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Isobaric Vapor–Liquid Equilibria for Acetone + Chloroform + Benzene and the Three Constituent Binary Systems

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Vapor-liquid equilibrium data for acetone + chloroform + benzene and for the three constituent binary systems acetone + chloroform, chloroform + benzene, and benzene + acetone have been measured at 101.3 kPa by using a dynamic equilibrium still. The experimental data have been correlated and predicted to appreciable accuracy using the Wilson equation.

Introduction

This paper deals with the measurement of vapor–liquid equilibria (VLE) at 101.3 kPa for the ternary system acetone + chloroform + benzene and the three constituent binary systems. It also discusses correlation and prediction of experimental VLE data using the Wilson equation (*1*). Moreover, it compares our binary data with the predictions of evaluated Wilson parameters (*2*) and Reinders' data (*3*) with the predictions of our parameters.

Experimental Section

Apparatus and Procedure. A liquid–vapor ebullition type equilibrium still, described in detail in ref 4, was used for measuring VLE. The still has two ebulliometers connected in series. Two electric heaters were used, one in the liquid-phase and the other in the vapor-phase boiling vessels.

Vapor and liquid equilibrium compositions were determined by using a Shimazu gas chromatograph type GC-3BT equipped with a thermal conductivity cell. PEG 1500 was used as column packing and helium as the carrier gas at a flow rate of 33 cm^3 min^{-1}. The column temperature was maintained at 338 K. Compositions were determined to better than 1% by the relative area method (*5*). The equilibrium temperature was measured with an accuracy of 0.01 K by using a Hewlett-Packard quartz thermometer Model 2804A, calibrated at the triple point of water. The pressure in the still was measured by a Fortin type mercury barometer. Since the barometric pressure changed slightly, the experimental temperatures were corrected to 101.3 kPa.

Materials. Acetone, chloroform, and benzene were special grade pure reagents, supplied by Wako Pure Chemicals Co. Acetone was used after its minute water content was removed with calcium sulfate, using molecular sieves 3A. Chloroform was treated with sulfuric acid, neutralized with sodium hydroxide, washed with water, dried overnight on potassium carbonate, and then distilled. The purities of the materials were checked by gas chromatographic analysis and found to be better than 99.9 mol %. The densities and normal boiling points of the purified reagents are shown in Table I.

Experimental Results

Binary Systems. Table II and Figures 1–3 show the experimental VLE data at a pressure P = 101.3 kPa for the three systems acetone + chloroform, chloroform + benzene, and

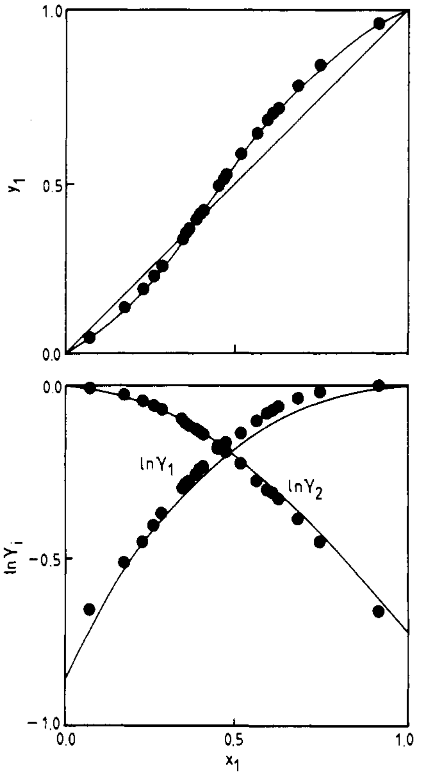

Figure 1. Vapor-phase mole fraction y_1 and activity coefficients γ_i for the binary system acetone (1) + chloroform (2) at 101.3 kPa as a function of liquid-phase mole fraction x_1: (●) experimental values. The curves are calculated by using Wilson equation.

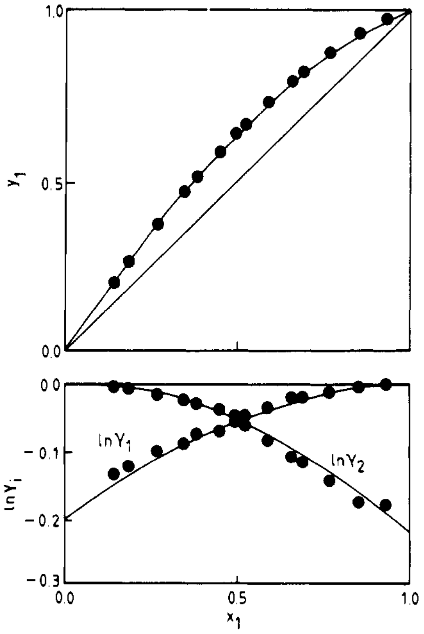

Figure 2. Vapor-phase mole fraction y_1 and activity coefficients γ_i for the binary system chloroform (1) + benzene (2) at 101.3 kPa as a function of liquid-phase mole fraction x_1: (●) experimental values. The curves are calculated by using Wilson equation.

