Vapor−Liquid Equilibria for the Ternary System Acetone + Methanol + Water at 101.325 kPa

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The vapor−liquid equilibrium at 101.325 kPa has been measured for the ternary system acetone + methanol + water in an equilibrium still with circulation of phases. Satisfactory results were obtained for the prediction of activity coefficients and the equilibrium compositions with group contribution models (ASOG, UNIFAC, UNIFAC−Dortmund, and UNIFAC−Lyngby). Small standard deviations of vapor molar fraction and temperature were calculated. Azeotropic behavior was observed only in the acetone + methanol mixture. The correlation parameters for the Tamir−Wisniak and UNIQUAC equations were presented.

Introduction

Experimental data collections of vapor−liquid equilibria for ternary or higher order complexity are scarce due to the time-consuming experimental procedure to obtain a complete description of the mixture. As an extension of our earlier work concerning phase equilibria, both vapor−liquid and liquid−liquid (Orge et al., 1995; Iglesias et al., 1997), and thermochemical properties (Rodriguez et al., 1998), in this work we present phase equilibria of a ternary mixture. In this mixture, the pure component water is an effective solvent in the acetone + methanol extractive rectification with a direct volatility separation process. Vapor−liquid equilibria (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 complete and fully updated experimental data in order to fit the group interaction parameters and reproduce the behavior of systems at other operating conditions. As a continuation of previous work concerning mixtures which show convenient thermodynamic topology for extractive distillation, this paper presents VLE results for the mixture acetone + methanol + water at a pressure of 101.325 kPa. The literature contains isobaric values for this ternary system (Griswold and Buford, 1949; Bunch et al., 1963; Kato et al., 1971; Verhoeye and Schepper, 1973); however, a new experimental study was necessary due to the observed composition and temperature discrepancies in the available isobaric data. A comparison was made in order to test the experimental accuracy. The application of group contribution methods leads to satisfactory predictions in terms of activity coefficients and compositions. Current correlations of temperature and activity coefficients with composition are presented.

Experimental Section

Chemicals. Acetone and methanol were Merck chromatographic grade, and water was Millipore quality (organic total mass < 5 ppb, resistivity 18.2 MΩ·cm). Purification was attempted by ultrasonic degassing and drying with molecular sieves (type 3A or 4A, 1/16 in.). The purity of materials was checked by gas chromatography and found to be better than 99.84 mol % for acetone, methanol, and water. These tests of the solvents showed purities in accordance with vendor specifications. Their purity was also checked by determining their densities and refractive indices at 298.15 K and their normal boiling temperatures T_b (Table 1), prior to the experiments.

Apparatus and Procedure. VLE measurements were carried out under an atmosphere of dry argon (less than 2 ppmv water) in a modified all-glass Othmer-type ebulliometer with recirculation of both phases (Ocón and Espantoso, 1958). Thermal isolation was ensured, as the whole apparatus was insulated except for the part corresponding to the vapor condenser. Boiling temperatures of mixtures were measured with a Yokogawa 7563 digital thermometer with a precision of $\pm 10^{-2}$ K (temperature scale IPTS-68 with a 1975 update in accordance with the device instruction manual), calibrated with an Anton Paar MKT-100 digital thermometer (precision $\pm 10^{-3}$, temperature scale ITS-90) over the entire range of work temperatures. Pressure was kept constant at (101.325 ± 10^{-2}) kPa with a controller device which introduced argon to the apparatus in order to maintain the pressure difference with respect to the pressure in the laboratory. Each experiment was continued at least for 1 h after the boiling temperature had become stable. Samples of both liquid and vapor phases were taken to low temperature with a built-in refrigeration device and sealed in ice-cooled graduated test tubes to prevent evaporation leakage. Once the sample temperature became stable in the PolyScience controller bath model 9510 with a temperature stability of $\pm 10^{-2}$ K, the samples were analyzed by measuring their refractive indices and densities at 298.15 K. The densities of the pure liquid and mixtures were measured with an Anton Paar DSA-48 densimeter with a precision of $\pm 2 \times 10^{-5}$ g·cm^{-3}, and the refractive indices n_D, with an automatic refractometer ABBEMAT-HP (Dr. Kernchen) with a precision of $\pm 10^{-5}$. The estimated uncertainties of the mole fractions were determined as $\pm 10^{-3}$ for the liquid phase and $\pm 2 \times 10^{-3}$ for the vapor phase.

