

Isobaric Vapor–Liquid Equilibria for Binary Systems of Acetic Acid + Benzene, Chloroacetic Acid + Benzene, and Dichloroacetic Acid + Benzene at 101.33 kPa

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Vapor–liquid equilibria (VLE) data for acetic acid + benzene, chloroacetic acid + benzene, and dichloroacetic acid + benzene binary systems have been measured at 101.33 kPa using a recirculating still. The experimental data were checked with the Herington method, which showed thermodynamic consistency. The Wilson, nonrandom two-liquid (NRTL), and universal quasi-chemical (UNIQUAC) activity coefficient models, combined with the Hayden–O’Connell equation, to account for the nonideality of the vapor phase due to the association of the acetic acid, were used to correlate the VLE data. The Wilson model correlated the experimental results better than the NRTL and UNIQUAC models.

Introduction

Chloroacetic acid is an important intermediate for medicine, dyes, pesticide, and other organic synthesis. During the process of chloroacetic acid production, the mother liquor with a certain amount of chloroacetic acid is produced. Generally, the mother liquor can be utilized further by deep chlorination to synthesize trichloroacetyl chloride, where a gas containing hydrogen chloride, acetic acid, chloroacetic acid, and dichloroacetic acid is produced. The gas needs to be absorbed to obtain hydrochloric acid by removing acetic acid, chloroacetic acid, and dichloroacetic acid. For such a purpose, benzene is often selected as a solvent to separate acetic acid, chloroacetic acid, and dichloroacetic acid from the gas, which can be recovered by distillation. It is known that vapor–liquid equilibria (VLE) data are vital to the simulation and design of the distillation process. Until now, many papers report the isobaric VLE data of the systems of acetic acid with toluene, octane, water, isopropyl acetate, *n*-pentyl acetate, *N*-methyl pyrrolidone, and *N*-methyl acetamide.^{1–4} However, for the systems of benzene with acetic acid, chloroacetic acid, and dichloroacetic acid, only the isobaric VLE data for the benzene + acetic acid system are reported.^{5,6} To our knowledge, no experimental study of the VLE of benzene with chloroacetic acid and dichloroacetic acid at 101.33 kPa has been found.

Acetic acid molecules strongly associate with each other to form stable dimers in both the liquid and the vapor phases. The deviation from ideal gas behavior caused by the dimerization of acetic acid molecules and interaction between two molecules in the vapor phase is described with the Hayden–O’Connell⁷ (HOC) equation, which is commonly used to calculate the VLE of the systems with associating components. The nonidealities in the liquid phase are considered by the Wilson model,⁸ nonrandom two-liquid model (NRTL),⁹ and universal quasi-chemical theory (UNIQUAC) model.¹⁰ In the present work, the Wilson, NRTL, and UNIQUAC models were combined with the HOC method for correlating the VLE of the binary systems.

Experimental Section

Chemicals. Analytical reagent benzene (Ruijinte Chemical Reagent Co., Tianjin) had the purity of 0.995. Acetic acid (AR, 0.995 mass fraction), chloroacetic acid (AR, 0.995), and dichloroacetic acid (AR, 0.990) were purchased from Guoyao Chemical Reagent Co., Shanghai, and the purities of the chemicals were checked by high-performance liquid chromatography (HPLC; LC-6A, Shimadzu Scientific Instruments) and gas chromatography (GC-960, Shanghai Haixin Chromatography Co., Ltd.). All of the chemicals were used without further purification.

Apparatus and Procedures. In this work, the VLE data were determined using a recirculating still of the modified Rose type as described by Huang.¹¹ In this still, both liquid and condensed vapor phases are continuously recirculated to provide intimate contact of the phases and ensure that equilibrium can be established rapidly. In each experiment, equilibria conditions were assumed when a constant vapor temperature was obtained for at least 30 min and the samples of the liquid and condensed vapor were withdrawn for analysis.

The temperature was measured by using a calibrated mercury thermometer with the uncertainty of ± 0.1 K. The pressure was maintained at 101.3 kPa by a U-shaped differential manometer in which the fluctuation was held within 0.03 kPa with a two-step automatic control system. The estimated uncertainty of the pressure measurement was less than ± 0.50 kPa. The liquid and condensed vapor samples were analyzed by a GC-960 gas chromatograph (GC) equipped with a flame ionization detector, which the column was an FFAP capillary column. The carrier gas was hydrogen flowing at $50 \text{ mL} \cdot \text{min}^{-1}$, and the column temperature was 473 K. The injector and detector temperatures were (428 and 473) K, respectively. The GC was calibrated using different mixtures of known compositions, prepared gravimetrically by an electronic balance (uncertainty of ± 0.0001 g). The uncertainty of the measured mole fraction was ± 0.003 .

