J. Chem. Eng. Data **1997,** *42*, 434−437

Articles

Vapor−Liquid Equilibria of 2-Methoxy-2-methylbutane + Methanol + Water at 101.32 kPa

Alberto Arce,* Antonio Blanco, José Martínez-Ageitos, and Ana Soto

Department of Chemical Engineering, University of Santiago de Compostela, E-15706 Santiago, Spain

Isobaric vapor−liquid equilibrium data for the system 2-methoxy-2-methylbutane + methanol + water were determined at 101.32 kPa using a distillation apparatus recycling both liquid and vapor phases. The VLE data were satisfactorily correlated using the Wilson, NRTL, and UNIQUAC equations for liquid phase activity coefficients and adequately predicted using the ASOG-KT, UNIFAC, UNIFAC−Dortmund, and UNIFAC−Lyngby group contribution methods.

Introduction

2-Methoxy-2-methylbutane (TAME or *tert*-amyl methyl ether) is useful as a gasoline additive because of its ability to prevent nocking and to improve octane rating. In this study we report VLE data for the ternary system TAME + methanol + water. The results were correlated using the Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) equations and compared with the predictions of the ASOG-KT (Kojima and Tochigi, 1979; Tochigi *et al.*, 1990), UNIFAC (Fredenslund *et al.*, 1977), UNIFAC−Dortmund (Weidlich and Gmehling, 1987; Gmehling *et al.*, 1993), and UNIFAC−Lyngby (Larsen *et al.*, 1987) group contribution methods. Physical properties for the range of homogeneous mixtures of the ternary system were obtained previously (Arce *et al.*, 1996a).

Experimental Section

Materials. Water was purified using a Milli-Q Plus system. Methanol was supplied by Merck with nominal purity >99.7 mass %, and 2 methoxy-2 methylbutane (TAME) was supplied by Fluka Chemika with nominal purity >98.9 mass %. The purities of the components were verified chromatographically; none was subjected to further purification. The methanol and TAME contained 0.03 and 0.02 mass % water, respectively, as determined by a Metrohm 737 KF coulometer. The densities and refractive indices of the pure components at 298.15 K, and their boiling points at 101.32 kPa, are compared with literature data in Table 1.

Apparatus and Procedure. The experimental data were obtained in a Labodest apparatus, that recycles both liquid and vapor phases (Fischer Labor und Verfahrenstechnik, Germany). Distillation was carried out under an inert atmosphere of argon, at a constant pressure of 101.32 kPa. Pressure was measured to a precision of ±0.01 kPa with a Fischer digital manometer, and temperature to a precision of ±0.02 K with a Heraeus Quatt 100 thermometer.

The compositions of the vapor and liquid phases were determined by densimetry and refractometry using previously published data for the composition dependence of the densities and refractive indices of the mixtures studied (Arce et al., 1996a). Densities were measured to within ±0.000 01 g·cm^{-3} in an Anton Paar 60 digital vibrating tube densimeter equipped with a DMA 602 measuring cell, and refractive indices to within ±0.0001 with an ATAGO RX-1000 refractometer. In both cases, a Hetotherm thermostat was used to maintain the temperature at (298.15 ± 0.02) K. The maximum deviation of the equilibrium mixture composition measurements is assumed to be ±0.002 mole fraction, as indicated by comparison of selected results with those for samples prepared by weighing.

Table 1. Densities (*d*), Refractive Indices (n_D), and Boiling Points (T_b) of the Pure Components

	d(298.15 K)/g·cm^{-3}		n_D (298.15 K)		T_b (101.32 kPa)/K	
component	exp	lit.	exp	lit.	exp	lit.
water	0.9970	0.997 05[a]	1.3324	1.332 50[a]	373.16	373.15[a]
methanol	0.7866	0.786 37[a]	1.3264	1.326 52[a]	337.65	337.696[a]
TAME	0.7657	0.765 77[c]	1.3858	1.385 8[c]	359.33	359.39[b]

[a] Riddick *et al.*, 1986. [b] Krähenbühl and Gmehling, 1994. [c] Linek, 1987.

Experimental Results and Data Treatment

Results. Isobaric VLE data were only determined for the totally miscible mixtures of the three components. The experimentally determined compositions of the liquid and vapor phases, and the corresponding equilibrium temperatures, are listed in Table 2, and Figure 1 shows the isotherms for the ternary system. The binodal curve (dashed line) shown in the figure is taken from Arce *et al.* (1994) and marks the miscibility limit of the three liquid components at 298.15 K.

