_{13}	Λ_{31}	Λ_{23}	Λ_{32}	$\gamma_{1,\text{calcd}}$	$\gamma_{1,\text{exptl}}$	$\Delta\gamma_1$
1	364.55	10.0521	0.7062	1.5499	0.4319	0.7653	0.0711	0.9913	0.9093	0.0902
2	369.35	9.7778	0.7078	1.5435	0.4360	0.7674	0.0736	0.9357	0.8434	0.1095
3	370.55	9.7115	0.7082	1.5419	0.4370	0.7679	0.0743	0.9179	0.8636	0.0629
4	372.20	9.6217	0.7087	1.5397	0.4384	0.7686	0.0751	0.9103	0.9028	0.0082
5	375.60	9.4418	0.7098	1.5353	0.4412	0.7700	0.0770	0.9089	0.8960	0.0143
6	375.73	9.4351	0.7098	1.5352	0.4413	0.7700	0.0770	0.9062	0.9040	0.0025
7	379.46	9.2454	0.7110	1.5305	0.4444	0.7715	0.0790	0.9138	0.9729	0.0607
8	381.75	9.1327	0.7116	1.5276	0.4462	0.7724	0.0803	0.9212	0.8764	0.0510
9	383.80	9.0341	0.7123	1.5251	0.4479	0.7732	0.0814	0.9213	0.8051	0.1443
10	384.25	9.0127	0.7124	1.5246	0.4482	0.7734	0.0816	0.9572	0.9596	0.0025
11	390.15	8.7416	0.7141	1.5175	0.4529	0.7757	0.0849	0.9513	0.9367	0.0157
12	392.85	8.6229	0.7149	1.5144	0.4550	0.7767	0.0864	0.9438	0.8770	0.0761
13	402.00	8.2437	0.7174	1.5042	0.4620	0.7801	0.0914	0.9442	0.9065	0.0416
14	404.83	8.1332	0.7182	1.5011	0.4641	0.7811	0.0930	0.9960	0.9545	0.0434
15	404.90	8.1305	0.7182	1.5010	0.4642	0.7811	0.0931	0.9993	1.1140	0.1030
16	411.20	7.8953	0.7199	1.4944	0.4688	0.7833	0.0966	0.9683	1.1242	0.1386
17	418.75	7.6311	0.7219	1.4867	0.4743	0.7859	0.1009	1.0554	1.0985	0.0393
18	421.45	7.5410	0.7225	1.4840	0.4762	0.7868	0.1024	1.0415	1.0344	0.0069
19	430.45	7.2562	0.7247	1.4754	0.4825	0.7897	0.1076	1.0428	0.9740	0.0707
20	440.65	6.9596	0.7271	1.4661	0.4894	0.7929	0.1134	1.0689	1.0114	0.0569

The deviations between the calculated results using the Wilson and NRTL equations and experimental results of vapor-phase mole fraction Δy_1 and temperature change ΔT of the four binary systems are listed in Table 4, which indicate that the correlated results are quite satisfactory.

Measurements and Predictions for Ternary Systems. The VLE data for the benzene−toluene−NFM ternary system were measured at 101.33 kPa and shown in Table 5 and Figure 7. The predicted results of the benzene−toluene−NFM system using the Wilson equation are listed in Table 6.

It was found that the predictions and the accuracy are acceptable for engineering design.

Conclusions

Experimental VLE data for four binary systems of toluene + NFM, *o*-xylene + NFM, *m*-xylene + NFM, and *p*-xylene + NFM were determined at 101.33 kPa. It can be seen from the experimental VLE data of the benzene−toluene system and the boiling point of ethanol that the performance of the modified Rose−Williams still is favorable. The benzene−toluene system satisfied thermodynamic consistency as validated by using the Herington semiempirical method which indicates the equipment is reliable. Analysis of the experimental data of the four binary systems by using the Wilson and NRTL equations shows that both equations generally give satisfactory results. The VLE data of the benzene−toluene−NFM ternary system were measured and predicted using the Wilson equation, which shows that BIPs adjusted on the binary system can be used for the prediction of multicomponent-system VLE.

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