Results and Discussion

Experimental Data. The VLE data for the binary systems of acetic acid + benzene, chloroacetic acid + benzene, and

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Table 1. Experimental VLE Data and Calculation Results for the Systems of Acetic Acid (1) + Benzene (2), Chloroacetic Acid (1) + Benzene (2), and Dichloroacetic Acid (1) + Benzene (2) at 101.33 kPa

T/K	x_1	y_1	Wilson		NRTL		UNIQUAC	
			γ_1	γ_2	γ_1	γ_2	γ_1	γ_2
Acetic Acid (1) + Benzene (2)								
383.95	0.9881	0.9165	1.0001	1.4077	1.0001	1.9294	1.0001	1.9278
380.95	0.9682	0.8347	1.0006	1.3821	1.0005	1.8973	1.0005	1.8963
378.65	0.9499	0.775	1.0014	1.3594	1.0013	1.8672	1.0014	1.8672
375.85	0.9316	0.7027	1.0026	1.3388	1.0025	1.8388	1.0026	1.8345
372.85	0.9006	0.6202	1.0053	1.3043	1.0055	1.7881	1.0053	1.7861
369.95	0.8545	0.5493	1.0108	1.2575	1.0120	1.7128	1.0116	1.7138
367.35	0.8196	0.4898	1.0162	1.2271	1.0189	1.6593	1.0175	1.6543
365.35	0.7862	0.4467	1.0221	1.2007	1.0272	1.6095	1.0246	1.6075
364.05	0.7583	0.4141	1.0276	1.1806	1.0354	1.5690	1.0354	1.5680
361.95	0.6916	0.3644	1.0425	1.1386	1.0606	1.4766	1.0616	1.4776
359.95	0.6288	0.3045	1.0586	1.1069	1.0922	1.3978	1.0953	1.3938
358.85	0.5707	0.2703	1.0749	1.0827	1.1295	1.3307	1.1285	1.3397
357.05	0.4991	0.2319	1.1203	1.0390	1.2690	1.1877	1.2676	1.1887
355.85	0.3574	0.1987	1.1429	1.0261	1.3615	1.1362	1.3603	1.1325
354.65	0.2168	0.1562	1.1939	1.0085	1.6503	1.0530	1.6546	1.0542
353.65	0.1073	0.0831	1.2350	1.0019	2.0144	1.0138	2.0178	1.0126
Chloroacetic Acid (1) + Benzene (2)								
444.75	0.9579	0.5881	1.0003	1.1344	1.0001	1.0794	0.9994	0.5043
436.85	0.9474	0.4903	1.0005	1.1350	1.0002	1.0791	0.9990	0.5080
424.35	0.9276	0.3732	1.0009	1.1345	1.0004	1.0780	0.9981	0.5151
416.95	0.8852	0.3049	1.0024	1.1230	1.0011	1.0724	0.9950	0.5307
408.05	0.8679	0.2134	1.0032	1.1212	1.0015	1.0712	0.9933	0.5374
395.45	0.8061	0.1208	1.0070	1.1063	1.0033	1.0636	0.9845	0.5626
389.65	0.7631	0.0971	1.0105	1.0953	1.0051	1.0580	0.9756	0.5814
383.25	0.7217	0.0749	1.0145	1.0858	1.0071	1.0528	0.9647	0.6007
376.85	0.6429	0.0435	1.0238	1.0674	1.0121	1.0429	0.9361	0.6406
371.95	0.5792	0.0331	1.0330	1.0544	1.0172	1.0355	0.9041	0.6765
365.45	0.4087	0.0131	1.0643	1.0261	1.0357	1.0183	0.7674	0.7909
363.15	0.3429	0.0108	1.0791	1.0182	1.0451	1.0131	0.6907	0.8424
360.95	0.2841	0.0084	1.0937	1.0124	1.0545	1.0091	0.6103	0.8912
358.45	0.1953	0.0065	1.1181	1.0058	1.0709	1.0044	0.4736	0.9647
355.85	0.1211	0.0052	1.1399	1.0022	1.0864	1.0017	0.3654	1.0131
354.35	0.0709	0.0019	1.1564	1.0007	1.0983	1.0006	0.3305	1.0249
Dichloroacetic Acid (1) + Benzene (2)								
463.15	0.9881	0.9365	1.0000	0.8169	1.0000	0.9655	0.9999	0.3959
457.75	0.9682	0.8147	0.9998	0.8227	1.0000	0.9663	0.9996	0.4017
452.65	0.9499	0.7350	0.9995	0.8277	0.9999	0.9669	0.9990	0.4073
443.55	0.9216	0.5927	0.9990	0.8316	0.9998	0.9672	0.9982	0.4129
434.05	0.8806	0.4232	0.9978	0.8393	0.9997	0.9683	0.9960	0.4229
425.25	0.8196	0.2647	0.9928	0.8627	0.9988	0.9724	0.9853	0.4514
418.85	0.7862	0.2053	0.9899	0.8712	0.9983	0.9739	0.9785	0.4642
403.45	0.6916	0.1058	0.9785	0.8947	0.9962	0.9782	0.9497	0.5047
394.65	0.6288	0.0716	0.9685	0.9097	0.9942	0.9811	0.9209	0.5356
387.95	0.5707	0.0533	0.9573	0.9232	0.9920	0.9838	0.8859	0.5675
381.05	0.4821	0.0414	0.9323	0.9474	0.9867	0.9888	0.7933	0.6375
369.25	0.3562	0.0330	0.9007	0.9667	0.9797	0.9928	0.6613	0.7218
365.05	0.2856	0.0253	0.8769	0.9779	0.9741	0.9952	0.5479	0.7884
361.45	0.2197	0.0177	0.8523	0.9866	0.9682	0.9971	0.4264	0.8575
358.35	0.1406	0.0128	0.8205	0.9943	0.9603	0.9988	0.2745	0.9433
355.45	0.0834	0.0097	0.7952	0.9980	0.9537	0.9995	0.1818	0.9935

