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Vapor–Liquid Equilibria for the Ternary System Methyl Ethyl Ketone + Cyclohexane + Heptane at 101.325 kPa

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This paper reports vapor–liquid equilibrium results for methyl ethyl ketone + cyclohexane + heptane mixtures at a constant pressure of 101.325 kPa. The equilibrium data have been correlated with the NRTL equation and compared with those predicted by the ASOG, UNIFAC, and modified UNIFAC group contribution methods.

Introduction

In previous works (*1–5*) we presented results on vapor–liquid equilibria measurements for ternary mixtures containing cyclohexane. The aim of the present study was to establish new vapor–liquid equilibrium (VLE) results for the ternary system methyl ethyl ketone (MEK) + cyclohexane + heptane at 101.325 kPa. No literature values are available for this system.

The results obtained have been compared with those predicted by the ASOG (*6*), UNIFAC (*7*), and modified UNIFAC (*8*) methods.

Experimental Section

Apparatus and Procedure. The VLE measurements were carried out under an atmosphere of argon in a modified Othmer-type ebulliometer with recirculation of both phases (*9*). The boiling temperatures T of the mixtures were measured with a Yokogawa 7563 digital thermometer with a precision of ±0.01 K. Pressure P was kept constant at 101.325 ± 0.01 kPa by introducing argon to make up the pressure difference with respect to pressure in the laboratory. Each experiment was continued for 1 h after the boiling temperature had become stable. Samples of both the liquid and vapor phases were analyzed by measuring their refractive indexes and densities at 298.15 K using a PolyScience bath, model 96190, with a temperature stability of ±0.02 K. Densities ρ of the pure liquid and mixtures were measured with an Anton Paar DMA-46 densimeter with a precision of ±0.0001 g·cm^{-3} and refractive indexes n_D by the automatic refractometer GPR 11-37X, Index Instruments, with a precision of ±0.000 01. The estimated uncertainties of mole fractions are ±0.001 for the liquid phase and ±0.002 for the vapor phase.

Purity of Materials. The liquids used MEK, cyclohexane (better than 99.5 mol %), and heptane (better than 99.0 mol %) were Merck chromatographic grade. No further purification was attempted because the purity of materials had been previously checked by gas chromatography. The analysis showed that the major peak area exceeds 99.6%. Their purities also had been checked by determining their densities and refractive indexes at 298.15 K and their normal boiling temperatures (Table 1).

Results and Discussion

The experimental density ρ and refractive index n_D values at 298.15 K for this ternary system as a function of x_i have previously been reported (*17*). The composition dependence of these properties has been calculated by means of the following equation:

$$Q = k_0 + \sum_{i=1}^{3}\sum_{j=1}^{m} A_{ij}x_i^{\,j} \qquad (1)$$

where Q is $\rho/(\text{g·cm}^{-3})$ or n_D and x_i is the mole fraction of component i. As a result of the crossing of density and refractive index isolines, the composition can be determined from the density, the refractive index, and the parameters k_0 and A_{ij}.

The VLE results are given in Table 2 with values of the activity coefficients γ_i calculated from the relation

$$\gamma_i = \phi_i y_i P / \{\phi_i^{\,s} x_i P_i^{\,s} \exp[v_i^{\,L}(P - P_i^{\,s})/RT]\} \qquad (2)$$

where the fugacity coefficients, ϕ_i and $\phi_i^{\,s}$, were obtained using a value of the second virial coefficient calculated by the method of Hayden and O'Connell (*18*).

Figure 1 gives the corresponding liquid and vapor compositions for the ternary mixture. Table 3 lists the properties of the pure components required to calculate γ_i.

The boiling temperatures of the system were correlated by the equation proposed Tamir and Wisniak (*20*):

$$T = \sum_{i=1}^{N} x_i T_i^{\circ} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2] + x_1x_2x_3[D_1 + D_2(x_1 - x_2) + D_3(x_1 - x_3) + D_4(x_2 - x_3)] \qquad (3)$$

where N is the number of components (N = 3), T_i° is the boiling temperature of the pure components i, and A_{ij}, B_{ij},

Table 1. Densities ρ, Refractive Indexes n_D, and Normal Boiling Temperatures T_b of the Pure Components