Demonstration of the thermodynamic consistency of the experimental VLE for the binary system methanol + TAME and correlation of the corresponding *x*, *y*, *P*, and *T* data were detailed in a previous paper (Arce *et al.*, 1996b). A deviation of $D = 0.855$ (less than 3) in the Wisniak $L-W$ test (Wisniak, 1993) and D less than D_{max} for all points in the McDermott−Ellis consistency test (McDermott and Ellis, 1965) confirm the thermodynamic consistency of the experimental VLE data for the ternary system.

S0021-9568(96)00283-X CCC: $14.00

Table 2. Isobaric Vapor−Liquid Equilibrium Data for the System 2-Methoxy-2-methylbutane (1) + Methanol (2) + Water (3): Mole Fractions x_i and y_i of Each Component i in the Liquid and Vapor Phases, Respectively, at Temperature T_b and Pressure 101.32 kPa

T_b/K	x_1	x_2	y_1	y_2
348.53	0.9340	0.0547	0.6687	0.2629
346.31	0.9100	0.0736	0.6094	0.3030
343.02	0.8473	0.1168	0.5283	0.3258
340.68	0.7827	0.1825	0.4604	0.4550
340.18	0.7468	0.2013	0.4525	0.4257
339.65	0.7269	0.2245	0.4367	0.4652
339.36	0.6896	0.2492	0.4301	0.4505
338.69	0.6506	0.2938	0.4077	0.5006
338.20	0.6216	0.3270	0.3929	0.5339
338.57	0.6155	0.3007	0.4025	0.4797
338.98	0.6001	0.2733	0.4127	0.4189
338.32	0.5482	0.3344	0.3913	0.4748
337.09	0.4218	0.4866	0.3355	0.5917
336.82	0.3869	0.5289	0.3232	0.6136
337.31	0.3873	0.4853	0.3377	0.5675
337.91	0.3700	0.4458	0.3573	0.5104
338.30	0.3783	0.4027	0.3763	0.4667
338.37	0.3974	0.3888	0.3799	0.4595
338.47	0.4196	0.3672	0.3833	0.4522
338.59	0.4534	0.3438	0.3928	0.4358
337.86	0.3851	0.4403	0.3588	0.5117
337.30	0.3262	0.5237	0.3263	0.5754
336.96	0.2794	0.5893	0.3013	0.6215
337.33	0.2820	0.5518	0.3150	0.5859
337.70	0.2848	0.5122	0.3316	0.5485
338.04	0.2842	0.4778	0.3483	0.5123
338.33	0.3006	0.4342	0.3665	0.4754
338.71	0.2930	0.3925	0.3838	0.4395
338.35	0.2536	0.4590	0.3575	0.4876
338.12	0.2306	0.5006	0.3394	0.5203
337.85	0.2019	0.5582	0.3107	0.5687
337.73	0.1944	0.5802	0.2973	0.5916
337.57	0.1674	0.6288	0.2734	0.6309
337.77	0.1754	0.5952	0.2897	0.6015
338.19	0.1718	0.5385	0.3159	0.5520
338.45	0.1649	0.5031	0.3369	0.5147
338.67	0.1562	0.4528	0.3593	0.4761
338.72	0.1746	0.4179	0.3746	0.4524
338.80	0.1636	0.4128	0.3815	0.4411
338.80	0.1785	0.4015	0.3843	0.4366
338.68	0.1565	0.4452	0.3608	0.4740
338.60	0.1357	0.5049	0.3296	0.5206
338.56	0.1196	0.5523	0.2990	0.5655
338.54	0.1046	0.5962	0.2652	0.6113
338.55	0.0920	0.6367	0.2359	0.6522
338.65	0.1004	0.5890	0.2695	0.6048
338.75	0.1014	0.5615	0.2855	0.5811
338.84	0.1035	0.5268	0.3093	0.5449
338.88	0.1049	0.4836	0.3327	0.5107
338.93	0.1016	0.4569	0.3524	0.4833
338.91	0.1024	0.4303	0.3680	0.4604
338.96	0.0893	0.4243	0.3704	0.4557
339.16	0.0755	0.4532	0.3442	0.4892
339.32	0.0682	0.4468	0.3372	0.4955
339.45	0.0577	0.4267	0.3433	0.4851
339.52	0.0472	0.3934	0.3559	0.4669
339.63	0.0383	0.3758	0.3625	0.4561
340.24	0.0328	0.3943	0.3285	0.4909
337.67	0.6181	0.3612	0.3764	0.5997
337.16	0.5497	0.4217	0.3565	0.6119
336.76	0.5053	0.4684	0.3416	0.6325
336.55	0.4423	0.5163	0.3270	0.6372
336.40	0.3917	0.5587	0.3120	0.6496