Table 2. Correlation Parameters and Average Absolute Deviations for the Binary Systems of Acetic Acid (1) + Benzene (2), Chloroacetic Acid (1) + Benzene (2), and Dichloroacetic Acid (1) + Benzene (2)

model	A_{12}^a J·mol ⁻¹	A_{21} J·mol ⁻¹	α_{12}	r	q	Δy^b	ΔT^c K
Acetic Acid (1) + Benzene (2)							
Wilson	935.4	-322.43				0.0169	1.05
NRTL	-321.09	233.43	0.27			0.0205	1.16
UNIQUAC	-104.79	308.07		(1) 2.195 (2) 0.365	(1) 2.072 (2) 0.120	0.0185	1.11
Chloroacetic Acid (1) + Benzene (2)							
Wilson	941.07	-404.08				0.0116	0.78
NRTL	-217.63	545.50	0.31			0.0126	0.85
UNIQUAC	-314.49	538.68		(1) 2.767	(1) 2.488	0.0126	0.85
Dichloroacetic Acid (1) + Benzene (2)							
Wilson	256.89	-999.41				0.0113	0.76
NRTL	-681.40	536.73	0.40			0.0119	0.80
UNIQUAC	-905.97	1039.00		(1) 3.362	(1) 2.908	0.0146	0.95

^a The binary adjustable parameters for the models are as follows: Wilson, $A_{ij} = (g_{ij} - g_{ii})$; NRTL, $A_{ij} = (g_{ij} - g_{ji})$; UNIQUAC, $A_{ij} = (u_{ij} - u_{ji})$. ^b $\Delta y = (1/N)|y_{\text{calcd}} - y_{\text{exptl}}|$. ^c $\Delta T = (1/N)|T_{\text{calcd}} - T_{\text{exptl}}|$.

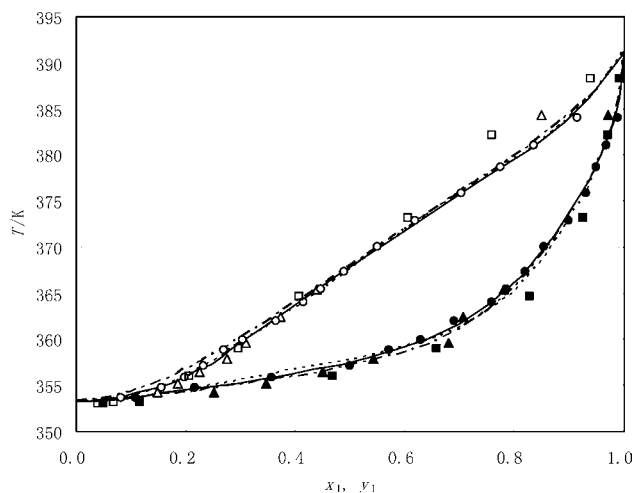


Figure 1. T - x - y phase equilibrium for the acetic acid (1) + benzene (2) system at 101.33 kPa: ●, x , T experimental data; ○, y , T experimental data; ▲, x , T experimental data (Garner, 1954); △, y , T experimental data (Garner, 1954); ■, x , T experimental data (Othmer, 1928); □, y , T experimental data (Othmer, 1928); —, Wilson; -·-, NRTL; ···, UNIQUAC.

