366 J. Chem. Eng. Data 2006, 51, 366−370

Isobaric Vapor−Liquid Equilibria for Binary Mixtures of 1,2-Dibromoethane with Benzene, Toluene, Fluorobenzene, and Bromobenzene at Atmospheric Pressure

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Vapor−liquid equilibria at atmospheric pressure for binary mixtures of 1,2-dibromoethane + benzene, + toluene, + fluorobenzene, and + bromobenzene have been determined. They have been correlated satisfactorily with the Wilson equation and have been shown to be thermodynamically consistent.

Introduction

Halogenated hydrocarbons find applications as solvents, reaction media, reaction intermediates, and refrigerants. Increasing concern about their environmental impact has resulted in more stringent regulations being imposed on plant design. This, in turn, requires more detailed knowledge of the relevant phase equilibria. We have previously reported vapor−liquid equilibria (VLE) for binary mixtures of chlorinated alkanes and chlorinated alkanes with heptane[1] and for binary mixtures of halogenated benzenes.[2] In this continuing series, we report new measurements of VLE at atmospheric pressure for binary mixtures of 1,2-dibromoethane + benzene, + toluene, + fluorobenzene, and + bromobenzene.

Experimental Section

Chemicals. The 1,2-dibromoethane was supplied by Merck and had a minimum mass fraction purity of 99.0 %. The benzene, toluene, fluorobenzene, and bromobenzene were supplied by Fluka and had minimum mass fraction purities of 99.8 %, 99.5 %, 99.5 %, and 99.0 %, respectively. These were all used without further purification. In Table 1, the measured normal boiling points are compared with the values reported in the literature and with the values obtained from the Antoine constants used in this work. It also shows the density values for the pure substances, and these are compared with the values reported in the literature. The agreement is generally satisfactory.

Table 1. Normal Boiling Point and Density (ρ) at 293.2 K for the Pure Components

	normal boiling point/K		ρ/g·cm^{-3}	
chemical	exptl (Antoine)	lit	exptl	lit
1,2-dibromoethane	404.3 (404.4)	404.5[3]	2.17924	2.1791[3]
benzene	353.3 (353.4)	353.2[4]	0.87653	0.8765[4]
toluene	383.8 (383.8)	383.8[4]	0.86681	0.8669[4]
fluorobenzene	357.8 (357.8)	357.9[4]	1.02227	1.0225[4]
bromobenzene	429.3 (429.3)	429.2[4]	1.49523	1.4950[4]

Table 2. Vapor−Liquid Equilibria for Benzene (1) + 1,2-Dibromoethane (2) System at Atmospheric Pressure[a]

P_{exp}/kPa	T_{exp}/K	T_{corr}/K	x_1	y_1	γ_1	γ_2
101.77	354.4	353.3	1.0000	1.0000		
101.74	355.5	354.5	0.9592	0.9904	0.998	1.129
101.75	358.1	357.1	0.8672	0.9663	0.996	1.109
101.74	360.8	359.8	0.7713	0.9370	1.002	1.093
101.72	364.2	363.2	0.6701	0.8996	1.002	1.073
101.73	367.0	366.0	0.5852	0.8625	1.016	1.062
101.71	369.7	368.7	0.5192	0.8274	1.018	1.050
101.70	373.3	372.3	0.4312	0.7732	1.037	1.036
101.72	377.0	376.0	0.3523	0.7107	1.056	1.030
101.72	380.4	379.3	0.2973	0.6583	1.062	1.010
101.76	383.2	382.0	0.2492	0.6028	1.082	1.010
101.76	385.8	384.6	0.2146	0.5546	1.082	1.000
101.72	388.1	387.0	0.1756	0.4943	1.110	1.006
101.68	390.2	389.2	0.1496	0.4463	1.113	1.001
101.85	393.2	391.8	0.1175	0.3794	1.131	1.001
101.88	397.2	395.7	0.0751	0.2726	1.158	1.001
101.94	400.2	398.5	0.0507	0.1982	1.167	0.993
101.95	403.2	401.5	0.0227	0.0975	1.197	0.999
101.86	405.8	404.3	0.0000	0.0000		

[a] T_{corr} is the boiling temperature at 101.325 kPa.

