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Phase Equilibria in the Systems Ethyl Methanoate + 1-Bromopropane, Ethyl Methanoate + Cyclohexane, and Ethyl Methanoate + 1-Bromopropane + Cyclohexane

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Vapor−liquid equilibrium at 101.3 kPa has been determined for the binary systems ethyl methanoate + 1-bromopropane and ethyl methanoate + cyclohexane and the ternary system ethyl methanoate + 1-bromopropane + cyclohexane. The two binary systems exhibit positive deviations from ideality and the binary ethyl methanoate + cyclohexane has an azeotrope that boils at 325.9 K and contains 82.2 mol % ethyl methanoate. The data were correlated by the Redlich−Kister, Wilson, NRTL, UNIQUAC, and Wisniak−Tamir equations, and the appropriate parameters are reported. The activity coefficients of the ternary system can be predicted from those of the pertinent binary systems. No ternary azeotrope is present.

The present work was undertaken to measure vapor−liquid equilibria (VLE) data for the title systems for which no isobaric data are available. Isobaric data for the binary system 1-bromopropane + cyclohexane have been published by Wisniak et al. (1995a); the system presents positive deviations from ideality, and the data are well represented by the Redlich−Kister expansion. Data for the system ethyl methanoate + cyclohexane have been reported by Ohta and Nagata (1980) at 323.15 K and at 66.66 kPa; the system exhibits moderate positive deviations from ideal behavior and presents an azeotropic point, and the equilibrium data are well represented by the Wilson and UNIQUAC models.

Experimental Section

Purity of Materials. Ethyl methanoate (99.3 mass %+) was purchased from Merck, 1-bromopropane (99.85 mass %+) from Aldrich, and cyclohexane (99.9 mass %+) from Phillips. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties and purity (as determined by glc) of the pure components appear in Table 1.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (Boublikova and Lu, 1969) was used in the VLE measurements. The experimental features have been described in a previous publication (Wisniak and Tamir, 1975). Temperature was measured with a Lauda Model R42/2 digital thermometer provided with a PT-10 probe (calibrated by the National Standards Laboratories of Israel), 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 3 m long and 0.2 cm in diameter, packed with SE-30 and operated at 323.15 K for the binary system with 1-bromopropane and 353.15 K for the binary system with cyclohexane; injector and detector temperatures were 493.15 and 543.15 K, respectively. Very good separation for the binary and ternary systems was achieved under these conditions, and repetitive calibration analyses were carried out 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 fits had correlation coefficients $R^2 > 0.99$. The accuracies in the determination of pressure P and temperature T were at least ±0.1 kPa and ±0.02 K, respectively.

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
ethyl methanoate (99.3)	1.3579[a]	327.40[a]
	1.3575[b]	327.46[b]
1-bromopropane (99.85)	1.4319[a]	343.90[a]
	1.4317[b]	344.15[b]
cyclohexane (99.9)	1.4233[a]	353.84[a]
	1.42354[b]	353.888[b]

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

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 2−4 and Figures 1−4, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln(Py_i/P_i^\circ x_i) + (B_{ii} - V_i^{\mathrm{L}})(P - P_i^\circ)/RT + (P/2RT)\sum\sum y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where T and P 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

$$\delta_{ij} = 2\mathrm{B}_{ij} - \mathrm{B}_{jj} - \mathrm{B}_{ii} \quad (2)$$

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° were calculated according to the Antoine equation:

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

where the Antoine constants A_i, B_i, and C_i are reported in

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Table 2. Experimental Vapor−Liquid Equilibrium Data for Ethyl Methanoate (1) + 1-Bromopropane (2) at 101.3 kPa

