

GENERAL RESEARCH

Vapor–Liquid Equilibria and Excess Properties of Cyclohexane–1,1-Dimethylpropyl Methyl Ether (TAME) Mixtures

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Vapor–liquid equilibrium (VLE) data are reported for the binary mixtures formed by cyclohexane and the branched ether 1,1-dimethylpropyl methyl ether (*tert*-amyl methyl ether or TAME). A Gibbs–Van Ness type apparatus was used to obtain total vapor pressure measurements for cyclohexane–TAME mixtures as a function of composition at 298.15, 308.15, 318.15, and 328.15 K. These data are analyzed together with isothermal VLE data previously obtained at 313.15 K and excess enthalpies and volumes previously determined at 298.15 K for these mixtures. The Peng–Robinson equation of state and the Wong–Sandler mixing rule, the lattice-fluid (LF) model, the Flory theory, the UNIQUAC model, and the modified UNIFAC (Dortmund) model are used to correlate or predict the VLE data and excess properties of cyclohexane–TAME mixtures.

Introduction

Branched ethers have been the subject of numerous investigations in recent years because of their use as additives in lead-free gasoline. The development of reliable models to describe the so-called “oxi-gasoline” requires an accurate knowledge of the thermodynamic properties for the involved mixtures. This is the reason for the increasing interest in the study of the phase equilibrium and other thermodynamic properties of the binary hydrocarbon–branched ether mixtures. Marsh et al.¹ have recently published a review paper on the thermophysical properties for the mixtures formed by branched ethers and nonpolar solvents. 1,1-Dimethylethyl methyl ether (*tert*-butyl methyl ether or MTBE) is the primary oxygenated compound being used, but it dissolves easily in water, and the health risks caused by the contamination of drinking water with MTBE in California make this compound a controversial gasoline additive. This problem increases the importance of 1,1-dimethylpropyl methyl ether (*tert*-amyl methyl ether or TAME), which is already one of the most widely used branched ethers.

The purpose of this paper is to report experimental VLE data for the cyclohexane–1,1-dimethylpropyl methyl ether system at 298.15, 308.15, 318.15, and 328.15 K and to discuss these data together with VLE data previously obtained by Chamorro et al.² at 313.15 K and other excess property data taken from the literature. Zhu et al.³ have reported that the cyclohexane–TAME system exhibits moderately endothermic mixing at

298.15 K. Linek⁴ and Witek et al.⁵ reported positive excess volumes (V_m^E) at 298.15 K. Both sets of data are in good agreement, and the V_m^E data obtained by Witek et al. will also be considered in this paper.

Several thermodynamic models will be used to analyze VLE, H_m^E , and V_m^E data for the cyclohexane–TAME mixtures: the Peng–Robinson (PR) equation of state (EOS)⁶ and the Wong–Sandler mixing rule,⁷ the lattice-fluid (LF) model,^{8,9} the Flory theory,¹⁰ the UNIQUAC model,¹¹ and the modified UNIFAC (Dortmund) model.¹²

Experimental Section

Cyclohexane was purchased from Carlo Erba (RPE-ACS), with a purity higher than 99.5%. TAME (Fluka, 97% purity) was fractionally distilled over 0.3-nm molecular sieves for several hours. The middle distillate used in the present work (approximately 50% of the initial amount) had a purity better than 99.6%, as determined by a gas chromatographic analysis. Chemicals were handled under a dry nitrogen atmosphere and were degassed by reflux distillation for several hours following a procedure described elsewhere.¹³

VLE data were measured using a Gibbs–Van Ness type static apparatus.¹⁴ Binary liquid solutions of known composition were prepared in a test cell by volumetric injection of degassed liquids using calibrated pistons. The accuracy of the mole fraction is estimated to be about 0.0001 in the dilute region and about 0.0003 in the middle of the concentration range. Cell and piston injectors were immersed in a water bath whose temperature was controlled to within ± 0.002 K. The temperature was measured with a quartz thermometer, Testo 781, with an accuracy of 0.01 K. The total vapor pressure was measured when phase equilibrium was reached using a differential MKS Baratron pressure gauge with a resolution of 0.08% of the reading. The pressure accuracy is estimated to be 0.01 kPa.

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Table 1. Properties of Pure Components Used in This Study

	<i>T</i> (K)	<i>V</i> _m (cm ³ mol ⁻¹)	$\kappa_T \times 10^9$ (Pa ⁻¹)	$\alpha \times 10^4$ (K ⁻¹)	<i>p</i> (kPa)	literature values range <i>p</i> (kPa)
cyclohexane	298.15	108.70 ^a	1.12 ^b	12.15 ^c	13.03	12.67–13.05 ^d
	308.15	110.04 ^a	1.22 ^b	12.15 ^c	20.15	20.03–20.11 ^d
	318.15	111.43 ^a	1.33 ^b	12.15 ^c	29.87	29.81–30.22 ^{d,e}
	328.15	112.89 ^a	1.46 ^b	12.15 ^c	43.37	43.51–44.15 ^d
TAME	298.15	133.44 ^f	1.26 ^f	9.71 ^f	10.04	10.01–10.10 ^{g-i}
	308.15	134.65 ^f	1.53 ^f	9.62 ^f	15.99	15.79–15.88 ^{h-j}
	318.15	135.86 ^f	1.80 ^f	9.52 ^f	24.04	23.99–24.13 ^{h-j}
	328.15	136.85 ^f	2.07 ^f	9.43 ^f	35.58	35.36–35.57 ^{h-j}

^a Reference 15. ^b Reference 16. ^c Reference 17. ^d Reference 18. ^e Reference 19. ^f Reference 20. ^g Reference 21. ^h Reference 22. ⁱ Reference 23. ^j Reference 24.