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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]	1.356 05	1.355 96[a]	329.35	329.44[a]
		0.785 47[b]		1.355 96[b]		329.23[b]
methanol	0.7863	0.786 64[a]	1.326 76	1.326 52[a]	337.86	337.85[a]
		0.786 64[b]		1.326 52[b]		337.687[b]
water	0.9970	0.997 05[a]	1.332 50	1.332 50[a]	373.13	373.15[a]
		0.997 047 4[b]		1.332 503[b]		373.15[b]

[a] Riddick et al. (1986). [b] TRC Thermodynamic Tables (1994).

Table 2. Experimental Vapor−Liquid Equilibrium Data: Temperature T, Liquid-Phase (x_i) and Vapor-Phase (y_i) Mole Fraction, Activity Coefficient γ_i for Acetone (1) + Methanol (2) + Water (3) at 101.325 kPa, and Root Mean Square Deviation from the UNIQUAC Correlation (in Parentheses in the Final Row)

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
329.31	0.936	0.032	0.949	0.028	1.019	1.248	4.530	333.48	0.361	0.108	0.721	0.117	1.745	1.310	1.554
329.35	0.915	0.049	0.933	0.043	1.022	1.268	4.234	333.56	0.334	0.341	0.579	0.310	1.518	1.087	1.725
329.36	0.889	0.068	0.907	0.066	1.024	1.395	3.891	333.82	0.403	0.174	0.694	0.162	1.489	1.108	1.700
329.40	0.892	0.059	0.918	0.051	1.031	1.235	3.983	333.84	0.141	0.790	0.257	0.716	1.592	1.065	1.944
329.42	0.885	0.062	0.910	0.058	1.029	1.343	3.785	334.02	0.366	0.216	0.654	0.199	1.537	1.082	1.741
329.47	0.866	0.074	0.900	0.065	1.039	1.263	3.564	334.07	0.252	0.495	0.449	0.451	1.533	1.066	1.951
329.47	0.805	0.122	0.852	0.117	1.058	1.365	2.694	334.07	0.308	0.351	0.567	0.312	1.581	1.042	1.755
329.54	0.757	0.170	0.817	0.156	1.077	1.309	2.271	334.14	0.352	0.212	0.659	0.192	1.603	1.067	1.679
329.56	0.817	0.109	0.865	0.098	1.055	1.278	3.110	334.52	0.370	0.162	0.664	0.163	1.517	1.162	1.789
329.57	0.842	0.089	0.883	0.079	1.044	1.258	3.465	334.55	0.114	0.815	0.223	0.749	1.668	1.048	1.941
329.58	0.835	0.093	0.876	0.084	1.045	1.294	3.372	334.64	0.265	0.374	0.527	0.351	1.680	1.075	1.623
329.62	0.804	0.114	0.857	0.103	1.059	1.281	3.044	334.68	0.205	0.533	0.405	0.504	1.672	1.076	1.664
329.66	0.896	0.042	0.923	0.033	1.023	1.146	4.266	334.68	0.325	0.132	0.677	0.144	1.751	1.255	1.586
329.67	0.779	0.140	0.831	0.136	1.058	1.385	2.491	334.82	0.300	0.162	0.648	0.174	1.812	1.226	1.575
329.75	0.696	0.218	0.778	0.194	1.107	1.253	2.017	334.88	0.100	0.828	0.185	0.784	1.576	1.065	2.048