Apparatus and Procedure. A Fischer (Germany) VLE still (model 0601) was used for the experimental determination of VLE at atmospheric pressure. The equilibrium temperatures in the re-circulating still were measured with a built-in calibrated platinum resistance thermometer PT 100 to an uncertainty of ± 0.1 K. The pressure was measured by an electronic pressure gauge to an uncertainty of ± 0.01 kPa. These uncertainties were established by determining the boiling temperatures of pure solvents and by intercomparison of the pressure gauge with a Fortin barometer. In this apparatus, when VLE was reached, as indicated by constant temperature readings for the liquid and vapor phases, the system was maintained in this state for at least a further 30 min. After that, the equilibrium temperature and pressure were recorded, and samples of the liquid and condensed vapor were withdrawn for analysis. These samples were then analyzed for composition by density measurements. An Anton-Paar DMA 4500 digital density meter (UK) with an uncertainty of ± 10^{-5} g·cm^{-3} was used for this purpose. In the analysis, the density dependence on composition was first established by preparing standard binary mixtures of different mole factions and measuring their density. These data were then fitted to a low-order polynomial that was used to obtain compositions of the samples taken from the still. Such a method of analysis can be very effective whenever the difference in density between the two components is at least 0.10 g·cm^{-3}. The uncertainties of pressure, temperature and composition

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10.1021/je050231r CCC: $33.50

Table 3. Vapor−Liquid Equilibria for Toluene (1) + 1,2-Dibromoethane (2) System at Atmospheric Pressure[a]

P_{exp}/kPa	T_{exp}/K	T_{corr}/K	x_1	y_1	γ_1	γ_2
102.09	384.9	383.8	1.0000	1.0000		
102.10	385.5	384.4	0.9543	0.9719	1.000	1.091
102.11	386.8	385.7	0.8740	0.9201	0.997	1.082
102.12	387.5	386.3	0.8281	0.8891	0.999	1.081
102.12	388.7	387.5	0.7527	0.8361	1.000	1.071
102.11	389.8	388.7	0.6793	0.7825	1.003	1.058
102.11	391.1	389.9	0.6122	0.7307	1.006	1.045
102.12	392.3	391.1	0.5382	0.6702	1.015	1.038
102.13	393.2	392.0	0.4914	0.6298	1.020	1.030
102.12	394.5	393.3	0.4252	0.5686	1.028	1.023
102.13	395.9	394.7	0.3574	0.5007	1.037	1.017
102.13	396.6	395.4	0.3241	0.4659	1.044	1.014
102.05	397.2	396.2	0.2863	0.4245	1.055	1.012
102.12	398.5	397.3	0.2371	0.3668	1.069	1.009
102.11	399.9	398.7	0.1852	0.3011	1.083	1.003
102.14	400.5	399.3	0.1592	0.2657	1.095	1.004
102.15	402.3	401.0	0.1027	0.1828	1.118	0.999
102.15	403.0	401.7	0.0790	0.1443	1.127	0.999
102.12	404.7	403.5	0.0246	0.0484	1.159	0.999
102.11	405.5	404.3	0.0000	0.0000		

[a] T_{corr} is the boiling temperature at 101.325 kPa.

Table 4. Vapor−Liquid Equilibria for Fluorobenzene (1) + 1,2-Dibromoethane (2) System at Atmospheric Pressure[a]

P_{exp}/kPa	T_{exp}/K	T_{corr}/K	x_1	y_1	γ_1	γ_2
101.94	358.4	357.8	1.0000	1.0000		
101.93	359.3	358.7	0.9566	0.9858	1.003	1.295
101.92	361.7	361.1	0.8618	0.9528	1.002	1.229
101.93	364.1	363.5	0.7635	0.9167	1.013	1.170
101.92	367.0	366.4	0.6683	0.8772	1.018	1.129
101.91	369.8	369.2	0.5630	0.8286	1.054	1.100
101.90	371.8	371.2	0.5046	0.7977	1.070	1.078
101.90	375.1	374.5	0.4114	0.7378	1.109	1.050
101.91	377.7	377.1	0.3553	0.6959	1.128	1.043
101.90	379.5	378.9	0.3123	0.6589	1.159	1.022
101.89	382.4	381.9	0.2614	0.6072	1.182	1.020
101.90	384.2	383.6	0.2272	0.5665	1.211	1.007
101.88	387.0	386.5	0.1860	0.5076	1.231	1.007
102.01	389.2	388.3	0.1575	0.4622	1.265	0.999
102.05	391.9	390.9	0.1267	0.4031	1.286	1.006
102.08	394.0	392.9	0.0998	0.3434	1.324	0.998
102.11	396.3	395.1	0.0791	0.2898	1.337	0.999
102.11	398.6	397.4	0.0557	0.2217	1.375	0.998
102.13	401.0	399.8	0.0352	0.1504	1.396	0.996
102.14	403.4	402.2	0.0163	0.0763	1.447	1.000
102.09	405.4	404.3	0.0000	0.0000		

[a] T_{corr} is the boiling temperature at 101.325 kPa.

measurement are estimated to be ± 0.01 kPa, ± 0.1 K, and ± 0.0001, respectively.