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Table I. Density ρ and Normal Boiling Points T_b of the Components

	ρ(298.15 K)/(g cm^{-3})		T_b/K	
component	exptl	lit.	exptl	lit.
acetone	0.7841	0.78440 (*6*)	329.25	329.44 (*6*)
chloroform	1.4798	1.47998 (*6*)	334.35	334.88 (*6*)
benzene	0.8734	0.8736 (*7*)	353.25	353.24 (*7*)

Table II. Isobaric Vapor–Liquid Equilibrium Data (Liquid-Phase Mole Fraction x_i, Vapor-Phase Mole Fraction y_i, and Temperature T) and Activity Coefficients γ_i for Binary Systems at 101.3 kPa

x_1	y_1	T/K	γ_1	γ_2
	Acetone (1) + Chloroform (2)			
0.075	0.049	335.26	0.520	0.999
0.177	0.137	336.60	0.596	0.977
0.229	0.191	337.10	0.635	0.962
0.262	0.230	337.34	0.665	0.949
0.285	0.259	337.44	0.688	0.939
0.345	0.339	337.60	0.743	0.908
0.357	0.356	337.62	0.754	0.900
0.365	0.366	337.62	0.759	0.897
0.387	0.396	337.61	0.776	0.885
0.395	0.408	337.58	0.785	0.879
0.404	0.420	337.55	0.791	0.875
0.452	0.488	337.35	0.829	0.843
0.466	0.510	337.20	0.845	0.831
0.474	0.520	337.19	0.847	0.826
0.519	0.579	336.82	0.873	0.799
0.564	0.641	336.34	0.905	0.760
0.594	0.679	335.88	0.924	0.739
0.610	0.697	335.57	0.933	0.732
0.624	0.715	335.31	0.943	0.719
0.684	0.780	334.39	0.967	0.677
0.747	0.840	333.38	0.985	0.632
0.918	0.961	330.68	1.000	0.512
	Chloroform (1) + Benzene (2)			
0.142	0.203	350.92	0.876	0.996
0.185	0.262	350.15	0.886	0.994
0.269	0.373	348.64	0.905	0.986
0.347	0.468	347.21	0.917	0.978
0.384	0.513	346.42	0.929	0.973
0.449	0.583	345.31	0.932	0.964
0.496	0.634	344.28	0.946	0.956
0.524	0.666	343.75	0.955	0.939
0.590	0.730	342.43	0.967	0.919
0.659	0.791	340.93	0.981	0.898
0.693	0.817	340.33	0.981	0.890
0.768	0.872	338.82	0.989	0.866
0.857	0.928	337.05	0.996	0.838
0.935	0.969	335.53	0.999	0.835
	Benzene (1) + Acetone (2)			
0.117	0.074	330.49	1.362	1.008
0.128	0.081	330.63	1.355	1.009
0.151	0.095	330.90	1.333	1.012
0.267	0.166	332.36	1.245	1.032
0.270	0.167	332.39	1.237	1.034
0.327	0.202	333.16	1.200	1.049
0.373	0.231	333.86	1.172	1.062
0.398	0.247	334.20	1.160	1.072
0.450	0.279	335.06	1.124	1.095
0.502	0.317	335.97	1.107	1.114
0.534	0.339	336.54	1.091	1.133
0.554	0.353	336.94	1.080	1.145
0.572	0.370	337.31	1.082	1.150
0.613	0.399	338.14	1.057	1.184
0.730	0.512	341.03	1.032	1.268
0.807	0.601	343.36	1.014	1.358
0.861	0.679	345.38	1.007	1.425

