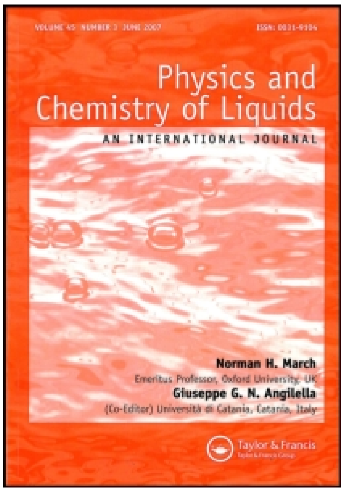

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Phase Equilibria in the Systems Oxolane Vinyl Acetate, Oxolane Ethyl 1,1-Dimethylethyl Ether and Vinyl Acetate Ethyl 1,1-Dimethylethyl Ether

Jaime Wisniak[a]; Hugo Segura[b]
[a] Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel [b] Departamento de Ingeniería Química, Universidad de Concepción, Concepción, Chile

To cite this Article Wisniak, Jaime and Segura, Hugo(2000) 'Phase Equilibria in the Systems Oxolane Vinyl Acetate, Oxolane Ethyl 1,1-Dimethylethyl Ether and Vinyl Acetate Ethyl 1,1-Dimethylethyl Ether', Physics and Chemistry of Liquids, 38: 5, 553 — 565

To link to this Article: DOI: 10.1080/00319100008030303

URL: http://dx.doi.org/10.1080/00319100008030303

Phys. Chem. Liq., 2000, Vol. 38, pp. 553–565
Reprints available directly from the publisher
Photocopying permitted by license only

PHASE EQUILIBRIA IN THE SYSTEMS OXOLANE + VINYL ACETATE, OXOLANE + ETHYL 1,1-DIMETHYLETHYL ETHER AND VINYL ACETATE + ETHYL 1,1-DIMETHYLETHYL ETHER

JAIME WISNIAK[a,]* and HUGO SEGURA[b]

[a] *Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel;* [b] *Departamento de Ingeniería Química, Universidad de Concepción, Concepción, Chile*

(Received 3 August 1999)

Vapor–liquid equilibrium at 94 kPa has been determined for the binary systems oxolane (THF) + vinyl acetate, oxolane + ethyl 1,1-dimethylethyl ether (ETBE) and vinyl acetate + ethyl 1,1-dimethylethyl ether. The three systems present slight to moderate positive deviations from ideal behavior and, to a first approximation, can be considered to behave like regular solutions. An azeotrope is present in the system vinyl acetate + ETBE that boils at 340.40 K and contains 49.8% mol vinyl acetate. The activity coefficients of the systems were correlated reasonable well with its composition by the Wohl, Wilson, UNIQUAC and NRTL models. The boiling points of the binary systems were correlated with the Wisniak-Tamir equation.

Keywords: Vapor–liquid equilibrium; ETBE; vinyl acetate; oxolane

1. INTRODUCTION

This work is part of our program to determine vapor–liquid equilibria (VLE) in systems formed of oxygenates and other organics, mainly gasoline components. Phase equilibria data of oxygenated mixtures are important for predicting the vapor phase composition that would

---

*Corresponding author. e-mail: wisniak@bgumail.bgu.ac.il be in equilibrium with hydrocarbon mixtures. No isothermal or isobaric VLE data are available for the three binaries reported here.

2. EXPERIMENTAL SECTION

2.1. Purity of Materials

Ethyl 1,1-dimethylethyl ether (96.0 + mass%) was purchased from TCI (Japan) and purified to 99.9 + mass% by distillation using a 1-m high × 30 mm diameter Normschliffgerätebau adiabatic distillation column (packed with 3 × 3 mm SS spirals) working at a 1:100 reflux ratio. Oxolane (99.9 mass%) and vinyl acetate (99.3 + mass%) were bought from Aldrich and used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table I. Appropriate precautions were taken when handling ETBE in order to avoid peroxide formation.

