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Vapor–Liquid Equilibria for the Ternary System Acetone + Methanol + Chlorobenzene at 101.325 kPa

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This paper reports vapor–liquid equilibrium results for the acetone + methanol + chlorobenzene mixture at a constant pressure of 101.325 kPa. The equilibrium data have been compared with those predicted by ASOG, UNIFAC, UNIFAC-Dortmund, and UNIFAC-Lyngby group contribution methods, with lower standard deviations of the vapor molar fraction and temperature being calculated by the latter.

Introduction

Distillation has been used as an effective method of separation in the chemical processing industry, and vapor–liquid equilibrium (VLE) data are essential for development, design, and simulation of separation sequences of mixtures. Therefore, the purpose of the study of the thermodynamic equilibrium in the current mixture is the attractive possibility of the application of chlorobenzene as the solvent in the acetone + methanol extractive rectification, using a reverse volatility separation process.

VLE data are usually obtained from experimental measurements, but can also be estimated from available predictive VLE models of group contribution methods such as ASOG (Kojima and Tochigi, 1979), UNIFAC (Fredenslund *et al.*, 1977), UNIFAC-Lyngby (Larsen *et al.*, 1987), and UNIFAC-Dortmund (Weidlich and Gmehling, 1987). These methods require a complete a fully updated experimental data bank in order to fit the group interaction parameters and reproduce the behavior of systems in operation conditions elsewhere.

In previous works (Arce *et al.*, 1990; Gama and Tojo, 1992; Tojo *et al.*, 1994) we presented results on vapor–liquid equilibrium measurements for ternary mixtures. The aim of the present study is to mesure VLE data for the ternary system acetone + methanol + chlorobenzene at 101.325 kPa. No values are available for this system in the open literature. The results obtained have been compared with those predicted by the ASOG, UNIFAC, UNIFAC-Lyngby, and UNIFAC-Dortmund group contribution methods.

Experimental Section

Chemicals. Acetone, methanol, and chlorobenzene were Merck chromatographic grade. No further purification was attempted because the purity of materials had been previously checked by gas chromatography (better than 99.84 mol % for acetone and methanol and better than 99.81 mol % for chlorobenzene). These tests of the solvents showed purities in accordance with purchaser specifications. Their purity had also been checked by determining their density and refractive indices at 298.15 K and their normal boiling temperatures T_b (Table 1).

Apparatus and Procedure. VLE measurements were carried out under an atmosphere of argon N-55 in a modified all-glass Othmer-type ebulliometer with recirculation of both phases (Ocón and Espantoso, 1958). Thermal isolation was assured as the whole apparatus was insulated except for the part corresponding to vapor condensation. Boiling temperatures T of mixtures were measured with a Yokogawa 7563 digital thermometer with a precision of $\pm 10^{-2}$ K (temperature scale IPTS-75). The pressure P was kept constant at (101.325 ± 10^{-2}) kPa by a controller device which introduced argon to the apparatus in order to maintain the pressure difference with respect to pressure in the laboratory. Each experiment was continued for 1 h after the boiling temperature had become stable. Samples of both liquid and vapor phases were taken to low temperature by a built-in refrigeration device and sealed in ice-cooled graduated test tubes to prevent evaporation leakage. Once the samples became thermostatized, they were analyzed by measuring their refractive indices and densities at 298.15 K using a PolyScience controller bath, model 9510, with a temperature stability of $\pm 10^{-2}$ K. Densities ρ of the pure liquid and mixtures were measured with an Anton Paar DMA-46 densimeter with a precision of $\pm 10^{-4}$ g·cm^{-3} and refractive indice n_D by an automatic refractometer, ABBEMAT-HP Dr Kernchen, with a precision of $\pm 10^{-5}$. Estimated uncertainties of mole fractions were determined as $\pm 10^{-3}$ for the liquid phase and $\pm 2 \times 10^{-3}$ for the vapor phase.

Results and Discussion

Experimental density ρ and refractive index n_D values at 298.15 K for this ternary system as a function of x_i have previously been reported (Orge *et al.*, 1994). As a result of interpolation the composition can be determined.