Table 1 lists values for the molar volumes, isothermal compressibilities, thermal expansion coefficients, and vapor pressures of cyclohexane and TAME at the temperatures studied. Pure-component vapor pressure values obtained in this work are compared to those previously reported. The sources for the pure-component properties are also given in Table 1. The vapor pressures measured in this work are in good agreement with literature values, and this is considered an indication of the chemicals' purity.

Results and Discussion

VLE Measurements. VLE measurements for cyclohexane–TAME were carried out at 298.15, 308.15, 318.15, and 328.15 K. Results were analyzed using a modified Barker's method and the maximum likelihood principle.²⁵ The temperature, *T*, and the amount of substance for components 1 and 2 were considered to be the independent variables in the data reduction. Equations of material balance were included to take into account the amounts of substances present in the vapor phase.

The excess Gibbs energy, G_m^E , of the liquid phase was assumed to be described by an (m/n) Padé approximant and is given by

$$\frac{G_m^E}{RT} = x_1(1 - x_1) \frac{\sum_{i=0}^m P_i(2x_1 - 1)^i}{1 + \sum_{j=1}^n Q_j(2x_1 - 1)^j} \quad (1)$$

where P_i and Q_j are adjustable parameters and x_1 is the mole fraction of cyclohexane. Data for the cyclohexane–TAME mixtures at the four temperatures studied are adequately described by (3/0) Padé approximants. This makes eq 1 equivalent to a Redlich–Kister equation. The vapor phase is described using the virial equation. Values for the second virial coefficients of the pure components and the cross virial coefficients were calculated by means of the Hayden and O'Connell method.²⁶

Table 2 lists values for the cyclohexane liquid composition, x_1 , and the total pressure, *p*, at the four temperatures studied, together with the calculated total pressure, p_{calc} ; the hydrocarbon vapor composition, y_1 ; the excess Gibbs energy, G_m^E ; the activity coefficients, $\ln \gamma_1$ and $\ln \gamma_2$, for cyclohexane and TAME, respectively; the Padé coefficients, P_i , for the representation of G_m^E in eq 1 and their uncertainties; and the standard deviations between experimental and calculated values of x_1 , σ_x , *p*, and σ_p . Figure 1 shows plots of the total pressure versus liquid and vapor compositions for the

temperatures studied. Deviations from Raoult's law are very small and a positive azeotrope is present in the region $x_1 > 0.92$ at all of the temperatures. Figure 2 shows plots of vapor composition versus liquid composition obtained in this study together with literature values² available at 313.15 K. As can be observed, there is nearly no temperature effect on the vapor compositions.

Values for the excess Gibbs energy of the cyclohexane–TAME system are positive, with maxima ranging from 205 J mol⁻¹ at 298.15 K to 106 J mol⁻¹ at 328.15 K. These maxima appear at approximately the same mole fraction ($x_1 \approx 0.5$) for all of the temperatures studied. Figure 3 shows plots of G_m^E values versus x_1 for the four temperatures studied.

VLE, H_m^E , and V_m^E Data Correlation. The UNIQUAC model¹¹ was used to correlate the isothermal VLE data. The experimental data previously reported² at 313.15 K are in good agreement with the VLE data reported in this paper and were also included in the correlation. The interaction parameters of this model, A_{ji} , were considered to vary linearly with temperature according to

$$A_{ji} = A_{ji,1} + A_{ji,2}(T - 298.15) \quad (2)$$

The values for $A_{ji,1}$ and $A_{ji,2}$ were obtained by simultaneous correlation of the H_m^E and VLE data. The resulting values are $A_{12,1} = -37.09$ K, $A_{12,2} = -0.7484$, $A_{21,1} = 58.45$ K, and $A_{21,2} = 0.7339$. Values for the standard deviations between experimental and calculated excess enthalpies, σ_H , using the UNIQUAC model are given in Table 3. Values for the percent ratio of σ_H and the maximum values of the excess enthalpy, $\sigma_H(\%)$ are also listed. Values for the standard deviations between experimental and calculated vapor pressures, σ_p , using the UNIQUAC model are given in Table 4. Values for the percent ratio of σ_p and the maximum value of vapor pressure, $\sigma_p(\%)$, are also listed. Values for the standard deviations indicate that such a correlation procedure leads to a simultaneous and very accurate description of VLE and H_m^E data; values for $\sigma_p(\%)$ are always lower than 1% and the value of $\sigma_H(\%)$ is 0.3%.