2.2. Apparatus and Procedure

An all glass vapor – liquid equilibrium apparatus model 602, manufactured by Fischer Labor- und Verfahrenstechnik (Bonn, Germany), was used in the equilibrium determinations. Details of the equipment and its operation appear in a previous publication [1]. The equilibrium temperature is measured with a Hart Scientific thermometer, model 1502, provided with a 4 mm diameter Pt-100 temperature sensor, with an accuracy of ± 0.005 K. The total pressure of the system is controlled by a vacuum pump capable to work at pressures down to 0.25 kPa. The

TABLE I Mole percent GLC purities (mass%), refractive index n_D at the Na D line, and normal boiling points T of pure components

	n_D		T_b (101.33 *kPa*)/*K*	
Component (*purity*/*mass*%)	*exptl.*	*lit.*	*exptl.*	*lit.*
oxolane (99.9)	1.4045[a] [298.15 K]	1.4049[b] [298.15 K]	339.15[a]	339.12[b]
vinyl acetate (99.3)	1.3932[a] [298.15 K]	1.3934[b] [298.15 K]	345.71[a]	345.32[c]
ethyl 1,1-dimethylethyl ether (99.8)	1.37594[a] [293.15 K]	1.37564[b] [293.15 K]	345.85[a]	345.86[d]

[a] Measured; [b] TRC a-6170 [13]. DIPPR [6]; [c] Swamy and Van Winkle [3]; [d] Krähenbühl and Gmehling [14].

pressure is measured by a Vac Probs with an accuracy of ± 0.07 kPa; a 5-L Erlenmeyer flask connected between the separating chamber and the Vac Probs dampens the pressure variations to no more than 0.01 kPa. Samples, taken by syringing out 0.7 mL after the system had achieved equilibrium, were analyzed by gas chromatography on a DANI model GC 1000 apparatus equipped with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SP-2100. Injector, detector, and column temperatures for the three binaries were (473.15, 493.15 and 313.15) K respectively. Very good separation was achieved under these conditions, and calibration analyses using synthetic mixtures were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fits had a correlation coefficient R^2 better than 0.99. Concentration measurements were accurate to better than ± 0.005 mole fraction.

3. RESULTS

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 94$ kPa are reported in Tables II–IV

TABLE II Experimental vapor-liquid equilibrium data for oxolane (1) + vinyl acetate (2) at 94.00 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}/$ $cm^3\,mol^{-1}$	$-B_{22}/$ $cm^3\,mol^{-1}$	$-B_{12}/$ $cm^3\,mol^{-1}$
343.18	0.000	0.000					
342.83	0.035	0.046	1.087	1.001	874	1204	1071
342.77	0.048	0.059	1.019	1.002	874	1205	1072
342.48	0.081	0.101	1.043	1.002	876	1207	1074
342.28	0.101	0.129	1.075	0.999	877	1209	1075
342.00	0.128	0.151	1.002	1.014	879	1211	1078
340.51	0.303	0.343	1.007	1.033	888	1224	1089
340.44	0.322	0.391	1.083	0.987	889	1225	1089
340.16	0.351	0.397	1.017	1.030	891	1228	1091
340.05	0.374	0.419	1.011	1.033	891	1229	1092
339.98	0.418	0.467	1.011	1.022	892	1229	1093
339.60	0.460	0.505	1.005	1.036	894	1233	1096
339.31	0.497	0.564	1.049	0.990	896	1235	1098
338.54	0.608	0.649	1.011	1.050	901	1242	1104
338.47	0.617	0.662	1.018	1.038	902	1243	1105
338.00	0.738	0.771	1.006	1.045	905	1247	1108
337.34	0.864	0.887	1.010	1.016	910	1253	1113
336.80	0.959	0.966	1.008	1.033	913	1258	1118
336.83	1.000	1.000					

TABLE III Experimental vapor–liquid equilibrium data for oxolane (1) + ethyl 1,1-dimethylethyl ether (3) at 94.00 kPa

