Vapor−Liquid Equilibria and Density Measurement for Binary Mixtures of Benzene + Nonane, Methylbenzene + 1,2-Dimethylbenzene, 1,3-Dimethylbenzene + 2,3,4,5-Tetrahydrothiophene-1,1-dioxide (Sulfolane), 1,2-Dimethylbenzene + Sulfolane, 1,2-Dimethylbenzene + *N*-Methylformamide (NMF), 1,3-Dimethylbenzene + NMF, and 1,4-Dimethylbenzene + NMF from (333.15 to 353.15) K at Vacuum Conditions[†]

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Vapor−liquid equilibria at (333.15, 343.15, and 353.15) K for seven binary mixtures of benzene + nonane, methylbenzene + 1,2-dimethylbenzene, 1,3-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, 1,2-dimethylbenzene + *N*-methylformamide (NMF), 1,3-dimethylbenzene + NMF, and 1,4-dimethylbenzene + NMF have been obtained at pressures ranging from (0.01 to 101.3) kPa. The Wilson, nonrandom two-liquid (NRTL), and universal quasichemical (UNIQUAC) activity coefficient models have been employed to correlate experimental data to find intermolecular parameters. The nonideal behavior of the vapor phase has been considered by using the Peng−Robinson equation of state in calculating the vapor mole fraction. Liquid and vapor densities were measured by using two vibrating tube densitometers to determine liquid excess molar volumes. Six systems of benzene + nonane, 1,3-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, 1,2-dimethylbenzene + NMF, 1,3-dimethylbenzene + NMF, and 1,4-dimethylbenzene + NMF mixtures present large positive deviations from the ideal solution and belong to endothermic mixtures because their excess Gibbs energies are positive. Only one system of the methylbenzene + 1,2-dimethylbenzene mixture may present a slight exothermic mixing deviation from the ideal solution. Temperature-dependent intermolecular parameters in the three models were obtained in this study.

1. Introduction

Vapor−liquid equilibrium (VLE) data are essential for engineering design of separation processes and unit operations. It is useful for an extension of a few thermodynamic models commonly applied for designing petrochemical related processes. Accurate densities of vapor and liquid phases are critical and important to result in a proper size in the process design of many separation equipments. For an ideal system, it is relatively easy to estimate the VLE. However, the densities of vapor and liquid phases are important to give a proper size in the process design of many pieces of separation equipment. The aim of this study is to obtain isothermal binary VLE data from (333.15 to 353.15) K at vacuum conditions for seven binary systems containing aromatics and straight-chain hydrocarbons mixed with *N*-methylformamide (NMF) or with 2,3,4,5-tetrahydrothiophene-1,1-dioxide (sulfolane) that is usually used as an extractive solvent in recovering aromatics in petroleum industries. Then, binary interactional parameters in liquid-phase models by using a gamma (γ)−phi (ϕ) relationship are obtained to increase separation efficiencies of the extraction towers. Three immiscible binary mixtures of 1,2-dimethylbenzene + NMF, 1,3-dimethylbenzene + NMF, and 1,4-dimethylbenzene + NMF systems become miscible at the temperatures of (333.15, 343.15, and 353.15) K.

A few commonly used liquid-phase activity coefficient models have been described in detail.[1] The VLE data of the 1,3-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide mixture from (412.81 to 445.89) K and the 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide mixture from (419.16 to 468.49) K have been respectively measured at 101.33 kPa by Yu et al.[2] Vapor pressures of benzene have been measured at 333.15 K by Karvo,[3] and vapor pressures of 2,3,4,5-tetrahydrothiophene-1,1-dioxide have been measured at 333.15 K by Domanska et al.[4] Calvar et al. had measured the density for a binary mixture of benzene + nonane at 313.15 K and at atmospheric pressure.[5] Isothermal density and compressibility of the 1,3-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide and 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide mixtures have been measured at 298.15 K and at atmospheric pressure by Yu and Li.[6] Zhou et al. have reported that the carbonyl bond of NMF has a strong electron pair donating ability and is capable of forming OH−OC hydrogen bonds.[7] The VLE data of the NMF + water mixture from (0.344 to 7.176) kPa and the NMF + methanol mixture from (0.0398 to 32.983) kPa have been respectively measured at 313.15 K by Zielkiewicz.[8] The density data of the NMF at 298.15 K and the NMF + methanol mixture at 313.15 K have been also measured in his earlier study by Zielkiewicz.[9] Lee et al. measured VLE data and density data of the benzene + NMF

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Table 1. Critical Constants and Molar Volumes Constants of Pure Compounds

property	*n*-nonane	benzene	toluene	*o*-xylene	*m*-xylene	*p*-xylene	sulfolane	NMF
formula	C_9H_{20}	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}	$C_4H_8O_2S$	C_2H_3NO
molecular weight	128.25	78.113	92.140	106.17	106.17	106.17	120.16	59.067
T_b/K	423.97	353.24	383.78	412.27	412.27	411.51	559.96	472.66
T_c/K	594.60	562.16	591.80	630.33	617.05	616.23	829.73	721.00
P_c/kPa	2290.0	4898.0	4106.0	3734	3536.0	3511.0	4799.6	5620.0
ω	0.4434	0.2100	0.2621	0.3104	0.3258	0.3215	0.3823	0.4100
ρ^L (kg·m^{-3})[a]								
333.15 K	684.448	833.635	828.479	844.148	827.641	825.094	1229.44	966.589
343.15 K				836.741	820.015	816.353		957.591
353.15 K	668.291	811.947	808.907	826.835	809.789	807.177	1212.73	948.909
ρ^L (kg·m^{-3})[b]								
333.15 K	685.961	835.696	830.467	845.839	829.305	825.521	1231.12	967.521
343.15 K				837.421	820.476	816.734		958.801
353.15 K	669.919	814.086	810.890	828.528	811.602	807.646	1214.39	950.010

[a] Calculated liquid density using the API model in the PRO-II software.[26] [b] Experimental density in this study.

mixture at (333.15 and 353.15) K.[10] VLE data of the methylbenzene + NMF mixture were also measured. Harris et al. have measured VLE data of the benzene + NMF mixture at 363.15 K from (1.95 to 137.28) kPa.[11] Beilstein's handbook reported that the liquid density of NMF is 0.9961 g·cm^{-3} and 0.9976 g·cm^{-3} at 298.15 K.[12,13] Isothermal VLE data at (333.15, 343.15, and 353.15) K under vacuum conditions for three mixtures of 1,2-dimethylbenzene + NMF, 1,3-dimethylbenzene + NMF, and 1,4-dimethylbenzene + NMF were studied by Chen et al.[14]

Experimental $P-x$ data were measured from (333.15 to 353.15) K under vacuum ranging from (0 to 101.3) kPa for four binary mixtures of benzene + nonane, methylbenzene + 1,2-dimethylbenzene, 1,3-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, and 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide by Chen et al.[15] These phase equilibrium calculations were carried out by adopting the Peng−Robinson (PR) equation of state[16] for the vapor phase and the Wilson,[17] nonrandom two-liquid (NRTL),[18] and universal quasichemical (UNIQUAC)[19] activity coefficient models for the liquid phase. This paper reported experimental $P-T-x$ diagrams containing NMF solvent and 2,3,4,5-tetrahydrothiophene-1,1-dioxide solvent, respectively.