The VLE results are given in Table 2 with the values of activity coefficients γ_i calculated from the relation

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

where the liquid molar volume, ν_i^L, was calculated from the Yen and Woods equation (Yen and Woods, 1966) and fugacity coefficients, ϕ_i and ϕ_i^S, were obtained using a value of the second virial coefficient calculated by the Hayden and O'Connell method (Hayden and O'Connell, 1975), characterizing the vapor phase deviation from ideal behavior and P_i^S is the vapor pressure calculated from Antoine's equation (eq 2), where A, B, and C are fitting

$$\log(P_i^S/\text{kPa}) = A - \frac{B}{T/\text{K} + C} \qquad (2)$$

parameters. Figure 1 gives the corresponding liquid and vapor composition for the ternary mixture, the properties of the pure components required to calculte γ_i being listed in Table 3. Boiling temperatures of the system were

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Table 1. Densities ρ, Refractive Indices n_D, and Normal Boiling Temperatures T_b of the Pure Components

	ρ(298.15 K)/(g·cm^{-3})		n_D(298.15 K)		T_b/K	
component	exptl.	lit.	exptl	lit.	exptl	lit.
acetone	0.7841	0.784 40[a] 0.785 47[b]	1.356 05	1.355 96[a] 1.355 96[b]	329.35	329.44[a] 329.23[b]
methanol	0.7863	0.786 64[a] 0.786 64[b]	1.326 76	1.326 52[a] 1.326 52[b]	337.86	337.85[a] 337.687[b]
chlorobenzene	1.1008	1.101 03[c] 1.101 1[b]	1.521 76	1.522 0[c] 1.521 38[b]	404.92	404.84[a] 404.91[b]

[a] Riddick and Bunger (1986). [b] *TRC Thermodynamic Tables* (1994). [c] Nakanishi *et al.* (1968).

Table 2. Experimental Vapor–Liquid Equilibrium Data: Temperatures T, Liquid-Phase x_i and Vapor-Phase y_i Mole Fractions, and Activity Coefficients γ_i for Acetone (1) + Methanol (2) + Chlorobenzene (3) at 101.325 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
358.17	0.102	0.149	0.184	0.617	0.745	1.971	1.177	337.47	0.061	0.700	0.090	0.853	1.138	1.239	2.425
339.65	0.324	0.153	0.457	0.473	1.013	2.904	1.219	337.42	0.061	0.722	0.096	0.848	1.225	1.196	2.629
334.01	0.291	0.274	0.391	0.566	1.159	2.417	1.157	337.40	0.059	0.741	0.091	0.851	1.200	1.170	2.961
334.75	0.342	0.253	0.419	0.537	1.031	2.413	1.239	335.66	0.120	0.684	0.187	0.768	1.275	1.225	2.576
334.21	0.360	0.251	0.479	0.485	1.141	2.248	1.042	335.10	0.099	0.704	0.180	0.775	1.527	1.230	2.550
332.72	0.429	0.209	0.561	0.409	1.177	2.417	1.025	336.93	0.004	0.981	0.026	0.960	4.742	1.015	9.986
332.49	0.506	0.150	0.708	0.267	1.263	2.238	0.911	336.16	0.024	0.954	0.068	0.913	2.335	1.023	9.280
334.54	0.498	0.097	0.744	0.227	1.260	2.715	0.804	335.60	0.041	0.916	0.091	0.881	1.826	1.052	7.226
339.94	0.404	0.089	0.708	0.241	1.243	2.537	0.899	335.75	0.061	0.863	0.119	0.840	1.605	1.058	5.951
337.30	0.090	0.419	0.111	0.832	0.957	2.032	1.201	335.81	0.075	0.813	0.128	0.823	1.404	1.098	4.806
336.88	0.094	0.439	0.112	0.831	0.942	1.968	1.277	335.27	0.098	0.792	0.174	0.782	1.485	1.095	4.498
328.96	0.890	0.102	0.882	0.112	1.008	1.601	11.533	334.11	0.178	0.694	0.253	0.705	1.232	1.182	3.847
328.97	0.851	0.131	0.839	0.151	1.003	1.682	7.720	333.75	0.185	0.690	0.279	0.684	1.324	1.169	3.500
328.72	0.760	0.210	0.760	0.228	1.025	1.600	6.062	333.36	0.246	0.626	0.308	0.654	1.107	1.253	3.623
329.78	0.785	0.127	0.788	0.196	0.994	2.177	2.463	333.18	0.224	0.653	0.304	0.658	1.209	1.216	3.838
331.67	0.696	0.168	0.759	0.219	1.013	1.700	2.033	332.43	0.268	0.612	0.365	0.605	1.240	1.232	3.203
329.90	0.574	0.240	0.643	0.335	1.106	1.949	1.611	332.17	0.301	0.587	0.392	0.579	1.198	1.245	3.249
330.45	0.522	0.241	0.591	0.385	1.099	2.177	1.375	332.02	0.314	0.576	0.409	0.562	1.202	1.239	3.359
330.63	0.434	0.308	0.545	0.431	1.211	1.891	1.244	330.91	0.426	0.466	0.498	0.475	1.117	1.357	3.381
331.13	0.402	0.320	0.497	0.476	1.174	1.965	1.275	330.89	0.439	0.441	0.519	0.456	1.131	1.379	2.732
332.32	0.313	0.439	0.374	0.592	1.094	1.689	1.743	330.95	0.481	0.408	0.542	0.431	1.075	1.409	3.169
332.85	0.274	0.481	0.343	0.621	1.125	1.582	1.816	330.55	0.542	0.356	0.585	0.389	1.044	1.481	3.417
333.35	0.221	0.543	0.308	0.654	1.239	1.447	1.909	330.54	0.564	0.342	0.609	0.366	1.044	1.452	3.658
333.71	0.211	0.450	0.277	0.686	1.150	1.801	1.312	330.18	0.579	0.328	0.624	0.351	1.055	1.475	3.628
334.30	0.185	0.371	0.238	0.713	1.105	2.221	1.287	329.95	0.629	0.290	0.677	0.301	1.060	1.449	3.805
336.50	0.122	0.495	0.130	0.816	0.849	1.741	1.509	329.86	0.653	0.267	0.686	0.293	1.038	1.533	3.715
336.85	0.084	0.560	0.117	0.831	1.109	1.544	1.531	361.95	0.083	0.137	0.079	0.707	0.354	2.158	1.064
336.65	0.079	0.624	0.129	0.818	1.313	1.376	1.857	365.35	0.139	0.078	0.330	0.413	0.801	2.003	1.117
337.45	0.061	0.668	0.102	0.842	1.301	1.282	2.116	353.61	0.246	0.092	0.376	0.496	0.717	3.004	1.021