The free-volume theory of Flory¹⁰ has been recently recommended to predict H_m^E data for mixtures involving an hydrocarbon and a branched ether.²⁷ In this work, the theory of Flory is used to describe VLE, H_m^E and V_m^E data for the cyclohexane–TAME system. Each fluid is characterized by three characteristic magnitudes, p^* , v^* , and T^* , which are evaluated from volumetric properties (molar volumes, cubic expansion coefficients, and isothermal compressibilities). The mixing rules introduce a binary parameter for the energy interaction, X_{AB} . An entropic correction parameter, Q_{AB} , is introduced into

Table 2. Vapor–Liquid Equilibrium Data and Coefficients and Standard Deviations for G^E Representation by Eq 1 for Cyclohexane (1)–TAME (2) at 298.15, 308.15, 318.15, and 328.15 K

x_1	P (kPa)	P_{calc} (kPa)	y_1	G_m^E (J mol ⁻¹)	$\ln \gamma_1$	$\ln \gamma_2$	x_1	P (kPa)	P_{calc} (kPa)	y_1	G_m^E (J mol ⁻¹)	$\ln \gamma_1$	$\ln \gamma_2$
cyclohexane (1)–TAME (2), $T = 298.15$ K							cyclohexane (1)–TAME (2), $T = 318.15$ K						
0.0000	10.04	10.04	0.0000	0	0.0000	0.0000	0.0000	24.04	24.04	0.0000	0	0.0000	0.0000
0.0495	10.33	10.33	0.0771	23	0.2130	-0.0012	0.0419	24.55	24.54	0.0614	20	0.1883	-0.0003
0.0868	10.57	10.57	0.1349	44	0.2338	-0.0027	0.0839	25.09	25.06	0.1209	41	0.1919	-0.0005
0.1262	10.84	10.84	0.1929	68	0.2421	-0.0036	0.1223	25.49	25.52	0.1721	61	0.1872	0.0001
0.1853	11.24	11.22	0.2718	104	0.2352	-0.0022	0.1617	25.95	25.97	0.2215	80	0.1769	0.0018
0.2333	11.50	11.50	0.3283	131	0.2182	0.0024	0.2066	26.41	26.44	0.2735	99	0.1610	0.0054
0.2832	11.76	11.76	0.3805	155	0.1941	0.0108	0.2473	26.85	26.84	0.3173	115	0.1444	0.0103
0.3231	11.93	11.95	0.4184	172	0.1725	0.0202	0.2845	27.19	27.17	0.3552	127	0.1287	0.0160
0.3793	12.17	12.17	0.4675	190	0.1415	0.0370	0.3336	27.54	27.56	0.4024	140	0.1086	0.0250
0.4479	12.39	12.40	0.5231	203	0.1060	0.0620	0.3748	27.88	27.86	0.4405	148	0.0930	0.0335
0.4877	12.52	12.51	0.5544	205	0.0878	0.0781	0.4139	28.16	28.12	0.4757	153	0.0799	0.0420
0.5277	12.61	12.61	0.5856	205	0.0715	0.0948	0.4511	28.35	28.34	0.5088	155	0.0689	0.0504
0.5538	12.67	12.67	0.6059	202	0.0622	0.1058	0.4947	28.58	28.59	0.5473	156	0.0581	0.0601
0.5909	12.75	12.75	0.6352	197	0.0504	0.1215	0.5406	28.82	28.83	0.5877	155	0.0488	0.0700
0.6231	12.81	12.81	0.6609	191	0.0417	0.1350	0.5793	28.99	29.02	0.6218	152	0.0424	0.0782
0.6536	12.85	12.86	0.6856	183	0.0346	0.1476	0.6180	29.17	29.20	0.6558	148	0.0371	0.0862
0.6813	12.89	12.90	0.7084	174	0.0290	0.1588	0.6545	29.34	29.35	0.6880	142	0.0327	0.0938
0.7108	12.93	12.94	0.7331	164	0.0238	0.1705	0.6953	29.51	29.51	0.7237	135	0.0282	0.1031
0.7377	12.97	12.97	0.7559	154	0.0198	0.1812	0.7312	29.68	29.64	0.7550	127	0.0245	0.1124
0.7727	13.01	13.00	0.7861	139	0.0153	0.1952	0.7714	29.79	29.77	0.7899	117	0.0203	0.1252
0.8169	13.04	13.04	0.8250	118	0.0105	0.2136	0.8066	29.89	29.86	0.8202	106	0.0165	0.1394
0.8575	13.06	13.06	0.8614	97	0.0069	0.2323	0.8481	29.94	29.95	0.8560	92	0.0119	0.1616
0.8935	13.07	13.07	0.8945	76	0.0042	0.2512	0.8836	29.98	29.99	0.8871	76	0.0080	0.1868
0.9231	13.08	13.07	0.9225	57	0.0024	0.2692	0.9348	29.98	30.01	0.9335	48	0.0031	0.2370
0.9443	13.07	13.07	0.9429	42	0.0013	0.2840	1.0000	29.87	29.87	1.0000	0	0.0000	0.0000
1.0000	13.03	13.03	1.0000	0	0.0000	0.0000	$P_0 = 0.236 \pm 0.001$; $P_1 = -0.009 \pm 0.005$; $P_2 = 0.017 \pm 0.006$; $P_3 = 0.090 \pm 0.012$; $\sigma_x = 0.000007$; $\sigma_p = 23$ Pa						