Results and Discussion

The results of the VLE measurements are given in Tables 2 to 5. The measured boiling temperatures have been corrected to standard atmospheric pressure using known pure component vapor pressures. By assuming the over small temperature ranges, the liquid phase activity coefficients are constant. This was done as follows. The vapor pressure of the mixture is given by

$$P = \gamma_1 x_1 P_1^{o} + \gamma_2 x_2 P_2^{o} \tag{1}$$

Differentiation of the above gives an expression from which the temperature correction can be obtained:

$$\frac{dP}{dT} = \gamma_1 x_1 \frac{dP_1^{o}}{dT} + \gamma_2 x_2 \frac{dP_2^{o}}{dT} \tag{2}$$

Table 5. Vapor−Liquid Equilibria for 1,2-Dibromoethane (1) + Bromobenzene (2) System at Atmospheric Pressure[a]

P_{exp}/kPa	T_{exp}/K	T_{corr}/K	x_1	y_1	γ_1	γ_2
101.81	404.6	404.3	1.0000	1.0000		
101.83	405.3	404.9	0.9655	0.9791	0.999	1.170
101.84	406.4	406.0	0.8979	0.9381	0.999	1.134
101.83	407.3	406.9	0.8466	0.9067	1.000	1.108
101.83	408.3	407.9	0.7875	0.8703	1.005	1.081
101.85	409.3	408.8	0.7339	0.8355	1.010	1.067
101.86	410.7	410.2	0.6654	0.7872	1.012	1.055
101.86	411.5	411.0	0.6222	0.7572	1.019	1.043
101.87	412.9	412.4	0.5577	0.7083	1.025	1.029
101.86	413.8	413.3	0.5174	0.6752	1.029	1.025
101.87	415.1	414.6	0.4618	0.6275	1.036	1.017
101.88	416.2	415.6	0.4180	0.5861	1.042	1.017
101.88	417.1	416.5	0.3845	0.5532	1.045	1.013
101.86	418.1	417.6	0.3446	0.5118	1.049	1.009
101.87	419.5	419.0	0.2951	0.4573	1.057	1.004
101.88	420.4	419.8	0.2660	0.4235	1.064	1.003
101.86	421.4	420.9	0.2326	0.3808	1.065	1.001
101.82	422.1	421.7	0.2038	0.3426	1.072	1.003
101.79	423.1	422.8	0.1744	0.3019	1.074	0.998
101.76	424.0	423.8	0.1430	0.2564	1.086	0.998
101.75	425.8	425.6	0.0930	0.1756	1.094	0.998
101.74	426.7	426.5	0.0697	0.1356	1.103	0.997
101.75	428.0	427.8	0.0371	0.0749	1.109	0.997
101.76	429.4	429.3	0.0000	0.0000		

[a] T_{corr} is the boiling temperature at 101.325 kPa.

Table 6. Antoine Constants for Pure Components

component	Antoine equation constants	temperature range/K	source(s)
1,2-dibromoethane	$A = 14.5753$ $B = 3648.11$ $C = -37.9709$	334.0−520.7	fitted to data reported in ref 5
benzene	$A = 13.9829$ $B = 2850.50$ $C = -49.0068$	341.8−429.4	fitted to data reported in ref 6
toluene	$A = 13.8668$ $B = 3009.12$ $C = -58.3949$	333.2−433.2	fitted to data reported in ref 6
fluorobenzene	$A = 13.4828$ $B = 2575.88$ $C = -67.24$	333.0−422.0	fitted to data reported in ref 7
bromobenzene	$A = 13.3849$ $B = 3060.99$ $C = -80.1075$	341.8−429.4	fitted to data reported in ref 8

Pure component vapor pressures were represented by the Antoine equation written in the following form:

$$\ln P_i^{o}/\text{kPa} = A_i - \frac{B_i}{(T/\text{K} + C_i)} \tag{3}$$

where P_i^{o} is the vapor pressure; T is the temperature and the constants; and A_i, B_i, and C_i are the Antoine equation constants for component i.