T/K	x_1	y_1	γ_1	γ_3	$-B_{11}/$ $cm^3\ mol^{-1}$	$-B_{33}/$ $cm^3\ mol^{-1}$	$-B_{13}/$ $cm^3\ mol^{-1}$
343.47	0.000	0.000					
343.08	0.063	0.089	1.166	0.984	872	1385	1063
342.43	0.118	0.162	1.155	0.981	876	1392	1069
342.30	0.124	0.165	1.124	0.988	877	1393	1070
342.27	0.132	0.176	1.128	0.985	877	1394	1070
341.57	0.153	0.199	1.124	1.003	882	1401	1075
340.87	0.202	0.252	1.101	1.016	886	1409	1081
340.04	0.370	0.439	1.074	0.991	891	1419	1088
339.68	0.410	0.476	1.062	0.999	894	1423	1091
339.00	0.481	0.536	1.041	1.028	898	1430	1096
339.15	0.499	0.549	1.023	1.030	897	1429	1095
338.80	0.534	0.581	1.023	1.041	900	1433	1098
338.38	0.640	0.682	1.015	1.037	903	1438	1102
338.40	0.663	0.705	1.012	1.027	902	1437	1101
337.90	0.729	0.763	1.012	1.043	906	1443	1106
337.82	0.806	0.826	0.993	1.073	906	1444	1106
337.76	0.809	0.829	0.995	1.073	907	1445	1107
337.75	0.841	0.857	0.990	1.078	907	1445	1107
337.40	0.889	0.899	0.993	1.103	909	1449	1110
337.48	0.902	0.910	0.988	1.111	909	1448	1109
337.38	0.916	0.921	0.988	1.141	909	1449	1110
337.28	0.928	0.933	0.991	1.133	910	1451	1111
337.27	0.943	0.946	0.989	1.154	910	1451	1111
336.83	1.000	1.000					

TABLE IV Experimental vapor–liquid equilibrium data for vinyl acetate (2) + ethyl 1,1-dimethylethyl ether (3) at 94.00 kPa

T/K	x_2	y_2	γ_2	γ_3	$-B_{22}/$ $cm^3\ mol^{-1}$	$-B_{33}/$ $cm^3\ mol^{-1}$	$-B_{23}/$ $cm^3\ mol^{-1}$
343.47	0.000	0.000					
343.65	0.016	0.024	1.496	0.986	1197	1378	1078
341.84	0.141	0.181	1.357	1.003	1213	1398	1092
340.65	0.280	0.322	1.263	1.029	1223	1412	1102
340.47	0.352	0.381	1.194	1.050	1225	1414	1103
340.27	0.445	0.456	1.137	1.085	1227	1416	1105
340.28	0.447	0.454	1.127	1.093	1227	1416	1105
340.32	0.467	0.472	1.120	1.095	1226	1415	1105
340.49	0.487	0.493	1.114	1.087	1225	1413	1103
340.41	0.501	0.503	1.108	1.098	1225	1414	1104
340.30	0.572	0.550	1.065	1.164	1226	1416	1105
340.35	0.638	0.623	1.078	1.153	1226	1415	1104
340.53	0.639	0.608	1.044	1.195	1224	1413	1103
340.78	0.721	0.676	1.020	1.270	1222	1410	1101
341.00	0.755	0.710	1.015	1.286	1220	1408	1099
341.16	0.771	0.724	1.007	1.303	1219	1406	1098
341.10	0.802	0.757	1.014	1.331	1219	1407	1098

TABLE IV (Continued)

T/K	x_2	y_2	γ_2	γ_3	$-B_{22}/$ $cm^3\ mol^{-1}$	$-B_{33}/$ $cm^3\ mol^{-1}$	$-B_{23}/$ $cm^3 mol^{-1}$
342.54	0.919	0.887	0.987	1.451	1207	1391	1087
342.73	0.934	0.905	0.984	1.489	1205	1389	1085
342.86	0.948	0.923	0.984	1.526	1204	1387	1084
342.93	0.948	0.924	0.983	1.503	1203	1386	1083
343.45	0.976	0.964	0.979	1.520	1199	1381	1079
343.18	1.000	1.000					