$P_0 = 0.3314 \pm 0.0008$; $P_1 = -0.001 \pm 0.003$; $P_2 = -0.085 \pm 0.004$; $P_3 = 0.087 \pm 0.007$; $\sigma_x = 0.00001$; $\sigma_p = 6$ Pa							cyclohexane (1)–TAME (2), $T = 308.15$ K						
0.0000	15.99	15.99	0.0000	0	0.0000	0.0000	0.0000	35.58	35.58	0.0000	0	0.0000	0.0000
0.0496	16.38	16.38	0.0729	21	0.1825	-0.0009	0.0347	36.15	36.17	0.0497	18	0.1832	0.0004
0.0987	16.83	16.81	0.1442	45	0.2010	-0.0023	0.0749	36.81	36.80	0.1031	37	0.1594	0.0018
0.1397	17.18	17.18	0.2005	67	0.2039	-0.0027	0.1056	37.24	37.23	0.1413	49	0.1426	0.0034
0.1829	17.54	17.55	0.2556	90	0.1980	-0.0015	0.1315	37.59	37.57	0.1722	59	0.1294	0.0052
0.2237	17.86	17.87	0.3034	110	0.1864	0.0015	0.1568	37.90	37.89	0.2012	67	0.1174	0.0072
0.2603	18.13	18.14	0.3431	126	0.1728	0.0058	0.1909	38.28	38.29	0.2389	76	0.1028	0.0103
0.3220	18.55	18.55	0.4044	150	0.1463	0.0168	0.2420	38.80	38.83	0.2932	87	0.0841	0.0154
0.3635	18.82	18.79	0.4425	162	0.1278	0.0265	0.2886	39.30	39.29	0.3409	95	0.0703	0.0204
0.4099	19.06	19.03	0.4830	172	0.1076	0.0392	0.3335	39.67	39.71	0.3858	100	0.0596	0.0252
0.4709	19.29	19.30	0.5341	180	0.0836	0.0580	0.3802	40.12	40.11	0.4318	104	0.0509	0.0300
0.5153	19.47	19.47	0.5707	181	0.0684	0.0728	0.4264	40.52	40.49	0.4766	105	0.0443	0.0345
0.5606	19.62	19.63	0.6078	179	0.0551	0.0883	0.4689	40.83	40.83	0.5175	106	0.0397	0.0382
0.5970	19.73	19.74	0.6378	174	0.0459	0.1010	0.5229	41.28	41.24	0.5688	106	0.0352	0.0426
0.6331	19.83	19.84	0.6677	168	0.0380	0.1135	0.5635	41.59	41.54	0.6070	104	0.0324	0.0459
0.6738	19.93	19.94	0.7018	159	0.0304	0.1278	0.6044	41.81	41.83	0.6449	103	0.0298	0.0495
0.7119	20.03	20.02	0.7341	149	0.0244	0.1413	0.6432	42.08	42.10	0.6804	100	0.0274	0.0536
0.7654	20.12	20.12	0.7800	131	0.0173	0.1614	0.6803	42.30	42.34	0.7139	97	0.0249	0.0585
0.7990	20.17	20.16	0.8094	118	0.0135	0.1751	0.7195	42.59	42.59	0.7486	93	0.0219	0.0654
0.8468	20.21	20.21	0.8518	96	0.0087	0.1974	0.7631	42.83	42.83	0.7866	87	0.0182	0.0760
0.8878	20.23	20.23	0.8890	75	0.0052	0.2205	0.8085	43.04	43.06	0.8257	79	0.0140	0.0917
0.9232	20.23	20.23	0.9222	55	0.0027	0.2446	0.8492	43.23	43.22	0.8605	69	0.0100	0.1111
0.9691	20.19	20.20	0.9674	24	0.0005	0.2838	0.8931	43.38	43.36	0.8986	55	0.0059	0.1394
1.0000	20.15	20.15	1.0000	0	0.0000	0.0000	0.9262	43.43	43.42	0.9282	42	0.0031	0.1672
$P_0 = 0.282 \pm 0.001$; $P_1 = 0.012 \pm 0.004$; $P_2 = -0.053 \pm 0.005$; $P_3 = 0.076 \pm 0.009$; $\sigma_x = 0.00001$; $\sigma_p = 12$ Pa							1.0000	43.37	43.37	1.0000	0	0.0000	0.0000
							$P_0 = 0.155 \pm 0.001$; $P_1 = -0.008 \pm 0.004$; $P_2 = 0.074 \pm 0.004$; $P_3 = 0.032 \pm 0.009$; $\sigma_x = 0.00001$; $\sigma_p = 24$ Pa						

the expression for the chemical potential. A value of 15.76 J cm^{-3} was obtained for the energy interaction parameter, X_{AB} , from the H_m^E data. The value for the Q_{AB} parameter obtained from the VLE data was 0.020 J cm^{-3} . Tables 3 and 4 summarize results for the correlation of the H_m^E and VLE data by means of the Flory theory. Calculated excess enthalpies are very accurate; a value of 1% was obtained for $\sigma_H(\%)$. Vapor pressure values calculated using Flory's theory are very accurate; the value of $\sigma_p(\%)$ compares favorably with those also reported in Table 4 for the other correlation procedures.

