152 J. Chem. Eng. Data **2003,** *48*, 152−157

Liquid−Liquid Equilibrium and Excess Enthalpies in Binary Systems Methylcyclohexane + Methanol and Methylcyclohexane + *N,N*-Dimethylformamide

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Liquid−liquid equilibrium and excess enthalpies were studied for the two binary systems: methylcyclohexane + methanol and methylcyclohexane + *N*,*N*-dimethylformamide. Points of the binodal curve in the vicinity of the critical point were established in both of the systems by means of the cloud-point method. Equilibrium compositions were determined at different temperatures using the direct analytical method and the volume method. Excess enthalpies as functions of composition were determined at 298.15 K and 313.15 K using a Hart 4410 microcalorimeter with continuous-flow mixing cells. The results were correlated by the modified Wilson equation. A prediction of the liquid−liquid equilibrium and the excess enthalpy by the modified UNIFAC contribution method (Dortmund) was compared to the experimental values.

Introduction

Methanol and dimethylformamide are widely used solvents, and the knowledge of their thermodynamic properties in relation to other compounds is of significant importance to many industrial processes. Methylcyclohexane is an important raw material: it is used in feed to catalytic crude-oil refining where it decomposes to toluene, a high-octane gasoline component.

In the present paper, liquid−liquid equilibrium and excess enthalpy were studied in the systems methylcyclohexane + methanol and methylcyclohexane + *N*,*N*-dimethylformamide. No literature values concerning properties presented in this work have been found for the system methylcyclohexane + *N*,*N*-dimethylformamide. Some liquid−liquid equilibrium data have been published for the system methylcyclohexane + methanol but are very incomplete: Kiser et al.[1] give only solubilities of methylcyclohexane in methanol at several temperatures, and Nagata et al.[2] published one single tie line.

The results were correlated by the modified Wilson equation. Liquid−liquid equilibrium and excess enthalpy were predicted using the modified UNIFAC contribution method (Dortmund),[3] and the prediction was compared to the experimental values.

Experimental Section

Methanol and *N*,*N*-dimethylformamide [C_3H_9NO (abbr. N,N-DMF)] were supplied by Sigma-Aldrich and were employed as delivered. Methylcyclohexane [C_7H_{14}] was supplied by Acros Organics (for excess enthalpy measurements) and Sigma-Aldrich (for liquid−liquid equilibrium measurements). Because the presence of even a small water content in the substances affects the equilibrium in the vicinity of the critical point in a significant way, extra dry compounds by Sigma-Aldrich were employed in measuring liquid−liquid equilibrium. 1-Butanol (Sigma-Aldrich, HPLC grade) was used as the internal standard for the quantitative GC analysis of methylcyclohexane and *N*,*N*-DMF. Purities declared by the manufacturers and the water contents in substances used in the experiments are presented in Table 1. The water contents were determined in our laboratory using the Karl Fischer titration.

Table 1. Purity, Water Content, and Density of the Measured Compounds

compound	purity[a] mass %	water content mass %	ρ/g·cm^{-3} at 298.15 K this work	literature data
methanol	99+%[b]	0.006	0.78655	0.78637[4] 0.78664[5]
methylcyclohexane	99+%[b]	0.005	0.76496	0.76500[6]
	99.8%[c]	0.015	0.76497	
N,*N*-DMF	99.8%[b]	0.006	0.94381	0.9439[4]
	99.9%[d]	0.006	0.94388	

[a] As provided by the manufacturer. [b] Sigma-Aldrich anhydrous compounds. [c] Acros Organics dried over molecular sieves. [d] Sigma-Aldrich dried over molecular sieves.

Densities of the chemicals were measured at 298.15 K using an Anton Paar DMA 5000 Density Meter and were compared to literature values (see Table 1).

To obtain liquid−liquid equilibrium data, three experimental methods were employed: the cloud-point, the direct analytical, and the volume method. The cloud-point method was used to acquire binodal-curve data in the vicinity of the critical point, and the direct analytical and the volume methods were employed to determine compositions of the conjugated phases.