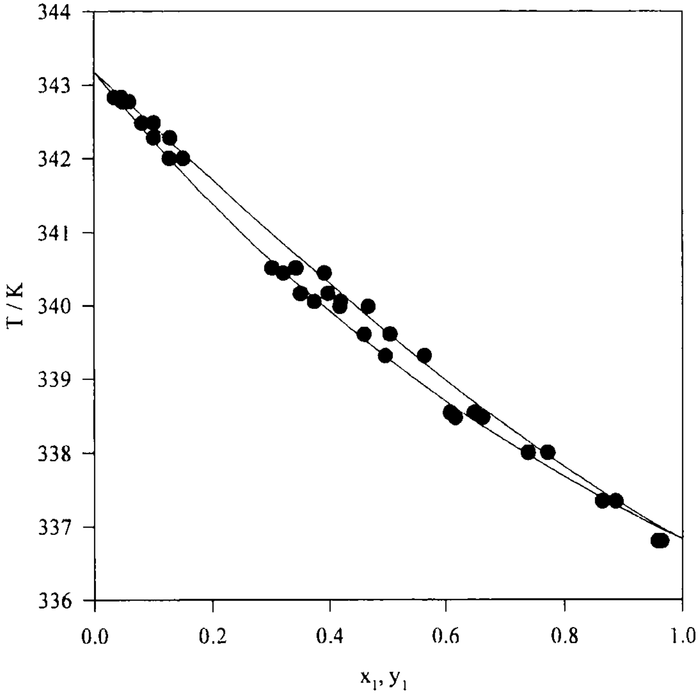

FIGURE 1 Experimental data for the system oxolane (1) + vinyl acetate (2) at 94.00 kPa. Experimental data (•). Smoothed data using the regular model, Eq. (4), with the A parameter given in Table VI (—).

and Figures 1–6, together with the activity coefficients γ_i that were calculated from the following equation [2]

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

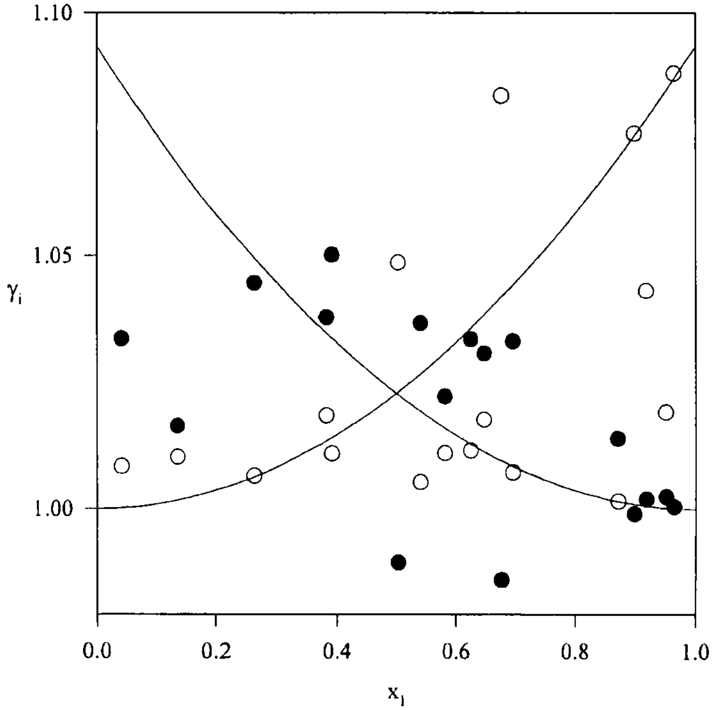

FIGURE 2 Activity coefficient plot of the system oxolane (1) + vinyl acetate (2) at 94.00 kPa. Experimental data (•, o). Smoothed data using the regular model, Eq. (4), with the A parameter given in Table VI (—).

where T and P are the boiling point and the total pressure, V_i^L is the molar liquid volume of component i, P_i^0 is the pure component vapor pressure, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} 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. Equation (1) is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure

