Isobaric Vapor−Liquid Equilibria in the Systems Methyl Acetate + 1-Hexene and 1-Hexene + 2-Propanol

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Vapor−liquid equilibria at 101.3 kPa have been determined for the binary systems methyl acetate + 1-hexene and 1-hexene + 2-propanol. The binary system methyl acetate + 1-hexene exhibits positive deviations from ideal behavior and an azeotrope that boils at 325.38 K and contains 39.1 mol % 1-hexene. The binary system 1-hexene + 2-propanol presents strong deviations from ideality and an azeotrope that boils at 331.67 K and contains 79.60 mol % 1-hexene. 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.

Introduction

Vapor−liquid equilibrium for the binary system methyl acetate (1) + 1-hexene (2) has been measured by Gmehling (1983) at 323.15 K as part of a program to determine the UNIFAC interaction parameters between the C=C and the CCOO groups; the system showed positive deviations from ideality, and the activity coefficients at infinite dilution were reported as $\gamma_1^\infty = 2.36$ and $\gamma_2^\infty = 3.02$. Vapor−liquid equilibrium data and azeotrope composition for the binary system 1-hexene (2) + 2-propanol (3) have been measured by Kudryavtseva et al. (1969) at various temperatures. Both systems include a component of very small dipole moment (1-hexene) and a second component with a large dipole moment. In addition, solutions of alcohols and hydrocarbons are characterized by large deviations from ideality; for example, in the related system hexane (1) + 2-propanol (2) Wisniak and Akunis (1995) found that at very high dilution $\gamma_1 > 5$ and $\gamma_2 > 10$. The system 1-hexene + 2-propanol is of interest to determine the influence of unsaturation on the nonideality of such solutions. The present work was undertaken to measure vapor−liquid equilibrium (VLE) data for the title systems for which no isobaric data are available.

Experimental Section

Purity of Materials. Methyl acetate (99.5+ mol %), 1-hexene (99.8+ mol %), and 2-propanol (99.9+ mol %) 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.

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 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

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/mol %)	n_D (298.15 K)	T/K
methyl acetate (99.5)	1.3588[a]	330.05[a]
	1.3589[b]	330.09[b]
1-hexene (99.8)	1.3852[a]	336.65[a]
	1.38502[b]	336.635[b]
2-propanol (99.9)	1.3754[a]	355.51[a]
	1.3752[b]	355.41[b]

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

Table 2. Experimental Vapor−Liquid Equilibrium Data for Methyl Acetate (1) + 1-Hexene (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}/$ (cm³ mol⁻¹)	$-B_{22}/$ (cm³ mol⁻¹)	$-B_{12}/$ (cm³ mol⁻¹)	G^E/RT
330.65	0	0	0					0
333.15	0.060	0.142	2.1156	1.0162	921	1296	1101	0.060
331.86	0.094	0.203	2.0427	1.0178	930	1308	1112	0.083
330.09	0.162	0.297	1.8272	1.0278	943	1326	1127	0.121
327.30	0.329	0.448	1.4981	1.1006	964	1355	1152	0.197
327.00	0.367	0.475	1.4367	1.1214	967	1358	1155	0.205
326.86	0.375	0.480	1.4272	1.1302	968	1360	1156	0.210
325.51	0.493	0.548	1.2988	1.2654	979	1374	1169	0.248
325.44	0.496	0.551	1.3016	1.2668	979	1375	1170	0.250
325.42	0.548	0.573	1.2249	1.3459	979	1375	1170	0.245
325.39	0.609	0.609	1.1724	1.4270	979	1376	1170	0.236
325.48	0.640	0.634	1.1602	1.4416	979	1375	1169	0.227
325.52	0.669	0.655	1.1424	1.4824	978	1374	1169	0.219
325.72	0.711	0.675	1.1018	1.5842	977	1372	1167	0.202
325.99	0.774	0.730	1.0844	1.6687	975	1369	1164	0.178
326.00	0.794	0.737	1.0661	1.7854	975	1369	1164	0.170
326.25	0.827	0.764	1.0522	1.8917	973	1366	1162	0.152
326.75	0.855	0.796	1.0422	1.9217	969	1361	1157	0.130
327.58	0.914	0.861	1.0247	2.1531	962	1352	1150	0.088
327.88	0.924	0.869	1.0132	2.2712	960	1349	1147	0.074
328.24	0.942	0.895	1.0121	2.3225	957	1345	1144	0.061
328.49	0.950	0.907	1.0077	2.3960	955	1343	1142	0.051
330.09	1	1						0
γ_i^{∞} [a]			2.65	2.94				