Although the theory of Flory does not include any volumetric parameter, in principle this model can be

used to predict V_m^E data. Figure 4 shows plots of the experimental H_m^E and V_m^E data and the values calculated by means of Flory's theory for the cyclohexane–TAME system at 298.15 K. As indicated by the arrows, H_m^E data are represented on the left axis and V_m^E data on the right axis. The H_m^E data are correctly described by the model. However, calculated excess volumes are only a poor estimation of the experimental V_m^E values. This could be due to the polarity of the ether molecule.

Correlations using the Peng–Robinson equation of state⁶ and the Wong–Sandler mixing rule⁷ were also carried out. In this rule, the composition dependence is based on the use of the excess Helmholtz energy, A_m^E ,

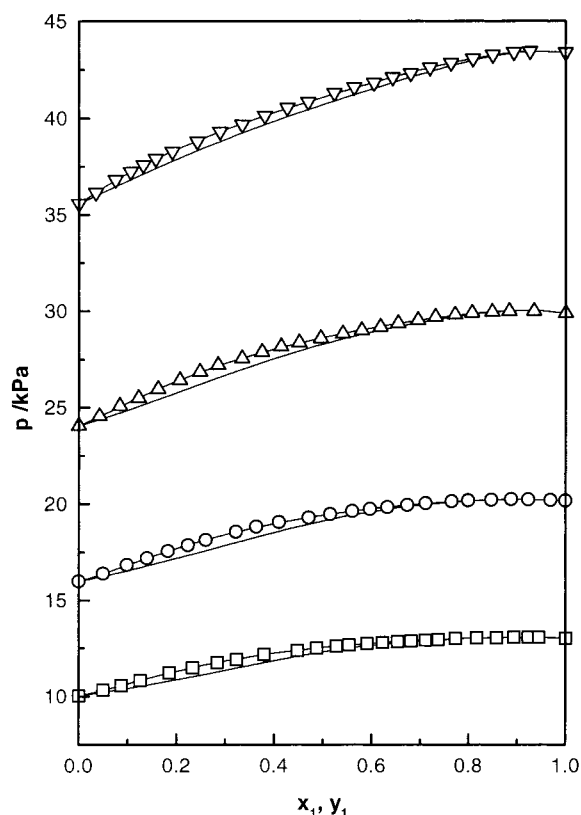


Figure 1. VLE data for the cyclohexane (1)-TAME (2) system: \square , 298.15 K; \circ , 308.15 K; \triangle , 318.15 K; ∇ , 328.15 K; and —, calculated values.

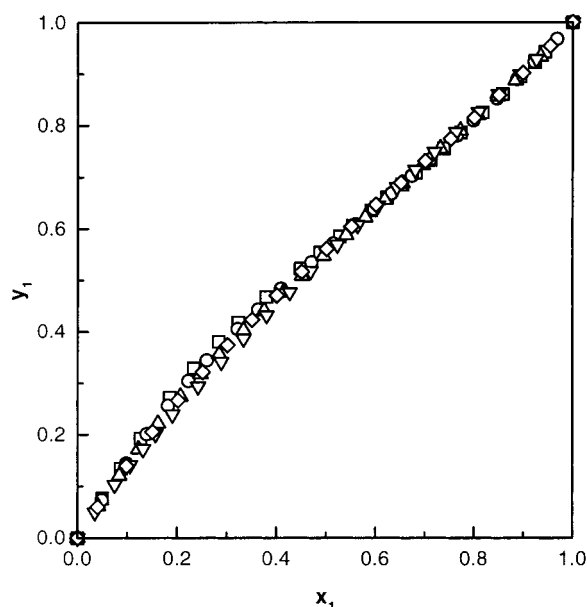


Figure 2. y_1 versus x_1 values for the cyclohexane (1)-TAME (2) system: \square , 298.15 K; \circ , 308.15 K; \diamond , 313.15 K; \triangle , 318.15 K; and ∇ , 328.15 K. Data at 313.15 K are taken from Chamorro et al.²

to combine the EOS and an activity coefficient model. Because the Helmholtz and Gibbs excess energy terms are indistinguishable at low pressures, the above-mentioned UNIQUAC model is used to evaluate G_m^E . As usual when an EOS is used, a cross term appears, which, in this case, is a cross virial coefficient

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right) \right] (1 - k_{ij}) \quad (3)$$

