J. Chem. Eng. Data **1996,** *41,* 1079−1082

Isobaric Vapor−Liquid Equilibria in the Systems Methyl Ethanoate + Oxolane and Oxolane + Toluene

Jaime Wisniak*

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

The vapor−liquid equilibrium at 101.3 kPa has been determined for the binary systems methyl ethanoate + oxolane (tetrahydrofuran) and oxolane + toluene. The binary system methyl ethanoate + oxolane exhibits positive deviations from ideal behavior, while the binary system oxolane + toluene presents moderate negative deviations from ideality. No azeotropes are present. The activity coefficients and boiling point of the solution were correlated with its composition by the Redlich−Kister, Wohl, Wilson, UNIQUAC, NRTL, and Wisniak−Tamir equations.

Oxolane (tetrahydrofuran) is an intermediate for the production of adipic acid and hexamethylenediamine used in the manufacture of nylon 6 and may also be used for the production of 1,4-butanediol, it possesses a very high dipole moment (1.7) and is used in many processes as a solvent. Vapor−liquid equilibrium for the binary system oxolane + toluene has been measured by Deshpande and Oswal (1975) and Oswal and Deshpande (1988) at (289.15 and 303.15) K, by Rivenq (1975) at (200, 300, 400, 600, and 760) mmHg, by Klon-Palczewska et al. (1980) at 760 mmHg, and by Nazarov et al. (1978) at 760 mmHg. Deshpande and Oswal (1975) calculated also the excess Gibbs function of the system at 303.15 K and found that the excess entropy of mixing was negative, indicating a solute−solvent specific interaction. Rivenq (1975) reported $T-x-y$ data only and analyzed the composition of the phases in equilibrium by measuring the dielectric constant of the same. Calculation of the activity coefficients from the data reported by Klon-Palczewska et al., Nazarov et al., and Rivenq indicates that the system deviates negatively from ideal behavior and that the data reported are not thermodynamically consistent for mole fractions of oxolane larger than 0.7. No vapor−liquid equilibrium data are available for the binary system methyl ethanoate (1) + oxolane (2). The binary system methyl methanoate + oxolane includes two components with large dipole moments while the system oxolane + toluene contains a component with a small dipole moment. The present work was undertaken to measure vapor−liquid equilibria (VLE) data for the title systems for which isobaric data are not available or are not reliable.

Experimental Section

Purity of Materials. Methyl ethanoate (99.5+ mass %), oxolane (99.8+ mass %), and toluene (99.94+ mass %) were purchased from Merck. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purities (as determined by GLC) of the pure components appear in Table 1.

Table 1. Mole Percent GLC Purities, Refractive Index n_D at the Na D Line, and Normal Boiling Points T of Pure Components

component (purity/mass %)	n_D (298.15 K)	T/K
methyl ethanoate (99.5)	1.3588[a]	330.05[a]
	1.3589[b]	330.09[b]
oxolane (99.8)	1.4050[a]	339.15[a]
	1.4049[b]	339.12[b]
toluene (99.94)	1.4926[a]	383.95[a]
	1.49411[b]	383.78[b]

[a] Measured. [b] TRC (1974).

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (Boublikova and Lu, 1969) was used in the VLE measurements. The general experimental features have been described in a previous paper (Wisniak and Tamir, 1975). Temperature was measured with a Lauda Model R42/2 digital thermometer provided with a PT-10 probe, and the total pressure of the system was determined from the boiling temperature of distilled water in a Swietoslawski ebulliometer. All analyses were carried out by gas chromatography on a Gow-Mac Series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 2 m long and 0.2 cm in diameter packed with SE-30 on 80−100 mesh SUPELCOPORT and operated at 333.15 K for the binary with methyl ethanoate and 373.15 K for the binary with toluene. The temperatures at the injector and detector were 493.15 and 543.15 K, respectively. Very good separation for the binary systems was achieved under these conditions, and repetitive gravimetric calibration analyses were carried out with synthetic mixtures to convert the peak ratio to the mass composition of the sample. Concentration measurements were accurate to better than ±0.008 mole fraction unit. The pertinent polynomial fit had a correlation coefficient R^2 better than 0.99. The accuracies in the determination of the pressure P and temperature T were at least ±0.1 kPa and ±0.02 K, respectively.