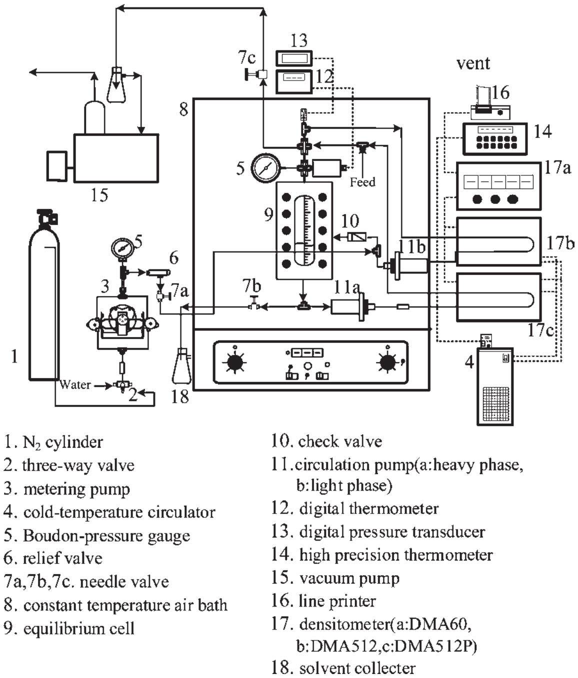

Figure 1. Schematic flow diagram of an experimental setup for vapor−liquid phase equilibrium measurement.

2. Experimental Section

2.1. Chemicals. Deionized water was prepared using a milli-Q purification system, and 99.99 % nitrogen was obtained from Air Product Co. (Taiwan). Both are used for the calibration of pressure- and temperature-related constants for two densitometers. All of the chemicals were standard-grade reagents and purchased from a local supplier, such as benzene (Fluka, ≥ 99.5 % GC, H_2O ≤ 0.03 %, evap. ≤ 0.001 %), methylbenzene (Sigma-Aldrich, ≥ 99.8 % GC, H_2O ≤ 0.001 %, evap. ≤ 0.0005 %), 1,2-dimethylbenzene (Alfa Aesar, ≥ 99 % GC), 1,3-dimethylbenzene (Alfa Aesar, ≥ 99 % GC), 1,4-dimethylbenzene (Alfa Aesar, ≥ 99 % GC), NMF (Sigma-Aldrich, ≥ 99 % GC), 2,3,4,5-tetrahydrothiophene-1,1-dioxide (Fluka, ≥ 98 % GC, H_2O ≤ 2 %), and nonane (Alfa Aesar, purum ≥ 99 % GC), used without further purification. Table 1 lists critical constants of eight pure compounds as well as calculated densities using the API model in the PRO-II software and experimental densities obtained from this study.

2.2. Apparatus and Procedures. The equilibrium system was previously designed by Chang et al.[20] and used with a little modification. The temperature was studied from (333.15 to 353.15) K and pressure measured from (0 to 101.3) kPa. Figure 1 shows the system mainly consists of a 80 mL equilibrium cell (9) equipped with a side-view glass window, a digital pressure transducer (13), a data acquisition set (17a), and two densitometers (17b, 17c). Two magnetic circulation pumps (11a, 11b) were used to speed up the achievement of the equilibrium, which is a mixed device of static and dynamic methods.

Table 2. Comparison of Experimental Liquid Densities with Calvar et al.[5] for the Nonane (1) + Benzene (2) Mixture at 313.15 K

x_1 mol	$\rho^{L,exp}$ g·cm^{-3}	x_1[a] mol	ρ[a] g·cm^{-3}
0	0.8575	0	0.8574
0.050	0.8438	0.0501	0.8397
0.1	0.8323	0.0982	0.8254
0.2	0.8114	0.1966	0.8008
0.302	0.7932	0.2948	0.7806
0.401	0.7766	0.4008	0.7638
0.502	0.7618	0.5	0.7495
0.599	0.7483	0.6003	0.7373
0.699	0.7355	0.6994	0.7262
0.799	0.7240	0.7987	0.7172
0.899	0.7131	0.8975	0.7093
0.94	0.7079	0.9465	0.7057
1	0.7025	1	0.7022

[a] Calvar et al.[5] have indicated that liquid densities of nonane and benzene are 0.7022 g·cm^{-3} and 0.8574 g·cm^{-3} at 313.15 K under atmospheric pressure, respectively.

Table 3. Experimental VLE Data of the Benzene (1) + Nonane (2) Mixture at (333.15 and 353.15) K

P kPa	x_1 mol	ρ^V $kg \cdot m^{-3}$	ρ^L $kg \cdot m^{-3}$	V^E $10^3\ m^3 \cdot mol^{-1}$	$V^{E,cal}$ $10^3\ m^3 \cdot mol^{-1}$	y_1^{cal} NRTL	y_1^{cal} UNIQUAC	y_1^{cal} Wilson
				333.15 K				
3.97	0.000	0.1868	685.961	0.000	0.000	0.0000	0.0000	0.0000
12.63	0.100	0.4286	700.985	−1.804	−1.677	0.7132	0.7119	0.7137
19.62	0.200	0.6271	715.957	−3.141	−2.977	0.8259	0.8261	0.8258
24.94	0.302	0.7759	731.175	−4.032	−3.915	0.8748	0.8754	0.8746
29.26	0.404	0.8955	746.508	−4.518	−4.463	0.9039	0.9043	0.9037
33.25	0.502	1.0062	761.194	−4.605	−4.626	0.9237	0.9239	0.9237
36.57	0.599	1.0965	775.788	−4.355	−4.437	0.9399	0.9399	0.9400
40.56	0.699	1.2055	790.766	−3.748	−3.879	0.9549	0.9547	0.9549
44.22	0.799	1.3030	805.683	−2.802	−2.956	0.9693	0.9692	0.9693
47.88	0.899	1.3983	820.654	−1.563	−1.668	0.9841	0.9841	0.9841
49.54	0.940	1.4413	826.713	−0.953	−1.035	0.9904	0.9904	0.9903
51.03	0.969	1.4805	831.191	−0.522	−0.551	0.9951	0.9952	0.9951
52.45	1.000	1.5172	835.696	0.000	0.000	1.0000	1.0000	1.0000
				353.15 K				
10.28	0.000	0.4513	669.919	0.000	0.000	0.0000	0.0000	0.0000
25.59	0.101	0.8384	684.481	−3.322	−1.714	0.6457	0.6441	0.6462
37.58	0.199	1.1500	698.728	−4.394	−3.002	0.7757	0.7759	0.7756
42.56	0.248	1.2788	705.756	−4.780	−3.507	0.8095	0.8101	0.8093
47.70	0.300	1.4124	713.217	−5.059	−3.944	0.8361	0.8368	0.8359
56.56	0.399	1.6408	727.581	−5.346	−4.491	0.8726	0.8732	0.8725
63.51	0.499	1.8142	741.992	−5.265	−4.670	0.8995	0.8997	0.8994
70.16	0.599	1.9788	756.286	−4.823	−4.474	0.9214	0.9213	0.9214
78.46	0.701	2.187	771.023	−4.043	−3.894	0.9415	0.9413	0.9415
85.24	0.799	2.3494	785.210	−3.015	−2.975	0.9603	0.9601	0.9603
92.23	0.899	2.5125	799.582	−1.650	−1.678	0.9796	0.9796	0.9795
100.00	1.000	2.6900	814.086	0.000	0.000	1.0000	1.0000	1.0000

In each experiment, the cell was first charged with 50 mL of a pure liquid or a binary mixture with a certain composition. Then, the system pressure reached the bubble point of the liquid by using a vacuum pump (15) operation. At this pressure, the temperature of the cell was indicated by a K-type digital thermometer (12) and controlled within ± 0.01 K by an air bath (8). Equilibrium was usually reached after (20 to 40) min; then, the unchanged vibration periods of the liquid and vapor phases were recorded by a printer (16). Vibration periods of vapor and liquid phases were measured by two densitometers (Anton-Paar, DMA512 and DMA512P) and a digital data processor (DMA60). The temperature in the vibrating-tube housing of the densitometer was thermally controlled by a high-precision circulator (Julabo, F10-HC) (4) at the same temperature of the cell. The temperature in the circulator was determined using a standard platinum thermometer (Hart Scientific, model 1506) (14). An equilibrium state was assured when the vibration period of the density tube is stable at least for two minutes after a one hour steady state period and when no vapor condensation occurred in the vapor phase densitometer tube. The densities of two phases can be obtained from individual calibration equation described by Chang and Chen.[21] The apparatus employed for the density calibration by using a N_2 cylinder (1), a metering pump (3), a few valves (6, 7a,b,c), a Bourdon pressure gauge (5), and a solvent collector (18) is shown in Figure 1. Table 2 lists a comparison of liquid-phase density in this study at 313.15 K with that of Calvar et al. for the nonane + benzene mixture at 313.15 K. The small difference of these liquid-density data represents the accuracy of density data measurement in this study.

