g_{ij}	interaction parameter in the NRTL equation
u_{ij}	interaction parameter in the UNIQUAC equation
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
v_i	liquid molar volume of component i
r_i	relative van der Waals volume of component i
q_i	relative van der Waals surface area of component i

Greek Letters

α_{12}	nonrandomness parameter in NRTL equation
γ_i	activity coefficient of component i
λ_{ij}	interaction parameter in the Wilson equation

Subscripts

exptl	experimental
calcd	calculated

Superscript

∞	value at infinite dilution

Registry No. 1-Hexene, 592-41-6; 1-octene, 111-66-0; 1-decene, 872-05-9; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; butyl acetate, 123-86-4.

Literature Cited

(1) Wichterle, I.; Linek, J.; Hala, E. "Vapor-Liquid Equilibrium Data Bibliography"; Elsevier: Amsterdam, 1973; 4 parts.
(2) Gmehling, J.; Onken, U. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA Chemistry Data Series: Frankfurt, 1977/78; Vol. I, Part 1, 2a.
(3) Gmehling, J.; Onken, U.; Arlt, W.; Grenzheuser, P.; Weidlich, U. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA Chemistry Data Series; Frankfurt, 1978; Vol. I, 10 parts.
(4) Derr, E. L.; Deal, C. H. *J. Chem. Eng. Symp. Ser. No. 32*, **1969**, *3*, 40.
(5) Kojima, K.; Tochigi, K. "Prediction of Vapor-Liquid Equilibria by the ASOG Method"; Kodansha: Tokyo, 1979.
(6) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
(7) Fredenslund, A.; Gmehling, J.; Rasmussen, P. "Vapor-Liquid Equilibria Using UNIFAC"; Elsevier: Amsterdam, 1977.
(8) Skjold-Jørgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. *Ind. Eng. Chem., Process Des. Dev.* **1979**, *18*, 714.
(9) Gmehling, J.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem., Process Des. Dev.* **1982**, *21*, 118.
(10) Gmehling, J.; Onken, U.; Arlt, W., presented at the 87th AIChE Meeting, Boston, MA, 1979.
(11) Onken, U.; Gmehling, J.; Arlt, W., presented at the 2nd International Conference on Phase Equilibria and Fluid Properties in Chemical Industry, Berlin, 1980.
(12) Gmehling, J.; Onken, U.; Schulte, H. W. *J. Chem. Eng. Data* **1980**, *25*, 29.
(13) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 341.
(14) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. *AIChE J.* **1973**, *19*, 238.
(15) Christiansen, L. J.; Fredenslund, A. *AIChE J.* **1975**, *21*, 49.
(16) Margules, M. *Sitzungsber. Akad. Wiss., Wien* **1895**, *104*, 1243.
(17) Van Laar, J. J. *Z. Phys. Chem.* **1910**, *72*, 723.
(18) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(19) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(20) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.

Received for review October 6, 1981. Revised manuscript received July 19, 1982. Accepted August 12, 1982. I thank the "Bundesministerium für Forschung und Technologie" and Celanese Co., Corpus Christi, TX, for support of this work.

Gibbs Excess Free Energy of Methylcyclohexane + Benzene and Methylcyclohexane + Toluene Mixtures at 348.15 K

M. Diaz-Peña,* A. Crespo-Colin, and A. Compostizo

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, Madrid 3, Spain

Vapor pressures as a function of composition and at 348.15 K were measured for the binary mixtures consisting of methylcyclohexane + benzene (MC + B) and methylcyclohexane + toluene (MC + T). Values for the Gibbs excess free energy for these mixtures were calculated and the results compared to those predicted by applying Flory's theory to the same mixtures and other binary mixtures made up of either *n*-heptane or methylcyclohexane + *o*-, + *m*-, and + *p*-xylenes.

This paper deals with alicyclic + aromatic hydrocarbon binary mixtures. In particular we have selected methylcyclohexane + benzene (MC + B) and + toluene (MC + T) as representative mixtures.

