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Isothermal Vapor–Liquid Equilibrium of Binary Mixtures Containing Pyrrolidine

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We report measurements of the vapor–liquid equilibrium of pyrrolidine, and of binary mixtures of pyrrolidine separately with cyclohexane at 313.15 and 333.15 K, with water at 333.15 and 353.15 K, with ethanol at 313.15 and 333.35 K, and with tetrahydrofuran at 313.35 and 333.35 K. These data are correlated with five liquid activity coefficient models by the maximum likelihood parameter estimation method, including a correction for nonideal vapor-phase behavior. A comparison of our data with the predictions of the UNIFAC model is also included. The prediction of the UNIFAC model is so poor that a new functional group for the cyclic secondary amine group should be defined. In contrast, the prediction of the DISQUAC model is in excellent agreement with our data.

Introduction

Cyclic amines are solvents of interest in the chemical industry and in theoretical modeling because of their unique physicochemical nature. We have previously reported vapor–liquid equilibrium (VLE) data for mixtures containing tetrahydrofuran (*1*), which has a single cyclic ether group, and 1,3-dioxolane (*2*), which has two cyclic ether groups. We measured the VLE of these mixtures containing cyclic ethers in order to obtain liquid activity coefficients, which are of inherent interest and also of use in determining the importance of proximity effects, that is, the interference between close neighbor, nonalkyl functional groups in current group contribution activity coefficient models (*3*). In this paper, we report the VLE data for mixtures containing pyrrolidine. Pyrrolidine has a five-member ring structure similar to that of tetrahydrofuran; pyrrolidine and tetrahydrofuran differ only in that the latter has one cyclic ether group while the former has one cyclic secondary amine group. Another goal of our measurements is to examine whether the cyclic secondary amine group in pyrrolidine differs in the group-contribution context from a noncyclic secondary amine group, which could be tested by comparing our measurements with the prediction of the UNIFAC model (*4*). Since in the UNIFAC model the cyclic ether group in tetrahydrofuran is defined to be a different group than the noncyclic ether group, it may also be that the cyclic secondary amine group in pyrrolidine should be considered to be different from a noncyclic secondary amine group. In addition to determining the vapor pressure of pure pyrrolidine, four binary mixtures were measured, each at two isotherms: pyrrolidine with cyclohexane at 313.15 and 333.15 K, with water at 333.15 and 353.15 K, with ethanol at 313.15 and 333.35 K, and with tetrahydrofuran at 313.35 and 333.35 K.

Experiments

The experimental equipment and operating procedures have been described in detail previously (*5*). The VLE measurements were done with a Stage–Muller dynamic still. The temperature was measured with a platinum resistance thermometer (Rosemount Model 162N) accurate to 0.02 K with a resolution of 0.001 K. Pressures were measured with an accuracy of 0.02 kPa with use of a Wallace-Tiernan Model FA-187 precision mercury manometer. Vapor and liquid equilibrium samples were analyzed by a Hewlett-Packard Model 5730 gas chromatograph with a Model 3390 integrator, after calibration with gravimetrically prepared samples. The compositions determined in this way are accurate to better than 0.0005 in mole fraction.

Table I. Vapor Pressure of Pyrrolidine as a Function of Temperature

T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
313.170	17.300	335.265	43.290	348.162	69.080
315.570	19.250	335.330	43.360	348.455	69.740
322.980	26.520	340.028	51.700	351.940	78.580
327.015	31.340	340.620	52.840	354.735	86.190
330.143	35.470	344.475	60.720	357.785	95.170
331.450	37.390	344.575	60.950		

Table II. Antoine Constants for Pure Components and the Temperature Range (T) of Determination (This Work): $\log(P/\text{kPa}) = A - (B/[(T/\text{K}) + C])$

component	A	B	C	T range/K
pyrrolidine	5.934 36	1118.946	−74.922	313–359
cyclohexane	6.151 59	1301.67	−39.705	293–353
water	7.075 10	1657.46	−46.130	333–363
ethanol	7.168 79	1552.60	−50.731	303–351
tetrahydrofuran	6.441 02	1384.21	−26.997	303–333