	ρ(298.15 K)/(g·cm^{-3})		n_D(298.15 K)		T_b/K	
component	exptl	lit.	exptl	lit.	exptl	lit.
MEK	0.7995	0.799 74 (*10*) 0.799 57 (*11*)	1.3764	1.376 4 (*10*) 1.376 2 (*12*)	352.75	352.79 (*10*) 352.75 (*13*)
cyclohexane	0.7737	0.773 89 (*10*) 0.773 63 (*14*)	1.4232	1.423 54 (*10*) 1.423 3 (*1*)	353.95	353.87 (*10*) 353.90 (*1*)
heptane	0.6796	0.679 51 (*10*) 0.679 51 (*15*)	1.3849	1.385 11 (*10*) 1.385 01 (*15*)	371.55	371.57 (*10*) 371.59 (*16*)

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Table 2. Experimental Vapor–Liquid Equilibrium Temperatures T, Liquid-Phase x_i and Vapor-Phase y_i Mole Fractions, and Activity Coefficients γ_i for Methyl Ethyl Ketone (1) + Cyclohexane (2) + Heptane (3) at 101.325 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
351.45	0.959	0.029	0.936	0.050	1.019	1.867	2.232	358.85	0.039	0.520	0.151	0.564	3.248	0.937	0.955
350.65	0.910	0.047	0.870	0.076	1.023	1.827	2.509	360.35	0.070	0.343	0.300	0.389	3.448	0.942	0.747
350.15	0.871	0.052	0.832	0.080	1.038	1.734	2.328	363.15	0.079	0.199	0.319	0.254	2.968	0.979	0.764
349.55	0.806	0.071	0.760	0.108	1.046	1.775	2.180	352.25	0.187	0.361	0.396	0.366	2.175	1.066	0.971
349.25	0.741	0.088	0.731	0.113	1.106	1.491	1.880	350.85	0.232	0.361	0.457	0.360	2.105	1.099	0.870
348.95	0.625	0.132	0.669	0.150	1.214	1.340	1.539	352.25	0.171	0.454	0.369	0.439	2.215	1.020	0.939
348.55	0.558	0.199	0.604	0.220	1.243	1.314	1.519	352.15	0.188	0.488	0.338	0.475	1.857	1.028	1.063
347.75	0.517	0.270	0.559	0.293	1.276	1.317	1.500	351.55	0.178	0.522	0.355	0.495	2.090	1.020	0.943
347.35	0.481	0.329	0.528	0.346	1.313	1.292	1.456	351.45	0.191	0.565	0.304	0.542	1.675	1.035	1.193
346.95	0.464	0.368	0.511	0.380	1.336	1.285	1.433	351.95	0.161	0.622	0.293	0.584	1.891	0.997	1.050
346.65	0.448	0.403	0.496	0.412	1.358	1.284	1.378	351.45	0.151	0.657	0.270	0.620	1.888	1.017	1.083
347.85	0.396	0.381	0.485	0.379	1.444	1.205	1.300	350.55	0.169	0.663	0.301	0.608	1.931	1.017	1.059
349.05	0.346	0.366	0.464	0.363	1.525	1.155	1.227	350.45	0.152	0.699	0.272	0.644	1.949	1.024	1.100
348.85	0.309	0.430	0.435	0.418	1.607	1.139	1.162	347.35	0.289	0.584	0.390	0.539	1.620	1.131	1.224
348.65	0.290	0.479	0.415	0.453	1.647	1.116	1.179	347.35	0.262	0.624	0.371	0.566	1.703	1.112	1.202
347.85	0.335	0.460	0.441	0.442	1.553	1.161	1.222	346.35	0.351	0.549	0.433	0.513	1.529	1.184	1.206
347.85	0.299	0.514	0.413	0.484	1.630	1.137	1.182	345.85	0.417	0.497	0.462	0.488	1.396	1.264	1.334
346.95	0.377	0.466	0.457	0.454	1.473	1.212	1.248	345.65	0.482	0.443	0.495	0.457	1.301	1.338	1.483
346.65	0.400	0.458	0.467	0.450	1.432	1.233	1.307	345.75	0.544	0.394	0.525	0.434	1.218	1.426	1.519
362.95	0.090	0.045	0.229	0.066	1.900	1.113	1.058	345.85	0.596	0.352	0.559	0.399	1.178	1.466	1.827
360.45	0.138	0.058	0.393	0.067	2.276	0.959	0.945	346.35	0.648	0.295	0.597	0.355	1.137	1.530	1.912
358.75	0.136	0.197	0.372	0.221	2.300	0.978	0.906	346.95	0.699	0.241	0.639	0.306	1.105	1.587	2.053
356.95	0.220	0.158	0.457	0.168	1.840	0.971	0.953	347.85	0.746	0.189	0.684	0.250	1.076	1.612	2.182
353.35	0.001	0.993	0.016	0.975	15.883	0.998	2.648	348.95	0.789	0.144	0.738	0.189	1.058	1.539	2.306
353.35	0.003	0.949	0.060	0.914	18.781	0.978	0.981	348.95	0.668	0.156	0.660	0.184	1.121	1.388	1.828
353.25	0.017	0.900	0.140	0.824	8.389	0.933	0.766	349.75	0.607	0.135	0.634	0.153	1.155	1.299	1.659
352.55	0.033	0.849	0.187	0.765	5.836	0.939	0.740	350.85	0.540	0.114	0.601	0.125	1.188	1.212	1.536
351.95	0.055	0.801	0.177	0.754	3.337	1.000	0.881	350.85	0.438	0.237	0.515	0.249	1.258	1.159	1.403
351.25	0.086	0.747	0.255	0.672	3.171	0.976	0.824	352.75	0.359	0.190	0.500	0.200	1.404	1.093	1.205
351.65	0.103	0.689	0.317	0.608	3.229	0.947	0.672	351.65	0.459	0.135	0.561	0.146	1.274	1.171	1.355
358.35	0.024	0.588	0.169	0.621	6.005	0.926	0.813								