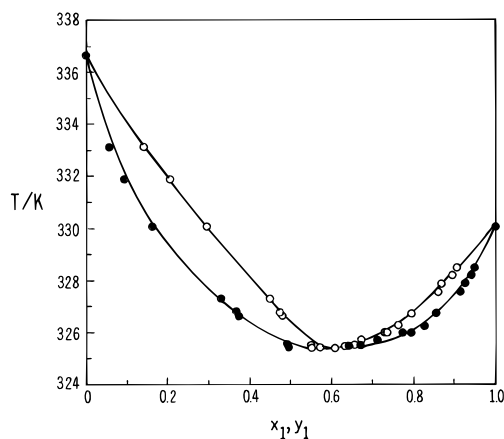[a] Calculated according to Wisniak et al. (1995).

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 SUPELCO-PORT and operated at 323.15 K. The temperatures at the injector and detector were 493.15 and 543.15 K, respectively. Very good separation was achieved under these conditions, and calibration analyses with gravimetrically

Table 3. Experimental Vapor–Liquid Equilibrium Data for 1-Hexene (2) + 2-Propanol (3) at 101.3 kPa

T/K	x_3	y_3	γ_2	γ_3	$-B_{22}/$ (cm^3 mol^{-1})	$-B_{33}/$ (cm^3 mol^{-1})	$-B_{23}/$ (cm^3 mol^{-1})	G^E/RT
333.65	1	1						0
332.49	0.873	0.843	1.0961	3.2289	1215	1304	1284	0.236
332.44	0.839	0.815	1.1044	3.0084	1213	1303	1283	0.261
331.58	0.798	0.793	1.1597	2.7976	1223	1311	1292	0.326
331.77	0.776	0.785	1.1740	2.5936	1221	1309	1290	0.338
332.38	0.752	0.775	1.1738	2.3819	1214	1303	1283	0.336
332.51	0.746	0.769	1.1690	2.3757	1212	1302	1282	0.336
332.53	0.657	0.737	1.2713	2.0014	1212	1302	1282	0.396
332.56	0.653	0.748	1.2976	1.8912	1212	1302	1281	0.391
332.76	0.594	0.727	1.3771	1.7363	1210	1300	1279	0.414
333.28	0.506	0.691	1.5125	1.5768	1204	1294	1274	0.434
333.96	0.445	0.689	1.6783	1.3708	1196	1288	1266	0.405
334.41	0.410	0.667	1.7400	1.3533	1191	1284	1261	0.406
335.00	0.361	0.643	1.8720	1.3025	1185	1278	1255	0.395
335.71	0.310	0.619	2.0502	1.2499	1177	1271	1248	0.377
337.09	0.261	0.578	2.1858	1.2139	1162	1258	1233	0.347
338.32	0.209	0.549	2.4967	1.1490	1149	1247	1221	0.301
339.71	0.182	0.513	2.5787	1.1281	1135	1234	1207	0.271
343.92	0.105	0.378	2.8976	1.1035	1093	1197	1166	0.200
344.39	0.092	0.364	3.1379	1.0895	1089	1193	1161	0.184
345.70	0.077	0.321	3.1976	1.0841	1076	1182	1149	0.164
350.95	0.024	0.126	3.4794	1.0667	1029	1139	1102	0.093
355.51	0	0						0
		$\gamma_i^{\infty\ a}$	4.03	4.99				

^{a} Calculated according to Wisniak et al. (1995).