In this study, pyrrolidine, cyclohexane, and tetrahydrofuran were purchased from the Aldrich Chemical Co. Water was found the main impurity in pyrrolidine (catalog no. P7380-3). Thus, the pyrrolidine was first purified to 99.9% by dehydration with molecular sieves. Cyclohexane (HPLC grade) and tetrahydrofuran (HPLC grade) were also dehydrated with molecular sieves so that the purity was higher than 99.9%. The water used was filtered, distilled, and deionized. The ethanol used was 200-proof (99.9%) dehydrated alcohol from U. S. Industrial Chemicals Corp. The vapor pressures we measured for cyclohexane, tetrahydrofuran, water, and ethanol agree with literature values (*6*–*8*). The vapor pressures of pyrrolidine that we measured, listed in Table I, also agree with literature values (*6*). The Antoine constants that we determined from our vapor pressure measurements are listed in Table II. The binary isothermal VLE data we measured are listed in Table III.

Results and Discussion

We correlated our measured vapor–liquid equilibrium data with five liquid activity coefficient models and virial coefficients from the correlation of Hayden and O'Connell (*9*) [see Table IV] by using the maximum likelihood parameter estimation method (*10*). The experimental data, together with the fit of the activity coefficient models that led to the best correlation, are plotted for each binary mixture in Figures 1–4. It is worth noting that the isothermal VLE data for pyrrolidine + cyclohexane at 298.15 K have also been reported in the literature (*11*). Our measured VLE data for pyrrolidine + cyclohexane at 313.15 and 333.15 K compare well with the data in the literature at 298.15 K, and all three sets could be correlated with the three-parameter Redlich–Kister equation. The sets of data at the three temperatures were found to be consistent in the

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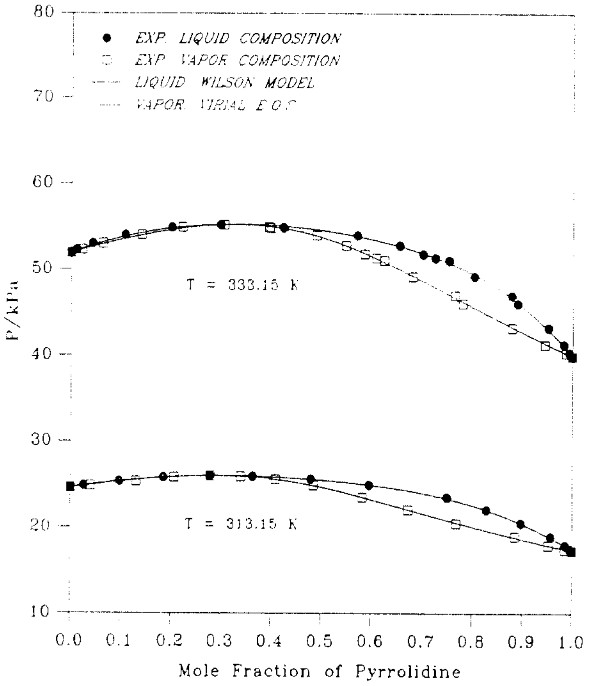

Figure 1. Vapor-liquid equilibrium for the pyrrolidine (1) + cyclohexane (2) system at 313.15 and 333.15 K. The points are our experimental data, and the lines resulted from the Wilson model.