First, points of the binodal curve in the critical region were established in the systems using the cloud-point method. The method consists of determining the temperature at which the second phase (i.e., turbidity) appears or disappears. An apparatus designed at our department after a work by Ochi et al.[7] was used to carry out the measurements (see Figure 1).

A mixture of a known composition was prepared in a thermostated cell and was brought to a temperature at which it was homogeneous. Then, the temperature was decreased at a definite rate (0.2 to 1 K/min) to find the

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10.1021/je020135f CCC: $25.00

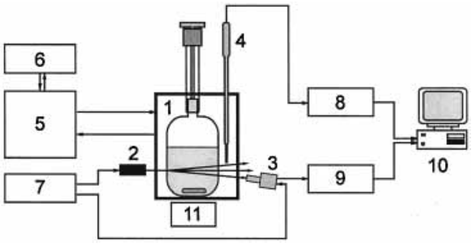

Figure 1. Apparatus for the cloud-point method. 1, measurement cell; 2, laser diode; 3, photodiode and amplifier; 4, thermometer; 5, thermostat; 6, temperature programmer; 7, power supply; 8, resistor bridge; 9, voltmeter; 10, PC; 11, magnetic stirrer.

narrowest possible temperature interval in which the second phase appeared. A Lauda RC6 CP Edition 2000 thermostat with a temperature programmer was employed for this purpose.

The change in turbidity was detected measuring the intensity of the light scattered by the mixture. A laser diode was the source of the light. The intensity of the scattered laser beam was detected by a photodiode connected to an amplifier which transformed the photocurrent to voltage. The temperature in the cell was measured by a Pt resistance thermometer connected to an ASL resistance bridge. The temperature and the intensity of the light were monitored during the measurements using a PC. Experimental uncertainties were found to be better than ±0.0002 mole fraction and ±0.01 K.

The cloud-point method does not permit the binodal curve to be determined in the whole concentration range. As the composition of the mixture becomes greatly different from that in the critical point, the change in turbidity becomes less accentuated and thus less precisely detectable. To obtain liquid−liquid equilibrium data in the noncritical region other methods were applied. The direct analytical and the volume method were employed in this work, allowing also to obtain compositions of the conjugated phases.

The direct analytical method consists of analyzing samples of the conjugated phases. In this work, capillary gas chromatography was employed. In the system methylcyclohexane + methanol, the concentration of methylcyclohexane was determined in both phases, because methanol was used as the GC solvent. In the system methylcyclohexane + *N*,*N*-DMF, the concentration of methylcyclohexane was determined in the solvent phase, whereas in the alkane phase, the *N*,*N*-DMF content was established.

Heterogeneous mixtures for sampling were prepared in a thermostated equilibrium cell.[8] The liquid mixture was thermostated to a required temperature, agitated for at least 8 h and then let stand for at least 12 h to allow the two phases to separate. Samples of each phase were then analyzed.

An HP 6890 gas chromatograph was employed to carry out the GC analyses. An HP-5 Cross-linked (5% − Phenyl) -methylpolysiloxane capillary column (30 m × 0.32 mm × 0.25 μm) was used. Helium at 1.1 mL/min was used as the carrier gas, and the following temperature program was applied: 318.15 K − 4 min, 25 K/min, 423.15 K − 2 min. The sample injection was effectuated in the splitless mode at 473.15 K. The chromatograph was calibrated with methanol solutions of known concentrations of methylcyclohexane, *N*,*N*-DMF, and 1-butanol, which was utilized as the internal standard. The data were fit to a calibration equation. Samples were then diluted with methanol to adjust their compositions approximately to those of calibration mixtures.

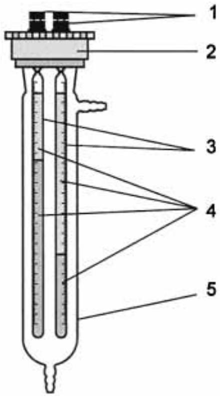

Figure 2. Apparatus for the volume method. 1, Teflon stoppers; 2, screw cap; 3, volume graduated ampules; 4, liquid equilibrium phases; 5, thermostated jacket.