336.19	0.3536	0.6005	0.2962	0.6717
336.19	0.3245	0.6204	0.2896	0.6732
336.05	0.2978	0.6501	0.2767	0.6904
335.98	0.2743	0.6762	0.2663	0.7041
335.90	0.2547	0.7010	0.2559	0.7197
335.83	0.2426	0.7164	0.2495	0.7285
335.85	0.2629	0.6970	0.2581	0.7195
335.80	0.2537	0.7082	0.2538	0.7254
335.76	0.2476	0.7173	0.2508	0.7302
335.76	0.2605	0.7055	0.2549	0.7269
335.74	0.2502	0.7180	0.2504	0.7325
335.71	0.2474	0.7228	0.2486	0.7359
335.68	0.2348	0.7369	0.2418	0.7439
335.66	0.2192	0.7533	0.2339	0.7527
337.34	0.0108	0.9879	0.0228	0.9772
337.56	0.0098	0.9764	0.0218	0.9720
338.13	0.0125	0.9338	0.0289	0.9495
338.50	0.0148	0.9013	0.0366	0.9297
338.97	0.0168	0.8610	0.0471	0.9046
339.52	0.0200	0.8142	0.0563	0.8791
340.27	0.0150	0.7739	0.0557	0.8612
341.18	0.0124	0.7216	0.0569	0.8368
342.03	0.0099	0.6732	0.0544	0.8188
342.50	0.0111	0.6279	0.0688	0.7882
342.53	0.0144	0.5842	0.1038	0.7441
343.36	0.0109	0.5450	0.0981	0.7319
344.21	0.0078	0.5089	0.0891	0.7252
345.36	0.0054	0.4551	0.0836	0.7061
345.29	0.0066	0.4054	0.1280	0.6560
341.92	0.0203	0.4188	0.2477	0.5666
340.25	0.0383	0.4193	0.3110	0.5149
336.52	0.0533	0.9338	0.0969	0.8991
337.27	0.0538	0.8785	0.1073	0.8630
337.88	0.0539	0.8256	0.1236	0.8270
338.57	0.0610	0.7354	0.1635	0.7578
339.08	0.0605	0.6750	0.1870	0.7095
339.63	0.0537	0.6282	0.1972	0.6814
339.80	0.0551	0.5624	0.2410	0.6181
339.94	0.0519	0.5038	0.2750	0.5683
340.28	0.0414	0.4573	0.2899	0.5424
336.38	0.2879	0.6339	0.2844	0.6675
336.30	0.2668	0.6595	0.2727	0.6829
336.29	0.2212	0.7010	0.2525	0.7039
336.18	0.1837	0.7482	0.2296	0.7349
336.16	0.1560	0.7837	0.2083	0.7617
336.85	0.1632	0.7095	0.2366	0.7026
337.15	0.1680	0.6746	0.2539	0.6722
337.11	0.1539	0.6968	0.2379	0.6933
337.04	0.1303	0.7388	0.2120	0.7286
337.02	0.1104	0.7753	0.1896	0.7582
337.04	0.0934	0.8068	0.1676	0.7872
337.51	0.1005	0.7437	0.1954	0.7380
337.74	0.1112	0.6969	0.2210	0.6978
335.63	0.1656	0.8167	0.2013	0.7926
335.78	0.1485	0.8258	0.1925	0.7970
335.83	0.1375	0.8376	0.1836	0.8063
336.13	0.1518	0.7914	0.2038	0.7684
336.18	0.1289	0.8207	0.1829	0.7937
336.26	0.1125	0.8407	0.1681	0.8102
336.37	0.0936	0.8641	0.1489	0.8323
336.77	0.1057	0.8105	0.1753	0.7851
337.27	0.1117	0.7483	0.1994	0.7390

Data Treatment. For vapor and liquid phases in equilibrium at pressure P and temperature T:

$$y_i\phi_i P = x_i\gamma_i P_i^{\mathrm{S}}\phi_i^{\mathrm{S}} \exp\left[\frac{V_i^{\mathrm{L}}(P - P_i^{\mathrm{S}})}{RT}\right] \tag{1}$$

where x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively, V_i^{L} is its molar volume in the liquid phase, γ_i is its activity coefficient, ϕ_i and ϕ_i^{S} are its coefficients of fugacity and fugacity at saturation, respectively, and P_i^{S} is its saturated vapor pressure. In this work, V_i^{L} was obtained from the empirical equation of Yen and Woods (1966), ϕ_i and ϕ_i^{S} were calculated by the method of Hayden and O'Connell (1975) from the second virial coefficient, and P_i^{S} was calculated from Antoine's equation

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

using the coefficients A, B, and C given in Table 3.