329.78	0.754	0.145	0.826	0.128	1.084	1.245	2.747	335.01	0.307	0.306	0.561	0.283	1.526	1.046	1.893
329.94	0.646	0.256	0.754	0.214	1.149	1.172	1.952	335.34	0.289	0.222	0.624	0.214	1.780	1.081	1.538
330.07	0.821	0.071	0.876	0.059	1.045	1.177	3.568	335.36	0.280	0.250	0.591	0.245	1.739	1.093	1.618
330.18	0.814	0.065	0.871	0.059	1.045	1.260	3.437	335.49	0.260	0.180	0.632	0.184	1.991	1.131	1.525
330.20	0.708	0.151	0.806	0.136	1.110	1.247	2.471	335.65	0.083	0.844	0.159	0.810	1.579	1.048	1.935
330.32	0.614	0.265	0.722	0.239	1.143	1.239	1.913	335.87	0.221	0.390	0.464	0.392	1.705	1.093	1.677
330.45	0.668	0.168	0.776	0.159	1.124	1.298	2.337	336.03	0.249	0.209	0.586	0.215	1.894	1.117	1.654
330.46	0.571	0.307	0.701	0.261	1.189	1.160	1.812	336.06	0.165	0.565	0.331	0.567	1.619	1.082	1.699
330.47	0.576	0.295	0.716	0.245	1.202	1.134	1.788	336.06	0.070	0.854	0.128	0.839	1.495	1.055	1.949
330.61	0.760	0.068	0.852	0.058	1.077	1.172	3.065	336.30	0.120	0.643	0.240	0.669	1.619	1.108	1.694
330.70	0.490	0.405	0.615	0.355	1.207	1.182	1.639	336.32	0.111	0.685	0.220	0.706	1.590	1.096	1.624
330.74	0.514	0.376	0.630	0.336	1.177	1.206	1.759	336.43	0.096	0.734	0.179	0.753	1.504	1.087	1.762
330.75	0.631	0.169	0.762	0.163	1.157	1.308	2.156	336.57	0.061	0.859	0.104	0.860	1.361	1.053	1.994
330.76	0.534	0.340	0.663	0.298	1.190	1.181	1.800	336.80	0.228	0.185	0.592	0.198	2.036	1.130	1.557
330.80	0.468	0.440	0.606	0.368	1.243	1.120	1.645	336.92	0.209	0.150	0.599	0.174	2.237	1.218	1.533
330.81	0.735	0.066	0.844	0.057	1.098	1.173	2.852	336.95	0.116	0.601	0.261	0.646	1.781	1.116	1.416
330.83	0.725	0.073	0.833	0.072	1.097	1.335	2.724	337.12	0.078	0.787	0.138	0.806	1.390	1.054	1.786
330.87	0.688	0.088	0.819	0.078	1.136	1.199	2.635	337.15	0.068	0.816	0.113	0.833	1.310	1.050	2.000
330.94	0.429	0.483	0.579	0.399	1.288	1.101	1.456	337.18	0.140	0.541	0.304	0.577	1.702	1.098	1.582
331.06	0.631	0.198	0.751	0.189	1.128	1.272	2.010	337.18	0.187	0.154	0.574	0.189	2.386	1.276	1.537
331.10	0.582	0.192	0.733	0.185	1.194	1.288	2.039	337.27	0.182	0.081	0.604	0.129	2.576	1.657	1.537
331.22	0.569	0.196	0.720	0.201	1.193	1.354	1.920	337.29	0.058	0.840	0.098	0.855	1.334	1.041	1.958
331.24	0.388	0.512	0.531	0.440	1.294	1.131	1.616	337.62	0.151	0.065	0.498	0.115	2.539	1.801	2.055