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 101.3$ kPa are reported in Tables 2 and 3 and Figures 1−3, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{12} P}{RT} \qquad (1)$$

where x_i and y_i are the equilibrium molar concentrations of component i in the liquid and vapor phases, T and P

---

* e-mail: wisniak@bgumail.bgu.ac.il.

Table 2. Experimental Vapor−Liquid Equilibria Data for Methyl Ethanoate (1) + Oxolane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ $\mathrm{cm^3\ mol^{-1}}$	$-B_{22}$/ $\mathrm{cm^3\ mol^{-1}}$	$-B_{12}$/ $\mathrm{cm^3\ mol^{-1}}$	G^E/RT
337.56	0.085	0.128	1.1774	1.0014	537	572	554	0.0152
337.02	0.124	0.177	1.1407	1.0037	539	575	557	0.0195
336.19	0.172	0.242	1.1465	1.0061	543	579	560	0.0286
335.48	0.233	0.309	1.1061	1.0132	546	582	564	0.0336
334.78	0.281	0.360	1.0956	1.0235	549	586	567	0.0424
334.50	0.305	0.390	1.1045	1.0180	550	587	568	0.0427
334.35	0.321	0.400	1.0813	1.0299	551	588	569	0.0451
333.70	0.384	0.460	1.0628	1.0432	554	591	572	0.0494
333.44	0.413	0.497	1.0754	1.0296	555	593	573	0.0472
332.96	0.474	0.552	1.0580	1.0391	557	595	576	0.0469
332.43	0.517	0.591	1.0572	1.0512	560	598	578	0.0529
332.08	0.581	0.645	1.0366	1.0671	561	600	580	0.0481
331.72	0.641	0.694	1.0259	1.0814	563	602	582	0.0445
331.53	0.671	0.723	1.0260	1.0782	564	603	583	0.0420
331.33	0.737	0.777	1.0115	1.0904	565	604	584	0.0312
331.02	0.760	0.798	1.0169	1.0975	566	606	585	0.0350
330.80	0.775	0.812	1.0219	1.0995	567	607	587	0.0381
330.75	0.802	0.834	1.0170	1.1006	567	607	587	0.0325
330.63	0.867	0.888	1.0048	1.1165	568	608	587	0.0188
330.37	0.904	0.918	1.0057	1.1370	569	609	589	0.0175
330.24	0.932	0.942	1.0051	1.1460	570	610	589	0.0140
330.20	0.949	0.956	1.0035	1.1550	570	610	590	0.0106
330.17	0.969	0.973	1.0011	1.1715	570	610	590	0.0060
330.05	1	1						
γ^{∞} [a]			1.18	1.19				

[a] Calculated according to Wisniak et al. (1995).

Table 3. Experimental Vapor−Liquid Equilibrium Data for Oxolane (2) + Toluene (3) at 101.3 kPa

T/K	x_3	y_3	γ_2	γ_3	$-B_{22}$/ $\mathrm{cm^3\ mol^{-1}}$	$-B_{33}$/ $\mathrm{cm^3\ mol^{-1}}$	$-B_{23}$/ $\mathrm{cm^3\ mol^{-1}}$	G^E/RT
379.06	0.069	0.181	0.8904	1.0023	725	1226	947	−0.0038
378.94	0.069	0.183	0.9003	1.0037	726	1227	948	−0.0058
378.10	0.084	0.224	0.9223	0.9918	730	1234	953	−0.0144
377.13	0.094	0.247	0.9309	1.0004	735	1242	959	−0.0064
376.10	0.110	0.284	0.9331	0.9981	740	1250	966	−0.0093
374.70	0.129	0.324	0.9409	1.0024	746	1262	975	−0.0058
368.27	0.237	0.516	0.9583	0.9909	779	1319	1018	−0.0171
367.03	0.260	0.549	0.9612	0.9868	785	1331	1027	−0.0201
365.10	0.297	0.600	0.9646	0.9792	796	1349	1041	−0.0255
360.94	0.382	0.697	0.9721	0.9609	819	1390	1071	−0.0355
359.25	0.421	0.734	0.9726	0.9488	829	1408	1084	−0.0421
358.50	0.447	0.757	0.9643	0.9309	833	1415	1090	−0.0559
356.60	0.486	0.788	0.9727	0.9281	844	1435	1105	−0.0518
355.17	0.522	0.814	0.9730	0.9168	853	1451	1117	−0.0559
348.32	0.718	0.919	0.9696	0.8522	896	1529	1175	−0.0672
343.42	0.870	0.970	0.9771	0.8151	929	1590	1220	−0.0468
342.84	0.884	0.974	0.9825	0.8142	933	1597	1225	−0.0395
339.15	1	1						
γ^{∞} [a]			0.82	0.84				