Liquid-vapor equilibrium data allow calculation of Gibbs excess free energy, G^E, a characteristic thermodynamic quantity suitable to study thermodynamic properties of liquid solutions.

Thus, we have measured at 348.15 K total vapor pressures, p, for the two aforementioned systems as a function of liquid and vapor composition, x and y, respectively, and throughout the whole concentration range.

The data herein contained and others previously published (*1*, *2*) for *n*-heptane and methylcyclohexane with *o*-, *m*-, and *p*-xylenes can be used to check liquid solution theories. From them, we have selected Flory's theory (*3*, *4*) as the most sensitive to G^E value changes.

Experimental Results

Vapor pressure was measured by a dynamic method. The ebulliometer was similar to one described in a previous paper (*5*).

The sources of the chemicals were the following: methylcyclohexane from Hopkin and Williams (for chromatography), benzene from Carlo Erba (for chromatography), and toluene from Merck (Uvasol). They were further purified by fractional distillation in a 35-theoretical-plate column at a 120 reflux ratio. Only the middle fraction was used, after it was dried over sodium wire. Purity of the used products, estimated by GLC using a flame ionization detector, was better than 99.8 mol %. The density at 298.15 K, the refractive index at 303.15 K, and the vapor pressure at various temperatures were reported earlier (*2*, *6*, *7*) where the data were compared to similar ones available in the published literature. Individual vapor pressure measurements are accurate to ±7 Pa, mole fractions to $\pm 5 \times 10^{-4}$, and temperature to ±0.01 K. It is estimated that G^E is accurate to better than 2.1 J mol^{-1} for the MC + B system and to better than 0.9 J mol^{-1} for the T + MC system.

Vapor- and liquid-phase composition at equilibrium was determined by refractive index measurements, n_D, at 303.15 K. This meant that we had to obtain first a calibrated curve of n_D

Table I. C_i Coefficients for the Relationship $n_D = \Sigma_{i=0}{}^{n} C_i x_1{}^{i}$ at 303.15 K, D_i Coefficients for Relationship 3 at 348.15 K, and Their Standard Deviations σ

	i				
	0	1	2	3	σ
			MC + B		
C_i	1.49477	−0.12521	0.06556	−0.01718	4×10^{-5}
D_i	1019.10	−27.29	−80.88	−225.89	1.84
			T + MC		
C_i	1.41797	0.05342	0.01655	0.00344	1×10^{-5}
D_i	810.29	25.43	71.41		1.05

Table II. Experimental Results for the Methylcyclohexane (1) + Benzene (2) System at 348.15 K

x_1	y_1	p/kPa	γ_1	γ_2	G^E/(J mol^{-1})
0		86.372			
0.0809	0.0605	84.762	1.3576	1.0038	81.6
0.1026	0.0760	84.261	1.3371	1.0053	100.0
0.1337	0.0975	83.577	1.3061	1.0092	126.2
0.1634	0.1181	82.870	1.2840	1.0128	149.0
0.1973	0.1412	81.984	1.2584	1.0172	171.0
0.2351	0.1667	80.859	1.2303	1.0220	189.3
0.2744	0.1935	79.716	1.2070	1.0285	208.4
0.3102	0.2164	78.640	1.1786	1.0373	220.8
0.3532	0.2459	77.274	1.1566	1.0467	234.3
0.3990	0.2777	75.760	1.1345	1.0585	244.7
0.4168	0.2903	75.194	1.1272	1.0640	249.2
0.4303	0.2997	74.715	1.1203	1.0681	250.2
0.4696	0.3277	73.319	1.1023	1.0814	252.5
0.4859	0.3394	72.733	1.0949	1.0877	252.6
0.5040	0.3528	72.086	1.0878	1.0950	253.2
0.5129	0.3597	71.723	1.0846	1.0977	252.1
0.5294	0.3720	71.115	1.0779	1.1052	251.2
0.5458	0.3853	70.477	1.0735	1.1111	250.5
0.5595	0.3960	69.933	1.0683	1.1172	248.3
0.5679	0.4024	69.605	1.0647	1.1217	246.7
0.5783	0.4114	69.184	1.0627	1.1254	246.0
0.6128	0.4403	67.757	1.0520	1.1421	238.8
0.6670	0.4891	65.316	1.0363	1.1697	219.9
0.6902	0.5112	64.240	1.0301	1.1835	210.3
0.7495	0.5739	61.339	1.0184	1.2197	183.6
0.7879	0.6199	59.228	1.0116	1.2418	159.2
0.8313	0.6773	56.743	1.0049	1.2712	129.0
0.9344	0.8515	50.185	0.9977	1.3339	48.3
0.9555	0.8949	48.768	0.9972	1.3531	31.1
1		45.728			