correlated by the equation proposed by Tamir and Wisniak (1978):

$$T = \sum_{i=1}^{N} x_i T_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2] + x_1 x_2 x_3 [D_1 + D_2(x_1 - x_2) + D_3(x_1 - x_3) + D_4(x_2 - x_3)] \quad (3)$$

where N is the number of components ($N = 3$), T_i^0 is the boiling temperature of pure component i, and A_{ij}, B_{ij}, C_{ij}, and D_i are correlation parameters. In Table 4 we report the parameters obtained for direct correlation of ternary data. The root mean square deviation for temperature calculated from eq 4 is $\sigma(T/\mathrm{K}) = 0.51$.

$$\sigma(T) = \{\sum (T_{\mathrm{exptl}} - T_{\mathrm{calcd}})^2/(\mathrm{ND})\}^{1/2} \quad (4)$$

$$\sigma(y_i) = \{\sum (y_{i,\mathrm{exptl}} - y_{i,\mathrm{calcd}})^2/(\mathrm{ND})\}^{1/2} \quad (5)$$

Figure 2 shows equilibrium isotherms on the liquid-phase composition diagram calculated from eq 3, using the parameters reported in Table 4. The shape of the curves indicates that the system does not exhibit azeotropic behavior out of the binary range of composition of the acetone + methanol mixture (estimated azeotrope, x_1 = 0.849).

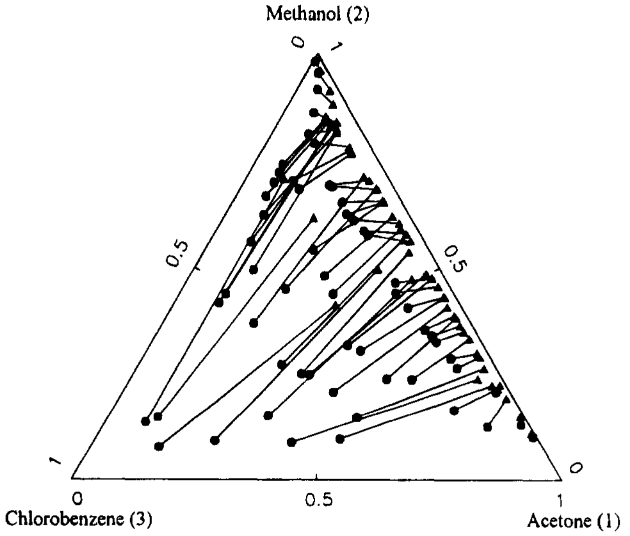

Figure 1. Composition (mole fractions x_i) diagram for acetone (1) + methanol (2) + chlorobenzene (3) at 101.325 kPa: (●) liquid phase, (▲) vapor phase.