331.31	0.365	0.540	0.519	0.454	1.342	1.102	1.615	337.72	0.147	0.441	0.360	0.483	1.871	1.104	1.593
331.34	0.561	0.198	0.763	0.145	1.277	0.969	2.136	337.75	0.043	0.870	0.070	0.890	1.267	1.028	1.901
331.35	0.625	0.104	0.787	0.103	1.182	1.311	2.278	337.76	0.144	0.489	0.316	0.534	1.682	1.098	1.700
331.52	0.344	0.566	0.492	0.482	1.342	1.105	1.579	337.81	0.098	0.567	0.224	0.650	1.747	1.150	1.565
331.59	0.536	0.218	0.701	0.213	1.219	1.272	1.946	337.95	0.034	0.894	0.051	0.915	1.130	1.020	1.994
331.62	0.514	0.250	0.692	0.227	1.254	1.183	1.891	337.96	0.019	0.939	0.028	0.954	1.129	1.012	1.783
331.69	0.560	0.118	0.768	0.118	1.272	1.307	1.956	338.01	0.158	0.123	0.549	0.174	2.633	1.418	1.586
331.75	0.304	0.613	0.455	0.519	1.396	1.089	1.701	338.18	0.172	0.137	0.566	0.186	2.477	1.355	1.466
331.85	0.467	0.284	0.661	0.251	1.307	1.139	1.944	338.34	0.020	0.907	0.024	0.923	0.920	0.999	2.906
332.06	0.524	0.126	0.752	0.124	1.316	1.259	1.921	338.69	0.117	0.387	0.346	0.464	2.199	1.165	1.526
332.20	0.282	0.625	0.425	0.545	1.381	1.099	1.784	339.09	0.082	0.529	0.206	0.645	1.844	1.163	1.495
332.52	0.411	0.315	0.630	0.270	1.385	1.072	1.939	339.76	0.144	0.076	0.543	0.146	2.704	1.792	1.513
332.55	0.478	0.162	0.734	0.142	1.384	1.099	1.834	340.21	0.069	0.481	0.202	0.631	2.070	1.199	1.381
332.62	0.254	0.631	0.405	0.556	1.444	1.091	1.782	340.82	0.108	0.083	0.501	0.170	3.199	1.847	1.474
332.62	0.193	0.740	0.341	0.637	1.602	1.064	1.798	341.38	0.071	0.317	0.282	0.459	2.695	1.269	1.494
332.85	0.342	0.420	0.560	0.357	1.466	1.047	1.822	341.88	0.066	0.264	0.298	0.418	3.025	1.363	1.459
332.95	0.378	0.328	0.608	0.288	1.433	1.079	1.847	342.87	0.060	0.229	0.305	0.386	3.287	1.395	1.437
333.05	0.431	0.195	0.693	0.176	1.428	1.109	1.812	344.69	0.051	0.205	0.307	0.385	3.731	1.453	1.262
333.05	0.254	0.588	0.423	0.523	1.487	1.082	1.771	345.78	0.043	0.158	0.293	0.329	4.031	1.541	1.380
333.09	0.234	0.641	0.385	0.570	1.471	1.081	1.832	349.09	0.028	0.120	0.241	0.267	4.567	1.468	1.462
333.20	0.316	0.447	0.530	0.385	1.488	1.045	1.837	355.95	0.009	0.062	0.220	0.148	11.180	1.234	1.299
333.24	0.166	0.768	0.297	0.677	1.599	1.063	1.968	356.15	0.004	0.081	0.160	0.192	18.521	1.221	1.342
333.29	0.421	0.152	0.705	0.150	1.475	1.195	1.746	359.99	0.001	0.048	0.162	0.116	42.620	1.073	1.240
(0.98)	(0.0009)	(0.0004)	(0.042)	(0.0257)	(5.036)	(0.199)	(0.308)								