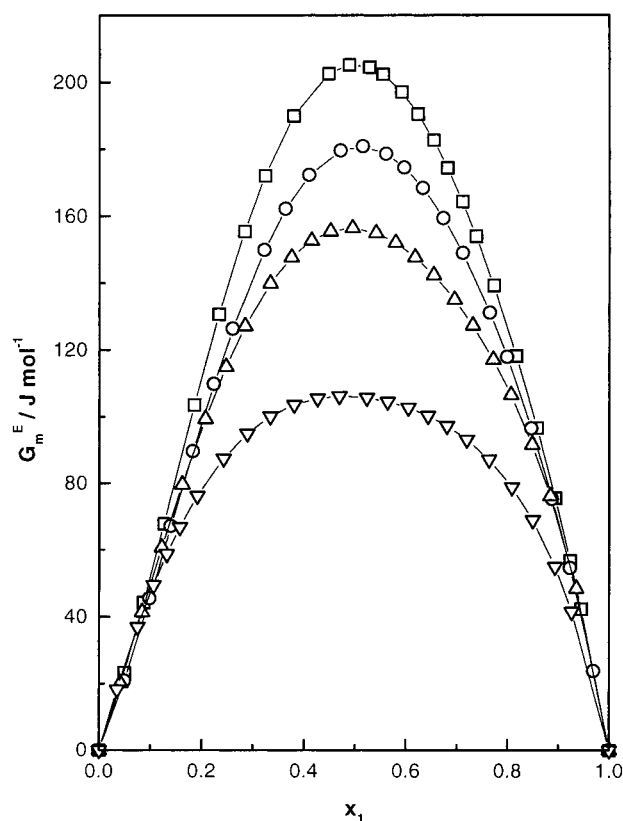


Figure 3. G_m^E versus x_1 values for the cyclohexane (1)-TAME (2) system: \square , 298.15 K; \circ , 308.15 K; \triangle , 318.15 K; and ∇ , 328.15 K.

Table 3. Excess Enthalpies for Cyclohexane (1)-TAME (2) at 298.15 K: Standard Deviations between Experimental and Calculated H_m^E , σ_H , and Percent Ratio of σ_H and the Maximum Value of the Excess Enthalpy, $\sigma_H(\%)$, for Correlations Using the UNIQUAC, Flory, and LF Models and Predictions Using the Modified UNIFAC (Dortmund) Model

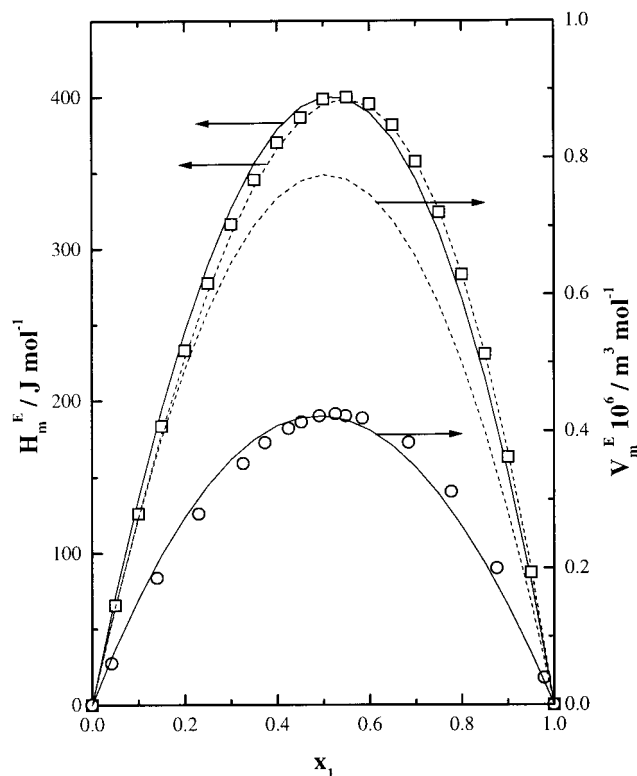
	UNIQUAC	Flory	LF	mod UNIFAC (Dortmund)
σ_H (J mol ⁻¹)	1	3	11	40
$\sigma_H(\%)$	0.3	1	3	10

where a and b are the cubic EOS parameters and k_{ij} is a binary interaction parameter. The Wong-Sandler mixing rule requires the parameters $k_{ij} = k_{ji}$ (considered to be temperature-independent) and the parameters of the excess Gibbs energy model, A_{ji} , (considered to be temperature-dependent according to eq 2). Values for these parameters were obtained by correlation of VLE data. The resulting values are $A_{12,1} = -26.11$ K, $A_{12,2} = 2.326$, $A_{21,1} = -43.15$ K, $A_{21,2} = -2.488$, and $k_{12} = 0.348$. Values for σ_p and $\sigma_p(\%)$ obtained using the PR EOS are given in Table 4. Values for the standard deviations indicate that the PR EOS provides a VLE correlation of accuracy similar to that of the UNIQUAC model, being slightly less accurate at the lowest temperature but slightly more accurate at the highest one. Experimental vapor pressures and those calculated using the PR EOS are plotted in Figure 5 for the five temperatures studied.