In subsequent calculations of the liquid phase activity coefficients, it is important that the selected vapor pressures span the entire temperature range of the relevant binary mixtures. Taking this into consideration, the Antoine constants were obtained by fitting experimental data taken from literature. This was done by minimizing the following objective function (OF) using Newton's method:

$$\text{OF} = \sum_{i=1}^{n} [P_i^{o}(\text{exp}) - P_i^{o}(\text{Antoine})]^2 \tag{4}$$

where the summation is over all data points. Table 6 gives the

Table 7. Wilson Equation Parameters (Using Barker's Method) and Component Molar Volumes

binary system	$V_1{}^a$/cm^3·mol^{-1}	$V_2{}^a$/cm^3·mol^{-1}	a_{12}/J·mol^{-1}	a_{21}/J·mol^{-1}	avg Δy_1	avg ΔT/K
benzene (1) + 1,2-dibromoethane (2)	88.88	86.18	1715.9	−955.9	0.0015	0.11
toluene (1) + 1,2-dibromoethane (2)	106.30	86.18	1525.6	−686.2	0.0017	0.03
fluorobenzene (1) + 1,2-dibromoethane (2)	93.76	86.18	1196.2	−28.6	0.0016	0.10
1,2-dibromoethane (1) + bromobenzene (2)	86.18	105.01	−79.8	608.6	0.0013	0.03

[a] Based on the experimental values of density at T = 293.15 K.

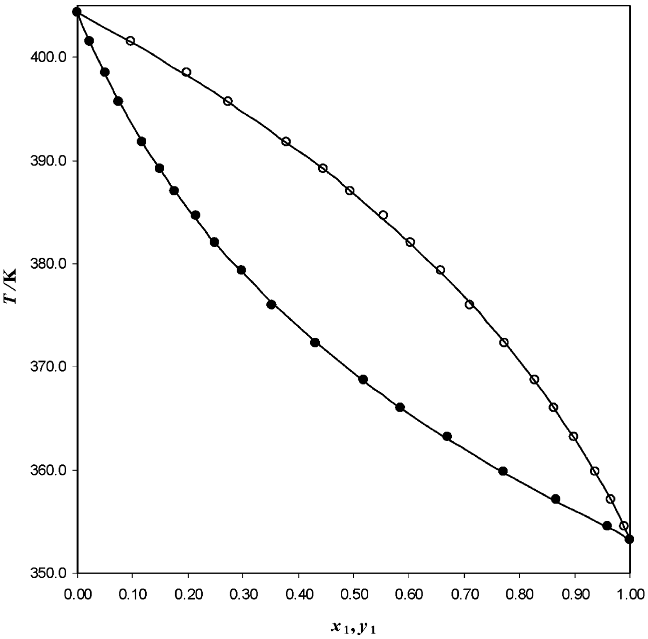

Figure 1. $T-x-y$ diagram for the benzene (1) + 1,2-dibromoethane (2) system at P = 101.325 kPa: ●, experimental x_1; ○, experimental y_1; solid line, Wilson equation fit using Barker's method.

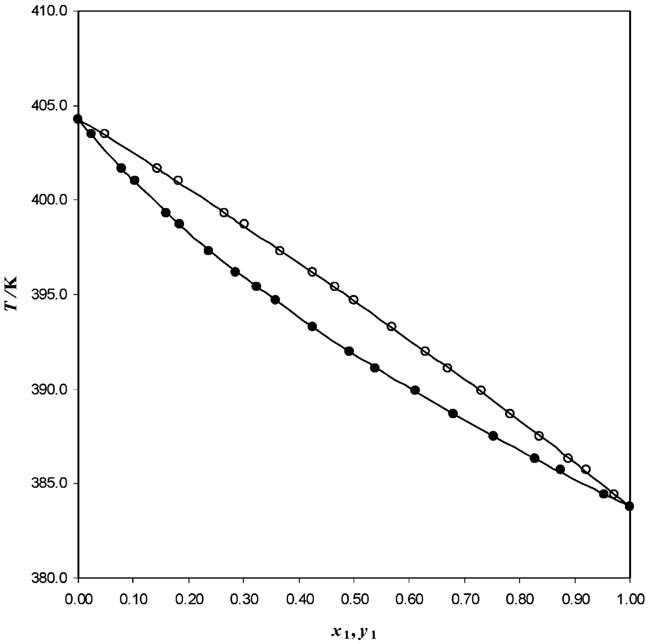

Figure 2. $T-x-y$ diagram for the toluene (1) + 1,2-dibromoethane (2) system at P = 101.325 kPa: ●, experimental x_1; ○, experimental y_1; solid line, Wilson equation fit using Barker's method.