Table 3. Physical Properties of the Pure Components Critical Pressure P_c, Mean Gyration Radius RD, Dipole Moment μ, Association Parameter ETA, Critical Temperature T_c, Critical Compressibility Factor Z_c, and Antoine Parameters A, B, and C

							Antoine parameters[a]		
	P_c/kPa	RD × 10^{10}/m	μ × 10^{30}/(C·m)	ETA	T_c/K	Z_c	A	B	C
MEK	4154.3 (*19*)	3.139 (*19*)	9.006 (*19*)	0.90 (*19*)	535.60 (*19*)	0.249 (*19*)	6.333 57 (*10*)	1368.210 (*10*)	36.650 (*10*)
cyclohexane	4053.0 (*10*)	3.261 (*19*)	0.000 (*19*)	0.00 (*19*)	553.15 (*10*)	0.271 (*10*)	5.969 88 (*10*)	1203.526 (*10*)	50.287 (*10*)
heptane	2735.8 (*19*)	4.267 (*19*)	0.000 (*19*)	0.00 (*19*)	540.26 (*19*)	0.259 (*19*)	6.027 30 (*10*)	1268.115 (*10*)	56.250 (*10*)

[a] $\log(P_v^s/\text{kPa}) = A - B/[(T/K) - C]$.

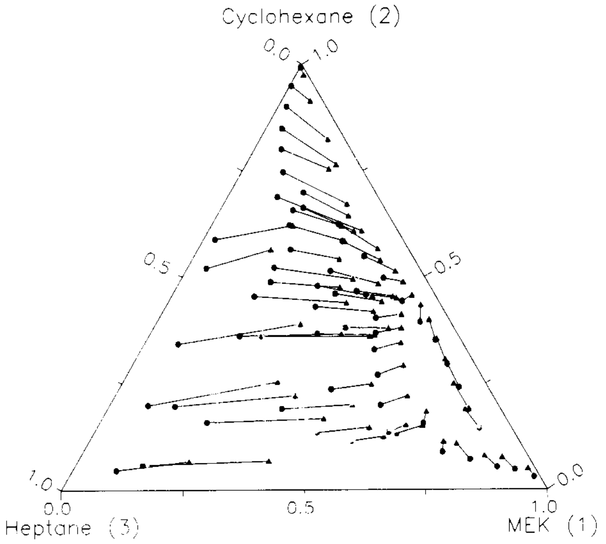

Figure 1. Composition (mole fractions x_i) diagram for methyl ethyl ketone (1) + cyclohexane (2) + heptane (3) at 101.325 kPa: (●) liquid phase, (▲) vapor phase.