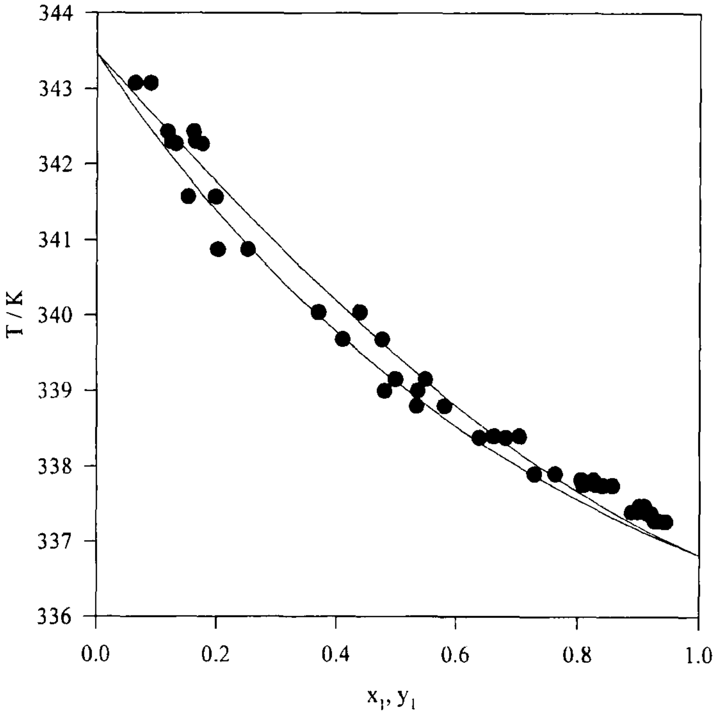

FIGURE 3 Experimental data for the system oxolane (1) + ETBE (3) at 94.00 kPa. Experimental data (●). Smoothed data using the regular model, Eq. (4), with the *A* parameter given in Table VI (—).

range under consideration. The pure component vapor pressures P_i^0 were calculated according to the Antoine equation:

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

where the Antoine constants A_i, B_i and C_i are reported in Table V. The pure component vapor pressure P_i^0 for vinyl acetate was taken from Swamy and Van Winkle [3] and for ETBE from Reich *et al.* [4]. The molar virial coefficients B_{ii} and B_{jj} were estimated by the method of Hayden and O'Connell [5] using the molecular parameters suggested by the authors and assuming the association parameter η to be zero for

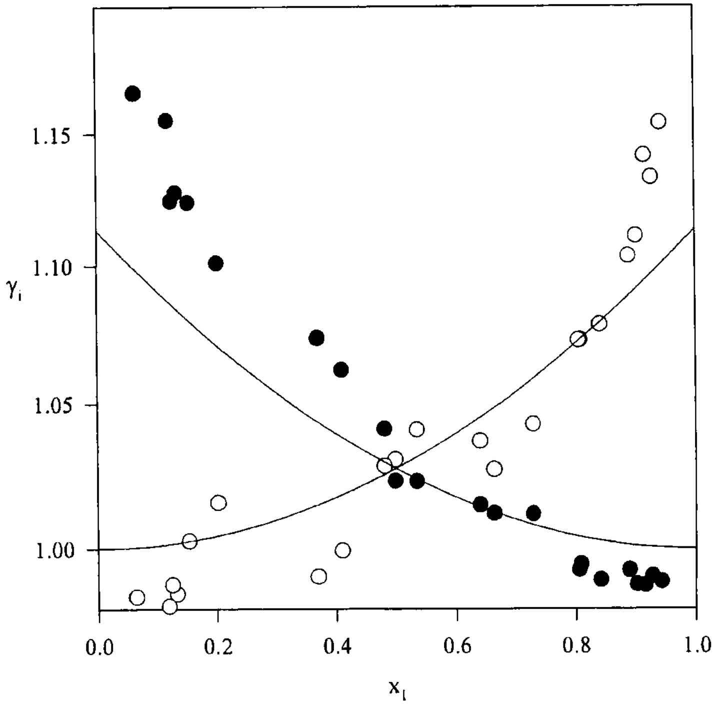

FIGURE 4 Activity coefficient plot of the system oxolane (1) + ETBE (3) at 94.00 kPa. Experimental data (•, o). Smoothed data using the regular model, Eq. (4), with the *A* parameter given in Table VI (—).