The volume method was an alternative to the direct analytical method. It consists of determining volumes of the individual equilibrium phases at two (or more) different ratios of the components. Compositions of the equilibrium phases were subsequently calculated from relations based on a mass balance.[9] The measurement was carried out using two calibrated 25 mL ampules placed in a thermostated jacket (see Figure 2).

The volume method is advantageous for systems showing mutual solubility of at least several mass percent, which is the case in systems presented in this paper and in similar ones. The method is not usable in systems with low mutual solubility.

Experimental uncertainties evaluated from the acquired data are ± 0.001 mole fraction units for the GC determination of methylcyclohexane and of *N*,*N*-DMF and ±0.005 mole fraction units for the volume method.

Excess enthalpies for the systems methylcyclohexane + methanol and methylcyclohexane + *N*,*N*-DMF were determined at 298.15 K and 313.15 K using a Hart 4410 microcalorimeter with modified continuous-flow mixing cells (model 4442) and high-pressure HPP 5001 pumps from Laboratorní přístroje. The calibration of the calorimeter was carried out by measuring the excess enthalpy for the reference systems hexane + cyclohexane and methanol + water. The composition uncertainty was found to be ±0.0005 mole fraction, and the enthalpy uncertainty was found to be ±2%. Fenclová et al.[10] give a detailed description of the instrument and its calibration.

Results and Discussion

Points of binodal curves in the critical region and compositions of conjugated phases were determined in the systems methylcyclohexane + methanol and methylcyclohexane + *N*,*N*-DMF. Binodal-curve data are summed up in Table 2, and tie-line data acquired by means of the direct analytical method and by the volume method are summarized in Table 3. Experimental liquid−liquid equilibrium data are presented in Figures 3 and 4. Good agreement between the three experimental methods applied in this work was observed.

Literature values found for the system methylcyclohexane + methanol[1,2] are compared to our results in Figures 3 and 4, but the literature data are too little to allow any substantial comparison to be made. They show, however, a satisfactory agreement with our data in the coincident experimental range.

Excess enthalpies were determined at 298.15 K and 313.15 K in the systems methylcyclohexane + methanol

Table 2. Binodal-Curve Mole Fractions for Systems Methylcyclohexane (1) + Methanol (2) and Methylcyclohexane (1) + *N*,*N*-Dimethylformamide (2)

T/K	x_1	*T*/K	x_1
	Methylcyclohexane (1) + Methanol (2)		
306.26	0.1920	317.60	0.4637
309.43	0.2119	317.34	0.5044
310.81	0.2231	317.11	0.5348
312.59	0.2399	317.00	0.5424
313.04	0.2452	316.96	0.5530
314.13	0.2604	316.51	0.5764
314.93	0.2721	315.82	0.6059
316.06	0.2955	314.79	0.6365
316.30	0.3042	313.69	0.6618
316.92	0.3263	312.53	0.6836
316.82	0.3265	310.69	0.7123
317.07	0.3389	308.02	0.7442
317.37	0.3701	303.02	0.7881
317.62	0.4463		
	Methylcyclohexane (1) + *N*,*N*-DMF (2)		
309.50	0.2135	322.84	0.4843
313.21	0.2413	322.85	0.5125
315.06	0.2590	322.85	0.5151
317.05	0.2809	322.81	0.5348
317.91	0.2926	322.85	0.5446
319.98	0.3275	322.64	0.5999
321.28	0.3584	322.45	0.6253
321.43	0.3668	321.91	0.6602
322.18	0.3939	320.39	0.7152
322.31	0.4040	319.29	0.7404
322.50	0.4196	316.59	0.7854
322.66	0.4358	313.95	0.8156
322.73	0.4497	311.64	0.8360