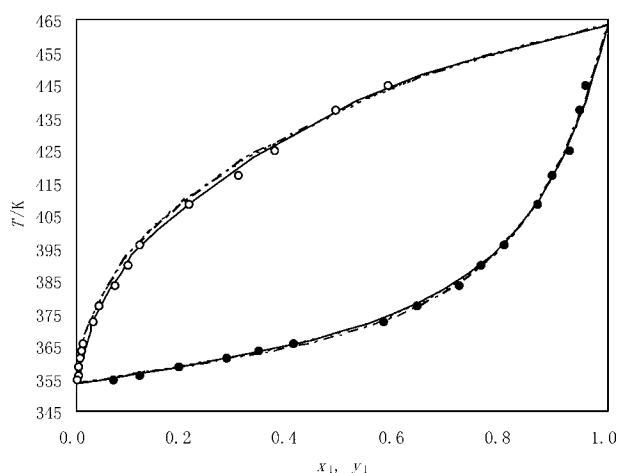


Figure 2. T - x - y phase equilibrium for the chloroacetic acid (1) + benzene (2) system at 101.33 kPa: ●, x , T experimental data; ○, y , T experimental data; —, Wilson; -·-, NRTL; ···, UNIQUAC.

dichloroacetic acid + benzene are listed in Table 1 and shown in Figures 1 to 3. Also, the experimental data of Garner et al.⁵ and Othmer⁶ are shown in Figure 1 to make a comparison to check the performance of the modified Rose still and experimental procedure. The x - T experimental data of this work shown in Figure 1 are close to those of Garner, except for one point at the composition of 0.68, but those of Othmer are away from the data of this work between the composition of 0.60 and 0.95. Meanwhile, the y - T data of this work are close to those of Garner and Othmer at the composition less than 0.7, and those of Garner and Othmer are away from the data of this work obviously when the composition is more than 0.7.

The Herington method¹² was used to check the thermodynamic consistency. Herington suggested that if $(D - J) < 10$, then the experimental points are considered to be thermodynamically consistent. The check results for the systems of acetic acid (1) + benzene (2), chloroacetic acid (1) + benzene (2), and dichloroacetic acid (1) + benzene (2) were -8.87 , -5.26 , and 2.97 , respectively, which indicates that the experimental data were thermodynamically consistent.

Vapor-Liquid Equilibria Model. The VLE equation can be expressed by the following equation

$$\hat{\phi}_i y_i p = x_i \gamma_i \phi_i^S p_i^S \left[\frac{V_i^L (p - p_i^S)}{RT} \right] \quad (1)$$

where $\hat{\phi}_i$ is the fugacity coefficient of component i in the mixture, ϕ_i^S is the fugacity coefficient at the saturated vapor pressure, y_i is the apparent mole fraction in the vapor phase, x_i is the mole fraction in the liquid phase, γ_i is the activity coefficient in the liquid phase, p is the system pressure, and p_i^S is the saturated vapor pressure.

At low pressure, the term $\exp[V_i^L (p - p_i^S)/RT]$ is approximately equal to 1, thus eq 1 can be rewritten as

$$\hat{\phi}_i y_i p = x_i \gamma_i \phi_i^S p_i^S \quad (2)$$

In the present work, the vapor-phase fugacity coefficients of benzene, chloroacetic acid, and dichloroacetic acid were calculated by using the virial equation. The vapor-phase fugacity coefficients of acetic acid were computed by using chemical theory¹³

$$\hat{\phi}_i = \frac{z_i}{y_i} \exp\left(\frac{B_i^{\text{Free}} \cdot p}{RT}\right) \quad (3)$$

where z_i is the true vapor-phase mole fraction of monomers, for the associating component A

$$z_i = \frac{\sqrt{1 + 4k_t y_A (2 - y_A)} - 1}{2k_t (2 - y_A)} \quad (4)$$

k_t is the dimerization equilibrium constant of associating component A, calculated by the following equation

$$\hat{\phi}_i = -\frac{B_A^D}{RT} p \exp\left(\frac{B_A^{\text{Free}} \cdot p}{RT}\right) \quad (5)$$

where B_i^{Free} and $B_A^D = B_{\text{bound}} + B_{\text{metastable}} + B_{\text{chem}}$ can be calculated by Hayden-O'Connell⁷ equation.