[a] Calculated according to Wisniak et al. (1995).

are the boiling point and the total pressure, V_i^L is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{2}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The pure component vapor pressures P_i^0 were calculated according to the Antoine equation

$$\log(P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \tag{3}$$

where the constants A_i, B_i, and C_i are reported in Table 4. The molar virial coefficients B_{ii} and B_{ij} were estimated according to the method of O'Connell and Prausnitz (1967) using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. The last two terms in eq 1 contributed less than 1% to the activity coefficients in the binary of oxolane with methyl ethanoate and less than 6% in the binary with toluene; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables 2 and 3 and are estimated accurate to within ±3% and ±6%, respectively, the higher relative error for the system oxolane + toluene is due to the large boiling temperature difference between the two pure components. The results reported in these tables indicate that the system methyl ethanoate + oxolane exhibits

Table 4. Antoine Coefficients,[a] Eq 3

compd	A_i	B_i	C_i
methyl ethanoate	6.186 213	1156.430	53.46
oxolane	6.120 043	1202.29	46.90
toluene	6.079 54	1344.8	53.67

[a] TRC (1974).

Table 5. Parameters and Deviations between Experimental and Calculated Values for the Different Models

A. Redlich–Kister, Eq 4

system	B	C	D	max % dev[a]	avg % dev[b]	rmsd[c]
2-propanol (1) + oxolane (2)	0.0709	−0.0028		2.7	1.0	0.003
oxolane (2) + toluene (3)	−0.0532	0.0021	−0.0102	8.8	4.0	0.013

B. Other Models[d]

model	system	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 2	0.1742	0.1718	0.6196		0.0034
	2 + 3	−0.1181	−0.2307	0.5924		0.0042
Wilson	1 + 2	−36.17[f]	530.22[f]			0.0027
	2 + 3	−41.44[f]	−349.51[f]			0.0031
NRTL	1 + 2	234.52[f]	236.17[f]		0.197	0.0018
	2 + 3	−221.29[f]	−229.62[f]		0.201	0.0021
UNIQUAC	1 + 2	658.04[f]	−433.03[f]			0.0024
	2 + 3	1116.65[f]	−1302.88[f]			0.0051

[a] Maximum % deviation. [b] Average % deviation. [c] Root mean square deviation. [d] All equations in ln γ_i form. [e] $\delta(y) = \sum|y_{\mathrm{exptl}} - y_{\mathrm{calcd}}|/N$ (N = number of data points). [f] J/mol.

Table 6. Coefficients in Correlation of Boiling Points, Eq 6, Average % Deviation and Root Mean Square Deviations in Temperature, rmsd (*T*/K)

system	C_0	C_1	C_2	C_3	max % dev %[a]	avg % dev[b]	msd[c]
methyl acetate (1) + oxolane (2)	−7.666 21	2.352 13	−0.693 81		0.32	0.08	0.01
oxolane (2) + tolene (3)	−21.835 01	13.446 61	0.108 88	−6.358 11	0.36	0.09	0.03

[a] Maximum % deviation. [b] Average % deviation. [c] Root mean square deviation.

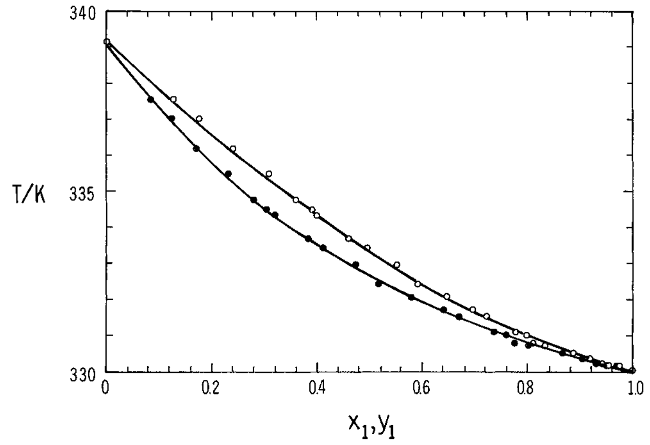

Figure 1. Boiling temperature diagram for the system methyl ethanoate (1) + oxolane (2) at 101.3 kPa.