					$\mathrm{cm^{-3}{\cdot}mol^{-1}}$			
T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$	$-B_{22}$	$-B_{12}$	G^E/RT
343.90	0	0						0
340.87	0.070	0.154	1.4275	1.0072	592	645	610	0.032
338.41	0.145	0.279	1.3522	1.0084	604	659	623	0.051
337.45	0.179	0.328	1.3235	1.0097	608	664	628	0.058
335.43	0.258	0.424	1.2678	1.0209	618	676	639	0.077
335.11	0.274	0.441	1.2511	1.0245	620	677	641	0.079
333.67	0.343	0.507	1.2057	1.0454	627	686	649	0.093
333.47	0.363	0.528	1.1935	1.0391	628	687	650	0.089
332.44	0.420	0.575	1.1606	1.0645	634	693	656	0.099
331.40	0.499	0.638	1.1204	1.0879	639	700	662	0.099
330.78	0.544	0.669	1.1004	1.1156	643	704	665	0.102
329.93	0.618	0.719	1.0711	1.1623	647	709	670	0.100
329.41	0.665	0.749	1.0552	1.2050	650	712	673	0.098
328.91	0.731	0.795	1.0362	1.2456	653	715	676	0.085
328.55	0.766	0.817	1.0275	1.2990	655	718	678	0.082
328.29	0.814	0.852	1.0178	1.3313	657	719	680	0.068
328.19	0.829	0.862	1.0151	1.3502	657	720	680	0.064
327.97	0.852	0.876	1.0114	1.4102	658	721	682	0.061
327.81	0.873	0.891	1.0084	1.4628	659	722	683	0.055
327.82	0.892	0.908	1.0062	1.4417	659	722	683	0.045
327.65	0.919	0.928	1.0034	1.5201	660	723	684	0.037
327.51	0.936	0.939	1.0021	1.6272	661	724	685	0.033
327.44	0.948	0.948	1.0014	1.7059	661	725	685	0.029
327.40	1	1						0
	$\gamma^{\infty\ a}$		1.72	1.68				

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

Table 3. Experimental Vapor−Liquid Equilibrium Data for Ethyl Methanoate (1) + Cyclohexane (3) at 101.3 kPa

					$\mathrm{cm^{-3}{\cdot}mol^{-1}}$			
T/ K	x_1	y_1	γ_1	γ_3	$-B_{11}$	$-B_{33}$	$-B_{13}$	G^E/RT
353.84	0	0					0	
350.36	0.013	0.090	3.4251	1.0221	781	1138	948	0.038
348.86	0.023	0.148	3.3020	1.0108	790	1150	958	0.038
345.98	0.043	0.250	3.2480	0.9902	806	1173	978	0.042
343.55	0.062	0.305	2.9591	1.0091	820	1194	995	0.076
341.30	0.081	0.361	2.8638	1.0164	834	1214	1011	0.101
336.01	0.146	0.490	2.5492	1.0338	867	1262	1052	0.165
334.52	0.188	0.529	2.2459	1.0538	877	1276	1064	0.194
332.15	0.233	0.559	2.0608	1.1320	893	1300	1083	0.263
331.18	0.282	0.591	1.8530	1.1595	899	1309	1091	0.280
330.11	0.335	0.631	1.7232	1.1734	907	1320	1100	0.289
329.00	0.414	0.659	1.5151	1.2748	915	1332	1110	0.314
328.07	0.472	0.687	1.4271	1.3418	921	1342	1118	0.323
327.31	0.570	0.718	1.2667	1.5253	927	1350	1125	0.316
326.55	0.675	0.757	1.1567	1.7854	932	1358	1131	0.287
326.58	0.693	0.762	1.1329	1.8506	932	1358	1131	0.276
325.99	0.764	0.796	1.0956	2.1029	937	1364	1136	0.245
326.25	0.780	0.801	1.0706	2.1778	935	1361	1134	0.225
325.90	0.803	0.814	1.0681	2.3130	937	1365	1137	0.218
326.07	0.845	0.840	1.0415	2.5132	936	1363	1136	0.177
326.05	0.855	0.850	1.0423	2.5210	936	1363	1136	0.169
326.04	0.871	0.858	1.0334	2.6799	936	1363	1136	0.156
326.39	0.915	0.897	1.0164	2.9121	934	1360	1133	0.106
327.40	1	1						0
	$\gamma^{\infty\ a}$		4.30	3.90				

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

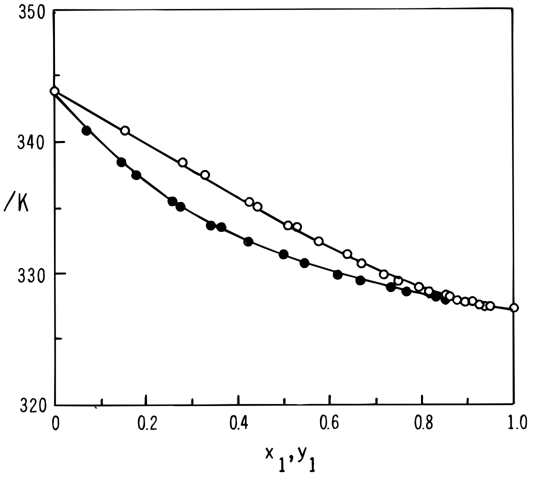

Figure 1. Boiling point diagram at 101.3 kPa for the system ethyl methanoate (1) + 1-bromopropane (2).