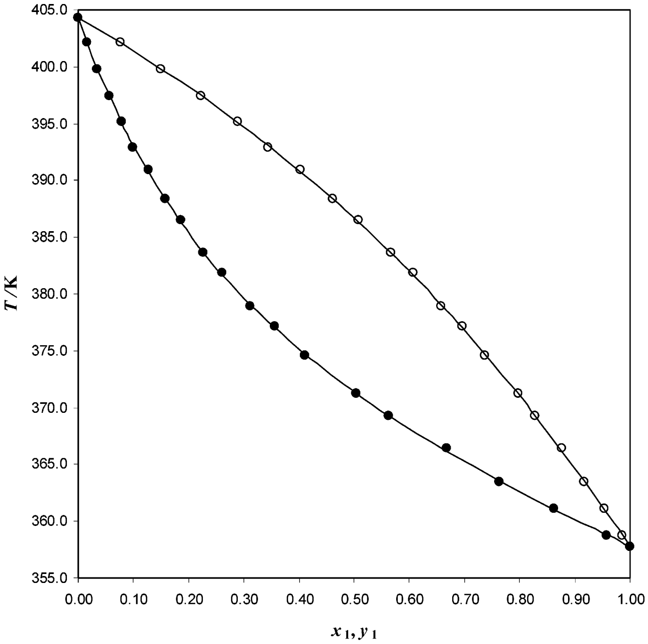

Figure 3. $T-x-y$ diagram for the fluorobenzene (1) + 1,2-dibromoethane (2) system at P = 101.325 kPa: ●, experimental x_1; ○, experimental y_1; solid line, Wilson equation fit using Barker's method.

Antoine constants, the range of applicability, and the sources of data.

Correlation and Thermodynamic Tests. The VLE results were correlated in two ways.

Wilson Equation Fitting Test. According to Wilson,[9] the excess Gibbs free energy of a binary mixture is given by

$$\frac{G^{\mathrm{E}}}{RT} = g = -x_1 \ln(x_1 + G_{12}x_2) - x_2 \ln(G_{21}x_1 + x_2) \tag{5}$$

where

$$G_{12} = \frac{V_2}{V_1}\exp\left(\frac{-a_{12}}{RT}\right) \quad \text{and} \quad G_{21} = \frac{V_1}{V_2}\exp\left(\frac{-a_{21}}{RT}\right) \tag{6}$$

The molar volume ratios can be assumed to be independent of temperature, and the value at 293.15 K was used in this work.

The Wilson parameters a_{12} and a_{21}were obtained by minimizing the objective function:

$$\mathrm{OF} = \sum_{i=1}^{n} [(g^* - g)^2]_i = \sum_{i=1}^{n} [\delta g^2]_i = \sum_{i=1}^{n} [((x_1 \ln \gamma_1^* + x_2 \ln \gamma_2^*) - (x_1 \ln \gamma_1 + x_2 \ln \gamma_2))^2]_i \tag{7}$$

where the superscript (*) denotes the experimental values and the summation is over all data points. The minimization was performed using a spreadsheet routine that is based on Newton's method. The parameters were then used to predict the boiling temperature and vapor phase compositions. This requires the Wilson expression for the liquid phase activity

Table 8. Summary of the Direct Consistency Test Results

binary system	a_{12}	a_{21}	avg $\Delta(y_1)$	avg $\Delta(T)$/K	RMS ($\delta(\ln(\gamma_1/\gamma_2))$)	comment
benzene (1) + 1,2-dibromoethane (2)	1342.7	−670.4	0.0009	0.15	0.008	highly consistent (class 1)
toluene (1) + 1,2-dibromoethane (2)	1180.0	−481.7	0.0015	0.04	0.012	highly consistent (class 1)
fluorobenzene (1) + 1,2-dibromoethane (2)	772.1	343.8	0.0021	0.13	0.019	highly consistent (class 1)
1,2-dibromoethane (1) + bromobenzene (2)	−378.7	1077.2	0.0011	0.07	0.011	highly consistent (class 1)

coefficients, the vapor phase being assumed to be ideal:

$$\ln \gamma_1 = -\ln(x_1 + G_{12}x_2) + x_2\left[\frac{G_{12}}{x_1 + G_{12}x_2} - \frac{G_{21}}{G_{21}x_1 + x_2}\right]$$

$$\ln \gamma_2 = -\ln(x_2 + G_{21}x_1) - x_1\left[\frac{G_{12}}{x_1 + G_{12}x_2} - \frac{G_{21}}{G_{21}x_1 + x_2}\right] \quad (8)$$