C_{ij}, and D_i are the correlation parameters. In Table 4 we report the parameters obtained for direct correlation of the ternary data. The root mean square deviation for temperature calculated from eq 7 is $\sigma(T/K) = 0.478$.

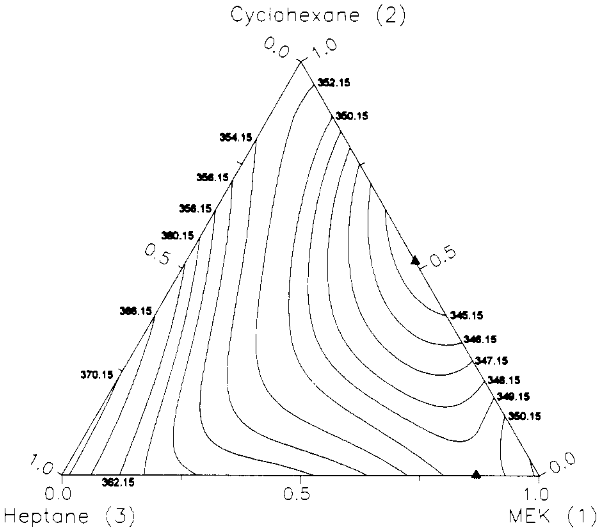

Figure 2. Isothermals for the ternary system methyl ethyl ketone (1) + cyclohexane (2) + heptane (3) at 101.325 kPa: coefficients from eq 3; (▲) estimated azeotropes.

Figure 2 shows the equilibrium isotherms on the liquid-phase composition diagram calculated from eq 3 and the parameters reported in Table 4. The shape of the curves indicates that the system does not exhibit azeotropic behavior.

Table 4. Correlation Parameters of T–x Data for Methyl Ethyl Ketone (1) + Cyclohexane (2) + Heptane (3) at 101.325 kPa

$A_{12} = -36.517$	$B_{12} = 6.850$	$C_{12} = 19.056$	
$A_{13} = -21.735$	$B_{13} = 12.058$	$C_{13} = -64.345$	
$A_{23} = -1.001$	$B_{23} = -30.853$	$C_{23} = -1.585$	
$D_1 = -83.418$	$D_2 = 1.778$	$D_3 = 54.418$	$D_4 = 152.244$

Table 5. Correlation Parameters and Root Mean Square Deviations for the System Methyl Ethyl Ketone (1) + Cyclohexane (2) + Heptane (3), for the NRTL Equation

Parameters		
$\Delta g_{12} = 460.63$	$\Delta g_{21} = 2638.60$	$\alpha_{12} = 0.04$
$\Delta g_{13} = 1505.32$	$\Delta g_{31} = 1078.14$	$\alpha_{13} = 0.15$
$\Delta g_{23} = -680.69$	$\Delta g_{32} = 516.73$	$\alpha_{23} = 0.29$

Root Mean Square Deviations			
$\sigma(T)/\mathrm{K} = 0.80$	$\sigma(y_1) = 0.04$	$\sigma(y_2) = 0.02$	$\sigma(y_3) = 0.03$

The ternary VLE data were correlated with the NRTL equation (*21*). The NRTL equation gives the activity coefficient for any component i in a multicomponent mixture as

$$\ln \gamma_i = \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{N} G_{ki} x_k} + \sum_{j=1}^{N} \left\{ \frac{x_j G_{ij}}{\sum_{k=1}^{N} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{m=1}^{N} x_m \tau_{mj} G_{mj}}{\sum_{k=1}^{N} G_{kj} x_k} \right) \right\} \qquad (4)$$

where

$$\tau_{ij} = \Delta g_{ij}/RT \qquad (5)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad (6)$$

The parameters for the NRTL equation $\Delta g_{ij}/(\mathrm{J{\cdot}mol^{-1}})$ and α_{ij}, together with the root mean square deviations for temperature $\sigma(T)$ and composition of the vapor phase $\sigma(y_i)$ calculated from eqs 7 and 8, where ND is the number of measurements, are reported in Table 5.

$$\sigma(T) = \{\sum (T_{\mathrm{exptl}} - T_{\mathrm{calcd}})^2/\mathrm{ND}\}^{1/2} \qquad (7)$$

$$\sigma(y_i) = \{\sum (y_{i,\mathrm{exptl}} - y_{i,\mathrm{calcd}})^2/\mathrm{ND}\}^{1/2} \qquad (8)$$