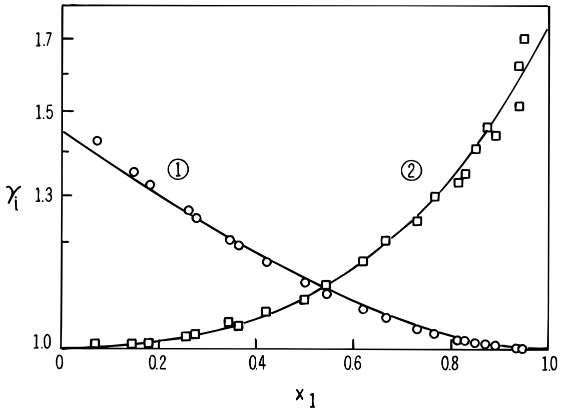

Figure 2. Activity coefficients for the system ethyl methanoate (1) + 1-bromopropane (2): experimental (○, □), predicted by the Wilson model (—).

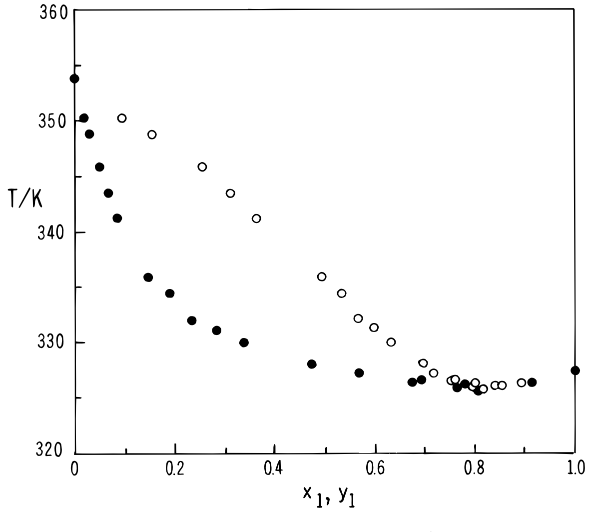

Figure 3. Boiling point diagram at 101.3 kPa for the system ethyl methanoate (1) + cyclohexane (3).

Table 5. The molar virial coefficients B_{ii} and B_{ij} were estimated by 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 3.0% to the activity coefficients, and their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Table 2−4 and are estimated accurately to within ±3%. Tables 2 and 3 contain also the activity coefficients at infinite dilution calculated by the method suggested by Wisniak et al. (1995b). As seen in Figures 1−4 the binary systems ethyl methanoate + 1-bromopropane and ethyl methanoate + cyclohexane exhibit positive deviations from ideality. Inspection of Figure 3 and Table 3 points to an azeotrope in the system

Table 4. Experimental Vapor−Liquid Equilibria Data for Ethyl Methanoate (1) + 1-Bromopropane (2) + Cyclohexane (3) at 94.4 kPa