Table III. Isobaric Vapor–Liquid Equilibrium Data (Liquid-Phase Mole Fraction x_i, Vapor-Phase Mole Fraction y_i, and Temperature T) and Activity Coefficients γ_i for Acetone (1) + Chloroform (2) + Benzene (3) System at 101.3 kPa

x_1	x_2	y_1	y_2	T/K	γ_1	γ_2	γ_3
0.019	0.061	0.056	0.086	351.00	1.574	0.859	0.998
0.054	0.522	0.074	0.632	342.73	0.894	0.936	0.962
0.059	0.535	0.080	0.643	342.42	0.892	0.938	0.956
0.063	0.292	0.120	0.364	346.00	1.149	0.874	1.001
0.067	0.883	0.046	0.929	336.13	0.533	0.995	0.861
0.071	0.571	0.089	0.672	341.58	0.843	0.941	0.962
0.075	0.279	0.143	0.343	345.76	1.159	0.867	1.003
0.075	0.296	0.141	0.364	345.56	1.148	0.872	0.999
0.083	0.851	0.061	0.904	336.62	0.564	0.989	0.899
0.092	0.650	0.099	0.740	340.07	0.753	0.953	0.945
0.095	0.487	0.132	0.569	342.56	0.914	0.906	1.000
0.096	0.261	0.182	0.312	345.32	1.168	0.852	1.007
0.101	0.278	0.189	0.329	344.98	1.162	0.852	1.004
0.106	0.680	0.107	0.761	339.41	0.719	0.956	0.956
0.110	0.611	0.124	0.694	340.50	0.781	0.938	0.976
0.111	0.408	0.172	0.475	343.28	1.003	0.882	1.004
0.118	0.792	0.099	0.846	337.44	0.630	0.970	1.011
0.124	0.495	0.166	0.564	341.94	0.896	0.900	1.012
0.130	0.151	0.264	0.169	345.11	1.264	0.798	1.016
0.145	0.574	0.170	0.642	340.60	0.812	0.920	1.000
0.164	0.544	0.199	0.600	340.74	0.839	0.902	1.025
0.164	0.422	0.236	0.466	342.10	0.963	0.865	1.025
0.167	0.325	0.268	0.355	342.89	1.055	0.834	1.030
0.172	0.192	0.313	0.202	343.57	1.181	0.784	1.034
0.180	0.682	0.180	0.721	338.70	0.730	0.922	1.143
0.191	0.635	0.199	0.685	339.25	0.749	0.924	1.044
0.194	0.210	0.338	0.218	342.87	1.152	0.789	1.034
0.200	0.615	0.214	0.662	339.44	0.766	0.916	1.043
0.203	0.570	0.230	0.608	339.92	0.802	0.894	1.094
0.221	0.564	0.253	0.599	339.76	0.815	0.894	1.062
0.226	0.596	0.246	0.632	339.35	0.783	0.904	1.072
0.235	0.335	0.345	0.339	341.38	1.008	0.806	1.074
0.241	0.256	0.380	0.250	341.61	1.079	0.770	1.066
0.251	0.099	0.438	0.090	341.67	1.199	0.711	1.048
0.265	0.179	0.429	0.165	341.22	1.124	0.732	1.071
0.274	0.359	0.380	0.352	340.53	0.976	0.800	1.100
0.276	0.434	0.356	0.435	340.10	0.916	0.831	1.102
0.293	0.488	0.354	0.489	339.54	0.870	0.846	1.118
0.302	0.511	0.354	0.510	339.24	0.851	0.851	1.146
0.313	0.318	0.435	0.295	339.95	0.996	0.768	1.124
0.339	0.591	0.360	0.590	338.26	0.790	0.878	1.166
0.342	0.215	0.503	0.184	339.48	1.072	0.715	1.102
0.343	0.276	0.484	0.243	339.45	1.028	0.738	1.120
0.377	0.411	0.471	0.375	338.68	0.927	0.787	1.169
0.384	0.387	0.486	0.347	338.60	0.942	0.774	1.177
0.440	0.144	0.616	0.105	337.49	1.084	0.642	1.120
0.448	0.267	0.588	0.211	337.64	1.009	0.697	1.176
0.578	0.336	0.682	0.255	335.88	0.955	0.707	1.307
0.608	0.318	0.713	0.232	335.44	0.963	0.688	1.348
0.642	0.289	0.747	0.203	334.90	0.972	0.672	1.339
0.684	0.091	0.803	0.052	333.44	1.029	0.566	1.245
0.768	0.117	0.858	0.066	332.48	1.008	0.576	1.327
0.878	0.053	0.929	0.026	330.85	1.005	0.525	1.390

benzene + acetone. The activity coefficients γ_i of component i, evaluated from eq 1, are listed in Table II and represented

$$\phi_i P y_i = \gamma_i P_i^S x_i \phi_i^S \exp[v_i^L (P - P_i^S)/RT] \qquad (1)$$

in Figures 1–3. The fugacity coefficients ϕ_i and ϕ_i^S in eq 1 were evaluated by using the second virial coefficients obtained by the Tsonopoulos method (*8*). The vapor pressure of the pure components P_i^S were obtained by using the Antoine equation constants provided by Boublik et al. (*9*). The liquid molar volumes v_i^L were calculated by the Rackett equation (*10*).