Table 3. Physical Properties of the Pure Components: Critical Presure 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

	P_c/kPa[a]	10^{10}RD/m[a]	$10^{30}\mu$/(C·m)[a]	ETA[a]	T_c/K[a]	Z_c[a]	Antoine constants[b] A	B	C
acetone	4760.0	2.740	9.540	0.90	509.10	0.241	6.35647	1277.030	−35.92
methanol	8094.0	1.536	5.704	1.63	512.58	0.224	7.02240	1474.080	−44.02
water	22119.247	0.615	6.104	1.70	647.37	0.230	7.13653	1695.167	−42.74

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

Table 4. Parameters of Tamir−Wisniak and UNIQUAC Equations for Acetone + Methanol + Water at 101.325 kPa

Parameters of Tamir−Wisniak Equation

$A_{12} = -8.8204$	$B_{12} = 16.6354$	$C_{12} = -28.3995$	$D_{12} = 2.1637$	
$A_{13} = -70.4737$	$B_{13} = 78.8043$	$C_{13} = -70.3315$	$D_{13} = 41.4474$	
$A_{23} = -46.4245$	$B_{23} = 28.5694$	$C_{23} = -65.2799$	$D_{23} = 110.0524$	
$E_1 = 36.3314$	$E_2 = -47.0283$	$E_3 = -124.8401$	$E_4 = -75.5656$	$\sigma = 0.45$

Parameters of UNIQUAC Equation

$F_{12} = -130.2535$	$F_{21} = -34.51268$	$F_{13} = -81.56071$	$F_{31} = -179.9613$
$F_{23} = -873.6794$	$F_{32} = 304.4958$		

Results and Discussion

Equilibrium Equation and Activity Coefficients. 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 (Iglesias et al., 1996). By interpolation, the composition can be determined. The VLE results are given in Table 2 with values of activity coefficients γ_i calculated from the relation

$$\gamma_i = \phi_i y_i P/\{\phi_i^{s} x_i P_i^{s} \exp[v_i^{L}(P - P_i^{s})/RT]\} \quad (1)$$

where the liquid molar volume v_i^L was calculated from the Yen and Woods equation (Yen and Woods, 1966), the fugacity coefficients ϕ_i and ϕ_i^S were obtained using the value of the second virial coefficient calculated by the Hayden and O'Connell (1975) method to characterize the vapor-phase deviation from ideal behavior, and P_i^S is the vapor pressure which was calculated from the Antoine equation

$$\log P_i^{S} = A - \frac{B}{T + C} \quad (2)$$

where A, B, and C are fitting parameters. Figure 1 gives the corresponding liquid and vapor compositions for the ternary mixture and the properties of the pure components required to calculate γ_i, which are listed in Table 3.

Temperature Correlation. To obtain general parameters of experimentally measured magnitudes, the Tamir−Wisniak (Tamir and Wisniak, 1978) equations were applied to correlate boiling temperatures, as in

$$T = \sum_{i=1}^{N} x_i T_i^{\circ} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + D_{ij}(x_i - x_j)^3] + x_1 x_2 x_3 [E_1 + E_2(x_1 - x_2) + E_3(x_1 - x_3) + E_4(x_2 - x_3)] \quad (3)$$

where N is the number of components ($N = 3$), T_i° is the boiling temperature of pure component i, and A_{ij}, B_{ij}, C_{ij}, D_{ij}, and E_i are correlation parameters, which are presented in Table 4. Figure 2 shows equilibrium isotherms on the liquid-phase composition diagram calculated from eq 3. 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 (Gueltekin, 1990; Dallinga et al., 1993). The root mean square deviation

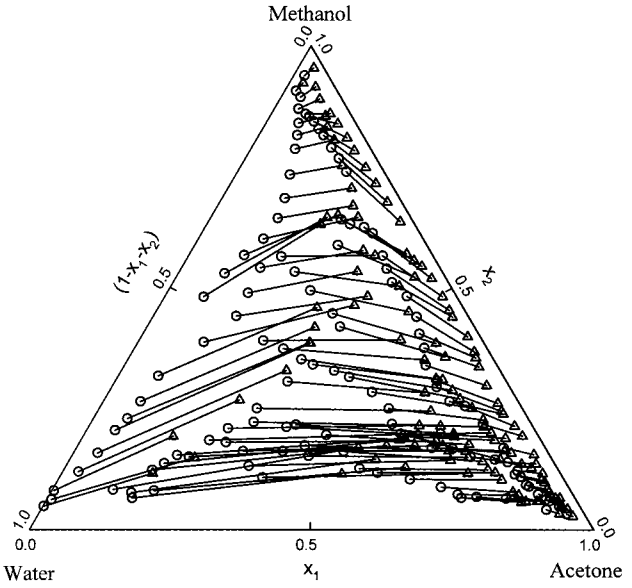

Figure 1. Composition (mole fractions x_i) diagram for acetone + methanol + water at 101.325 kPa: (○) liquid phase; (△) vapor phase.

for temperature from eq 3 is $\sigma = 0.62$ K, calculated with

$$\sigma(M) = \{\sum (M_{exptl} - M_{calcd})^2/ND\}^{1/2} \quad (4)$$

where M is a general magnitude (such as temperature, vapor-phase composition, etc.) and ND is the number of experimental data.