					activity coefficients			virial coefficients ($cm^3 \cdot mol^{-1}$)					
T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$-B_{12}$	$-B_{13}$	$-B_{23}$	$-B_{11}$	$-B_{22}$	$-B_{33}$
327.25	0.593	0.042	0.712	0.028	1.2114	1.1273	1.6610	927	801	1350	838	1125	1018
327.45	0.637	0.142	0.717	0.097	1.1265	1.1777	1.9498	926	800	1348	837	1124	1016
327.55	0.592	0.118	0.692	0.084	1.1649	1.2215	1.7887	925	799	1347	836	1123	1015
327.85	0.510	0.050	0.678	0.034	1.3137	1.1389	1.4952	923	797	1344	834	1120	1013
327.95	0.688	0.209	0.748	0.149	1.0690	1.2040	2.2766	922	796	1343	833	1119	1012
328.35	0.480	0.099	0.655	0.069	1.3244	1.1560	1.4705	919	794	1338	831	1115	1008
328.65	0.495	0.142	0.651	0.095	1.2640	1.1064	1.5548	917	792	1336	829	1113	1006
329.35	0.438	0.156	0.622	0.108	1.3369	1.1095	1.4485	913	788	1329	825	1107	1001
329.85	0.359	0.063	0.608	0.047	1.5656	1.1772	1.2699	909	784	1323	821	1102	996
330.25	0.509	0.371	0.627	0.265	1.1244	1.1166	1.8905	906	782	1319	819	1099	994
330.45	0.417	0.268	0.583	0.188	1.2653	1.0861	1.5246	905	781	1317	817	1097	992
330.45	0.327	0.081	0.590	0.060	1.6335	1.1512	1.2302	904	780	1316	817	1097	991
330.75	0.432	0.495	0.595	0.340	1.2345	1.0514	1.8541	902	778	1313	815	1095	989
330.95	0.456	0.472	0.581	0.353	1.1373	1.1422	1.8961	901	778	1312	814	1094	988
330.95	0.342	0.181	0.564	0.131	1.4735	1.1092	1.3107	901	778	1312	814	1094	988
331.05	0.298	0.031	0.589	0.024	1.7563	1.1759	1.1789	900	777	1311	813	1092	987
331.65	0.394	0.370	0.548	0.266	1.2136	1.0707	1.5834	896	773	1305	810	1087	983
331.75	0.382	0.383	0.549	0.271	1.2479	1.0530	1.5347	896	773	1304	809	1087	982
332.05	0.407	0.494	0.553	0.358	1.1698	1.0667	1.7717	894	771	1301	807	1084	980
332.15	0.373	0.525	0.521	0.389	1.2008	1.0856	1.7314	893	770	1300	806	1083	979
332.75	0.357	0.586	0.497	0.451	1.1714	1.1054	1.7717	889	767	1294	803	1078	974
332.85	0.296	0.373	0.482	0.280	1.3649	1.0738	1.3894	888	766	1293	802	1077	973
332.95	0.357	0.551	0.511	0.407	1.1979	1.0564	1.7005	888	765	1292	802	1077	973
333.15	0.268	0.335	0.465	0.256	1.4406	1.0820	1.3344	886	764	1289	800	1074	971
333.25	0.211	0.159	0.493	0.127	1.9332	1.1310	1.1428	885	763	1288	799	1074	970
333.55	0.306	0.608	0.460	0.464	1.2302	1.0669	1.6694	883	761	1286	798	1071	968
333.85	0.218	0.155	0.472	0.129	1.7582	1.1544	1.1849	881	760	1283	796	1069	966
333.85	0.287	0.473	0.454	0.358	1.2843	1.0477	1.4562	881	760	1282	796	1069	966
334.35	0.285	0.669	0.441	0.513	1.2369	1.0445	1.8243	878	757	1278	793	1065	962
334.75	0.179	0.035	0.496	0.033	2.1913	1.2593	1.0828	875	755	1274	790	1062	959
334.95	0.230	0.569	0.394	0.444	1.3433	1.0406	1.4504	874	753	1272	789	1060	957
335.15	0.207	0.414	0.395	0.331	1.4908	1.0632	1.2854	873	752	1270	788	1059	956
335.65	0.196	0.509	0.370	0.405	1.4488	1.0398	1.3322	869	749	1265	785	1054	952
336.05	0.177	0.373	0.374	0.310	1.6018	1.0729	1.2155	867	747	1262	783	1052	950
336.45	0.151	0.118	0.426	0.112	2.1092	1.2096	1.0768	864	744	1258	780	1048	946
336.75	0.188	0.774	0.335	0.628	1.3234	1.0228	1.6411	862	743	1255	778	1046	945
336.95	0.140	0.123	0.400	0.117	2.1085	1.2001	1.0989	861	742	1253	777	1044	943
337.25	0.161	0.743	0.302	0.612	1.3684	1.0218	1.4871	859	740	1250	775	1042	941
337.25	0.144	0.338	0.343	0.296	1.7394	1.0872	1.1596	859	740	1250	775	1042	941
337.45	0.151	0.611	0.306	0.506	1.4713	1.0199	1.3008	857	739	1248	774	1040	939
338.05	0.138	0.764	0.268	0.644	1.3883	1.0177	1.4523	854	735	1243	771	1036	935
338.45	0.116	0.371	0.293	0.338	1.7705	1.0868	1.1515	851	733	1239	768	1033	932
338.95	0.109	0.105	0.367	0.109	2.3413	1.2221	1.0494	848	730	1235	766	1029	929
339.75	0.093	0.364	0.254	0.349	1.8413	1.0986	1.1224	843	726	1227	761	1023	923
340.15	0.094	0.187	0.300	0.194	2.1285	1.1763	1.0678	841	724	1224	759	1020	921
340.75	0.078	0.097	0.318	0.113	2.6610	1.2864	1.0259	837	720	1218	755	1015	916
341.25	0.074	0.165	0.273	0.184	2.3685	1.2197	1.0459	834	718	1214	753	1012	913
341.45	0.073	0.325	0.222	0.332	1.9587	1.1110	1.0795	833	717	1213	752	1011	912
342.15	0.041	0.903	0.094	0.849	1.4500	1.0004	1.4427	829	713	1206	748	1005	907
343.15	0.020	0.706	0.061	0.697	1.9181	1.0173	1.2184	823	708	1197	742	998	900
345.55	0.049	0.143	0.207	0.178	2.3826	1.1954	0.9743	808	695	1177	729	981	885
346.25	0.036	0.040	0.193	0.057	2.9865	1.3492	1.0170	804	692	1171	726	946	880