The Peng-Robinson EOS could also be used to calculate volumetric properties. However, values for the excess volume predicted for cyclohexane-TAME by means of the PR EOS and the parameters obtained from the VLE correlation are negative, and for this reason, they are not shown in Figure 4. This points out the

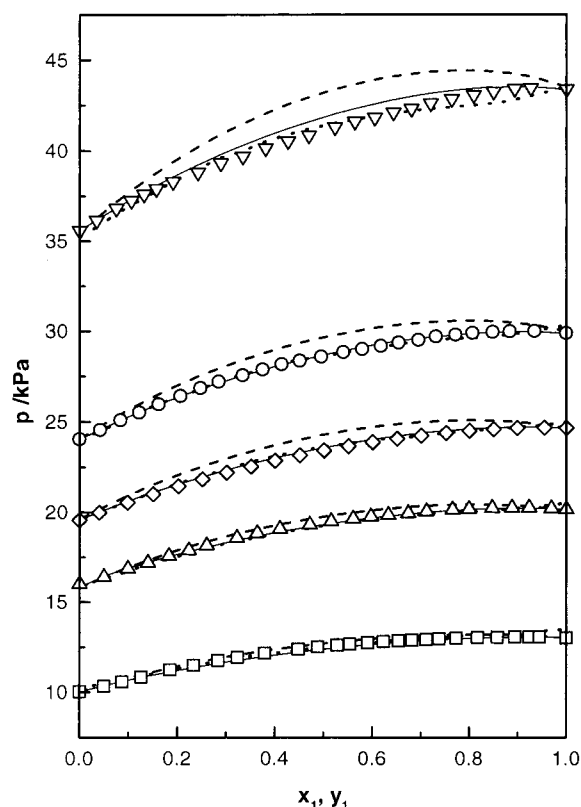
Table 4. Correlation and Prediction of VLE Data for Cyclohexane (1)–TAME (2) Using the PR Equation of State, the UNIQUAC, Flory, LF, and Modified UNIFAC (Dortmund) Models: Standard Deviations between Experimental and Calculated Vapor Pressures, σ_p , and Percent Ratio of σ_p and the Maximum Value of the Vapor Pressure, $\sigma_p(\%)$

	298.15 K ^a		308.15 K ^a		313.15 K ^b		318.15 K ^a		328.15 K ^a	
	σ_p (kPa)	$\sigma_p(\%)$	σ_p (kPa)	$\sigma_p(\%)$	σ_p (kPa)	$\sigma_p(\%)$	σ_p (kPa)	$\sigma_p(\%)$	σ_p (kPa)	$\sigma_p(\%)$
VLE correlation										
UNIQUAC	0.11	0.8	0.18	0.9	0.13	0.5	0.08	0.3	0.42	1.0
Flory	0.18	1.4	0.18	0.9	0.03	0.1	0.16	0.5	0.30	0.7
PR	0.14	1.1	0.15	0.7	0.16	0.6	0.14	0.5	0.33	0.8
LF	0.11	0.8	0.08	0.4	0.13	0.5	0.06	0.2	0.52	1.2
VLE prediction										
mod UNIFAC (Dortmund)	0.15	1.2	0.25	1.2	0.70	2.8	0.76	2.5	1.47	3.4

^a Present work. ^b Reference 2.**Figure 4.** H_m^E (□) and V_m^E (○) data for the cyclohexane (1)–TAME (2) system at 298.15 K: symbols, experimental data taken from Zhu et al.³ and Witeck et al.⁵ —, correlated using the LF model; and ---, calculated using the Flory theory.

difficulty of using these models to predict a property different from that used to calculate the interaction parameters.

VLE, H_m^E , and V_m^E data for the cyclohexane–TAME system were also correlated using the physical interaction model proposed by Sanchez and Lacombe: the lattice-fluid theory (LF).^{8,9} In the LF model, each fluid is characterized by the number of segments of the molecule, r , and two scaling constants, the closed-packed volume, v^* , and the characteristic temperature, T^* . Values for the cyclohexane and TAME parameters were taken from Lacombe and Sanchez⁸ and Coto et al.,¹⁸ respectively. The mixing rules include two binary parameters, the energy interaction parameter, ζ_{AB} , and the volume interaction parameter, ξ_{AB} . These two parameters adopt values close to unity and should be calculated from excess enthalpy data and volumetric properties, respectively. For reasons similar to those of Flory's theory, an entropic correction parameter, q_{AB} , is introduced in the expression for the chemical poten-

**Figure 5.** VLE data for cyclohexane (1)–TAME (2): □, 298.15 K; ○, 308.15 K; ◇, 313.15 K; △, 318.15 K; ▽, 328.15 K; —, correlated using the LF model; ···, correlated using the PR EOS; - - -, predicted using the modified UNIFAC (Dortmund) model. VLE data at 313.15 K are taken from Chamorro et al.²

tial. All of these binary parameters are assumed to be temperature-independent. The resulting values for these parameters are $\zeta_{AB} = 0.9834$, $\xi_{AB} = 1.0023$, and $q_{AB} = -0.024$.

Tables 3 and 4 summarize results for the correlation of the H_m^E and VLE data by means of the LF model. Values for σ_H , $\sigma_H(\%)$, σ_p , and $\sigma_p(\%)$ are listed in Tables 3 and 4. Calculated excess enthalpies can be considered accurate, as a value of 3% was obtained for $\sigma_H(\%)$. Calculated excess volumes are also accurate, as a value of $1.8 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ was obtained for the standard deviation between experimental and calculated excess volumes, σ_V , which corresponds to a value of 4% for $\sigma_V(\%)$, the percent ratio of σ_V and the maximum value for the excess volume. Figure 4 shows plots of H_m^E and V_m^E data calculated by means of the LF model. Both properties are correctly described by means of the LF model. Vapor pressure values calculated by means of the LF

model are also very accurate. $\sigma_p(\%)$ values obtained for this model compare favorably to those reported in Table 4 for the correlations obtained using the UNIQUAC model and the PR EOS. Experimental vapor pressures and those calculated using the LF model are shown in Figure 5 for the five temperatures studied. Values calculated by means of the UNIQUAC model are very similar to those obtained from the LF model, and for this reason, they are not shown in Figure 5.