Table 3. Conjugated Phases Mole Fractions for the Systems Methylcyclohexane (1) + Methanol (2) and Methylcyclohexane (1) + *N*,*N*-DMF(2)

	solvent phase	alkane phase
T/K	x_1'	x_1''
	Direct Analytical Method	
	Methylcyclohexane (1) + Methanol (2)	
293.15	0.135	0.831
298.15	0.150	0.812
303.15	0.174	0.792
308.15	0.202	0.750
313.15	0.251	0.680
	Methylcyclohexane (1) + N,N-DMF (2)	
293.15	0.138	0.920
298.15	0.156	0.903
303.15	0.180	0.881
308.15	0.205	0.854
313.15	0.242	0.816
	Volume Method	
	Methylcyclohexane (1) + Methanol (2)	
288.15	0.126	0.861
293.15	0.139	0.837
295.15	0.145	0.828
298.15	0.154	0.814
301.15	0.167	0.793
303.15	0.177	0.780
305.15	0.184	0.767
307.15	0.196	0.758
	Methylcyclohexane (1) + N,N-DMF (2)	
288.15	0.124	0.932
293.15	0.136	0.918
295.15	0.145	0.911
298.15	0.154	0.900
301.15	0.166	0.889
303.15	0.174	0.883
305.15	0.184	0.875
307.15	0.194	0.859

and methylcyclohexane + *N*,*N*-DMF. Experimental results are summarized in Table 4 and shown in Figures 5 and 6.

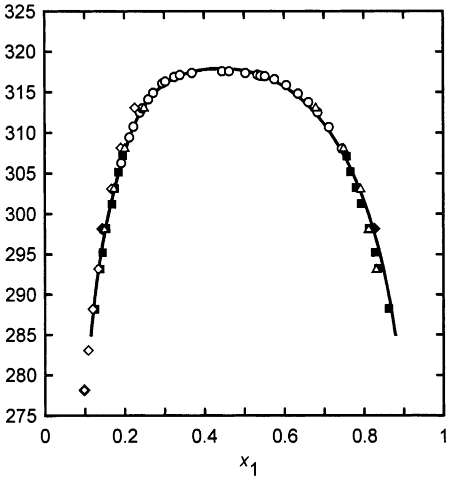

Figure 3. Liquid−liquid equilibrium in the system methylcyclohexane (1) + methanol (2). ○, cloud-point method; △, direct analytical method; ■, volume method; ◇, ref 1; ◆, ref 2; —, modified Wilson equation.

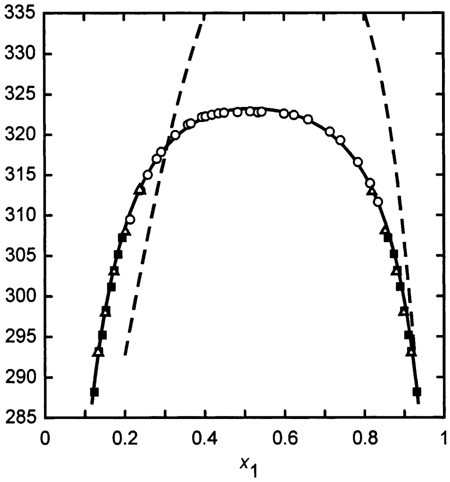

Figure 4. Liquid−liquid equilibrium in the system methylcyclohexane (1) + *N*,*N*-DMF (2). ○, cloud-point method; △, direct analytical method; ■, volume method; —, the modified Wilson equation; - - -, the modified UNIFAC method.

Correlation of the Experimental Data

The experimental results were correlated using the modified Wilson equation[11] which, to correlate data obtained in binary systems, combines the original Wilson[13] and the Redlich−Kister equation:[14]

$$Q = G^{E}/(RT) = Q_{W} + Q_{RK} \tag{1}$$

$$Q_{W} = -\sum_{i=1}^{N} x_i \ln \sum_{j=1}^{N} x_j (V_j/V_i) \exp(-\, a_{ij}/T^*) \tag{2}$$

$$Q_{RK} = \sum_{i=1}^{N-1} \sum_{j>i}^{N} x_i x_j \sum_{k=1}^{n_{ij}} B_{ijk} (x_i - x_j)^{k-1} \tag{3}$$

$$a_{ij} = \alpha_{ij} + \beta_{ij} T^* + \gamma_{ij}/T^* \tag{4}$$

$$B_{ijk} = \alpha_{ijk} + \beta_{ijk} T^* + \gamma_{ijk}/T^* \tag{5}$$

where Q is the dimensionless excess Gibbs energy; Q_W is the Wilson term; Q_{RK} the Redlich−Kister term; α_{ij}, β_{ij}, γ_{ij}, α_{ijk}, β_{ijk}, and γ_{ijk} are temperature-independent binary parameters; and V_i and x_i are molar volumes and mole fractions of the individual components, respectively.