Table 5. Antoine Coefficients, Eq 3 (TRC, 1974)

compound	A_i	B_i	C_i
ethyl methanoate	6.078 99	1101.00	57.17
1-bromopropane	6.035 55	1194.889	47.64
cyclohexane	5.964 07	1200.31	50.65

ethyl methanoate + cyclohexane which contains 82.2% mol hexane and boils at 325.9 K.

The excess Gibbs functions of the two binary systems are presented in Tables 2 and 3 and Figure 5 as the variation of the dimensionless number $\Delta G^E/RT$ (Gibbs number) with composition. The values of the parameter are positive over the entire composition range, the value at $x = 0.5$ for the binary ethyl methanoate−cyclohexane system is substantially larger than that for the binary ethyl methanoate−1-bromopropane system probably due to a larger steric influence of the cyclohexane molecule.

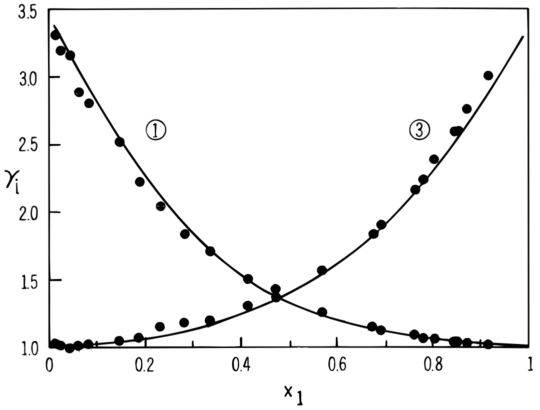

Figure 4. Activity coefficients for the system ethyl methanoate (1) + cyclohexane (3): experimental (●), predicted by the NRTL model (−).

The binary data reported in Tables 2 and 3 were found to be thermodynamically consistent by the area test (Van Ness and Abbott, 1982), the point-to-point test of Fredenslund (1977), and the L-W method of Wisniak (1993). For both binaries, the residuals of the Fredenslund test were

Table 6. Constants for the Redlich–Kister Model

A. Binaries (Eq 7)

System	b_{ij}	c_{ij}	d_{ij}	rmsd	% dev[a]	max % dev[b]
ethyl methanoate (1) + bromopropane (2)	0.1951	0.0306	0.0275	0.003	1.4	4.7
ethyl methanoate (1) + cyclohexane (3)	0.5388	−0.0002	0.0122	0.012	2.5	6.5
1-bromopropane (2) + cyclohexane (3)[c]	0.1568	−0.0071	0	0.004	1.5	4.6

B. Ternary (Eq 10)

											γ_1/γ_2			γ_1/γ_3		
	b_{12}	c_{12}	d_{12}	b_{13}	c_{13}	d_{13}	b_{23}	c_{23}	d_{23}	C_1	rmsd	max % dev	% dev	rmsd	max % dev	% dev
ethyl methanoate (1) + 1-bromopropane (2) + cyclohexane (3)	0.1951	0.0306	0.0275	0.5388	−0.0002	0.0122	0.1568	−0.0071	0	0	0.014	10.4	6.3	0.014	14.5	7.0
										0.00731	0.014	10.4	6.3	0.014	10.5	7.0