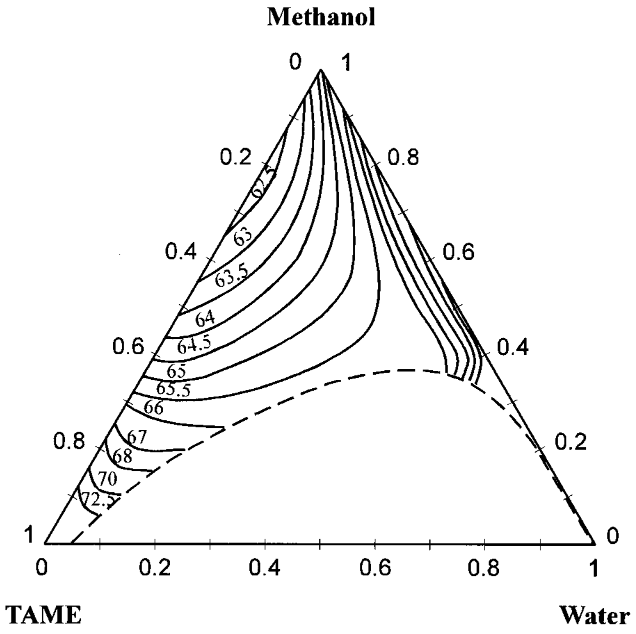

Figure 1. Isotherms for the VLE of the ternary system 2-methoxy-2-methylbutane (1) + methanol (2) + water (3) at 101.32 kPa.

Table 3. Antoine Coefficients *A*, *B*, and *C* for Equation 2

component	*A*	*B*	*C*	ref
water	7.072 62	−1657.160	−46.13	Reid *et al.*, 1987
methanol	7.205 19	−1581.993	−33.439	Riddick *et al.*, 1986
TAME	6.067 82	−1256.258	−50.100	Krähenbühl and Gmehling, 1994

Table 4. Correlation of the VLE Data for the System 2-Methoxy-2-methylbutane (1) + Methanol (2) + Water (3): Model Parameters and Mean Deviations (md) in the Equilibrium Temperature and Vapor Phase Compositions

model	parameters/J·mol^{-1}	md	mole fraction	
		T/K	md y_1	md y_2
UNIQUAC	$\Delta u_{12} = 3736.56$, $\Delta u_{21} = -460.407$ $\Delta u_{13} = 5522.04$, $\Delta u_{31} = 528.313$ $\Delta u_{23} = -208.505$, $\Delta u_{32} = 366.760$	0.17	0.0068	0.0059
WILSON	$\Delta\lambda_{12} = -316.444$, $\Delta\lambda_{21} = 5239.20$ $\Delta\lambda_{13} = 10410.60$, $\Delta\lambda_{31} = 10459.99$ $\Delta\lambda_{23} = -3078.92$, $\Delta\lambda_{32} = 3990.82$	0.91	0.0142	0.0279
NRTL (α=0.3)	$\Delta g_{12} = 803.856$, $\Delta g_{21} = 3473.17$ $\Delta g_{13} = 6246.31$, $\Delta g_{31} = 15425.80$ $\Delta g_{23} = -340.043$, $\Delta g_{32} = 1234.46$	0.18	0.0062	0.0067

Correlation. The experimental results were correlated by least-squares regression (Simplex method), the objective function minimized being

$$F = \sum_i \{x_i(\text{calc}) - x_i\}^2 \qquad (3)$$

where x is the mole fraction of component i in the liquid phase.

The models used for the liquid phase activity coefficients were the Wilson equation, NRTL equation, setting the nonrandomness parameter α to different values and selecting the value giving the best correlation, and the UNIQUAC equation, setting the area parameter q' to 0.96 for methanol and 1.0 for water and calculating r and q using group contribution methods. Table 4 lists the model parameters fitted for the ternary system, together with the mean deviations in T, y_1, and y_2. Figure 2 compares the experimental data with the UNIQUAC correlation (the number of points has been reduced for the sake of clarity).