These equations are, of course, solutions of the Gibbs−Duhem equation.

In this work, the experimental VLE data were first reduced using Barker's method[10] (i.e., using $\sum(\delta P)^2$ as the objective function), since this method is preferred for practical applications. The quality of the fitting of the VLE data was judged by how close the model predictions were to the experimental data in the $T-x-y$ and $y-x$ graphs and by the average absolute difference between predicted and experimental bubble point temperatures and vapor phase compositions. The Wilson parameters for each binary system, the molar volumes of the two components, and the average deviations in y_1 and T for each binary system are given in Table 7. Figures 1 to 4 show the experimental data and the Wilson equation fit for four systems. It can be seen that, by inspection of Figures 1 to 4 and Table 7 for the three binary systems, the VLE data are well fit.

Direct Consistency Test. Van Ness[11] proposed a new test that can be applied simultaneously to individual VLE data points as well as to VLE data sets as a whole. This test is called the direct test. Van Ness has shown that, if an isobaric VLE set of data is reduced with $\sum(\delta g)^2$ as the objective function, then the quantity on the right-hand side of the following equation is required by the Gibbs−Duhem equation to be zero for thermodynamic consistency:

$$\delta\left(\ln\left(\frac{\gamma_1}{\gamma_2}\right)\right) = x_1\frac{\mathrm{d}\ln\gamma_1^*}{\mathrm{d}x_1} + x_2\frac{\mathrm{d}\ln\gamma_2^*}{\mathrm{d}x_1} + \frac{H^{\mathrm{E}}}{RT^2}\frac{\mathrm{d}T}{\mathrm{d}x_1} \quad (9)$$

Therefore the residual, which is the difference between the experimental values and the Wilson equation values, on the left is a direct measure of deviations from the Gibbs−Duhem equation. The extent to which values of this residual fail to scatter about zero measures the departure of the data from thermodynamic consistency.

In this work, the experimental VLE data were fitted again to Wilson's equation by minimizing the objective function $\sum(\delta g)^2$ to obtain the Wilson equation parameters a_{12} and a_{21}. These parameters were then used to calculate the bubble point temperatures, vapor phase compositions, activity coefficients (γ_1 and γ_2), and the residual $\delta(\ln(\gamma_1/\gamma_2))$.

Finally, to test the VLE data for thermodynamic consistency, the residual $\delta(\ln(\gamma_1/\gamma_2))$ was plotted against x_1 to check whether these values scatter around zero, and the root-mean-square deviation was calculated and compared against the direct test consistency index proposed by Van Ness.[11] According to the classification of acceptable data given by Van Ness, the data for all four systems are class 1 as can be seen in Table 8.

Comparison with VLE Data Reported in the Literature. Kalra et al.[12,13] have reported isothermal VLE data for the binary systems of 1,2-dibromoethane + benzene and 1,2-dibromoethane + toluene at T = 308.15 K and T = 298.15 K. Gracia et al.[14] have also reported isothermal VLE data for the binary system of 1,2-dibromoethane + benzene at temperatures between 283.15 K and 323.15 K at intervals of 5 K. None of these is directly comparable with the data of this work.