[a] Percent average deviation. [b] Maximum percent deviation. [c] Wisniak, 1995b.

randomly distributed, as measured by the Durbin–Watson statistic. The ternary activity coefficients reported in Table 4 were found to be thermodynamically consistent, as tested by the L-W method of Wisniak (1993) and the McDermot–Ellis method (1965) modified by Wisniak and Tamir (1977). According to these references two experimental points *a* and *b* are considered thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \tag{4}$$

The local deviation D is given by

$$D = \sum_{i=1}^{N} (x_{ia} + x_{ib})(\ln \gamma_{ia} - \ln \gamma_{ib}) \tag{5}$$

where N is the number of components and the maximum deviation $D_{\max}$ is

$$\begin{aligned} D_{\max} = \sum_{i=1}^{N} (x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x + \\ 2\sum_{i=1}^{N} |\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{N} (x_{ia} + x_{ib})\frac{\Delta P}{P} + \sum_{i=1}^{N} (x_{ia} + \\ x_{ib}) B_i\{(T_a + C_i)^{-2} + (T_b + C_i)^{-2}\}\Delta T \end{aligned} \tag{6}$$

The errors in the measurements, Δx, ΔP, and ΔT, were as previously indicated. The first term in eq 6 was the dominant one. For the experimental points reported here D never exceeded 0.116 while the smallest value of $D_{\max}$ was 0.232.

The activity coefficients of the two binary systems were correlated by the Redlich–Kister equation (Walas, 1985)

$$\begin{aligned} \log \frac{\gamma_i}{\gamma_j} = b_{ij}(x_j - x_i) + c_{ij}(6x_i x_j - 1) + \\ d_{ij}(x_j - x_i)(1 - 8x_i x_j) \end{aligned} \tag{7}$$

where b_{ij}, c_{ij}, and d_{ij} are the constants for the pertinent binary system, by the Wilson model (Walas, 1985)

$$\ln \gamma_i = -\ln\left(\sum_{j=1}^{n} x_j A_{ij}\right) + 1 - \sum_{k=1}^{n} \frac{x_k A_{ki}}{\sum_{j=1}^{n} x_j A_{kj}} \tag{8}$$

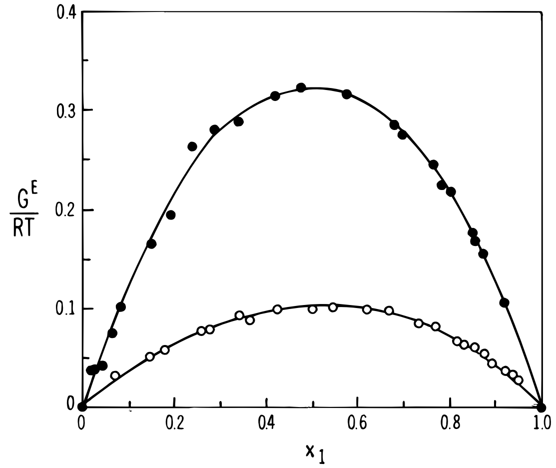

Figure 5. Variation of G^E/RT with concentration for the systems ethyl methanoate + 1-bromopropane (●) and ethyl methanoate + cyclohexane (○) at 101.325 kPa.

Table 7. Parameters and Deviations between Calculated and Experimental Vapor-Phase Mole Fractions and Temperatures

1. Binary Systems

	J·mol⁻¹				
model	A_{ij}	A_{ji}	α_{ij}	$\delta(y)$[a]	$\delta(T/K)$[b]
Ethyl Methanoate (1) + 1-Bromopropane (2)					
Wilson	−35.5314	1597.56		0.0051	0.219
NRTL	325.198	1066.29	0.493	0.0067	0.213
UNIQUAC	1409.62	−799.647		0.0043	0.173
Ethyl Methanoate (1) + Cyclohexane (3)					
Wilson	3024.72	1311.84		0.0075	0.280
NRTL	1836.18	1937.66	0.179	0.0081	0.296
UNIQUAC	−12.6038	1330.46		0.0081	0.303