Prediction. The VLE data were predicted using the ASOG-KT, UNIFAC (the structural and group interaction parameters recommended by Gmehling *et al.* (1982) were used), UNIFAC−Dortmund, and UNIFAC−Lyngby group contribution methods to calculate the liquid phase activity coefficients.

Table 5 lists the root mean squared deviations between the experimental VLE data and those predicted by each group contribution method, and Figure 3 compares the experimental data with those predicted using the UNIFAC−Lyngby method (the number of points has also been reduced for the sake of clarity).

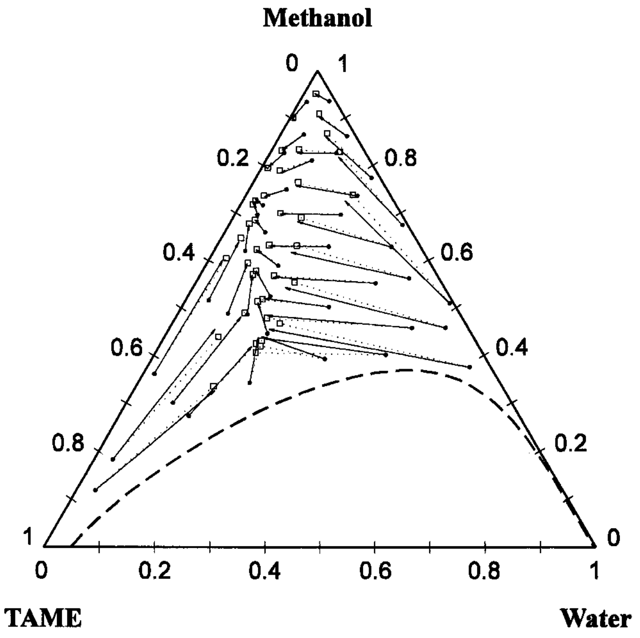

Figure 2. Experimental VLE data (→) and the corresponding UNIQUAC correlation (···□) for the ternary system 2-methoxy-2-methylbutane (1) + methanol (2) + water (3) at 101.32 kPa.

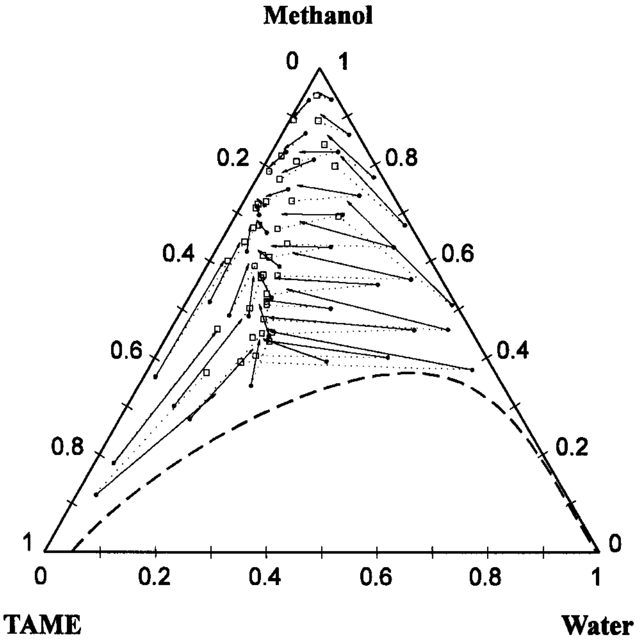

Figure 3. Comparison of the experimental (→) and UNIFAC−Lyngby predicted (···□) VLE data for the ternary system 2-methoxy-2-methylbutane (1) + methanol (2) + water (3) at 101.32 kPa.