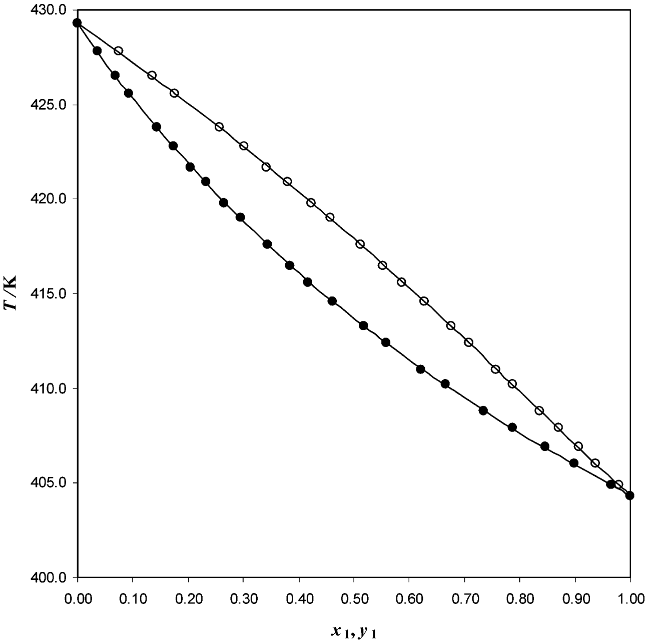

Figure 4. $T-x-y$ diagram for the 1,2-dibromoethane (1) + bromobenzene (2) system at P = 101.325 kPa: ●, experimental x_1; ○, experimental y_1; solid line, Wilson equation fit using barker's method.

Conclusions

In this work, VLE data have been determined for binary mixtures of 1,2-dibromoethane + benzene, + toluene, + fluorobenzene, and + bromobenzene. The data have been shown to be highly thermodynamically consistent. Further data and analyses for halogenated hydrocarbons will be reported at a later date.

Literature Cited

(1) Al-Hayan, M. N. M.; Newsham, D. M. T. Isobaric vapour−liquid equilibria for mixtures containing halogenated hydrocarbons at atmospheric pressure. I. Binary mixtures of trichloromethane + 1,2-dichloroethane, 1,2-dichloroethane + 1,1,2,2-tetrachloroethane, trichloromethane + 1,1,2,2-tetrachloroethane and *n*-heptane + 1,1,2,2-tetrachloroethane. *Fluid Phase Equilib.* **1999**, *166*, 91−100.

(2) Al-Hayan, M. N. M.; Newsham, D. M. T. Isobaric vapor−liquid equilibria for mixtures containing halogenated hydrocarbons at atmospheric pressure. II. Binary mixtures of fluorobenzene, chlorobenzene and bromobenzene. *Fluid Phase Equilib.* **2000**, *168*, 259−266.

(3) Riddick, J. A.; Bunger W. B.; Sakano T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986.

(4) Lide, D. R. *Handbook of Organic Solvents*; CRC Press: London, 1995.

(5) Yaws, C. L. *Handbook of Vapor Pressure*; Gulf Publishing Co.: Houston, TX, 1993; Vol. 2.

(6) Yaws, C. L. *Handbook of Vapor Pressure*; Gulf Publishing Co.: Houston, TX, 1993; Vol. 3.
(7) Jordan, T. E. *Vapor Pressure of Pure Compounds*; Interscience: New York, 1954.
(8) Boublik, T.; Fried, V.; Hala, E. *Vapour Pressure of Pure Substances*; Elsevier: Amsterdam, 1973.
(9) Wilson, G. M. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−131.
(10) Smith, J. M.; Van Ness, H. C.; Abbot, M. M. *Introduction to Chemical Engineering Thermodynamics*, 5th ed.; McGraw-Hill: Singapore, 1996.
(11) Van Ness, H. C. Thermodynamics in the treatment of vapor/liquid equilibrium (VLE) data. *Pure Appl. Chem.* **1995**, *67*, 859−872.
(12) Kalra, K. C.; Singh, K. C.; Soni, M.; Spah, D. C. Excess molar Gibbs free energies of (1,2-dibromoethane + an aromatic hydrocarbon) at 308.15 K. *J. Chem. Thermodyn.* **1990**, *22*, 771−775.
(13) Kalra, K. C.; Singh, K. C.; Spah, D. C. Thermodynamics of molecular interactions in 1,2-dibromoethane + benzene or toluene mixtures. *Fluid Phase Equilib.* **1991**, *66*, 211−220.
(14) Gracia, M.; Perez, P.; Valero, J. Vapor pressures of 1,2-dibromoethane + benzene at temperatures between 283.15 and 323.15 K. *Fluid Phase Equilib.* **1994**, *97*, 147−153.

Received for review June 16, 2005. Accepted January 23, 2006. The authors wish to thank Kuwait Foundation for the Advancement of Sciences (KFAS) and the Public Authority for Applied Education and Training (PAAET), Kuwait, for providing them with a grant that enabled them to conduct this research.

JE050231R