Table 4. Excess Enthalpy Data for the Systems Methylcyclohexane (1) + Methanol (2) and Methylcyclohexane (1) + *N,N*-DMF (2)

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
Methylcyclohexane (1) + Methanol (2) at 298.15 K			
0.0166	77.3	0.2819^a	441.1
0.0345	149.5	0.3251^a	442.8
0.0537	217.5	0.3736^a	445.2
0.0743	276.3	0.4283^a	449.7
0.0967	332.0	0.4907^a	452.0
0.1210	381.2	0.5623^a	453.0
0.1475^a	416.9	0.6453^a	456.7
0.1764^a	430.8	0.7429^a	463.2
0.2082^a	434.6	0.8061^a	455.9
0.2411^a	437.5	0.8590	421.7
0.2432^a	438.0	0.9056	371.1
Methylcyclohexane (1) + Methanol (2) at 313.15 K			
0.0166	83.7	0.3244^a	616.4
0.0343	159.4	0.3728^a	629.1
0.0534	233.7	0.4275^a	643.5
0.0741	300.6	0.4898^a	656.4
0.0964	363.3	0.5615^a	667.7
0.1206	421.6	0.6446^a	686.2
0.1470	475.0	0.7423	669.9
0.1758	521.2	0.8057	637.2
0.2075	559.2	0.8588	576.9
0.2411	583.3	0.9055	513.4
0.2424	588.6	0.9410	452.4
0.2812^a	605.7		
Methylcyclohexane (1) + *N*,*N*-DMF (2) at 298.15 K			
0.0310	248.1	0.4771^a	923.1
0.0633	433.7	0.5304^a	911.5
0.0969	679.3	0.5867^a	899.1
0.1320	875.3	0.6460^a	885.4
0.1685^a	955.5	0.7087^a	871.2
0.2068^a	977.2	0.7751^a	852.4
0.2467^a	976.3	0.8455^a	833.2
0.2893^a	974.7	0.9204^a	750.1
0.3322^a	965.0	0.9240	712.8
0.3781^a	951.8	0.9274	683.0
0.3782^a	944.7	0.9305	665.9
0.4264^a	936.6	0.9383	613.6
Methylcyclohexane (1) + *N*,*N*-DMF (2) at 313.15 K			
0.0310	242.5	0.4267^a	1313.2
0.0634	476.3	0.4773^a	1306.7
0.0970	696.6	0.5307^a	1286.7
0.1321	901.2	0.5869^a	1280.5
0.1687	1086.6	0.6462^a	1272.3
0.2069	1246.1	0.7089^a	1258.4
0.2469^a	1318.8	0.7753^a	1240.8
0.2887^a	1335.2	0.8457^a	1155.8
0.2887^a	1324.8	0.9204	762.6
0.3325^a	1328.0	0.9383	644.2
0.3784^a	1321.9	0.9552	495.5

[a] Data obtained in the heterogeneous region.

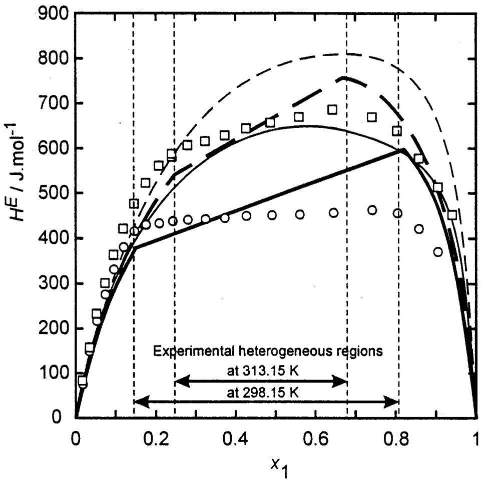

Figure 5. Excess enthalpy in the system methylcyclohexane (1) + methanol (2). ○, 298.15 K; □, 313.15 K; —, calculated data at 298.15 K; - - -, calculated data at 313.15 K; (bold lines − the modified Wilson equation, thin lines − the modified UNIFAC method).