Table III. Experimental Results for the Methylcyclohexane (2) + Toluene (1) System at 348.15 K

x_1	y_1	p/kPa	γ_1	γ_2	G^E/(J mol^{-1})
0		45.728			
0.1059	0.0952	45.402	1.2435	1.0049	79.5
0.1444	0.1286	45.206	1.2267	1.0071	103.0
0.1818	0.1589	44.987	1.1983	1.0117	122.8
0.2218	0.1926	44.675	1.1824	1.0142	139.4
0.2538	0.2231	44.406	1.1670	1.0186	155.2
0.2835	0.2427	44.226	1.1543	1.0231	165.1
0.3073	0.2621	44.019	1.1448	1.0264	172.6
0.3314	0.2808	43.810	1.1320	1.0316	179.3
0.3530	0.2983	43.614	1.1241	1.0356	185.0
0.3750	0.3160	43.380	1.1151	1.0396	188.4
0.4072	0.3418	43.060	1.1028	1.0471	194.3
0.4567	0.3820	42.547	1.0861	1.0602	201.2
0.5036	0.4207	41.995	1.0711	1.0739	202.6
0.5291	0.4437	41.662	1.0669	1.0787	202.4
0.5563	0.4672	41.319	1.0599	1.0877	201.6
0.5889	0.4962	40.894	1.0527	1.0989	199.7
0.6306	0.5333	40.310	1.0418	1.1170	193.2
0.6602	0.5611	39.851	1.0354	1.1293	186.1
0.6854	0.5857	39.434	1.0304	1.1396	178.4
0.7062	0.6062	39.086	1.0261	1.1499	171.5
0.7371	0.6392	38.553	1.0228	1.1616	162.2
0.7643	0.6674	38.062	1.0171	1.1795	150.3
0.7984	0.7059	37.457	1.0139	1.2004	138.5
0.8296	0.7430	36.809	1.0097	1.2200	121.2
0.8647	0.7882	36.028	1.0063	1.2400	99.9
0.8981	0.8340	35.304	1.0050	1.2650	82.3
0.9351	0.8887	34.358	1.0016	1.2967	53.1
1		32.567			

Table IV. Standard Deviations for Δy, Δp, and ΔG^E

system	$\sigma(\Delta y)$	$\sigma(\Delta p$/kPa)	$\sigma(\Delta G^E$/(J mol^{-1}))
MC + B	0.0016	0.022	2.92
T + MC	0.0008	0.015	1.19

vs. mole fraction. The measured values were fitted by applying a least-squares procedure to a polynomial of the type $n_D = \sum_{i=0}{}^{n} C_i x_1{}^{i}$, and the corresponding C_i values are shown in Table I.