In isothermal VLE data of seven binary mixtures at (333.15, 343.15, and 353.15) K, the vapor phase is at very low pressure (i.e., high vacuum), and it is difficult to measure the vapor-phase composition (y_i). Nevertheless, following similar studies of Jang et al.,[22] Klara et al.,[23] and Lee et al.,[24] a bubble-point temperature reduction method (i.e., given P, x_i to find T, y_i) was employed in this study, and the density of vapor and liquid phases was also measured. Both precisions of density in the liquid and vapor phases are within 0.00005 $g \cdot cm^{-3}$.

In our study, the experimental liquid-phase composition (x) was obtained by using a corresponding equation of $x = a\rho + b$ from the measured density (ρ) at a known liquid-phase composition. The regression coefficients of these straight lines all attain 0.999. The correction of liquid-phase composition shows that the deviation between the experimental and the prepared liquid composition is less than 0.001. The densitometer has a repeatability of about $5 \cdot 10^{-5}$ $g \cdot cm^{-3}$, and the electronic balance has the minimum reading of about $1 \cdot 10^{-5}$ g. The variation of the temperature was found to be less than ± 0.01 K, the accuracy of the pressure reading within ± 0.1 % for the full scale, and the liquid mole fraction of the component i (x_i) estimated to be deviated within ± 0.001.

3. Results and Discussion

3.1. P−x−y Phase Diagram and Density Data. The pressure-related constants of the two densitometers (K_P^L, K_P^V) were calibrated using water and nitrogen. Although the vibration frequency (τ) is not linear with respect to the density, the τ^2 is linear with respect to density, and K_P^L and K_P^V are linear with respect to pressure. Vapor and liquid densities for each experiment were calculated using the following equations:

$$K_P^{L,V} = \frac{\rho_{H_2O} - \rho_{N_2}}{\tau_{H_2O}^{\ 2} - \tau_{N_2}^{\ 2}} \tag{1}$$

$$\rho^L = \rho_{H_2O} + K_P^L[(\tau^L)^2 - (\tau_{H_2O})^2] \tag{2}$$

$$\rho^V = \rho_{N_2} + K_P^V[(\tau^V)^2 - (\tau_{N_2})^2] \tag{3}$$

For density measurement, two pressure-dependent calibration constants of the vapor and the liquid densitometer were determined at constant temperature, using water and nitrogen as calibrated fluids for all investigated pressures, and then, the density of each phase was obtained. Although densities of liquid and vapor phases were obtained, the vapor-phase composition (y_i) was calculated at system pressure (P) by knowing the liquid-

Table 4. Experimental VLE Data of the Methylbenzene (1) + 1,2-Dimethylbenzene (2) Mixture at (333.15 and 353.15) K

P kPa	x_1 mol	ρ^V $kg \cdot m^{-3}$	ρ^L $kg \cdot m^{-3}$	V^E $10^3\ m^3 \cdot mol^{-1}$	$V^{E,cal}$ $10^3\ m^3 \cdot mol^{-1}$	y_1^{cal} NRTL	y_1^{cal} UNIQUAC	y_1^{cal} Wilson
				333.15 K				
5.32	0.000	0.1767	845.800	0.000	0.000	0.0000	0.0000	0.0000
6.75	0.108	0.2341	844.136	0.031	0.026	0.2899	0.2888	0.2889
7.98	0.203	0.2838	842.673	0.054	0.044	0.4614	0.4612	0.4613
8.95	0.301	0.3241	841.173	0.065	0.058	0.5914	0.5912	0.5913
10.64	0.400	0.3906	839.661	0.056	0.065	0.6912	0.6912	0.6912
11.97	0.499	0.4071	838.134	0.069	0.068	0.7705	0.7705	0.7705
13.50	0.601	0.4874	836.576	0.057	0.065	0.8354	0.8355	0.8354
14.74	0.699	0.5349	835.072	0.061	0.057	0.8869	0.8869	0.8869
16.14	0.800	0.5882	833.533	0.040	0.044	0.9309	0.9310	0.9310
17.24	0.900	0.6303	831.999	0.016	0.025	0.9681	0.9682	0.9682
18.62	1.000	0.6829	830.467	0.000	0.000	1.0000	1.0000	1.0000
				353.15 K				
12.80	0.000	0.4397	828.500	0.000	0.000	0.0000	0.0000	0.0000
15.96	0.102	0.5491	826.692	0.028	0.029	0.2528	0.2528	0.2528
17.95	0.202	0.6184	824.931	0.054	0.052	0.4298	0.4298	0.4298
20.28	0.299	0.7003	823.222	0.067	0.067	0.5599	0.5600	0.5599
22.61	0.400	0.7824	821.449	0.078	0.077	0.6656	0.6656	0.6655
25.27	0.499	0.8765	819.705	0.074	0.080	0.7488	0.7489	0.7488
27.80	0.600	0.9796	817.918	0.072	0.077	0.8186	0.8186	0.8186
30.92	0.699	1.0979	816.176	0.056	0.067	0.8751	0.8751	0.8751
33.58	0.799	1.2001	814.417	0.045	0.051	0.9233	0.9233	0.9233
36.24	0.899	1.3022	812.661	0.013	0.029	0.9643	0.9643	0.9643
38.40	1.000	1.3863	810.890	0.000	0.000	1.0000	1.0000	1.0000

phase composition (x_i) and temperature (T), that is, to obtain P, y_i for a set of knowing T, x_i, which is similar to the work of Jang et al.[22] The excess molar volume of the liquid phase was obtained by the following equations:

$$V^E = \sum x_i M_i(\rho^{-1} - \rho_i^{-1}) \tag{4}$$

where ρ and ρ_i are the density of the liquid phase and the density of the pure components at the same P and T, respectively; M_i represents the molecular weight of the component i.

The calculated excess molar volume of the liquid phase is represented by the following equation. A_i is the regression coefficient.

$$V^{E,cal} = x_1 x_2 \sum A_i(x_1 - x_2)^i \tag{5}$$

Tables 3 to 9 present the experimental data of the liquid mole

Table 5. Experimental VLE Data of the 1,3-Dimethylbenzene (1) + 2,3,4,5-Tetrahydrothiophene-1,1-dioxide (2) Mixture at (333.15 and 353.15) K