Figure 1. Boiling temperature diagram for the system methyl acetate (1) + 1-hexene (2) at 101.3 kPa.

prepared samples were carried out to convert the peak ratio to the weight composition of the sample. Mole fractions were accurate to better than ±0.008. 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 to 4, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982):

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

where x_i and y_i are the equilibrium molar concentrations of component i in the liquid and vapor phases, 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
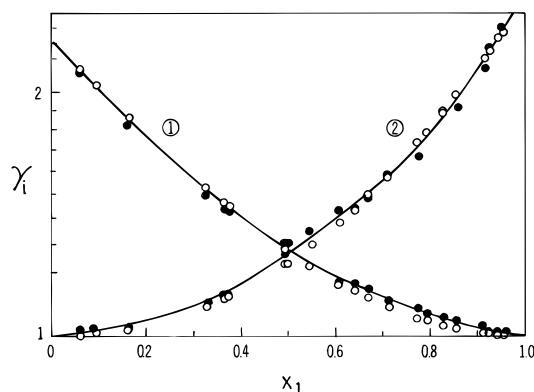
Figure 2. Activity coefficients for the system methyl acetate (1) + 1-hexene (2) at 101.3 kPa: experimental (●); predicted by UNIQUAC (○).
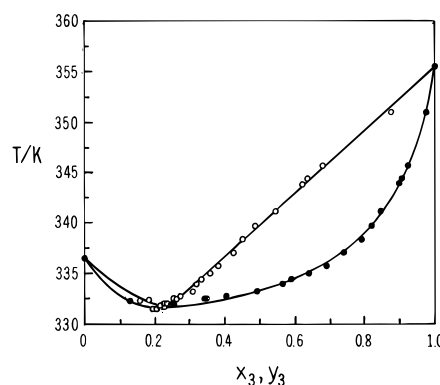
Figure 3. Boiling temperature diagram for the system 1-hexene (2) + 2-propanol (3) at 101.3 kPa.
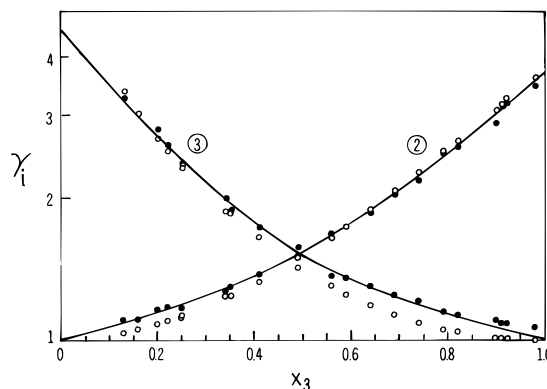
Figure 4. Activity coefficients for the system 1-hexene (2) + 2-propanol (3) at 101.3 kPa: experimental (●); predicted by NRTL (○).

$$\delta_{ij} = 2B_{ij} - 2B_{jj} - B_{ii} \quad (2)$$

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

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

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

**Table 4. Antoine Coefficients, Eq 3[a]**

compound	A_i	B_i	C_i
methyl acetate	6.186 213	1156.43	53.46
1-hexene	5.990 633	1152.971	47.30
2-propanol	7.242 683	1580.92	53.54

[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	E	max dev[a] %	av dev[b]%	rmsd[c]
methyl acetate (1) + 1-hexene (2)	0.3816	0.0125	0.0093	0.0316	2.8	1.3	0.003
1-hexene (2) + 2-propanol (3)	0.5780	−0.0373	−0.0419	0.0710	6.5	2.9	0.12

B. Other Models[d]

model	system	A_{12}	A_{21}	q_1/q_2	α	$\delta(y)$[e]
Wohl	1 + 2	0.83920	0.96869	0.702 54		0.0066
	2 + 3	1.64883	1.34338	0.923 99		0.017
Wilson	1 + 2	550.26[f]	133.707[f]			0.0067
	2 + 3	1133.00[f]	199.744[f]			0.0125
NRTL	1 + 2	360.68[f]	246.08[f]		0.084	0.0043
	2 + 3	257.17[f]	883.99[f]		0.207	0.017
UNIQUAC	1 + 2	−26.0621[f]	252.450[f]			0.0046
	2 + 3	−74.8959[f]	434.121[f]			0.021