The first three columns in Tables II and III contain the x, y, and p experimental results, which enabled the calculation of the activity coefficient, γ, through the following thermodynamic retationships:

$$\ln \gamma_1 = \ln (py_1/p^\circ{}_1 x_1) + (B_{11} - v^\circ{}_1)(p - p^\circ{}_1)/RT + py_2\delta_{12}{}^2/RT \tag{1}$$

$$\ln \gamma_2 = \ln (py_2/p^\circ{}_2 x_2) + (B_{22} - v^\circ{}_2)(p - p^\circ{}_2)/RT + py_1\delta_{12}{}^2/RT \tag{2}$$

The second virial coefficient, B, and the molar volume, v°, of toluene are respectively −1657 and 113.35 cm^3 mol^{-1} (*7*). The corresponding values for the other substances were given in previous papers (*2*, *8*). The interaction virial coefficient B_{12} was estimated as $\{(B_{11}{}^{1/3} + B_{22}{}^{1/3})/2\}^3$ and the numerical values are −1217 cm^3 mol^{-1} for MC + B and −1559 cm^3 mol^{-1} for T + MC. G^E values calculated from γ, gathered in the last columns of Tables II and III, were fitted to a polynomial of the type

$$G^E = x_1 x_2 \sum_{i=0}^{n} D_i (x_1 - x_2)^i \tag{3}$$

whose coefficients, D_i, and corresponding standard deviation, σ, are given in Table I.

A check of our experimental results was run by using an iterative procedure developed by Barker (*9*), which enables us to calculate the differences between experimental and calculated values. The corresponding standard deviations are given in Table IV.

Flory's Theory

If we assume ideal combinatorial entropy for molecules of similar size, Flory's theory (*3*) leads to the following expression for G^E:

$$\begin{aligned} G^E = {} & 3T\{(x_1 p^*{}_1 V^*{}_1/T^*{}_1) \ln [(\tilde{v}_1{}^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + \\ & (x_2 p^*{}_2 V^*{}_2/T^*{}_2) \ln [(\tilde{v}_2{}^{1/3} - 1)/(\tilde{v}^{1/3} - 1)]\} + \\ & x_1 p^*{}_1 V^*{}_1[(1/\tilde{v}_1) - (1/\tilde{v})] + \\ & x_2 p^*{}_2 V^*{}_2[(1/\tilde{v}_2) - (1/\tilde{v})] + x_1 V^*{}_1 \theta_2 \chi_{12}/\tilde{v} \end{aligned} \tag{4}$$

The pure-substance parameters $T^*{}_i$, $p^*{}_i$, $V^*{}_i$, and $\tilde{v}_i$ were evaluated from α and α/κ as described by Flory and their values are gathered in Table V. For mixtures $\tilde{v}$ was a function of the interaction energy χ_{12} and both parameters were obtained by an iterative procedure, which first required that initial values be given to $\tilde{v}$. The procedure ended when the difference between G^E experimental and theoretical values in two successive steps was smaller than a somewhat arbitrarily selected value. Calculation of θ_2 was done as shown in ref *3* and *4*, that

Table V. Parameters for the Pure Liquids at 348.15 K

substances	$10^3\alpha$/ K^{-1}	(α/κ)/ (J cm^{-3} K^{-1}	V^*/ (cm^3 mol^{-1})	T^*/K	p^*/ (J cm^{-3})	$\tilde{v}$
benzene	1.361[a]	0.945[d]	70.24	4882	606	1.3571
toluene	1.216[b]	0.921[e]	85.36	5125	565	1.3278
methylcyclo-	1.251[c]	0.828[f]	102.04	5061	514	1.3351
hexane						1.3694
n-heptane	1.424[c]	0.633[g]	115.11	4792	413	1.2934
o-xylene	1.055[b]	0.964[e]	98.75	5479	561	1.2995
m-xylene	1.083[b]	0.908[e]	100.16	5410	534	1.3045
p-xylene	1.106[b]	0.880[e]	100.26	5355	521	

[a] Reference *10*. [b] Reference *11*. [c] Reference *12*. [d] Reference *13*. [e] Reference *14*. [f] Reference *15*. [g] Reference *16*.