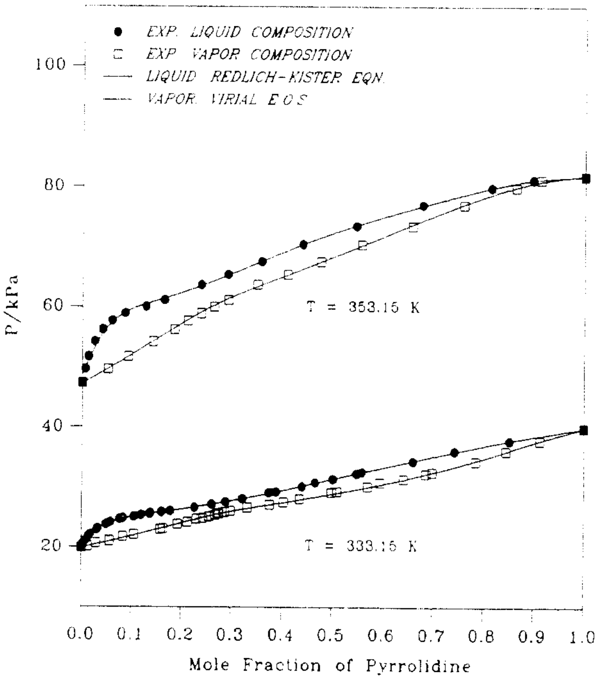

Figure 2. Vapor-liquid equilibrium for the pyrrolidine (1) + water (2) system at 333.15 and 353.15 K. The points are our experimental measurements, and the lines resulted from the Legendre polynomial expansion.

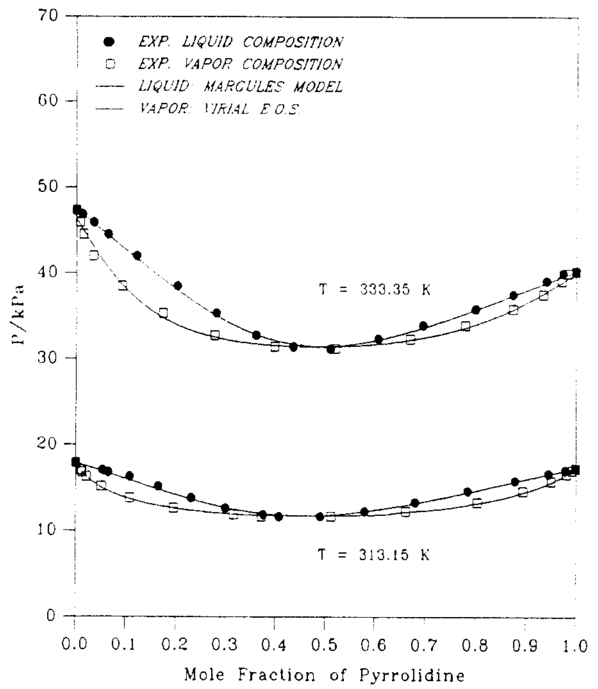

Figure 3. Vapor-liquid equilibrium for the pyrrolidine (1) + ethanol (2) system at 313.15 and 333.35 K. The points are our experimental measurements, and the lines resulted from the Margules model.

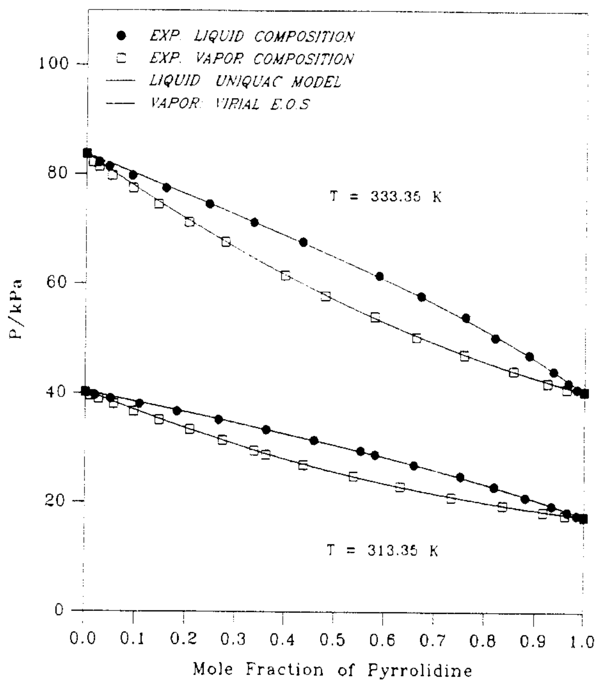

Figure 4. Vapor-liquid equilibrium for the pyrrolidine (1) + tetrahydrofuran (2) system at 313.35 and 333.35 K. The points are our experimental measurements, and the lines resulted from the UNIQUAC model.

sense that the Gibbs-Helmholtz equation below can be used to interrelate the data. No VLE data have been reported for the other pyrrolidine-containing systems, except vapor pressure measurements in dilute aqueous solutions (*12*).