[a] Maximum deviation %. [b] Average deviation (%). [c] Root mean square deviation. [d] All equations in ln γ_i form. [e] $\delta(y) = \Sigma|y_{exptl} - y_{calcd}|/N$ (N = number of data points). [f] Cal/mol.
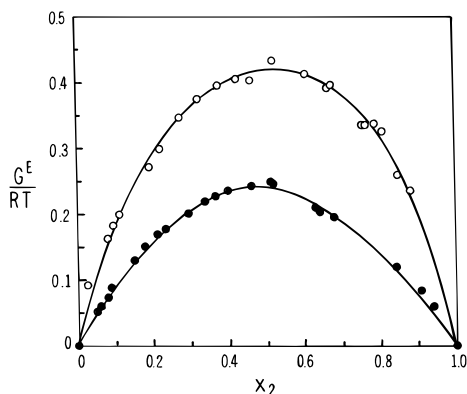
Figure 5. Variation of G^E/RT with concentration: methyl acetate + 1-hexene (●); 1-hexene + 2-propanol (○).

and assuming the association parameter η to be zero. The last two terms in eq 1 contributed less than 2.5% to the activity coefficient, and 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%. The results indicate that the binary system methyl acetate + 1-hexene exhibits positive deviations from ideal behavior and an azeotrope that boils at 325.38 K and contains 39.1 mol % 1-hexene. The binary system 1-hexene + 2-propanol presents strong deviations from ideality and an azeotrope that boils at 331.67 K and contains 79.60 mol % 1-hexene.

The vapor−liquid equilibrium data reported in Tables 2 and 3 were found to be thermodynamically consistent by the Redlich−Kister area test (1948) and by the L−W method of Wisniak (1993). The activity coefficients were correlated with the Redlich−Kister, Wohl, Wilson, NRTL, and UNIFAC equations (Walas, 1985). The following Redlich−Kister expansion was used (1948):

$$\ln(\gamma_1/\gamma_2) = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(1 - 8x_1x_2) + E(x_2 - x_1)^2(10x_1x_2 - 1) \quad (4)$$

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.

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

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

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 the system methyl acetate (1) + 1-hexene (2) very well, the best fit corresponding to the UNIQUAC correlation. In Figure 2 appear the experimental activity coefficients and the ones predicted by the UNIQUAC model. For the system 1-hexene (2) + 2-propanol (3) the fit was good except in the range of high concentration of 2-propanol, probably due to association effects in the alcohol. A comparison of the experimental activity coefficients and the ones predicted by the NRTL model is presented in Figure 4.

The excess Gibbs function G^E of the two binary systems is presented in Tables 2 and 3 and Figure 5 as the variation of the dimensionless number (Gibbs number) G^E/RT with the concentration of 1-hexene. It is seen that at $x = 0.5$ the value of the parameter for the system 1-hexene + 2-propanol is almost double that for the system methyl acetate + 1-hexene. 1-Hexene has a slight dipole moment (0.4) while methyl acetate and 2-propanol have large dipole moments (1.8 and 1.7, respectively), indicating that in the solution interactive forces are weaker and that the predominant effect is the dispersive one. In addition, solutions with 2-propanol are characterized by associating effects of the alcohol, reflected by the much larger values of G^E/RT.

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

$$T/K = \sum_{i=1}^{2}x_i(T_i^\circ/K) + x_1x_2\sum_{m=0}^{m}C_k(x_i - x_j)^k \quad (6)$$

In this equation T_i° is the boiling point of the pure component i and m is the number of terms in the series expansion of $x_i - x_j$. The various constants of eq 5 are reported in Table 6, which also contains information indicating the degree of goodness of the correlation.

Table 6. Coefficients in the 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_4	rmsd[a]/%	
methyl acetate (1) + 1-hexene (2)	−29.826 64	6.307 62	−20.616 39		0.06	0.35
1-hexene (2) + 2-propanol (3)	−47.455 11	−3.841 10	−56.012 82	−56.515 34	0.16	1.04

[a] Average deviation (%).

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