P kPa	x_1 mol	ρ^V $kg \cdot m^{-3}$	ρ^L $kg \cdot m^{-3}$	V^E $10^3\ m^3 \cdot mol^{-1}$	$V^{E,cal}$ $10^3\ m^3 \cdot mol^{-1}$	y_1^{cal} NRTL	y_1^{cal} UNIQUAC	y_1^{cal} Wilson
				333.15 K				
0.01	0.000	0.0005	1231.12	0.000	0.000	0.0000	0.0000	0.0000
0.31	0.010	0.0120	1227.11	−0.100	−0.116	0.9648	0.9643	0.9681
0.46	0.015	0.0177	1225.10	−0.150	−0.173	0.9761	0.9758	0.9782
0.60	0.020	0.0231	1223.09	−0.199	−0.229	0.9818	0.9816	0.9834
0.87	0.030	0.0337	1219.07	−0.344	−0.340	0.9876	0.9875	0.9886
2.47	0.100	0.0946	1190.81	−0.913	−1.054	0.9959	0.9959	0.9960
3.96	0.199	0.1517	1150.86	−1.670	−1.871	0.9976	0.9976	0.9976
4.79	0.299	0.1836	1110.94	−2.299	−2.466	0.9981	0.9982	0.9981
5.27	0.399	0.2019	1070.45	−2.708	−2.828	0.9984	0.9984	0.9983
5.52	0.501	0.2116	1029.46	−2.934	−2.955	0.9985	0.9985	0.9985
5.64	0.600	0.2160	989.939	−2.948	−2.843	0.9986	0.9986	0.9986
5.73	0.700	0.2193	949.485	−2.660	−2.494	0.9987	0.9986	0.9987
5.88	0.799	0.2251	909.766	−2.122	−1.912	0.9988	0.9988	0.9988
6.11	0.900	0.2339	869.443	−1.253	−1.074	0.9991	0.9991	0.9991
6.59	1.000	0.2520	829.305	0.000	0.000	1.0000	1.0000	1.0000
				353.15 K				
0.04	0.000	0.0018	1214.39	0.000	0.000	0.0000	0.0000	0.0000
1.01	0.015	0.0370	1208.34	−0.152	−0.184	0.9565	0.9560	0.9599
1.32	0.020	0.0480	1206.33	−0.205	−0.245	0.9668	0.9665	0.9694
1.94	0.030	0.0703	1202.30	−0.309	−0.363	0.9773	0.9771	0.9789
3.08	0.050	0.1117	1194.25	−0.505	−0.593	0.9859	0.9858	0.9867
5.49	0.100	0.1985	1173.97	−0.973	−1.125	0.9925	0.9925	0.9927
8.86	0.199	0.3201	1133.93	−1.772	−1.998	0.9957	0.9957	0.9956
10.98	0.299	0.3968	1093.91	−2.453	−2.635	0.9967	0.9967	0.9966
12.13	0.399	0.4383	1053.33	−2.881	−3.022	0.9972	0.9972	0.9971
12.64	0.501	0.4565	1012.24	−3.124	−3.159	0.9974	0.9974	0.9974
13.07	0.600	0.4723	972.621	−3.152	−3.041	0.9976	0.9975	0.9976
13.28	0.700	0.4799	932.070	−2.847	−2.668	0.9977	0.9976	0.9978
13.52	0.799	0.4885	892.257	−2.273	−2.046	0.9978	0.9978	0.9980
14.00	0.900	0.5058	851.836	−1.344	−1.149	0.9983	0.9984	0.9984
15.09	1.000	0.5448	811.602	0.000	0.000	1.0000	1.0000	1.0000

Table 6. Experimental VLE Data of the 1,2-Dimethylbenzene (1) + 2,3,4,5-Tetrahydrothiophene-1,1-dioxide (2) Mixture at (333.15 and 353.15) K

P kPa	x_1 mol	ρ^V kg·m^{-3}	ρ^L kg·m^{-3}	V^E 10^3 m^3·mol^{-1}	$V^{E,cal}$ 10^3 m^3·mol^{-1}	y_1^{cal} NRTL	y_1^{cal} UNIQUAC	y_1^{cal} Wilson
				333.15 K				
0.01	0.000	0.0005	1231.12	0.000	0.000	0.0000	0.0000	0.0000
0.25	0.010	0.0098	1227.27	−0.091	−0.101	0.9561	0.9553	0.9629
0.38	0.015	0.0147	1225.35	−0.128	−0.151	0.9702	0.9697	0.9747
0.49	0.020	0.0188	1223.42	−0.173	−0.200	0.9774	0.9770	0.9807
0.72	0.030	0.0276	1219.57	−0.261	−0.297	0.9847	0.9845	0.9868
2.02	0.100	0.0776	1192.25	−0.781	−0.921	0.9951	0.9951	0.9955
3.56	0.200	0.1364	1153.84	−1.470	−1.641	0.9973	0.9973	0.9973
4.40	0.300	0.1687	1115.37	−2.015	−2.160	0.9980	0.9981	0.9979
4.97	0.400	0.1904	1076.99	−2.399	−2.474	0.9984	0.9984	0.9982
5.22	0.499	0.2001	1038.59	−2.564	−2.583	0.9985	0.9985	0.9984
5.26	0.599	0.2016	1000.24	−2.572	−2.487	0.9985	0.9985	0.9985
5.28	0.699	0.2021	961.436	−2.309	−2.184	0.9985	0.9985	0.9986
5.34	0.801	0.1971	922.401	−1.849	−1.658	0.9984	0.9984	0.9987
5.35	0.899	0.1972	884.731	−1.102	−0.947	0.9984	0.9984	0.9987
5.44	1.000	0.2082	845.839	0.000	0.000	1.0000	1.0000	1.0000
				353.15 K				
0.04	0.000	0.0018	1214.39	0.000	0.000	0.0000	0.0000	0.0000
0.05	0.010	0.0020	1210.53	−0.089	−0.108	0.8856	0.8871	0.8982
0.18	0.015	0.0067	1208.60	−0.137	−0.161	0.9208	0.9218	0.9296
0.49	0.020	0.0178	1206.67	−0.185	−0.213	0.9395	0.9403	0.9462
1.08	0.030	0.0394	1202.81	−0.271	−0.317	0.9589	0.9594	0.9633
3.34	0.100	0.1211	1175.45	−0.827	−0.981	0.9876	0.9877	0.9884
6.06	0.200	0.2193	1136.98	−1.565	−1.748	0.9938	0.9938	0.9939
8.21	0.300	0.2966	1098.46	−2.142	−2.300	0.9959	0.9959	0.9957
9.57	0.400	0.3460	1060.02	−2.547	−2.635	0.9968	0.9968	0.9967
10.82	0.499	0.3909	1021.56	−2.731	−2.751	0.9974	0.9974	0.9972
11.41	0.599	0.4123	983.157	−2.748	−2.650	0.9977	0.9977	0.9976
11.68	0.699	0.4219	944.296	−2.466	−2.327	0.9978	0.9978	0.9979
11.78	0.801	0.4255	905.202	−1.972	−1.767	0.9979	0.9979	0.9981
11.95	0.899	0.4317	867.477	−1.183	−1.009	0.9981	0.9981	0.9983
12.66	1.000	0.4571	828.528	0.000	0.000	1.0000	1.0000	1.0000

Table 7. Experimental VLE Data of the 1,2-Dimethylbenzene (1) + NMF (2) Mixture at (333.15, 343.15, and 353.15) K