Discussion

The VLE data obtained for the range of homogeneous mixtures of the ternary TAME + methanol + water system show that this mixture does not form an azeotrope. The

Table 5. Prediction of the VLE Data for the System 2-Methoxy-2-methylbutane (1) + Methanol (2) + Water (3): Root Mean Squared (rms) Deviations in Equilibrium Temperature and Vapor Phase Compositions (Mole Fraction)

method	rms y_1	rms y_2	rms y_3	rms T/K
ASOG-KT	0.0269	0.0505	0.0334	1.47
UNIFAC	0.0471	0.0415	0.0241	1.77
UNIFAC−Dortmund	0.0543	0.0438	0.0187	2.25
UNIFAC−Lyngby	0.0302	0.0277	0.0089	1.44

Wisniak $L-W$ and McDermott−Ellis tests confirm the thermodynamic consistency of the experimental data. The UNIQUAC and NRTL (with $\alpha = 0.3$) models allow correlation of the experimental results, affording only minor deviations in composition and temperature, while the Wilson equation gives larger deviations, especially in the equilibrium temperatures. The best predictions of the VLE data were obtained using the UNIFAC−Lyngby method to calculate the liquid phase activity coefficients, while use of the UNIFAC−Dortmund method afforded the worst predictions, particularly as regards the equilibrium temperature (Table 5).

Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−118.

Arce, A.; Blanco, A.; Blanco, M.; Soto, A.; Vidal, I. Liquid-Liquid Equilibria of Water + Methanol + (MTBE or TAME) Mixtures. *Can. J. Chem. Eng.* **1994**, *72*, 935−938.

Arce, A.; Martínez-Ageitos, J.; Mendoza, J.; Soto, A. Densities, Refractive Indices, Speeds of Sound and Isentropic Compresibilities of Water + Methanol + 2-Methoxy-2-methylbutane at 298.15 K. *J. Chem. Eng. Data* **1996a**, *41*, 724−727.

Arce, A.; Martínez-Ageitos, J.; Soto, A. VLE Measurements of Binary Mixtures of Methanol, Ethanol, 2-Methoxy-2-methylpropane and 2-Methoxy-2-methylbutane at 101.32 kPa. *J. Chem. Eng. Data* **1996b**, *41*, 718−723.

Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria using UNIFAC: A Group-Contribution Method*; Elsevier: Amsterdam, 1977.

Gmehling, J.; Rasmussen, P.; Fredenslund, A. Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. 2. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118−127.

Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.

Hayden, J. G.; O'Connell, J. P. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−216.

Kojima, K.; Tochigi, K. *Prediction of Vapor-Liquid Equilibria by the ASOG Method*; Elsevier: Tokyo, 1979.

Krähenbühl, M. A.; Gmehling J. Vapor Presures of Methyl *tert*-Butyl Ether, Ethyl *tert*-Butyl Ether, Isopropyl *tert*-Butyl Ether, *tert*-Amyl Methyl Ether and *tert*-Amyl Ethyl Ether. *J. Chem. Eng. Data* **1994**, *39*, 759−762.

Larsen, B. L.; Rasmussen, P.; Fredenslund, A. A Modified UNIFAC Group Contribution Model for Prediction of Phase Equilibria and Heats of Mixing. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274−2286.

Linek, J. Excess Volumes and Refractive Indices in the Benzene - tert-amyl methyl ether and Cyclohexane - tert-amyl methyl ether Systems at 298.15 K. *Collect. Czech. Chem. Commun.* **1987**, *52*, 2839.

McDermott, C.; Ellis, S. R. M. A Multicomponent Consistency Test. *Chem. Eng. Sci.* **1965**, *20*, 293−296.

Reid, R. C.; Prausnitz, J. M.; Poling B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

Riddick, J. A.; Bunger, W. B.; Sakano, T. *Organic Solvents*, 4th ed.; John Wiley: New York, 1986.

Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

Tochigi, K.; Tiegs, D.; Gmehling, J.; Kojima, K. Determination of New ASOG Parameters. *J. Chem. Eng. Jpn.* **1990**, *23*, 453−463.

Weidlich, U.; Gmehling, J. A Modified UNIFAC Model. 1. Prediction of VLE, h^E, and γ^∞. *Ind. Eng. Chem. Res.* **1987**, *26*, 1372−1381.

Wilson, G. M. Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

Wisniak, J. A New Test for the Thermodynamic Consistency of Vapor-Liquid Equilibrium. *Ind. Eng. Chem. Res.* **1993**, *32*, 1531−1533.

Yen, L. C.; Woods, S. S. A Generalized Equation for Computer Calculation of Liquid Densities. *AIChE J.* **1966**, *12*, 95−99.

Received for review August 16, 1996. Accepted November 19, 1996.⊗ This work was partly financed by the DGICYT (Spain) under Project PB94-0658 and the Xunta de Galicia (Spain) under Project XUGA 20902B94.

JE9602834

⊗ Abstract published in *Advance ACS Abstracts*, January 1, 1997.