positive deviations from ideal behavior while the system oxolane + toluene presents moderate negative deviations from ideality. Tables 2 and 3 contain also the activity coefficients at infinite dilution calculated by the method suggested by Wisniak et al. (1995).

The vapor–liquid equilibria data reported in Tables 2 and 3 were found to be thermodynamically consistent by the L-W method of Wisniak (1993) and the point-to-point method of Van Ness et al. (1973) as modified by Fredenslund et al. (1977). For both binaries, the residuals of the Fredenslund test were randomly distributed, as measured by the Durbin–Watson statistic. The activity coefficients were correlated with the Redlich–Kister, Wohl, Wilson, NRTL, and UNIQUAC equations (Walas, 1985). The following Redlich–Kister expansion was used (1948):

$$\ln \gamma_1/\gamma_2 = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(1 - 8x_1x_2) \quad (4)$$

The values of the constants B, C, D, and E were determined by multilinear regression. The values of the pertinent parameters and statistics appear in Table 5.

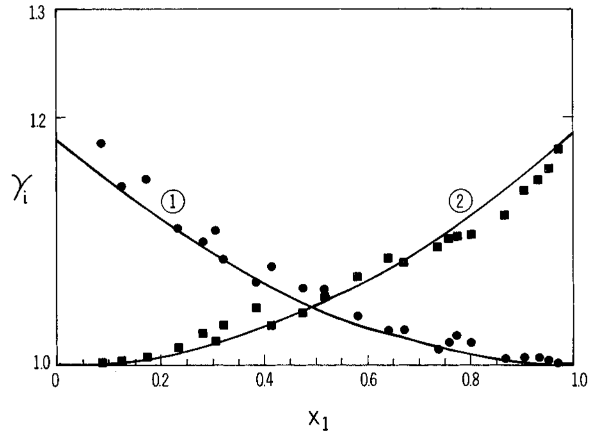

Figure 2. Activity coefficients for the system methyl ethanoate (1) + oxolane (2) at 101.3 kPa: experimental (●, □); predicted by NRTL (—).

The parameters of the Wohl, Wilson, NRTL, and UNIQUAC equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N,2} \left(\frac{\gamma_{i,\mathrm{exptl}} - \gamma_{i,\mathrm{calcd}}}{\gamma_{i,\mathrm{exptl}}} \right)^2 \quad (5)$$

They are reported in Table 5, together with the relative deviation of the vapor composition. Inspection of the results given in Table 5 shows that all four models fitted very well the system methyl ethanoate (1) + oxolane (2), the best fit corresponding to the NRTL correlation. A comparison of the experimental activity coefficients and the ones predicted by the NRTL model is presented in Figure 2. For the system oxolane (2) + toluene (3) the fit was good except in the range of high concentration of toluene, probably due to strong interaction effects (charge transfer or hydrogen bond) with the aromatic ring.

The excess Gibbs function G^E of the two binary systems is presented in Tables 2 and 3 as the variation of the dimensionless function G^E/RT with the concentration of oxolane. For the system methyl ethanoate + oxolane $G^E/$

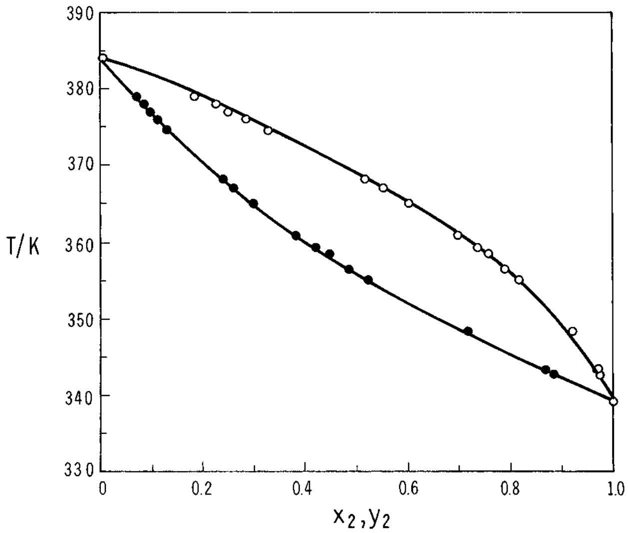

Figure 3. Boiling temperature diagram for the system oxolane (2) + toluene (3) at 101.3 kPa.