P kPa	x_1 mol	ρ^V kg·m^{-3}	ρ^L kg·m^{-3}	V^E 10^3 m^3·mol^{-1}	$V^{E,cal}$ 10^3 m^3·mol^{-1}	y_1^{cal} NRTL	y_1^{cal} UNIQUAC	y_1^{cal} Wilson
				333.15 K				
0.37	0.000	967.461	0.0079	0.000	0.000	0.0000	0.0000	0.0000
0.92	0.100	955.279	0.0212	−0.740	−0.773	0.6365	0.6367	0.6365
1.46	0.201	943.061	0.0360	−1.333	−1.382	0.7953	0.7952	0.7953
1.98	0.300	930.949	0.0524	−1.769	−1.811	0.8671	0.8670	0.8671
2.49	0.401	918.701	0.0700	−2.050	−2.075	0.9090	0.9090	0.9090
2.98	0.499	906.743	0.0889	−2.162	−2.163	0.9359	0.9359	0.9359
3.49	0.601	894.398	0.1099	−2.102	−2.079	0.9557	0.9557	0.9557
3.96	0.698	882.623	0.1312	−1.874	−1.830	0.96996	0.96997	0.96996
4.46	0.800	870.121	0.1556	−1.440	−1.392	0.9821	0.9821	0.9821
4.93	0.899	858.136	0.1804	−0.830	−0.791	0.9916	0.9916	0.9916
5.45	1.000	845.839	0.2087	0.000	0.000	1.0000	1.0000	1.0000
				343.15 K				
0.67	0.000	958.765	0.0138	0.000	0.000	0.0000	0.0000	0.0000
1.49	0.099	946.741	0.0330	−0.736	−0.770	0.5931	0.5934	0.5932
2.30	0.201	934.413	0.0552	−1.341	−1.389	0.7667	0.7666	0.7667
3.08	0.301	922.286	0.0789	−1.780	−1.823	0.8475	0.8473	0.8475
3.86	0.400	910.279	0.1051	−2.058	−2.083	0.8946	0.8945	0.8946
4.63	0.500	898.117	0.1338	−2.173	−2.174	0.9263	0.9263	0.9263
5.41	0.599	886.023	0.1652	−2.116	−2.092	0.9488	0.9488	0.9488
6.14	0.700	873.758	0.1980	−1.874	−1.833	0.9661	0.9661	0.9661
6.88	0.800	861.715	0.2331	−1.451	−1.399	0.9795	0.9796	0.9795
7.64	0.899	849.639	0.2713	−0.833	−0.795	0.9906	0.9906	0.9906
8.47	1.000	837.399	0.3149	0.000	0.000	1.0000	1.0000	1.0000
				353.15 K				
1.15	0.000	949.980	0.0231	0.000	0.000	0.0000	0.0000	0.0000
2.34	0.100	937.805	0.0507	−0.771	−0.805	0.5588	0.5592	0.5588
3.55	0.200	925.706	0.0826	−1.384	−1.435	0.7377	0.7376	0.7377
4.68	0.300	913.562	0.1164	−1.841	−1.886	0.8268	0.8267	0.8268
5.85	0.400	901.432	0.1549	−2.132	−2.160	0.8802	0.8801	0.8802
6.99	0.499	889.316	0.1963	−2.252	−2.254	0.9159	0.9159	0.9159
8.14	0.601	877.006	0.2420	−2.191	−2.166	0.9420	0.9420	0.9420
9.22	0.699	865.051	0.2884	−1.948	−1.903	0.9612	0.9612	0.9612
10.46	0.801	852.738	0.3442	−1.499	−1.445	0.9769	0.9769	0.9769
11.51	0.900	840.639	0.3970	−0.856	−0.817	0.9895	0.9895	0.9895
12.71	1.000	828.528	0.4587	0.000	0.000	1.0000	1.0000	1.0000

Table 8. Experimental VLE Data of the 1,3-Dimethylbenzene (1) + NMF (2) Mixture at (333.15, 343.15, and 353.15) K

P kPa	x_1 mol	ρ^V kg·m^{-3}	ρ^L kg·m^{-3}	V^E 10^3 m^3·mol^{-1}	$V^{E,cal}$ 10^3 m^3·mol^{-1}	y_1^{cal} NRTL	y_1^{cal} UNIQUAC	y_1^{cal} Wilson
				333.15 K				
0.37	0.000	967.461	0.0079	0.000	0.000	0.0000	0.0000	0.0000
0.98	0.100	953.656	0.0224	−0.872	−0.920	0.6732	0.6731	0.6732
1.69	0.200	939.829	0.0418	−1.575	−1.639	0.8208	0.8205	0.8208
2.31	0.301	925.816	0.0610	−2.104	−2.160	0.8863	0.8862	0.8863
2.92	0.400	912.150	0.0820	−2.435	−2.469	0.9225	0.9225	0.9224
3.54	0.501	898.304	0.1057	−2.575	−2.577	0.9463	0.9463	0.9462
4.18	0.601	884.463	0.1318	−2.509	−2.477	0.9630	0.9631	0.9630
4.70	0.701	870.672	0.1560	−2.229	−2.170	0.9755	0.9756	0.9755
5.32	0.800	856.867	0.1856	−1.724	−1.659	0.9854	0.9854	0.9854
5.94	0.899	843.274	0.2172	−0.997	−0.944	0.9932	0.9932	0.9932
6.58	1.000	829.305	0.2519	0.000	0.000	1.0000	1.0000	1.0000
				343.15 K				
0.67	0.000	958.765	0.0138	0.000	0.000	0.0000	0.0000	0.0000
1.74	0.100	944.911	0.0543	−0.894	−0.942	0.6394	0.6408	0.6389
2.69	0.201	931.014	0.0909	−1.615	−1.684	0.7978	0.7980	0.7977
3.55	0.300	917.240	0.1242	−2.148	−2.206	0.8693	0.8692	0.8693
4.48	0.401	903.309	0.1599	−2.493	−2.529	0.9109	0.9107	0.9110
5.56	0.499	889.710	0.2008	−2.635	−2.638	0.9375	0.9373	0.9376
6.38	0.601	875.637	0.2324	−2.568	−2.535	0.9570	0.9569	0.9571
7.33	0.698	862.285	0.2687	−2.295	−2.233	0.9710	0.9710	0.9711
8.27	0.800	848.058	0.3051	−1.767	−1.699	0.9828	0.9828	0.9828
9.22	0.899	834.428	0.3414	−1.021	−0.966	0.9920	0.9920	0.9920
10.17	1.000	820.443	0.3779	0.000	0.000	1.0000	1.0000	1.0000
				353.15 K				
1.15	0.000	949.980	0.0231	0.000	0.000	0.0000	0.0000	0.0000
2.55	0.099	936.271	0.0756	−0.905	−0.955	0.5962	0.5967	0.5962
4.02	0.201	922.151	0.1304	−1.655	−1.723	0.7696	0.7695	0.7696
5.40	0.300	908.470	0.1821	−2.195	−2.257	0.8491	0.8489	0.8491
6.77	0.400	894.594	0.2333	−2.549	−2.585	0.8966	0.8965	0.8966
8.13	0.500	880.820	0.2841	−2.696	−2.698	0.9279	0.9278	0.9279
9.53	0.600	866.999	0.3366	−2.630	−2.596	0.9503	0.9503	0.9503
10.91	0.699	853.268	0.3880	−2.342	−2.280	0.9671	0.9671	0.9671
12.25	0.800	839.222	0.4385	−1.808	−1.738	0.9805	0.9805	0.9805
13.71	0.900	825.505	0.4930	−1.040	−0.980	0.9911	0.9911	0.9911
15.12	1.000	811.602	0.5457	0.000	0.000	1.0000	1.0000	1.0000

fraction of one component i (x_i), the density of each phase (ρ^V, ρ^L), excess molar volume (V^E), and calculated excess molar volume ($V^{E,\ cal}$) of the liquid phase for seven binary systems from (333.15 to 353.15) K, respectively. Our experimental data show that liquid densities of nonane and benzene are 685.961 kg·m^{-3} and 835.696 kg·m^{-3} at 333.15 K under vacuum conditions, respectively. The excess molar volumes of the benzene + nonane mixture at (333.15 and 353.15) K present negative values, as shown in Table 3. Similarly, the negative excess molar volumes of 1,3-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide mixtures (Table 5), 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide (Table 6), 1,2-dimethylbenzene + NMF (Table 7), 1,3-dimethylbenzene + NMF (Table 8), and 1,4-dimethylbenzene + NMF (Table 9). However, the excess molar volumes of the methylbenzene

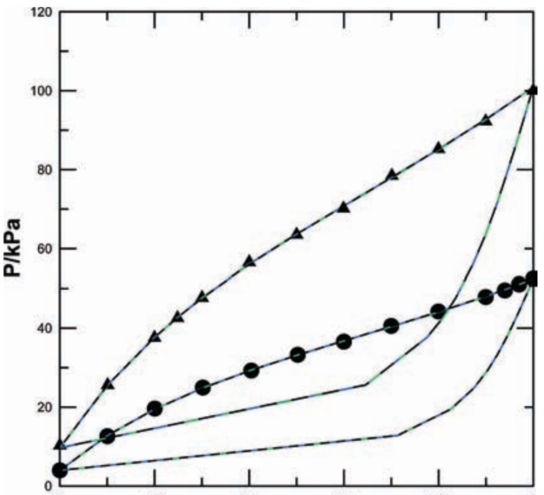

Figure 2. $P-x-y$ diagram of the benzene (1) + nonane (2) mixture at (333.15 and 353.15) K. ●, 333.15 K; ▲, 353.15 K; —, PR-NRTL; – –, PR-UNIQUAC; ---, PR-Wilson.