Ternary System. Table III shows the experimental VLE data for the acetone (1) + chloroform (2) + benzene (3) system at 101.3 kPa.

Correlation and Prediction

The activity coefficients γ_i were correlated by using the following Wilson equation.

Table IV. Wilson Parameters, Equations 2 and 3, and Deviations between Calculated and Experimental Vapor-Phase Mole Fractions Δy_i and Temperatures ΔT

Wilson parameters/ (J mol^{-1})	acetone (1) + chloroform (2)	chloroform (1) + benzene (2)	benzene (1) + acetone (2)	acetone (1) + chloroform (2) + benzene (3)
$\lambda_{12} - \lambda_{11}$	−349.3	−140.6	−75.1	no ternary parameters
$\lambda_{12} - \lambda_{22}$	−1586.4	−444.8	1360.2	

	acetone (1) + chloroform (2)		chloroform (1) + benzene (2)		benzene (1) + acetone (2)		acetone (1) + chloroform (2) + benzene (3)			
	Δy_1	ΔT/K	Δy_1	ΔT/K	Δy_1	ΔT/K	Δy_1	Δy_2	Δy_3	ΔT/K
average	0.005	0.40	0.002	0.07	0.004	0.07	0.007	0.002	0.006	0.39
maximum	0.012	0.67	0.004	0.16	0.009	0.34	0.012	0.016	0.015	0.54

$\Delta y_i = \Sigma_k | (y_{i,\mathrm{exp}} - y_{i,\mathrm{cal}})|_k/N$, $\Delta T = \Sigma_k | (T_{\mathrm{exp}} - T_{\mathrm{cal}})|_k/N$ (N, Number of data points), R = 8.314/(J mol^{-1} K^{-1})

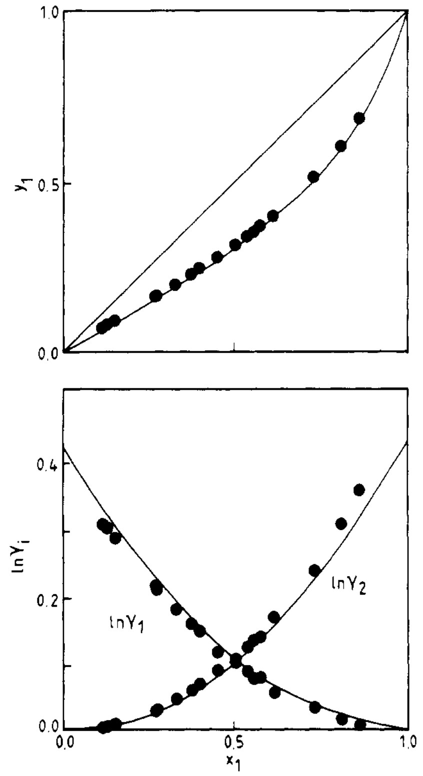

Figure 3. Vapor-phase mole fraction y_1 and activity coefficients γ_i for the binary system benzene (1) + acetone (2) at 101.3 kPa as a function of liquid-phase mole fraction x_1: (●) experimental values. The curves are calculated by using the Wilson equation.

$$\ln \gamma_i = -[\ln (\sum_{j=1}^{N} x_j \Lambda_{ij})] + 1 - \sum_{k=1}^{N} \left(\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{N} x_j \Lambda_{kj}} \right) \qquad (2)$$

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp \left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \qquad (3)$$

Table IV shows the Wilson parameters $\lambda_{ij} - \lambda_{ii}$ and $\lambda_{ij} - \lambda_{jj}$ of the binary systems i–j determined on the basis of the experimental data and the average deviations between the experimental and calculated vapor-phase compositions and bubble point temperatures. The calculated results using the Wilson equation (*1*) are shown by solid lines in Figures 1–3. The average deviations between the experimental and calculated vapor compositions using the recommended Wilson parameters (*2*) are 0.003 mole fraction for the acetone + chloroform system and 0.007 mole fraction for the benzene + acetone system.

The prediction of ternary VLE was carried out with the Wilson parameters in Table IV. Average and maximum deviations between the experimental and predicted vapor-phase composition and bubble point temperatures are 0.005, 0.016 mole fraction and 0.39, 0.54 K, respectively. The predicted vapor compositions of our parameters agree with Reinders' data (*3*) in the accuracy of 0.003 mole fraction on the average.

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