Prediction of vapor–liquid equilibria for the ternary system methyl ethyl ketone + cyclohexane + heptane at 101.325 kPa has been carried out by the ASOG (*6*), UNIFAC (*7*), and modified UNIFAC (*8*) methods. The group interaction parameters were those published by Hansen et al. (*22*) for the UNIFAC method and by Tochigi et al. (*23*) for the ASOG model. The results are compared with the calculated values, and the root mean square deviations for temperature $\sigma(T)$ and composition of the vapor phase $\sigma(y_i)$ were determined (Table 6). The modified UNIFAC method yields better results than the UNIFAC and ASOG methods.

Table 6. Root Mean Square Deviations between the Experimental and Calculated Temperatures $\sigma(T)$/K and Vapor-Phase Compositions $\sigma(y_i)$ of the Ternary Mixtures Methyl Ethyl Ketone (1) + Cyclohexane (2) + Heptane (3) Calculated by the ASOG, UNIFAC, and Modified UNIFAC (M-UNIFAC) Methods

method	$\sigma(T)$/K	$\sigma(y_1)$	$\sigma(y_2)$	$\sigma(y_3)$
ASOG	1.07	0.038	0.023	0.024
UNIFAC	1.80	0.035	0.023	0.022
M-UNIFAC	0.81	0.036	0.021	0.024

Registry Numbers Supplied by Author. Methyl ethyl ketone, 78-93-3; cyclohexane, 110-82-7; heptane, 142-82-5.

Literature Cited

(1) Arce, A.; Blanco, A.; Tojo, J. *Fluid Phase Equilib.* **1986**, *26*, 68.
(2) Arce, A.; Blanco, A.; Tojo, J. *J. Chem. Eng. Data* **1987**, *32*, 247.
(3) Arce, A.; Blanco, A.; Correa, A.; Tojo, J. *Can. J. Chem. Eng.* **1988**, *66*, 452.
(4) Arce, A.; Domínguez, A.; Tojo, J. *J. Chem. Eng. Data* **1990**, *35*, 30.
(5) Gama, L.; Tojo, J. *J. Chem. Eng. Data* **1992**, *37*, 20.
(6) Kojima, K.; Tochigi, K. *Prediction of Vapor-Liquid Equilibria by the ASOG Method*; Elsevier: Tokyo, 1979.
(7) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
(8) Larsen, B. L.; Rasmussen, P.; Fredenslund, Aa. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274.
(9) Ocón, J.; Espantoso, J. *An. Quím.* **1958**, *54B*, 413.
(10) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Techniques of Chemistry. *Organic Solvents*, 4th ed.; Wiley: New York, 1986; Vol. II.
(11) Takeo, M.; Nishii, K.; Nitta, T.; Katayama, T. *Fluid Phase Equilib.* **1979**, *3*, 123.
(12) Ohta, T.; Koyabu, J.; Nagata, I. *Fluid Phase Equilib.* **1981**, *7*, 65.
(13) Nagata, I.; Ohta, T.; Nakagawa, S. *J. Chem. Eng. Jpn.* **1976**, *9*, 276.
(14) Hiaki, T.; Tochigi, K.; Kojima, K. *Fluid Phase Equilib.* **1986**, *26*, 83.
(15) García, M.; Rey, C.; Peréz Villar, V.; Rodriguez, J. R. *J. Chem. Thermodyn.* **1984**, *16*, 603.
(16) Hanson, D. O.; Van Winkle, M. *J. Chem. Eng. Data* **1967**, *12*, 319.
(17) Ramallo, A. V.; Legido, J. L.; Tojo, J. *J. Chem. Thermodyn.* **1993**, *25*, 993.
(18) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(19) Prausnitz, J.; Anderson, T.; Greens, E.; Eckert, C.; Hsieh, R.; O'Connell, J. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1980.
(20) Tamir, A.; Wisniak, J. *Chem. Eng. Sci.* **1978**, *33*, 657.
(21) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(22) Hansen, H. K.; Rasmussen, P.; Fredenslund, Aa.; Schiller, M.; Gmeling, J. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352.
(23) Tochigi, K.; Tiegs, D.; Gmehling, J.; Kojima, K. *J. Chem. Eng. Jpn.* **1990**, *23*, 453.

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