RT is positive, while for oxolane + toluene G^E/RT is negative. The difference in sign and size is due to the different nature of the forces operating in both systems. Toluene has a small dipole moment (0.4 D), while methyl ethanoate and oxolane have large dipole moments (1.7 D each), indicating that in toluene solutions interactive forces are weaker and that the predominant effect is the dispersive one, in the system methyl methanoate + oxolane the dispersive forces are predominant.

The boiling points of the two binaries were correlated by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = \sum_{i=1}^{2} x_i T_i^0/K + x_1 x_2 \sum_{m=0} C_k (x_i - x_j)^k \qquad (6)$$

In this equation T_i^0 is the boiling point of the pure component *i* and *m* is the number of terms in the series expansion of $x_i - x_j$. The various constants of eq 6 are reported in Table 6, which also contains information indicating the degree of goodness of the correlation.

Literature Cited

Boublikova, L. K.; Lu, B. C.-Y. Isothermal Vapor–Liquid Equilibria for the Ethanol–*n*-Octane System. *J. Appl. Chem.* **1969**, *19*, 89–92.

Deshpande, D. D.; Oswal, S. L. Thermodynamics of Mixtures Containing p-Dioxan or Tetrahydrofuran. 1. Excess Gibbs Free Energies and Excess Volumes. *J. Chem. Thermodyn.* **1975**, *7*, 155–159.

Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor–Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

Klon-Palczewska, M.; Cholinski, J.; Wyrzykowska-Stankiewicz, D. Isobaric Vapor–Liquid Equilibrium in Binary Organic Solvent Mixtures. *Chem. Stosow.* **1980**, *24*, 197–210.

Nazarov, V. V.; Generalova, T. V.; Shalgyn, V. A.; Bernshtein, L. A. Liquid-Vapor Equilibrium in Diethyl Ether-Tetrahydrofuran and Tetrahydrofuran-Toluene Systems. *Zh. Prikl. Khim.* **1978**, *51*, 1198–1199.

O'Connell, J. P.; Prausnitz, J. M. Empirical Correlations of Second Virial Coefficients for Vapor–Liquid Equilibrium Calculations. *Ind. Eng. Chem., Process Des. Dev.* **1967**, *6*, 245–250.

Oswal, S. L.; Deshpande, D. D. Liquid-Vapor Equilibrium. Oxolane-Toluene. *Int. DATA Ser., Sel. Data Mixtures, Ser. A.* **1988**, 16–17.

Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

Rivenq, F. Ebulliometry of the Binary Tetrahydrofuran-Toluene. *Bull. Soc. Chim. Fr.* ***1975***, 2433–2434.

TRC-Thermodynamic Tables. Non-hydrocarbons; Thermodynamics Research Center, The Texas A & M University System, College Station, TX (Looseleaf data sheets, extant 1974).

Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions*; McGraw-Hill Book Co.: New York, 1982.

Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor–Liquid Equilibrium: Part 1. An Appraisal of Data Reduction Methods. *AIChE J.* **1973**, *19*, 238–244.

Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: London, **1985**.

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

Wisniak, J.; Tamir, A. Vapor–Liquid Equilibria In System Carbon Tetrachloride Acetic Acid. *J. Chem. Eng. Data* **1975**, *20*, 168–170.

Wisniak, J.; Tamir, A. Correlation of the Boiling Point of Mixtures. *Chem. Eng. Sci.* **1976**, *31*, 631–635.

Wisniak, J.; Segura, H.; Reich, R. Determination of Activity Coefficients at Infinite Dilution by Using the Weighted Volatility Function. *Phys. Chem. Liq.* **1995**, in press.

Received for review March 18, 1996. Accepted May 21, 1996.[⊗]

JE9601016

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.