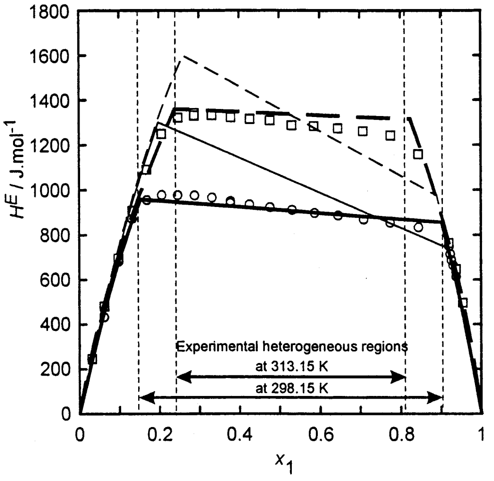

Figure 6. Excess enthalpy in the system methylcyclohexane (1) + *N*,*N*-DMF (2). ○, 298.15 K; □, 313.15 K; —, calculated data at 298.15 K; - - -, calculated data at 313.15 K; (bold lines − the modified Wilson equation, thin lines − the modified UNIFAC method).

Table 5. Critical Compositions and Critical Temperatures in Systems Methylcyclohexane (1) + Methanol (2) and Methylcyclohexane (1) + *N,N*-DMF (2)

x_c	T_c/K	δ_{x1c}^{c}	δ_{Tc}/K^c
Methylcyclohexane (1) + Methanol (2)			
0.4293^a	317.62^b	0.002	−0.24
Methylcyclohexane (1) + *N*,*N*-DMF (2)			
0.5147^a	322.82^b	0.002	0.14

[a] Determined from the experimental data by the Cailletet-Mathias rule. [b] Experimental values. [c] Difference between values obtained by the Cailletet-Mathias rule and those obtained in the correlation (mod. Wilson equation)

The number of parameters n_{ij} of the Redlich−Kister term depends on the system to be correlated. A temperature transformation $T^* = T/T_{ref}$ was introduced to improve the numerical stability of the calculation. In this work, T_{ref} equal to 300 K was used. Equations 4 and 5 express the general temperature dependence of the model parameters.

The correlation was effectuated using a procedure published by Řehák et al.[15] where the maximum-likelihood method[16] allows the parameters of the correlation model to be obtained. This method permits all of the available data to be correlated simultaneously, inclusive of excess enthalpy data obtained in heterogeneous regions, making the calculation more precise and comprehensive. The corresponding model equations can be found in a previous work.[12]

To make correlated data complete, literature vapor−liquid equilibrium values were added to the experimental results in the system methylcyclohexane + methanol.[17−19] These data were, however, upon a consistency test, found inconsistent. They were consequently attributed a lower statistical weight in the calculation.

Critical compositions and temperatures in the two studied systems were included in the correlation as well and are given in Table 5. Determining critical values (and namely critical compositions) experimentally appears to be a difficult task, and these values must be obtained in a

Table 6. Parameters of the Modified Wilson Equation for the System Methylcyclohexane (1) + Methanol (2) and Methylcyclohexane (1) + *N*,*N*-DMF (2)