VLE and H_m^E Data Prediction. Predictions of VLE data from pure-component data and the model parameters available in the literature are of great industrial interest and were carried out using the modified UNIFAC (Dortmund)^{12,29} model. For comparison purposes, H_m^E data were also predicted by means of this model. Values for σ_H and $\sigma_H(\%)$ are listed in Table 3. The predicted excess enthalpies cannot be considered accurate. Values for σ_p and $\sigma_p(\%)$ are listed in Table 4. As could be expected, predicted values are less precise than those correlated by means of the PR EOS or the UNIQUAC, LF, or Flory models. Experimental vapor pressures and those calculated by means of the modified UNIFAC (Dortmund) model are plotted in Figure 5, which clearly shows that this model overestimates deviations from ideal behavior. This effect is more important at the higher temperatures. However, in a previous study on the prediction of phase equilibria for binary and ternary mixtures involving MTBE and TAME,³⁰ we found that the modified UNIFAC (Dortmund) model leads to very accurate predictions for mixtures formed by a branched ether and a linear hydrocarbon. A better agreement with experiment could be attained by introducing more groups to distinguish between $-\text{CH}_2-$ groups in linear and in cyclic molecules, but increasing the number of groups might lead to a less useful group-contribution method.

Conclusions

Vapor pressure measurements were carried out for cyclohexane–TAME mixtures at 298.15, 308.15, 318.15, and 328.15 K. The system exhibits a nearly ideal behavior, but an azeotrope is found in the cyclohexane–rich region. There is no temperature effect on the vapor composition in the 298.15–328.15 K range.

Experimental VLE data reported here, and VLE data at 313.15 K, and H_m^E and V_m^E data at 298.15 K previously available for the cyclohexane–TAME mixtures are analyzed in terms of the Peng–Robinson equation of state and the Wong–Sandler mixing rule, the UNIQUAC, Flory, and lattice-fluid models, and the well-known UNIFAC (Dortmund) group-contribution model.

Because the temperature effect on G^E appears to be very regular, a simultaneous description of VLE and H_m^E data using the UNIQUAC model was successfully obtained. Both properties can be described by a unique set of four parameters.

The V_m^E data are well correlated by means of the LF model. However, prediction of V_m^E data using the PR EOS or the Flory theory is not possible. The H_m^E data are accurately correlated by means of the UNIQUAC, Flory, and LF models.

Several models provide a good correlation of VLE data. For VLE predictions, the modified UNIFAC (Dortmund) model is shown to lead to accurate predictions at the five temperatures studied.

Although a single binary mixture cannot be used to judge the applicability of different models, it should finally be noted that only the LF model is able to correlate simultaneously the VLE, H_m^E , and V_m^E data available for the cyclohexane–TAME mixtures. This successful correlation is attained using three adjustable temperature-independent parameters.

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Nomenclature

Latin Letters

A = Helmholtz energy
 A_{ij} = UNIQUAC model interaction parameters
 a = equation of state parameter
 b = equation of state parameter
 G = Gibbs energy
 H = enthalpy
 J = Joule
 K = Kelvin
 k = equation of state interaction parameter
 $\text{kPa} = 10^3 \text{ Pascal}$
 P_i = Padé approximant parameter
 p = vapor pressure
 Q_j = Padé approximant parameter
 Q_{AB} = entropic correction parameter, Flory's theory
 q_{AB} = entropic correction parameter, lattice-fluid theory
 R = gas constant
 T = temperature
 V = volume
 X_{AB} = energy interaction parameter (Flory theory)
 x = mole fraction in the liquid phase
 y = mole fraction in the vapor phase

Greek Symbols

α = thermal expansion coefficient
 γ = activity coefficient
 ξ_{AB} = energy interaction parameter (lattice-fluid model)
 κ = isothermal compressibility
 ξ_{AB} = volume interaction parameter (lattice-fluid model)
 σ = standard deviation
 $\sigma(\%)$ = percent ratio of the standard deviation and the maximum value of a magnitude

Superscripts

$*$ = characteristic magnitude for a fluid
 E = excess property

Subscripts

calc = calculated
 i, j = components of binary systems
 H = excess enthalpy
 m = molar property
 max = maximum
 p = vapor pressure
 V = excess volume
 x = liquid composition of component 1

Abbreviations

EOS = equation of state
 LF = lattice-fluid
 MTBE = 1,1-dimethylethyl methyl ether (*tert*-butyl methyl ether)
 PR = Peng–Robinson

TAME = 1,1-dimethylpropyl methyl ether (*tert*-amyl methyl ether)

VLE = vapor–liquid equilibrium

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