The liquid-phase activity coefficient was calculated by the solution models for the excess Gibbs energy, such as the Wilson, NRTL, and UNIQUAC models, and the relationship is

$$\ln \gamma_i = \left(\frac{\partial(nG^E/RT)}{\partial n_i} \right)_{T,P,n_j \neq i} \quad (6)$$

Calculation of Binary Vapor-Liquid Equilibria. The experimental data of the systems of acetic acid (1) + benzene (2), chloroacetic acid (1) + benzene (2), and dichloroacetic acid (1) + benzene (2) measured in this work were correlated by using the Wilson, NRTL, and UNIQUAC equations. For the VLE calculation at low pressure, the parameters of the Wilson, NRTL, and UNIQUAC models can be optimized by the objective function based on activity coefficients, which are more straightforward. Moreover, for the papers¹⁴⁻¹⁶ about the VLE of acetic acid, the objective function based on activity coefficients was often selected. In view of this, the objective function for the calculation is

$$F = \sum_{i=1}^N \{(\gamma_{1,\text{calcd}} - \gamma_{1,\text{exptl}})_i^2 + (\gamma_{2,\text{calcd}} - \gamma_{2,\text{exptl}})_i^2\} \quad (7)$$

where N is the number of the experimental data points and the subscripts exptl and calcd represent the experimental and calculated values. The summations are extended over all of the data points.

The estimated parameters for the systems of acetic acid + benzene, chloroacetic acid + benzene, and dichloroacetic acid

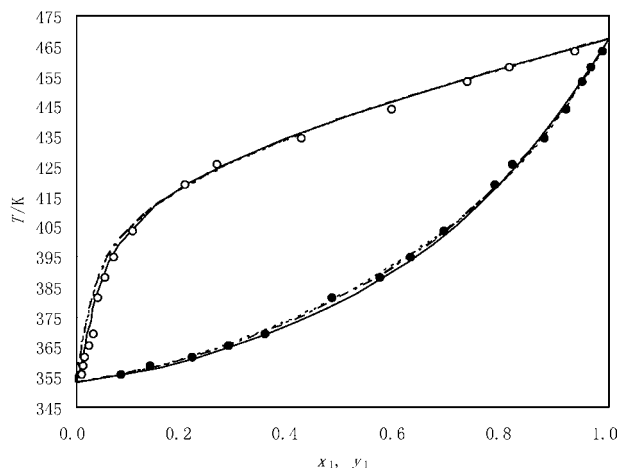


Figure 3. T - x - y phase equilibrium for the dichloroacetic acid (1) + benzene (2) system at 101.33 kPa: ●, x , T experimental data; ○, y , T experimental data; —, Wilson; - - -, NRTL; ···, UNIQUAC.

+ benzene and the average absolute deviation (AAD) between the calculated results using the Wilson, NRTL, and UNIQUAC equations and the experimental data are listed in Table 2.

From the AAD in Table 2, it can be seen that there is a good agreement between the calculated results by the Wilson, NRTL, and UNIQUAC equations and experimental data. For the calculation results of the acetic acid + benzene system by the three activity coefficient models shown in Figure 1, the Wilson model represents better results compared with those of NRTL and UNIQUAC models. The results calculated by the NRTL model show the largest deviation, which is also shown in Table 2. For the system of chloroacetic acid + benzene shown in Figure 2, the Wilson model still represents better calculation results. The lines calculated by the NRTL and UNIQUAC are almost overlapped and have the same deviations. For the system of dichloroacetic acid + benzene shown in Figure 3, the Wilson and NRTL models give better results compared to that of the UNIQUAC model. There is a little difference between the results of the Wilson and NRTL model. From the view of industrial application, the Wilson, NRTL, and UNIQUAC models can be used to calculate the VLE of the three binary systems.

Conclusions

VLE data for the binary systems of acetic acid + benzene, chloroacetic acid + benzene, and dichloroacetic acid + benzene were determined at 101.33 kPa. The experimental data were checked with the Herington method, which showed good

thermodynamic consistency. The experimental data of the systems were correlated by the Wilson, NRTL, and UNIQUAC models. The calculated results of the Wilson model show better agreement with experimental data compared with those of the NRTL and UNIQUAC models.

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