mixtures of ETBE. Physical properties for pure components were taken from DIPPR [6] and liquid volumes were approximated using the Rackett equation [7]. The last two terms in Eq. (1), particularly the second one that expresses the correction due to the non-ideal behavior of the vapor phase, contributed between 1 to 3% to the activity coefficients of the three binary systems; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables II–IV and are estimated accurate to within ± 3%. The results reported in these tables indicate that the binary systems containing oxolane show small deviations from ideal behavior, while the system vinyl acetate(2) + ETBE(3) deviates moderately from ideality and presents an azeotrope that boils at 340.40 K and contains 49.8 % mole vinyl acetate. The vapor–liquid equilibria data

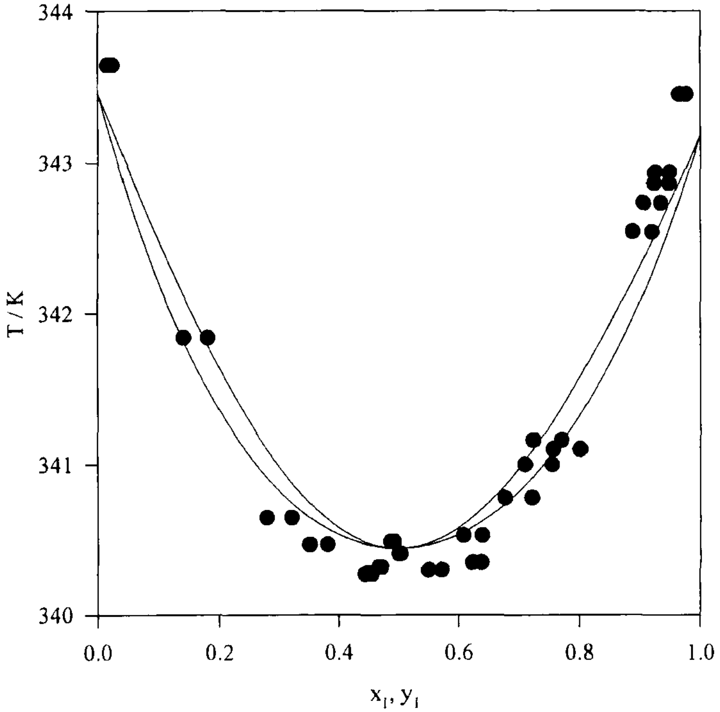

FIGURE 5 Experimental data for the system vinyl acetate (2) + ETBE (3) at 94.00 kPa. Experimental data (●). Smoothed data using the regular model, Eq. (4), with the *A* parameter given in Table VI (—).

reported in Tables II–IV were found to be thermodynamically consistent by the L-W point-to-point and area method of Wisniak [8], except at the very dilute ends and the point-to-point method of Van Ness *et al.* [9] as modified by Fredenslund *et al.* [10]. For the three sets of data, Fredenslund's test consistency criteria was met using a one parameter Legendre polynomial, or symmetric model, which reduces the functionality of the excess Gibbs energy G^E to the following relation

$$G^E = Ax_1x_2 \qquad (4)$$

Pertinent statistics, including the value of parameter *A* in Eq. (4) for each binary system, are presented in Table VI. In addition, it was found that the residuals of the Fredenslund test were randomly distributed, as measured by the Durbin-Watson statistic.