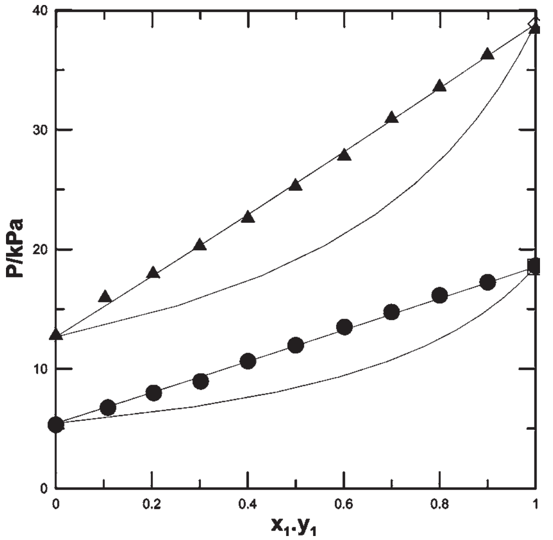

Figure 3. $P-x-y$ diagram of the methylbenzene (1) + 1,2-dimethylbenzene (2) mixture at (333.15 and 353.15) K. ●, 333.15 K;, ▲, 353.15 K; —, PR-NRTL; – –, PR-UNIQUAC; ---, PR-Wilson; □, 333.15 K (PRO-II); ◇, 353.15 K (PRO-II).

Table 9. Experimental VLE Data of the 1,4-Dimethylbenzene (1) + NMF (2) Mixture at (333.15, 343.15, and 353.15) K

P kPa	x_1 mol	ρ^V $kg \cdot m^{-3}$	ρ^L $kg \cdot m^{-3}$	V^E 10^3 $m^3 \cdot mol^{-1}$	$V^{E,cal}$ 10^3 $m^3 \cdot mol^{-1}$	y_1^{cal} NRTL	y_1^{cal} UNIQUAC	y_1^{cal} Wilson
				333.15 K				
0.37	0.000	967.461	0.0079	0.000	0.000	0.0000	0.0000	0.0000
1.07	0.101	953.153	0.0247	−0.912	−0.964	0.6883	0.6886	0.6883
1.76	0.201	938.932	0.0434	−1.640	−1.708	0.8294	0.8293	0.8294
2.40	0.300	924.819	0.0633	−2.179	−2.238	0.8906	0.8905	0.8906
3.05	0.400	910.762	0.0856	−2.525	−2.563	0.9253	0.9252	0.9253
3.71	0.500	896.493	0.1105	−2.673	−2.676	0.9481	0.9481	0.9481
4.31	0.600	882.334	0.1356	−2.608	−2.574	0.9641	0.9641	0.9641
4.95	0.700	868.075	0.1642	−2.318	−2.257	0.9763	0.9763	0.9763
5.56	0.800	853.939	0.1940	−1.797	−1.723	0.9857	0.9857	0.9857
6.21	0.900	839.770	0.2269	−1.030	−0.971	0.9935	0.9935	0.9935
6.85	1.000	825.539	0.2620	0.000	0.000	1.0000	1.0000	1.0000
				343.15 K				
0.67	0.000	958.765	0.0138	0.000	0.000	0.0000	0.0000	0.0000
1.71	0.100	944.552	0.0382	−0.926	−0.978	0.6490	0.6495	0.6491
2.74	0.200	930.324	0.0658	−1.672	−1.742	0.8034	0.8033	0.8034
3.72	0.300	916.152	0.0954	−2.227	−2.291	0.8730	0.8728	0.8730
4.70	0.400	901.907	0.1281	−2.586	−2.624	0.9132	0.9131	0.9132
5.65	0.501	887.537	0.1635	−2.738	−2.739	0.9582	0.9582	0.9582
6.65	0.600	873.479	0.2033	−2.670	−2.635	0.9582	0.9582	0.9582
7.58	0.700	859.306	0.2443	−2.375	−2.311	0.9723	0.9723	0.9723
8.54	0.800	845.071	0.2891	−1.839	−1.764	0.9834	0.9834	0.9834
9.51	0.899	830.948	0.3375	−1.058	−1.003	0.9924	0.9924	0.9924
10.50	1.000	816.664	0.3903	0.000	0.000	1.0000	1.0000	1.0000
				353.15 K				
1.15	0.000	949.980	0.0231	0.000	0.000	0.0000	0.0000	0.0000
2.64	0.100	935.754	0.0572	−0.948	−1.002	0.6056	0.6060	0.6056
4.10	0.200	921.474	0.0955	−1.714	−1.785	0.7744	0.7743	0.7744
5.54	0.300	907.258	0.1380	−2.283	−2.349	0.8535	0.8533	0.8535
6.98	0.400	893.081	0.1851	−2.649	−2.690	0.8997	0.8996	0.8997
8.40	0.500	878.818	0.2361	−2.805	−2.808	0.9303	0.9303	0.9303
9.87	0.600	864.525	0.2932	−2.736	−2.701	0.9521	0.9521	0.9521
11.28	0.701	850.269	0.3530	−2.433	−2.364	0.9684	0.9684	0.9684
12.71	0.800	836.094	0.4183	−1.886	−1.809	0.9812	0.9812	0.9812
14.15	0.900	821.910	0.4883	−1.082	−1.020	0.9914	0.9914	0.9914
15.61	1.000	807.649	0.5636	0.000	0.000	1.0000	1.0000	1.0000

+ 1,2-dimethylbenzene mixture at (333.15 and 353.15) K present positive values (Table 4). The minimum excess volume of mixing is 13.0 $cm^3 \cdot mol^{-1}$ for this system.

To our knowledge, densities of eight pure compounds at (333.15, 343.15, and 353.15) K under atmospheric pressure have not been found in the literature. In isothermal VLE of the 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide mixture, the vapor phase is at very low pressure. Hence, there are a few discrepancies of vapor pressure of 2,3,4,5-tetrahydrothiophene-1,1-dioxide between our data and those of Karvo at 333.15 K[3] and Domanska et al. at 353.15 K.[4]

Figures 2 to 8 display the experimental liquid mole fraction and the calculated $P-x-y$ phase diagram by using the Wilson, NRTL, and UNIQUAC models, respectively. For comparison, vapor pressures of methylbenzene at (333.15 and 353.15) K, calculated by the PRO-II software,[26] are also plotted in Figure 3. These three models fit experimental data well for all four binary systems. There may be an azeotropic point existing in two systems containing the 2,3,4,5-tetrahydrothiophene-1,1-dioxide component. Figure 9 displays the experimental excess molar volumes and calculated excess molar volumes of the methylbenzene and 1,2-dimethylbenzene system at (333.15 and 353.15) K showing positive deviations from the ideal solution.

Usually, the order of magnitude of the Gibbs excess energy (G^E) in a binary regular mixing solution is mainly determined by the excess enthalpy (H^E) and the excess entropy (S^E) through the relation of $G^E = H^E - T(S^E)$. Table 10 shows the methylbenzene + 1,2-dimethylbenzene mixture exhibiting a small negative G^E value which indicates it might be an exothermic system close to an ideal solution. The other three mixtures of the benzene + nonane, 1,3-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, and 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide mixtures presenting positive G^E values indicate that they belong to endothermic systems. Three dimethylbenzene + NMF mixtures exhibiting positive G^E values indicate that they belong to endothermic systems.