Activity Coefficient Correlation. The activity coefficients play a key role in vapor−liquid equilibria calculations, since Raoult's law provides no more than a rough approximation in common nonideal mixtures. For strongly nonideal mixtures, especially solutions of alcohols, water, and so forth, the UNIQUAC equation is likely to represent the data successfully. This equation offers three advantages: only two fitting parameters for each pair of compounds, a weaker dependence on temperature for such parameters, and surface fraction as a primary concentration variable. This equation is applicable to a wide range of mixtures with small or large molecules and to both vapor−liquid and liquid−liquid equilibria. The description of this model is widely presented in the open literature (Abrams and Prausnitz, 1978; Reid et al., 1986), and hence, it is not discussed here. The fitting parameters of this

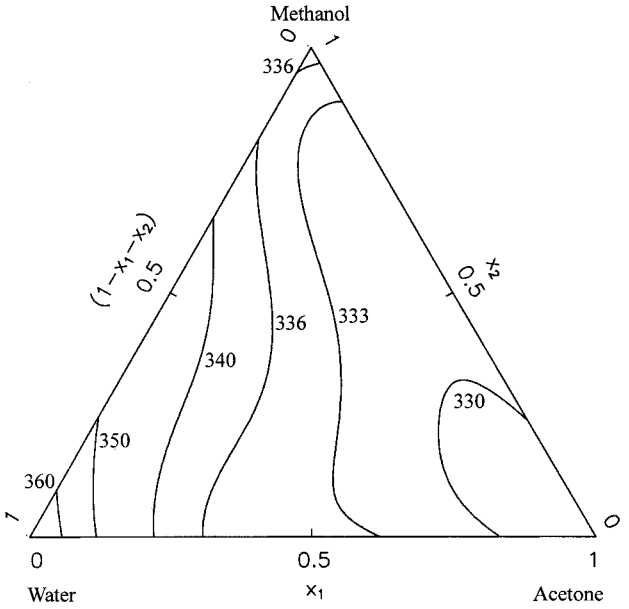

Figure 2. Isotherms (temperature in K) for the ternary system acetone + methanol + water at 101.325 kPa using eq 3 with coefficients from Table 4.

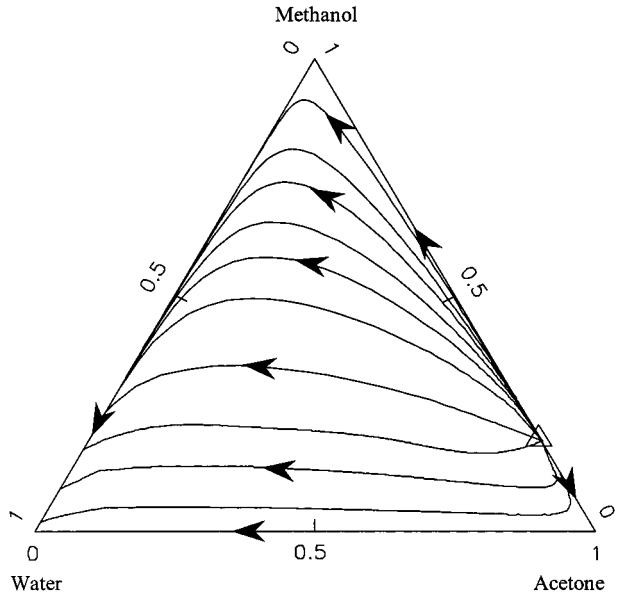

Figure 3. Residual curve map for the ternary system acetone + methanol + water at 101.325 kPa by the ASOG method: (△) experimental azeotrope (Dallinga et al., 1993).