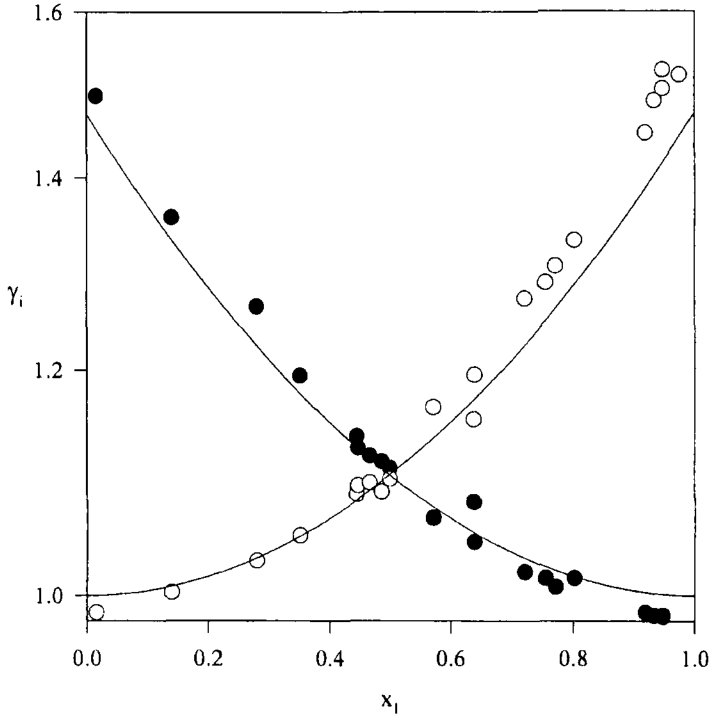

FIGURE 6 Activity coefficient plot of the system vinyl acetate (2) + ETBE (3) at 94.00 kPa. Experimental data (•, ○). Smoothed data using the regular model, Eq. (4), with the *A* parameter given in Table VI (—).

TABLE V Antoine coefficients, Eq. (3)

Compound	A_i	B_i	C_i
oxolane[a]	6.12142	1203.110	46.80
Vinyl acetate[b]	6.52501	1349.872	46.63
ethyl 1,1-dimethylethyl ether[c]	5.96651	1151.730	55.06

[a] TRC k-6170 [13]; [b] Fitted from the data of Swamy and Van Winkle [3]; [c] Reich *et al.* [4].

TABLE VI Consistency test statistics for the binary systems oxolane (1) + vinyl acetate (2), oxolane (1) + ETBE (3) and vinyl acetate (2) + ETBE (3)

System	A^a	$100 \times \Delta y^b$	$\Delta P^c/KPA$
1 + 2	0.092	0.65	0.23
1 + 3	0.107	0.45	0.65
2 + 3	0.388	0.53	0.67

[a] Zero th order Legendre polynomial (or Porter model) parameter in Eq. (4); [b] Average absolute deviation in vapor phase mole fractions $\Delta y = 1/N\sum_{i=1}^{N} |y_1^{exptl} - y_1^{calc}|$ (N : number of data points); [c] Average absolute deviation in pressure $\Delta P = 1/N\sum_{i=1}^{N} |P^{exptl} - P^{calc}|$.

TABLE VII Parameters and prediction statistics for different G^E models

					Bubble-point pressures			Dew-point pressures		
Model	*ij*	A_{ij} /	A_{ji} /	αij	ΔP (%)[f]	$100\times\Delta Y_1$	$100\times\Delta Y_2$	ΔP(%)	$100\times\Delta X_1$	$100\times\Delta X_2$
Wohl	1–2	0.08	0.11	0.75[e]	0.23	0.7	0.7	0.31	0.7	0.7
	1–3	0.10	−0.15	0.27	0.42	0.6	–	0.49	0.6	–
	2–3	0.35	0.01	0.30	0.38	–	0.6	0.40	–	0.6
NRTL[a]	1–2	1135.68	−764.89	0.30	0.23	0.7	0.7	0.30	0.7	0.7
	1–3	−1481.84	2115.82	0.30	0.64	0.5	–	0.64	0.5	–
	2–3	−196.47	1454.07	0.30	0.59	–	0.5	0.62	–	0.6
Wilson[a,b]	1–2	54.25	288.75		0.23	0.7	0.7	0.30	0.7	0.7
	1–3	3042.88	−2535.81		0.64	0.5	–	0.65	0.5	–
	2–3	2325.99	−1068.32		0.60	–	0.5	0.62	–	0.6
UNIQUAC[a,c]	1–2	−139.10	292.03		0.23	0.7	0.7	0.30	0.7	0.7
	1–3	−1115.63	1697.57		0.59	0.6	–	0.60	0.6	–
	2–3	−783.09	1366.60		0.59	–	0.5	0.62	–	0.6
UNIFAC[d]	1–2				0.67	0.8	0.8	0.76	0.8	0.8
	1–3				0.80	0.5	–	0.81	0.5	–
	2–3				6.13	–	1.7	5.54	–	1.8