The molar heats of mixing, H^E, were estimated from the fitted Wilson G^E model at two temperatures with the Gibbs-Helmholtz relation:

$$H^E = \partial(G^E/T)/\partial(1/T) \qquad (1)$$

where the partial derivative was approximated by the finite difference. The calculated values of H^E for mixtures of pyrrolidine with cyclohexane at temperatures ranging from 313.15 to 333.15 K are compared with directly measured data (*13*) at 298.15 K in Figure 5. There are no directly measured heats of mixing for the other mixtures we considered.

The Wilson model is best for correlating the experimental data for the pyrrolidine + cyclohexane mixture. The UNIQUAC model provides the best correlation of the pyrrolidine + tetrahydrofuran mixture, while the Margules model best correlates the experimental data for the pyrrolidine and ethanol mixture. However, no one model is satisfactory for all the mixtures studied here, and none of the five models gives a satisfactory correlation for the mixtures of pyrrolidine with water. These

Table III. Experimental Vapor Pressure P, Liquid Mole Fractions x_1, and Vapor Mole Fractions y_1 of Binary Mixtures at Constant Temperature T

T = 313.15 K			T = 313.15 K			T = 333.15 K			T = 333.15 K		
P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
Pyrrolidine (1) + Cyclohexane (2)											
24.614	0.0000	0.0000	23.500	0.7498	0.5824	51.886	0.0000	0.0000	51.790	0.7013	0.5856
24.865	0.0264	0.0403	22.040	0.8287	0.6729	52.270	0.0109	0.0219	51.360	0.7255	0.6093
25.380	0.0981	0.1313	20.470	0.8977	0.7677	53.000	0.0425	0.0630	51.070	0.7527	0.6243
25.820	0.1854	0.2067	18.900	0.9574	0.8857	53.980	0.1077	0.1404	49.210	0.8030	0.6810
26.000	0.2787	0.2799	17.900	0.9863	0.9524	54.870	0.2004	0.2218	46.980	0.8777	0.7645
25.920	0.3639	0.3399	17.300	0.9963	0.9849	55.170	0.2981	0.3054	46.040	0.8897	0.7801
25.600	0.4791	0.4087	17.270	1.0000	1.0000	54.880	0.4224	0.3946	43.230	0.9516	0.8779
24.920	0.5959	0.4848				54.790	0.4233	0.3984	41.250	0.9824	0.9447
						53.970	0.5709	0.4891	40.280	0.9936	0.9862
						52.800	0.6548	0.5480	39.920	1.0000	1.0000

T = 333.15 K			T = 333.15 K			T = 353.15 K			T = 353.15 K		
P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
Pyrrolidine (1) + Water (2)											
19.930	0.0000	0.0000	26.010	0.1775	0.2981	47.377	0.0000	0.0000	63.620	0.2383	0.3496
20.170	0.0020	0.0123	26.580	0.2270	0.3311	49.640	0.0061	0.0507	65.340	0.2920	0.4093
20.680	0.0041	0.0284	27.100	0.2614	0.3746	51.700	0.0121	0.0915	67.470	0.3581	0.4763
21.040	0.0079	0.0558	27.500	0.2890	0.4021	54.190	0.0239	0.1415	70.340	0.4398	0.5572
21.720	0.0139	0.0826	28.040	0.3225	0.4353	56.180	0.0405	0.1843	73.400	0.5469	0.6583
22.080	0.0179	0.1049	29.060	0.3740	0.4994	57.680	0.0591	0.2112	76.960	0.6785	0.7592
22.920	0.0310	0.1577	29.210	0.3879	0.5099	58.880	0.0851	0.2377	79.850	0.8146	0.8634
23.090	0.0321	0.1633	30.080	0.4397	0.5701	60.000	0.1272	0.2645	81.230	0.8975	0.9135
23.800	0.0496	0.1922	30.770	0.4671	0.5953	61.090	0.1644	0.2931	81.784	1.0000	1.0000
24.140	0.0579	0.2119	31.320	0.5026	0.6420						
24.680	0.0768	0.2305	32.230	0.5487	0.6860						
24.810	0.0832	0.2430	32.500	0.5597	0.6991						
25.050	0.1053	0.2553	34.310	0.6611	0.7847						
25.320	0.1200	0.2675	36.000	0.7435	0.8452						
25.540	0.1371	0.2750	37.750	0.8527	0.9130						
25.650	0.1381	0.2737	39.920	1.0000	1.0000						
25.840	0.1602	0.2869									