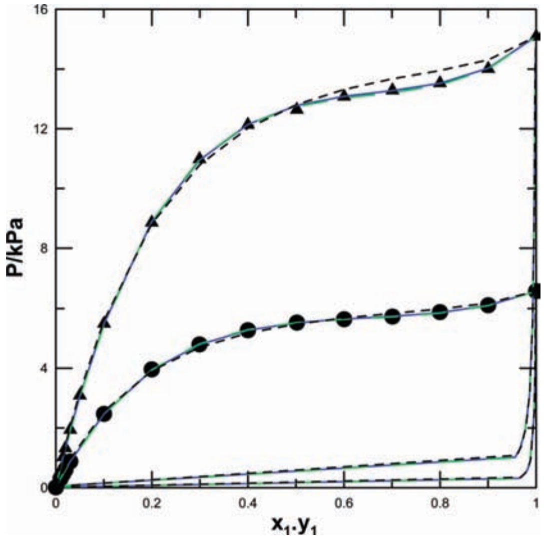

Figure 4. $P-x-y$ diagram of the 1,3-dimethylbenzene (1) + 2,3,4,5-tetrahydrothiophene-1,1-dioxide (2) mixture at (333.15 and 353.15) K. ●, 333.15 K; ▲, 353.15 K; —, PR-NRTL; − −, PR-UNIQUAC; ---, PR-Wilson.

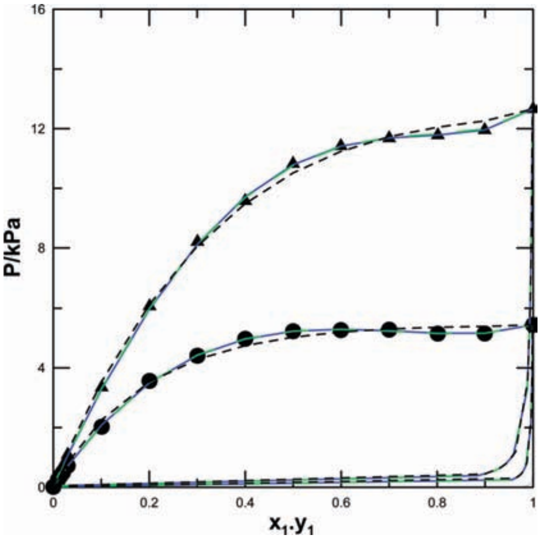

Figure 5. $P-x-y$ diagram of the 1,2-dimethylbenzene (1) + 2,3,4,5-tetrahydrothiophene-1,1-dioxide (2) mixture at (333.15 and 353.15) K. ●, 333.15 K; ▲, 353.15 K; −, PR-NRTL; −−, PR-UNIQUAC; ---, PR-Wilson.

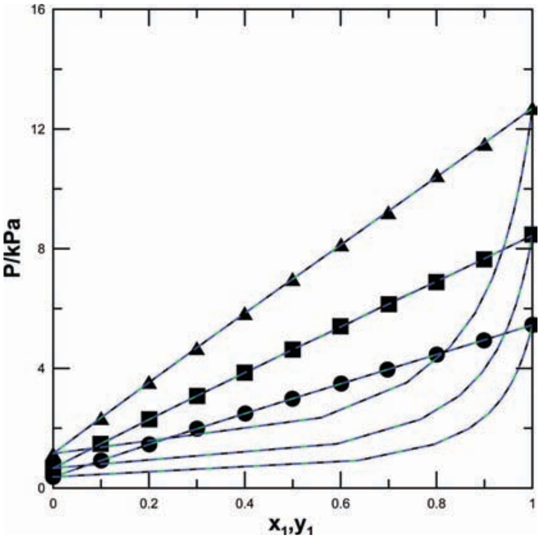

Figure 6. $P-x-y$ diagram of the 1,2-dimethylbenzene (1) + NMF (2) mixture at (333.15, 343.15, and 353.15) K. ●, 333.15 K; ■, 343.15 K; ▲, 353.15 K; −, PR-NRTL; −−, PR-UNIQUAC; ---, PR-Wilson.

3.2. Data Correlation. A classical VLE relationship between the activity coefficient (γ_i) and the fugacity coefficient (ϕ_i) shown in eq 6 was employed for the data correlation of experimental bubble pressure (P^{exp}) and liquid mole fraction (x_i).

$$P^{\text{exp}} = \sum_{i=1}^{2} \frac{\gamma_i x_i P_i^{\text{sat}} \phi_i^{\text{sat}} \exp[V_i^L(P - P_i^{\text{sat}})/RT]}{\phi_i} \qquad (6)$$

where ϕ_i^{sat} is the fugacity coefficient of pure component i in its saturated state, the saturated vapor pressure is denoted by P_i^{sat}, and V_i^{L} is the saturated liquid molar volume of pure component i. The Ponyting pressure correction was considered to be unity in this study. Then, γ_i can be calculated by giving experimental bubble pressure (P^{exp}) and liquid mole fraction (x_i). The γ_i was individually obtained by the Wilson,[17] NRTL,[18] or UNIQUAC[19] models. The ϕ_i and ϕ_i^{sat} were calculated by the Peng−Robinson equation of state (PR-EoS),[16] shown in eq 7. The simple van der Waals mixing rule[25] was used to evaluate the mixture parameters.

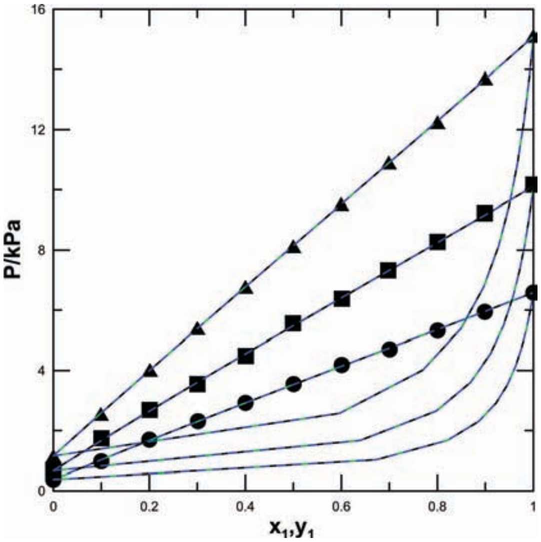

Figure 7. $P-x-y$ diagram of the 1,3-dimethylbenzene (1) + NMF (2) mixture at (333.15, 343.15, and 353.15) K. ●, 333.15 K; ■, 343.15 K; ▲, 353.15 K; −, PR-NRTL; −−, PR-UNIQUAC; ---, PR-Wilson.

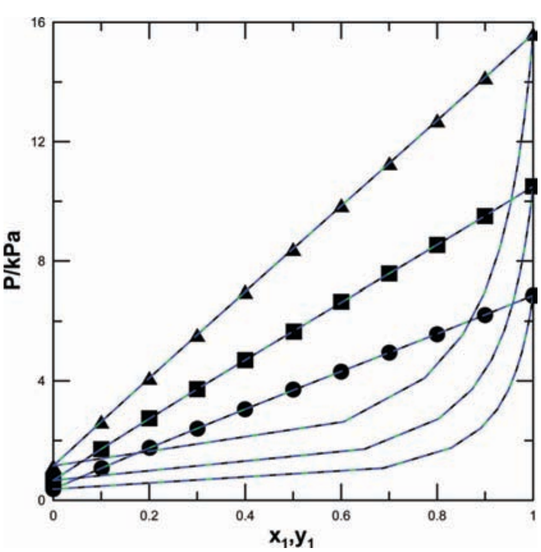

Figure 8. $P-x-y$ diagram of the 1,4-dimethylbenzene (1) + NMF (2) mixture at (333.15, 343.15, and 353.15) K. ●, 333.15 K; ■, 343.15 K; ▲, 353.15 K; −, PR-NRTL; −−, PR-UNIQUAC; ---, PR-Wilson.