[a] Parameters in J mol^{-1}; [b] Liquid volumes have been estimated from the Rackett equation (7); [c] Molecular parameters are those calculated from UNIFAC; [d] Calculations based on original UNIFAC [10, 12]; [e] "q" parameter for the Wohl's model. [f] $\Delta P = 100/N\sum_i^N |P_i^{\text{exptl}} - P_i^{\text{calc}}|/P_i^{\text{exptl}}$.

Table VI shows that the model of Eq. (4) gives a good representation of the data of the system and, that according to it, the three binaries may be assumed, to a first approximation, to behave like regular solutions.

The activity coefficients of the vinyl acetate + ETBE system were correlated well with the Wohl, NRTL, Wilson and UNIQUAC equations [11]. Pertinent parameters were obtained by minimizing the following objective function (*OF*)

$$OF = 100 \times \sum_{i=1}^{N} \left| y_{1,i}^{\text{exptl}} - y_{1,i}^{\text{calc}} \right| + \left| \frac{P_i^{\text{exptl}} - P_i^{\text{calc}}}{P_i^{\text{exptl}}} \right| \tag{5}$$

and are reported in Table VII, together with the relative deviation of equilibrium pressures and mole fractions. Inspection of the results given in Table VII shows that the four models fitted the binaries reasonable well. Table VII also includes the prediction based on the UNIFAC group contribution method [10, 12], which results less accurate than previous models, particularly for the system vinyl acetate (2) + ETBE (3).

It should be noted that the closeness of the boiling points of the pure components, compounded with the experimental error and the fact that the solutions are near ideal, is reflected in the dispersion between predicted and experimental values, as seen in the figures.

Acknowledgments

Yehudit Reizner helped in the experimental part. This work was partially financed by FONDECYT, Chile, project No. 1990402.

References

[1] Wisniak, J., Embon, G., Shafir, R., Segura, H. and Reich, R. (1997). *J. Chem. Eng. Data*, **42**, 1191.

[2] Van Ness, H. C. and Abbott, M. M. (1982). "*Classical Thermodynamics of Nonelectrolyte Solutions*", McGraw-Hill Book Co.

[3] Swamy, P. A. and Van Winkle, M. (1965). *J. Chem. Eng. Data*, **10**, 214.

[4] Reich, R., Cartes, M., Segura, H. and Wisniak, J. (1998). *Fluid Phase Equilibria*, **154**, 99.

[5] Hayden, J. and O'Connell, J. (1975). *Ind. Eng. Chem. Process Des. Dev.*, **14**, 209.

[6] Daubert, T. E. and Danner, R. P. (1989). *Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation.* Taylor & Francis: Bristol, PA.

[7] Rackett, H. G. (1970). *J. Chem. Eng. Data*, **15**, 514.

[8] Wisniak, J. (1993). *Ind. Eng. Chem. Res.*, **32**, 1531.

[9] Van Ness, H. C., Byer, S. M. and Gibbs, R. E. (1973). *AIChE J.*, **19**, 238.

[10] Fredenslund, Aa., Gmehling, J. and Rasmussen, P. (1977). "*Vapor-Liquid Equilibria Using UNIFAC. A Group Contribution Method*", Elsevier, Amsterdam.

[11] Walas, S. M. (1985). "*Phase Equilibria in Chemical Engineering*", Butterworth Publishers: Boston.

[12] Hansen, H. K., Rasmussen, P. and Fredenslund, Aa. (1991). *Ind. Eng. Chem. Res.*, **30**, 2355.

[13] *TRC-Thermodynamic Tables-Non-Hydrocarbons*; Thermodynamics Research Center: Texas A & M University System, College Station, TX, extant 1996.

[14] Krähenbühl, M. A. and Gmehling, J. (1994). *J. Chem. Eng. Data*, **39** 759.