Table VI. Values of the Segment Number Ratio r_1/r_2, the Surface Area Segment Ratio s_1/s_2, and the Interaction Parameter χ_{12} at $x = 0.5$ for the Systems at 348.15 K

system[a]	r_1/r_2	s_1/s_2	χ_{12}
MC + B	1.452	0.882	15.20
T + MC	0.836	1.061	11.93
o-X + MC	0.967	1.010	9.90
m-X + MC	0.981	1.006	7.76
p-X + MC	0.982	1.005	8.28
o-X + H	0.857	1.052	11.70
m-X + H	0.870	1.047	9.75
p-X + H	0.870	1.047	9.18

[a] MC = methylcyclohexane; B = benzene; T = toluene; X = xylene; H = *n*-heptane.

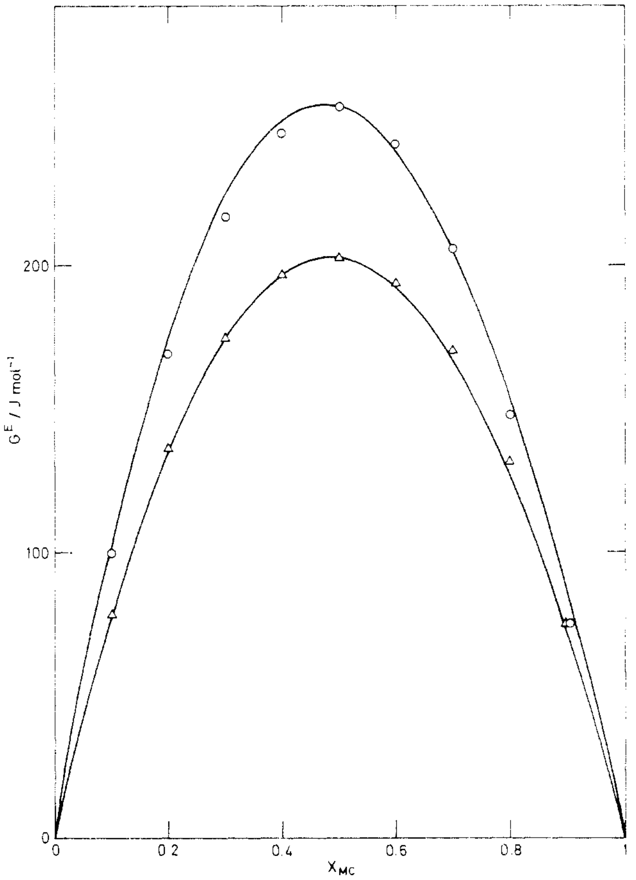

Figure 1. Comparison of theoretical (solid curve) and experimental G^E values at 348.15 K for the following systems: (○) methylcyclohexane (1) + benzene (2); (△) methylcyclohexane (2) + toluene (1).