Methylcyclohexane (1) + Methanol (2)	
$\alpha_{12} = 1.5944$	
$\alpha_{21} = 3.7402$	
$\alpha_{121} = -0.2848$	$\gamma_{121} = 0.3705$
$\alpha_{122} = 0$	$\gamma_{122} = 0$
$\alpha_{123} = 0.0211$	
molar volumes[a]	
$V_{m1} = 128.33\ \mathrm{cm^3 \cdot mol^{-1}}$	$V_{m2} = 40.74\ \mathrm{cm^3 \cdot mol^{-1}}$
Methylcyclohexane (1) + *N*,*N*-DMF (2)	
$\alpha_{12} = 0.5731$	
$\alpha_{21} = 2.5536$	
$\alpha_{121} = -1.4796$	$\gamma_{121} = 2.0851$
$\alpha_{122} = -0.1136$	$\gamma_{122} = 0$
$\alpha_{123} = -0.0741$	$\gamma_{123} = 0.2001$
molar volumes[a]	
$V_{m1} = 128.33\ \mathrm{cm^3 \cdot mol^{-1}}$	$V_{m2} = 77.49\ \mathrm{cm^3 \cdot mol^{-1}}$

[a] Reference 20.

different way. Critical compositions of the two studied systems were, apart from the above-described procedure, determined by the Cailletet−Mathias rule.[9] Maximum temperatures on corresponding binodal curves were considered to be the critical ones in this calculation. The critical temperature and composition are given in Table 5.

The calculated model parameters are listed in Table 6.

The correlation results are compared to the experimental ones in Figures 3−6. A very good description was attained on correlating liquid−liquid equilibrium data in both of the studied systems. Differences between critical values obtained from the experimental values by the Cailletet−Mathias rule and those attained in the correlation are given in Table 5. Correlation of the excess enthalpy data in the system methylcyclohexane (1) + *N*,*N*-DMF (2) led to a very good agreement with the experimental results, and the system methylcyclohexane (1) + methanol (2) was described satisfactorily.

Liquid−liquid equilibrium and excess enthalpy in both of the studied systems have also been predicted by the modified UNIFAC (Dortmund) contribution model.[3] The calculated values are compared to the experimentally obtained ones in Figures 4−6. The model predicts a heterogeneous region larger than the experimentally obtained one in the system methylcyclohexane + *N*,*N*-DMF (see Figure 4), which can be considered as a satisfactory result. On the other hand, it fails for the system methylcyclohexane + methanol in the method's declared temperature range (293.15 K to 398.15 K). The model assumes the system should be homogeneous in the whole concentration range. On extrapolating the model parameters to temperatures out of the declared temperature range, it has been found that the second phase should appear at temperatures lower than 248.15 K. Prediction of excess enthalpies is shown in Figures 5 and 6 and can be considered as relatively successful, because it depends to a large extent on the prediction of the corresponding liquid−liquid equilibria. It also follows from the prediction that the model correctly describes the excess heat capacity, because it characterizes appropriately the temperature dependence of the excess enthalpy.

Conclusion

Liquid−liquid equilibrium has been determined in the systems methylcyclohexane + methanol and methylcyclohexane + *N*,*N*-DMF by three different methods. The cloud-point method was employed to obtain points of binodal curves in critical regions, the direct analytical and volume methods enabled us to acquire compositions of conjugated phases. Results obtained by these three methods presented in Figures 3−4 are in a very good mutual agreement.

Excess enthalpies in the systems methylcyclohexane + methanol and methylcyclohexane + *N*,*N*-DMF at 298.15 K and 313.15 K have been obtained. The results were, together with liquid−liquid equilibrium data, employed to carry out correlation calculations using the modified Wilson equation. The model occurred to describe the acquired results very well, the calculation of the model parameters by the maximum-likelihood method permitting a simultaneous correlation of all of the available values.

A prediction by the modified UNIFAC model has been effectuated for the two studied systems. Although for the system methylcyclohexane + *N*,*N*-DMF the calculation corresponds qualitatively to experimentally obtained results, it assumes that the system methylcyclohexane + methanol should, at studied temperatures, be homogeneous in the whole concentration range, which is contradictory to reality.

Experimental liquid−liquid equilibrium results in the system methylcyclohexane + methanol were compared to literature values, but these are too incomplete to allow any conclusion to be made.

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Received for review July 18, 2002. Accepted October 7, 2002. This work was supported by the Ministry of Education of the Czech Republic under Grant CB MSM 2234 00008.

JE020135F