Prediction of vapor–liquid equilibria for the ternary system acetone + methanol + chlorobenzene at 101.325 kPa has been carried out by using the ASOG, UNIFAC, UNIFAC-Lyngby, and UNIFAC-Dortmund methods. The group interaction parameters were those published by

Table 3. Physical Properties of the Pure Components: Critical Pressures P_c, Mean Gyration Radius RD, Dipole Moment μ, Association Parameter ETA, Critical Temperature T_c, Critical Compressibility Factor Z_c, and Antoine Parameters A, B, and C

							Antoine parameters		
	P_c/kPa	RD × 10^{10}/m	μ × 10^{30}/(C·m)	ETA	T_c/K	Z_c	A	B	C
acetone	4760.0[a]	2.740[a]	9.540[a]	0.90[a]	509.10[a]	0.241[a]	6.35647[b]	1277.03[b]	−35.92[b]
methanol	8094.0[a]	1.536[a]	5.704[a]	1.63[a]	512.58[a]	0.224[a]	7.02240[b]	1.474.08[b]	−44.02[b]
chlorobenzene	4520.1[a]	3.568[a]	5.837[a]	0.00[a]	632.40[a]	0.268[a]	6.30963[b]	1556.60[b]	−43.15[b]

[a] Prausnitz *et al.* (1980). [b] Riddick *et al.* (1986).

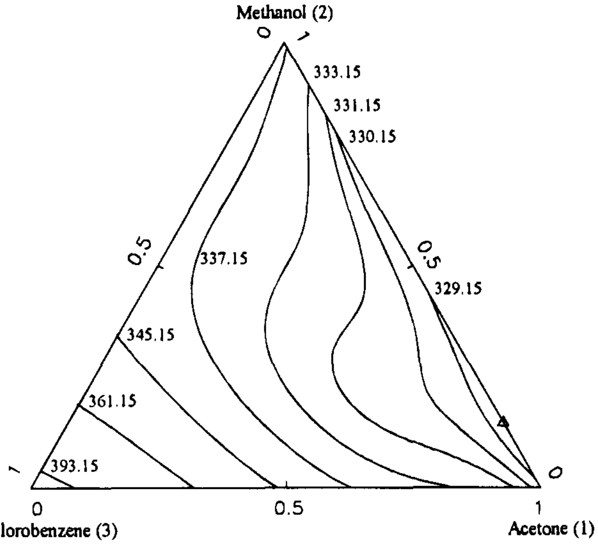

Figure 2. Isolines of temperature for the ternary system acetone (1) + methanol (2) + chlorobenzene (3) at 101.325 kPa using eq 3 with coefficients from Table 4: (△) estimated azeotrope.

Table 4. Correlation Parameters of T−x Data for Acetone (1) + Methanol (2) + Chlorobenzene (3) at 101.325 kPa

$A_{12} = -17.895$	$B_{12} = 16.239$	$C_{12} = -23.122$	
$A_{13} = -93.854$	$B_{13} = 10.538$	$C_{13} = 48.477$	
$A_{23} = -127.490$	$B_{23} = 105.730$	$C_{23} = -30.702$	
$D_1 = 42.525$	$D_2 = -38.668$	$D_3 = 47.559$	$D_4 = 91.938$

Table 5. Root Mean Square Deviations between the Experimental and Calculated Temperatures $\sigma(T/\mathrm{K})$ and Vapor-Phase Compositions $\sigma(y_i)$ of the Ternary Mixture Acetone (1) + Methanol (2) + Chlorobenzene (3) and Those Calculated by Using the ASOG, UNIFAC, UNIFAC-Lyngby, and UNIFAC-Dortmund Methods

method	$\sigma(T/\mathrm{K})$	$\sigma(y_1)$	$\sigma(y_2)$	$\sigma(y_3)$
ASOG	3.70	0.026	0.028	0.022
UNIFAC	3.96	0.024	0.033	0.025
UNIFAC-Lyngby	3.61	0.024	0.029	0.023
UNIFAC-Dortmund	4.03	0.025	0.028	0.024

Tochigi *et al.* (1990), Hansen *et al.* (1991), Larsen *et al.* (1987), and Gmehling *et al.* (1993) for the ASOG, UNIFAC, UNIFAC-Lyngby, and UNIFAC-Dortmund methods, respectively. Results are compared with calculated values, and root mean square deviations for temperature $\sigma(T)$ and composition of the vapor phase $\sigma(y_i)$ are shown (Table 5). Root mean square deviations for temperature $\sigma(T)$ and composition of the vapor phase $\sigma(y_i)$ calculated from eqs 4 and 5, where ND is the number of measurements, are reported in Table 5. The UNIFAC-Lyngby method yields better results than the other methods.

Registry Numbers Supplied by the Author. Acetone, 67-64-1; methanol, 67-56-1; chlorobenzene, 108-90-7.

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