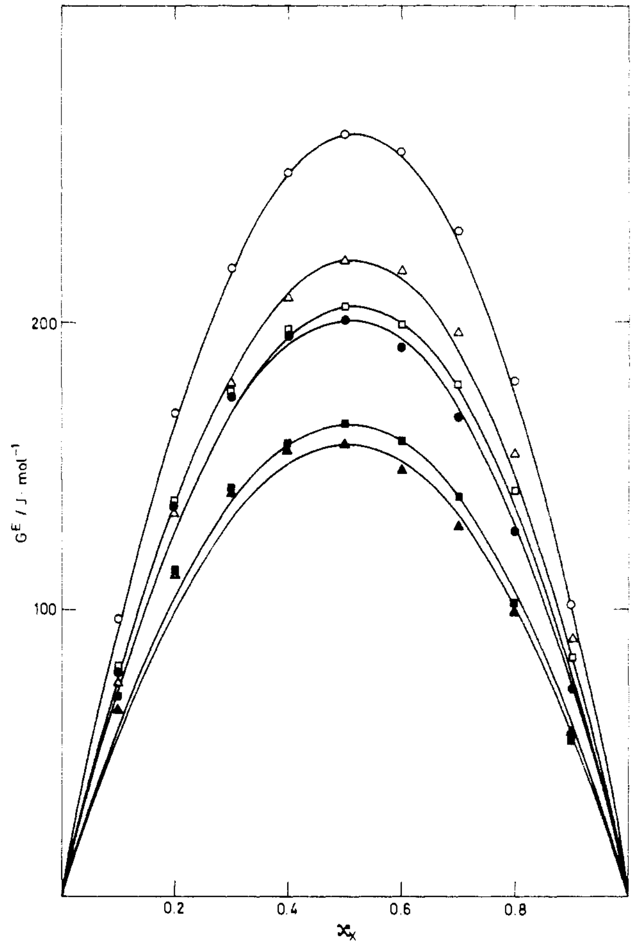

Figure 2. Comparison of theoretical (solid curve) and experimental G^E values at 348.15 K for the following systems: (○) *o*-xylene (1) + *n*-heptane (2); (△) *m*-xylene (1) + *n*-heptane (2); (□) *p*-xylene (1) + *n*-heptane (2); (●) *o*-xylene (1) + methylcyclohexane (2); (▲) *m*-xylene (1) + methylcyclohexane (2); (■) *p*-xylene (1) + methylcyclohexane (2).

is, from the surface area per segment ratio, s_1/s_2, and the segment number ratio of each molecule, r_1/r_2. Both ratio values are given in Table VI. The former ratio was taken to be equal to $(V^*_2/V^*_1)^{1/3}$, which comes from assuming spherical molecules. This simplification affected only the numerical value of χ_{12} but not the excess thermodynamic property. The ratio r_1/r_2 was made equal to V^*_1/V^*_2 since the same net volume or value per segment was taken for all substances.

The values of χ_{12} are indeed very nearly independent of composition. Values of χ_{12} at $x = 0.5$ were used to calculate G^E and are given in Table VI.

The solid curves in Figures 1 and 2 represent theoretical predictions for G^E and the points are the experimental values.

Using the parameter $\chi_{12}(G^E)$ values given in the last column of Table VI, we calculated V^E for the MC + B and T + MC systems at 343.15 and 353.15 K, respectively. The results are represented in Figure 3 together with experimental values obtained by Stookey (*17*). It ought to be kept in mind that the temperatures for χ_{12} and for the calculated V^E are different. This might contribute to an explanation of the observed differences.

Glossary

B_{ij}	second virial coefficient due to interaction of molecules *i* and *j* (*i*, *j* = 1, 2), cm^3 mol^{-1}
C_i	coefficients in $n_D = \sum_{i=0}^{n} C_i x_1^i$
D_i	coefficients for eq 3
G^E	excess Gibbs free energy, J mol^{-1}
n_D	refractive index
p	total pressure, kPa
$p°_i$	vapor pressure of pure species *i*, kPa
p^*_i	characteristic pressure of component *i*, J cm^{-3}
R	universal gas constant, J mol^{-1} K^{-1}
r_i	segment number of each molecule *i*