The experimental results were then used to obtain the binary parameters by using the PR-EoS[16] combined with various activity coefficient models of Wilson, NRTL, and UNIQUAC. The expressions for the activity coefficients for the Wilson,[17] NRTL,[18] and UNIQUAC[19] model are listed in the literature. The optimal interaction parameters for each binary system were obtained by minimizing the following objective function (Π).

$$\Pi = \left(\frac{100}{2n}\right) \sum_{k=1}^{n} \left[\left|\frac{P_k^{\text{cal}} - P_k^{\text{exp}}}{P_k^{\text{exp}}}\right|\right] \qquad (7)$$

The regression results are shown in Table 10. The root-mean-square deviations of ΔP were defined as follows:

$$\Delta P = \sqrt{\frac{\sum_{k}^{n} (P_k^{\text{cal}} - P_k^{\text{exp}})^2}{n}} \qquad (8)$$

Table 10. Optimal Binary Interaction Parameters in Wilson, NRTL, and UNIQUAC Correlations for Seven Binary Mixtures

	PR/NRTL[a]				PR/UNIQUAC[b]				PR/Wilson[c]			
T/K	A_{12}	A_{21}	δP^d	$G^E_{(x=0.5)}$	A_{12}	A_{21}	δP	$G^E_{(x=0.5)}$	A_{12}	A_{21}	δP	$G^E_{(x=0.5)}$
	(T/K)	(T/K)	(P/kPa)	($\mathrm{J \cdot mol^{-1}}$)	(T/K)	(T/K)	(P/kPa)	($\mathrm{J \cdot mol^{-1}}$)	(T/K)	(T/K)	(P/kPa)	($\mathrm{J \cdot mol^{-1}}$)
Benzene (1) + Nonane (2)												
333.15	−46.128	45.173	0.1780	399.22	326.29	−217.07	0.1779	398.08	4.4661	−4.4664	0.1780	399.76
353.15	79.51	−82.369	0.305332	449.97	27.201	−27.202	0.3058	447.83	−119.98	119.98	0.3050	450.57
Methylbenzene (1) + 1,2-Dimethylbenzene (2)												
333.15	79.255	168.41	0.1422	−5.8849	−149.44	304.96	0.1447	−6.4672	−71.271	329.7	0.1452	−6.4671
353.15	54.431	184.29	0.4342	−17.507	−161.54	319.32	0.4337	−17.507	−76.548	323.92	0.4371	−17.677
1,3-Dimethylbenzene (1) + 2,3,4,5-Tetrahydrothiophene-1,1-dioxide (2)												
333.15	576.33	178.13	0.0104	1229.5	263.20	−37.122	0.0162	1229.5	361.39	561.23	0.0795	1222.9
353.15	646.69	161.50	0.0461	1304.4	300.22	−53.273	0.0529	1304.0	359.22	633.84	0.2336	1296.7
1,2-Dimethylbenzene (1) + 2,3,4,5-Tetrahydrothiophene-1,1-dioxide (2)												
333.15	916.10	101.80	0.0312	1362.1	433.12	−102.56	0.0313	1361.5	320.49	1467.6	0.1621	1352.4
353.15	966.92	−64.348	0.1780	1090.2	493.53	−162.80	0.1803	1091.7	162.79	1045.1	0.2748	1099.8
1,2-Dimethylbenzene (1) + NMF (2)												
333.15	141.2	−93.305	0.4071	72.75	186.74	−142.4	0.4111	72.84	189.33	−136.14	0.4117	73.05
343.15	104.1	−72.033	1.4520	52.11	208.25	−178.5	1.4507	52.20	177.78	−132.71	1.4596	52.33
353.15	88.674	−63.833	2.3493	41.09	218.49	−195.17	2.3648	41.10	172.96	−131.91	2.3684	41.51
1,3-Dimethylbenzene (1) + NMF (2)												
333.15	63.878	−37.166	2.8087	50.41	232.37	−206.66	2.8113	50.54	170.18	−127.41	2.8480	50.04
343.15	117.11	−80.348	5.4118	58.09	188.75	−150.09	5.4042	57.05	169.34	−126.15	5.3544	60.18
353.15	−85.004	109.60	2.1277	34.15	337.90	−315.60	2.1385	34.11	142.51	−112.38	2.1703	34.64
1,4-Dimethylbenzene (1) + NMF (2)												
333.15	8.596	22.923	0.9653	64.95	268.25	−236.60	0.9653	64.95	157.12	−116.68	0.9870	65.37
343.15	−46.148	77.989	1.1749	58.71	311.15	−280.26	1.1744	58.74	147.46	−111.65	1.1663	59.22
353.15	13.106	2.5791	0.7786	32.44	268.99	−253.28	0.7764	32.44	158.67	−123.70	0.7622	32.96

[a] NRTL: $A_{12} = (g_{12} - g_{22})/R$; $A_{21} = (g_{21} - g_{11})/R$; $\alpha = 0.3$; NRTL interaction energy between i and j ($g_{ji} - g_{ii}$). [b] UNIQUAC: $A_{12} = (U_{12} - U_{22})/R$; $A_{21} = (U_{21} - U_{11})/R$; UNIQUAC interaction energy between i and j ($U_{ji} - U_{ii}$). [c] Wilson: $A_{12} = (\lambda_{12} - \lambda_{22})/R$; $A_{21} = (\lambda_{21} - \lambda_{11})/R$; Wilson interaction energy between i and j ($\lambda_{ij} - \lambda_{jj}$). [d] $\delta P = (\sum_{i=1}^{n}(P_i^{\mathrm{cal}} - P_i^{\mathrm{exp}})^2/n)^{1/2}$.

The deviation between experimental and calculated equilibrium bubble pressures is reasonably small, and it is indicated that these three activity coefficient models are suitable to represent the binary experimental data. The calculated $P-x-y$ diagrams of seven binary systems are shown in Figures 2 to 8, respectively. As expected, nevertheless, there is little difference among three liquid activity coefficient models for the seven binary systems studied. Table 10 shows the calculated excess Gibbs energy (G^E) at equal mole fractions using the Wilson, NRTL, and UNIQUAC models.

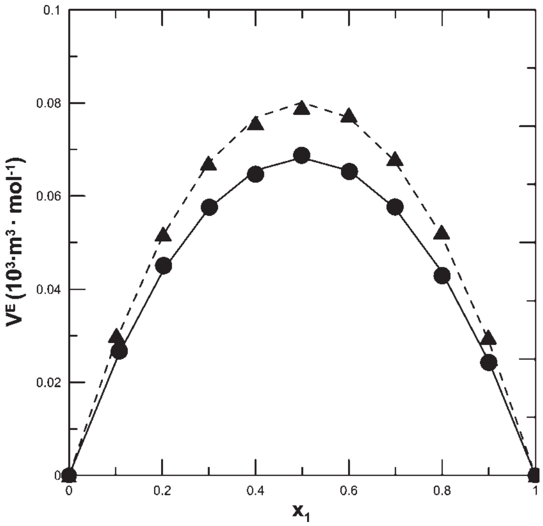

Figure 9. Excess molar volumes of the methylbenzene (1) + 1,2-dimethylbenzene (2) mixture at (333.15 and 353.15) K. ●, 333.15 K; ■, 353.15 K; —, 333.15 K by eq 5; ---, 353.15 K by eq 5.

4. Conclusions

Vapor−liquid equilibria of seven binary mixtures of benzene + nonane, methylbenzene + 1,2-dimethylbenzene, 1,3-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, 1,2-dimethylbenzene + NMF, 1,3-dimethylbenzene + NMF, and 1,4-dimethylbenzene + NMF have successfully been obtained from (333.15 to 353.15) K at vacuum conditions in this study. Experimental data of phase densities, liquid mole fractions, and system pressures were determined using the bubble-point method coupled with two vibration densitometers. Three activity coefficient models have been employed to correlate the experimental data, and the results are satisfactory. The calculated activity coefficient (γ_i) and excess Gibbs energy (G^E) negative values reveal that the methylbenzene + 1,2-dimethylbenzene mixture was slightly close to the ideal solution. However, six systems of benzene + nonane, 1,3-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, 1,2-dimethylbenzene + 2,3,4,5-tetrahydrothiophene-1,1-dioxide, 1,2-dimethylbenzene + NMF, 1,3-dimethylbenzene + NMF, and 1,4-dimethylbenzene + NMF mixtures show an apparent positive deviation from the ideal solution. Only the excess molar volume of the methylbenzene + 1,2-dimethylbenzene system presents a positive deviation (Figure 9). The associated binary interaction parameters between each component for seven mixtures were finally obtained from the optimal correlation of our experimental data.

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