T = 313.15 K			T = 313.15 K			T = 333.35 K			T = 333.35 K		
P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
Pyrrolidine (1) + Ethanol (2)											
17.877	0.0000	0.0000	11.670	0.4904	0.5122	47.334	0.0000	0.0000	31.180	0.5099	0.5196
17.050	0.0544	0.0105	12.270	0.5802	0.6616	46.830	0.0123	0.0076	32.340	0.6067	0.6701
16.800	0.0652	0.0128	13.330	0.6805	0.8027	45.900	0.0357	0.0073	33.930	0.6955	0.7780
16.310	0.1085	0.0213	14.640	0.7837	0.8942	44.500	0.0644	0.0143	35.810	0.7988	0.8737
15.180	0.1653	0.0511	15.810	0.8781	0.9503	41.990	0.1216	0.0350	37.490	0.8739	0.9338
13.840	0.2311	0.1082	16.640	0.9453	0.9808	38.470	0.2027	0.0922	39.100	0.9408	0.9715
12.650	0.3001	0.1961	17.070	0.9792	0.9930	35.320	0.2806	0.1734	40.000	0.9740	0.9844
11.900	0.3762	0.3162	17.270	1.0000	1.0000	32.760	0.3604	0.2771	40.230	1.0000	1.0000
11.670	0.4075	0.3722				31.430	0.4352	0.3976			

T = 313.35 K			T = 313.35 K			T = 333.35 K			T = 333.35 K		
P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1
Pyrrolidine (1) + Tetrahydrofuran (2)											
40.200	0.0000	0.0000	28.790	0.5815	0.3616	83.690	0.0000	0.0000	57.800	0.6718	0.4789
39.640	0.0195	0.0100	26.920	0.6594	0.4364	82.140	0.0260	0.0123	54.030	0.7614	0.5793
39.060	0.0501	0.0264	24.900	0.7524	0.5381	81.310	0.0452	0.0245	50.250	0.8203	0.6626
38.070	0.1082	0.0559	22.950	0.8194	0.6316	79.700	0.0914	0.0508	47.090	0.8874	0.7591
36.720	0.1827	0.0958	21.010	0.8810	0.7335	77.450	0.1588	0.0926	44.160	0.9373	0.8566
35.180	0.2652	0.1469	19.490	0.9344	0.8361	74.520	0.2452	0.1439	42.000	0.9679	0.9248
33.360	0.3624	0.2071	18.360	0.9664	0.9159	71.180	0.3361	0.2046	40.880	0.9849	0.9639
31.410	0.4579	0.2729	17.730	0.9854	0.9615	67.620	0.4340	0.2775	40.230	1.0000	1.0000
29.500	0.5526	0.3376	17.430	1.0000	1.0000	61.510	0.5879	0.3981			

data could only be correlated with a five-parameter Legendre polynomial expansion. The VLE phase envelope of the pyrrolidine + water mixture has a peculiar shape, which is not fit well by existing excess Gibbs free energy models. It is interesting to compare the shape of the VLE phase envelope for this mixture with that of diethylamine + methanol mixture measured by Srivastava and Smith (*14*). They found a double azeotrope in the diethylamine + methanol mixture at one isotherm and only a single azeotrope at another isotherm; the pyrrolidine + water mixture shows incipient azeotropic behavior. The reason why we compare these two systems is because of their similar molecular interactions. Pyrrolidine and diethylamine are both secondary amines; the former is cyclic and the latter noncyclic. Water and methanol, the second components, are both hydrogen-bonding molecules. Consequently, these two mixtures should have a similar phase behavior. Although there is no azeotrope in the pyrrolidine + water mixture in the temperature range we measured, the shape of the phase envelope suggests the mixture may form an azeotrope at different temperatures. Thus, while the shape of the pyrrolidine + water phase envelope is unusual, the behavior is plausible. The data for this system, and indeed for all the systems studied, satisfy the point-to-point consistency test.