model are presented in Table 4, and root mean square deviations for T, x_i, y_i, and γ_i are presented in Table 2, following the experimental data. In Figure 3 the corresponding residual curve map can be observed (UNIQUAC parameters were applied to calculations). In accordance with that, the capability of this solvent (water) as a potential extractive agent is highly selective for methanol due to hydrogen bonds as well as an adequate molecular volume. A direct distillation sequence (acetone as the first distillate product in the extractive column and methanol as the second distillate product in the solvent recovery column) is possible, attending to the ternary obtained topology (Doherty, 1985; Foucher et al., 1991; Laroche et al., 1991). Furthermore, a surprisingly low solvent concentration in the extractive column is necessary for high-purity separation and economical operation conditions (reflux and column feed ratio).

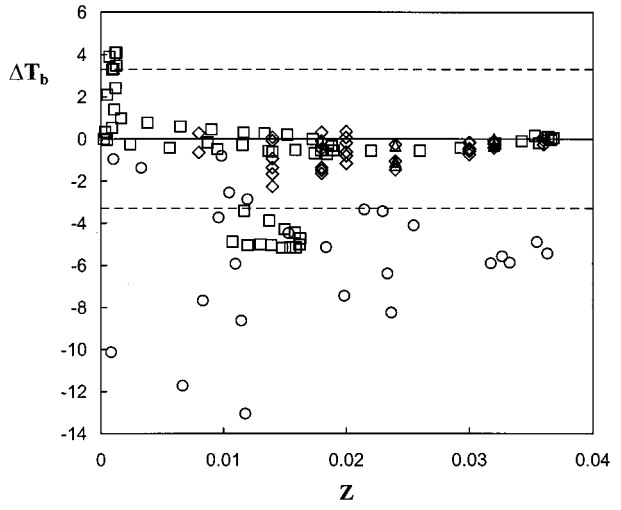

Figure 4. Deviations of boiling temperatures (ΔT_b/ K) for acetone + methanol + water: (− − −) ±1% deviation from our experimental data; (○) Griswold and Buford (1949); (□) Bunch et al. (1963); (◇) Kato et al. (1971); (△) Verhoeye and Schepper (1973).

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

method	$\sigma(T/K)$	$\sigma(y_1)$	$\sigma(y_2)$	$\sigma(y_3)$
ASOG	0.92	0.040	0.028	0.030
UNIFAC	1.44	0.035	0.027	0.025
UNIFAC−Lyngby	1.92	0.057	0.040	0.043
UNIFAC−Dortmund	1.09	0.057	0.041	0.043

Prediction Models. Predictions of vapor−liquid equilibria for the ternary system acetone + methanol + water at 101.325 kPa have been carried out with the ASOG, UNIFAC, UNIFAC−Lyngby, and UNIFAC−Dortmund group contribution methods. The group interaction parameters were those published by Tochigi et al. (1990), Hansen et al. (1991), Larsen et al. (1987), and Gmehling et al. (1993), for these methods, respectively. Results are compared with calculated values, and root mean square deviations for temperature $\sigma(T)$ and the composition of the vapor phase $\sigma(y_i)$ are shown in Table 5. The lowest deviations from experimental data were found for the ASOG method.

Comparison of Data. Figure 4 shows the boiling temperature deviations corresponding to literature data points from the experimental data of this paper. The abscissa is an arbitrary parameter (z) which expresses the product of the total mole fractions in the mixture. In a simple way, we could describe this figure as an easy and clear procedure to locate trends or zones in the composition diagram where high or low deviations exist from a set of experimental data. In general terms, good agreement is observed between our experimental data and those reported by Bunch et al. (1963), Kato et al. (1971), and Verhoeye and Schepper (1973), although the last one reports only six experimental points for the ternary mixture. Large deviations are observed between our data and the data reported by Griswold and Buford (1949), which could induce significant errors in composition measurement in rectification processes or design calculations.

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