2. Ternary System

	% dev[c]			max % dev[d]		
	γ_1	γ_2	γ_3	γ_1	γ_2	γ_3
ethyl methanoate (1) + 1-bromopropane (2) + cyclohexane (3)	4.6	4.2	2.5	13.9	13.6	10.9

[a] $\delta(y) = \sum|y_{\text{exptl}} - y_{\text{calc}}|/N$. [b] $\delta(T/K) = \sum|T_{\text{exptl}} - T_{\text{calc}}|/N$ (N = number of experimental points). [c] Average % deviation. [d] Maximum % deviation.

where A_{ij}, A_{ki}, and A_{kj} are the Wilson binary parameters, by the NRTL model (Walas, 1985)

$$\ln \gamma_i = x_j^2\left[\tau_{ji}\left(\frac{G_{ji}}{x_i + x_j G_{ji}}\right)^2 + \left(\frac{\tau_{ij} G_{ji}}{(x_j + x_i G_{ij})^2}\right)\right] \tag{9}$$

where τ_{ij} and G_{ij} are the NRTL parameters, and also by

Table 8. Coefficients in Correlation of Boiling Points, Eqs 10 and 11, Root Mean Square Deviations in Temperature, rmsd (*T*/K), and Percent Deviation

A. Equation 10

system	C_0	C_1	C_2	C_3	rmsd(*T*/K)	% dev[b]	max % dev[c]
ethyl methanoate (1) + 1-bromopropane (2)	−17.3828	8.74725	−7.64619		0.02	0.1	0.31
ethyl methanoate (1) + cyclohexane (3)[d]	−46.4787	8.41682	−66.3331	89.8022	0.20	1.3	3.1
1-bromopropane (2) + cyclohexane (3)	−13.6198	4.52251	-0.93737		0.01	0.09	0.21

	A	*B*	*C*	rmsd(*T*/K)[a]	% dev[b]	max % dev[c]
ethyl methanoate (1) + 1-bromopropane (2) + cyclohexane (3)	−181.9704	−32.6047		0.4	3.7	9.7

B. Equation 11

$A_{12} = -18.840$ $B_{12} = -52.025$ $C_{12} = -15.679$ rmsd(*T*/K) = 0.05
$A_{13} = 14.349$ $B_{13} = 35.473$ $C_{13} = 4.581$ % dev[b] = 0.4
$A_{23} = 1.161$ $B_{23} = -61.652$ $C_{23} = -2.370$ max % dev[c] = 2.0

[a] rmsd(*T*/K): root mean square deviation, $\{\sum(T_{\text{exptl}} - T_{\text{calc}})^2\}^{0.5}/N$. [b] Average % deviation. [c] Maximum % deviation. [d] Wisniak et al. (1995).

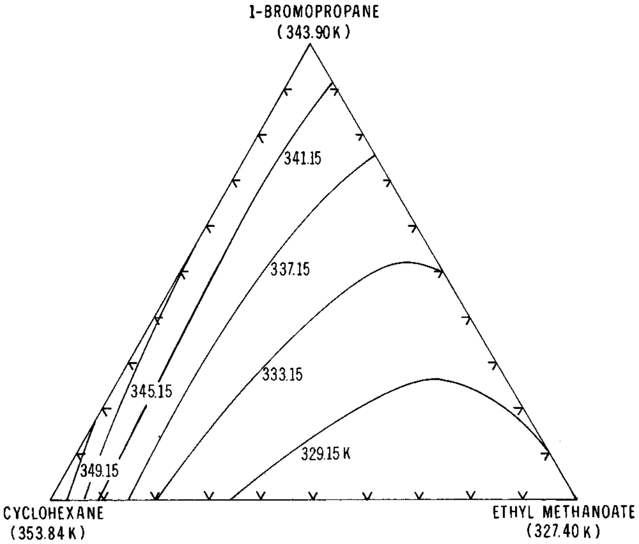

Figure 6. Isothermals for the ternary system ethyl methanoate (1) + 1-bromopropane (2) + cycloehexane (3) at 101.325 kPa from 329.15 to 349.15 K, every 4 K. Coefficients from eq 12.