The predictive UNIFAC model with parameters reported in the literature (*15*) results in poor predictions for all the mixtures studied here. This confirms our suspicion and the findings of

Table IV. Second Molar Virial Coefficients B_{ij} and Liquid Molar Volumes V_i ($cm^3\ mol^{-1}$) as a Function of Temperature T

component	T/K	V_i	B_{ii}	B_{12}
pyrrolidine (i = 1)	313.15	84.7	-1235	
	313.35	84.7	-1233	
	333.15	86.6	-1054	
	333.35	86.6	-1052	
	353.15	88.4	-914	
cyclohexane (i = 2)	313.15	111.9	-1691	-1278
	333.15	114.6	-1423	-1081
water (i = 2)	333.15	18.4	-912	-479
	353.15	18.8	-637	-415
ethanol (i = 2)	313.15	59.2	-1652	-985
	333.35	60.9	-1201	-847
tetrahydrofuran (i = 2)	313.35	83.4	-1118	-1101
	333.35	84.8	-958	-937

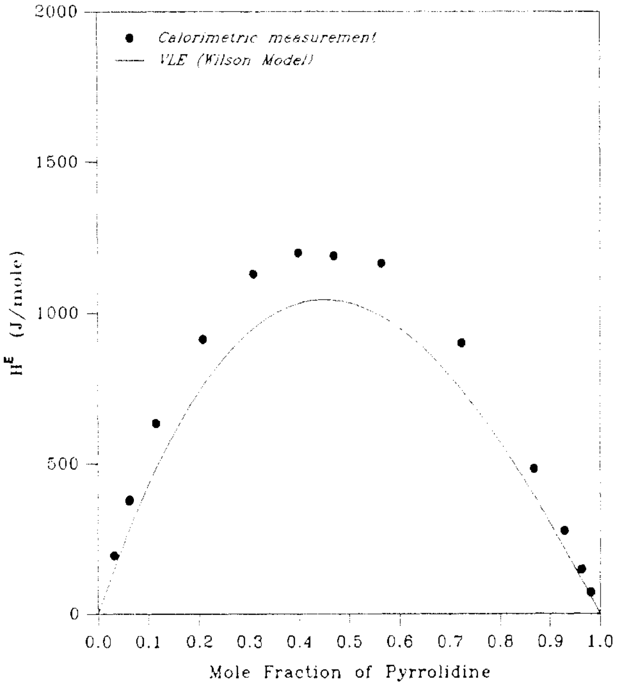

Figure 5. Molar excess enthalpy, H^E, for the pyrrolidine (1) + cyclohexane (2) system. The points are direct calorimetric measurements (*13*), and the lines resulted from the values of G^E generated from our vapor-liquid equilibrium measurements.

Tine and Kehiaian (*16*) that the cyclic secondary amine group in pyrrolidine may have to be considered a different functional group from the noncyclic secondary amine group in future improvements of the UNIFAC model. It is also worth noting that our VLE data reported here can be reproduced by the DISQUAC model with reported parameters (*17*), with average deviations in pressure of the order of 0.5 kPa and in composition of 0.01 or better.

Acknowledgment

We thank Dr. H. Kehiaian for his comments and for providing us with the results of the DISQUAC calculations.

Registry No. Pyrrolidine, 123-75-1; cyclohexane, 110-82-7; ethanol, 64-17-5; tetrahydrofuran, 109-99-9.

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Thermodynamics of Binary Mixtures Containing Alkanenitriles. 1. Excess Enthalpies of Some *n*-Alkanenitrile + *n*-Alkane or + Cyclohexane Mixtures

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A Tian-Calvet-type calorimeter was used to determine excess enthalpies, H^E, as a function of concentration at atmospheric pressure and 298.15 K for some binary liquid mixtures containing linear alkanenitriles of the general formula $CH_3(CH_2)_{n-2}CN$ (n = 2, 3, 4, 5) with *n*-alkanes (hexane, heptane) or cyclohexane.

Introduction

This work is part of a systematic study of the thermodynamic properties of organic mixtures, TOM Project (*1*-*16*), with the purpose of characterizing the type and magnitude of molecular interactions in binary liquid mixtures and to improve the group contribution models currently used to predict thermodynamic