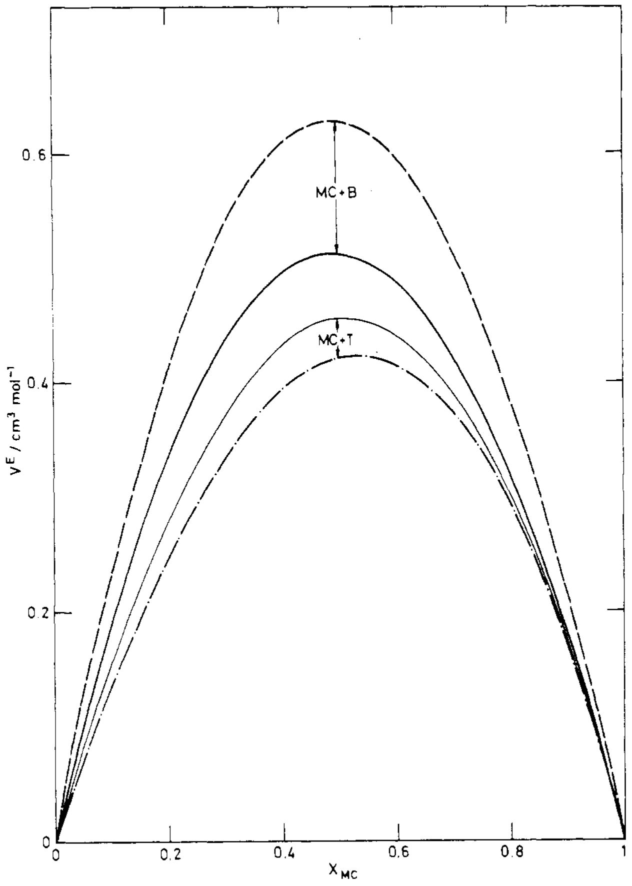

Figure 3. Experimental and calculated V^E values: (heavy solid curve) calculated curve for MC + B at 343.15 K; (- - -) corresponding experimental curve; (light solid curve) calculated curve for MC + T at 353.15 K; (-··-) corresponding experimental curve.

s_i	surface area per segment of each molecule i
T	absolute temperature, K
T^*_i	characteristic temperature of component i, K
v°_i	molar volume of pure species i, cm^3 mol^{-1}
V^*_i	characteristic molar volume of component i, cm^3 mol^{-1}
$\tilde{v}_i$	reduced volume of component i
$\tilde{v}$	reduced volume of the mixture
V^E	excess volume, cm^3 mol^{-1}
x_i	liquid-phase mole fraction of i
y_i	vapor-phase mole fraction of i

Greek Letters

α	thermal expansion coefficient, K^{-1}
α/κ	thermal pressure coefficient, J cm^{-3} K^{-1}
γ_i	activity coefficients of compound i at temperature T
Δ	difference between experimental and calculated values
δ_{12}	$= B_{11} + B_{22} - 2B_{12}$
θ_2	site fraction
σ	standard deviation
χ_{12}	parameter to express the difference between interactions of neighboring pairs of like and unlike species

Registry No. Methylcyclohexane, 108-87-2; toluene, 108-88-3; benzene, 71-43-2.

Literature Cited

(1) Díaz Peña, M.; Compostizo, A.; Crespo Colin, A. *J. Chem. Thermodyn.* **1980**, *12*, 259.
(2) Díaz Peña, M.; Compostizo, A.; Crespo Colin, A. *J. Chem. Thermodyn.* **1979**, *11*, 447.
(3) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(4) Abe, A.; Flory, P. J. *J. Chem. Soc.* **1965**, *87*, 1838.
(5) Díaz Peña, M.; Rodriguez Cheda, D. *An. Quím.* **1970**, *66*, 721.
(6) Díaz Peña, M.; Crespo Colin, A.; Compostizo, A. *J. Chem. Thermodyn.* **1978**, *10*, 1101.
(7) Díaz Peña, M.; Crespo Colin, A.; Compostizo, A. *J. Chem. Thermodyn.* **1978**, *10*, 337.
(8) Díaz Peña, M.; Compostizo, A.; Crespo Colin, A.; Escudero, I. *J. Chem. Thermodyn.* **1981**, *10*, 337.
(9) Barker, J. A. *Aust. J. Chem.* **1953**, *6*, 207.
(10) Wood, S. E.; Austin, A. E. *J. Am. Chem. Soc.* **1945**, *67*, 480.
(11) Egloff, G. "Physical Constants of Hydrocarbons"; Reinhold: New York, 1946.
(12) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1965.
(13) Díaz Peña, M.; Cavero, B. *An. Quím.* **1964**, *60B*, 357.
(14) Shraiber, L. S. *Isr. J. Chem.* **1975**, *13*, 185.
(15) Wada, Y. *J. Phys. Soc. Jpn.* **1949**, *4*, 280.
(16) Holder, G. A.; Whalley, E. *Trans. Faraday. Soc.* **1962**, *58*, 2095.
(17) Stookey, D. J.; Sallak, H. M.; Smith, B. D. *J. Chem. Thermodyn.* **1973**, *5*, 741.

Received for review December 31, 1981. Revised manuscript received June 24, 1982. Accepted September 24, 1982.