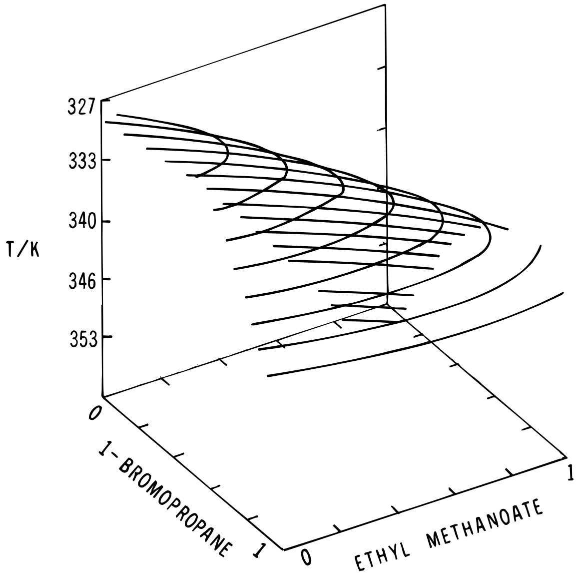

Figure 7. Three-dimensional graph $T-x_1-x_2$.

the UNIQUAC local concentration model (Abrams and Prausnitz, 1975). The constants of the corresponding models appear in Tables 6 and 7, together with corresponding statistical parameters. A comparison between the experimental activity coefficients and those predicted by the Wilson equation appears in Figure 2 for the binary system ethyl methanoate + 1-bromopropane, and a comparison between the experimental activity coefficients and the NRTL model appears in Figure 4 for the binary system ethyl methanoate + cyclohexane.

The ternary activity coefficients were correlated very well by the Wilson model (eq 8), using the binary parameters, as shown by the statistical parameters given in Table 7.

The activity coefficients for the ternary system were also correlated by the following Redlich−Kister expansion (Hala et al., 1967):

$$\begin{aligned}\ln \gamma_1/\gamma_2 = {}& b_{12}(x_2 - x_1) - c_{12}[(x_1 - x_2)^2 - 2x_1x_2] + \\ & d_{12}(x_2 - x_1)[(x_1 - x_2)^2 - 4x_1x_2] + x_3[b_{13} + \\ & c_{13}(2x_1 - x_3) + d_{13}(x_1 - x_3)(3x_1 - x_3) - b_{23} - \\ & c_{23}(2x_2 - x_3) - d_{23}(x_2 - x_3)(3x_2 - x_3) + C_1(x_2 - x_1)] \qquad (10)\end{aligned}$$

where b_{ij}, c_{ij}, and d_{ij} are constants for the pertinent binary system and C_1 is a ternary constant. The equations for the two other pairs of activity coefficients were obtained by cyclic rotation of the indices. All the constants in eq 10 are assumed to be independent of the temperature. Data for the binary system 1-bromopropane + cyclohexane have already been reported (Wisniak et al., 1995a). The ternary Redlich−Kister coefficient was obtained by a Simplex optimization technique. The differences between the values of the root mean square deviation for the activity coefficient for the two cases—with and without the ternary constant C_1 (Table 6)—are statistically not significant, suggesting that ternary data can be predicted directly from the binary systems.

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

$$\begin{aligned}T/\text{K} = {}& \sum_{i=1}^{n} x_i T_i^\circ/\text{K} + \sum_{i,j=1}^{n} \{x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k\} + \\ & x_1x_2x_3\{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \qquad (11)\end{aligned}$$

In this equation n is the number of components ($n = 2$ or 3), T_i° is the boiling point of the pure component i, and m is the number of terms in the series expansion of $(x_i - x_j)$. C_k are the binary constants where A, B, C, and D are ternary constants. The following equation, of the same structure, has been suggested by Tamir (1981) for the direct correlation of ternary data, without the use of binary data:

$$T/\mathrm{K} = \sum_{i=1}^{3} x_i T_i + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + ...] + x_1 x_3 [A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + ...] + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + ...] \quad (12)$$

In eq 12 coefficients A_{ij}, B_{ij}, and C_{ij} are not binary constants; they are multicomponent parameters determined directly from the data. Direct correlation of $T(x)$ for ternary mixtures can be very efficient as reflected by a lower percent average deviation and rmsd and a smaller number of parameters than those for eq 11. Both equations may require a similar number of constants for similar accuracy, but the direct correlation allows an easier calculation of boiling isotherms (Figures 6 and 7). The various constants of eqs 11 and 12 are reported in Table 8, which also contains information indicating the degree of goodness of the correlation. It is clear that for the ternary system in question a direct fit of the data gives a much better fit.

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