Liquid–Liquid Equilibrium of Cyclohexane–*n*-Hexane–Methanol Mixtures: Effect of Water Content

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Experimental liquid–liquid equilibrium data for the ternary system cyclohexane–*n*-hexane–methanol and for the binary systems *n*-hexane–methanol and cyclohexane–methanol are presented over a temperature range from 284 to 298 K at pressure of 0.1 MPa. Attention is given to the effect of the purity of methanol as far as the water content is concerned. The data are correlated by means of excess Gibbs energy models (NRTL and UNIQUAC), and the binary interaction parameters are reported.

Introduction

In recent years much attention has been given to hydrocarbon–alcohol mixtures (*1*, *2*). Thermodynamic properties of such systems are of theoretical interest since hydrogen-bonding effects, present in one component, are diluted by the nonpolar behavior of the other component.

Among the possible hydrocarbon–alcohol systems, the ternary system cyclohexane–*n*-hexane–methanol has been considered by IUPAC as a test system for the comparison of thermodynamic models in equilibrium data correlation because accurate vapor–liquid equilibrium (VLE) data are available in the literature. Unfortunately liquid–liquid equilibrium (LLE) data for the same system have not been measured so far; thus any comparison of models cannot be made. In this context it should be pointed out that LLE data must be considered a more severe test for any thermodynamic model than VLE data. The goal of this investigation is to provide LLE data for binary and ternary systems as a function of temperature from 283.15 to 298.15 K.

The binary systems *n*-hexane–methanol and cyclohexane–methanol exhibit partial miscibility. While a general good agreement among different sets of literature experimental data is encountered for the cyclohexane–methanol system, the data for the *n*-hexane–methanol are scattered. The upper critical solution temperature of this binary system lies, depending upon the data set, between 308.15 and 318.15 K. Consequently, before starting the investigation on the ternary systems, two binary systems have been measured and the resulting data compared with the literature values.

The influence of methanol impurity (water content) on the binary and ternary liquid–liquid equilibria is also studied, and experimental results are presented and discussed.

Apparatus and Materials

Liquid–liquid equilibrium data for ternary and binary systems are measured by using the equilibrium cells described in ref *3*. All the measurements are performed at atmospheric pressure.

The mixtures are equilibrated at the given temperature by agitation with a magnetic stirrer for at least 2 h, followed by a settling period of about 20 h. For each of the two phases, four samples are withdrawn by an hypodermic syringe and the composition is determined via GLC analysis. The syringe was kept at the sample temperature in order to avoid sample modifications.

The mixtures are analyzed by a thermal conductivity gas chromatograph (C. Erba) equipped with a Shimadzu Cromatopac E-1A integrator; a 4-m column packed with Porapak was used. The chromatographic factors are determined from mixtures of known composition, checked by density measurement, representing both phases: the uncertainty in mole fraction is estimated to be ±0.0005 mole fraction.

Mutual solubilities in the binary systems are determined through cloud-point measurements. The experimental setup is similar to that used by Fabries et al. (*4*). The experimental procedure consists of introducing a binary mixture of known composition in an equilibrium cell. The mixture is stirred and the temperature is slowly increased until the phase separation disappears. This event is observed by the diffraction of the light passing through the solution and detected by means of a photoresistor. A different measurement of the miscibility temperature is performed in the cooling sequence, i.e., cooling the sample from temperatures at which a homogeneous mixture is present to temperatures where phase separation occurs. For each composition two heating and cooling sequences are performed. Generally, very good agreement is obtained between the different values detected (always in the range of the experimental error of the measured temperature).

The composition of the binary mixtures is determined from the volumes of methanol and hydrocarbon added to the cell by using hypodermic syringes and checked via GLC; the uncertainty in mole fraction is estimated to be ±0.0005 mole fraction.

The temperature is measured by a quartz thermometer (Battara, Model 2) with a Pt 100 probe. Probe calibration were performed by using a platinum resistance thermometer (Rosemount, Model 162 CE) and checked at the water triple point. The inaccuracy in the equilibrium temperature measurements is ±0.01 K.

An A. Paar densimeter Model 602 (*5*) was used for checking the density of the different chemicals in order to assure the purity before the equilibrium determinations and for determining the composition of the binary mixtures from the volumetric readings. Estimation of the inaccuracy in density measurements is ±0.000 01 g/cm^3.

n-Hexane and cyclohexane were Fluka GLC grade and were used without any other purification. No detectable impurities were found by GLC analysis and by density measurements.

Fluka 99.9 mol % methanol was distilled two times over sodium metal in a 2-m column packed with glass helices (estimated number of stages 150) by using different reflux ratios.

The purity of methanol checked after purification via density measurements was >99.99%.

Special attention was paid to prevent water contamination and oxidation of the chemicals after their purification. *n*-Hexane and cyclohexane were stored in bottles over sodium metal, and methanol was stored over 3A molecular sieves.

Results and Discussion

Binary Systems. One of the most likely explanations for the data scattering of the binary system *n*-hexane–methanol is the presence of water as an impurity in the methanol.

A very accurate method for determining traces of water in methanol is the density check, on account of the relatively big

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Table I. Experimental Densities (g/cm^3) for the System Water–Methanol as a Function of Water Mole Fraction at 298.15 K

x_{H_2O}	δ, g/cm^3	x_{H_2O}	δ, g/cm^3	x_{H_2O}	δ, g/cm^3
0.0000	0.786 65	0.0471	0.794 56	0.2373	0.828 62
0.0123	0.788 81	0.0863	0.801 32	0.3009	0.837 64
0.0227	0.790 54	0.1612	0.814 56	0.3584	0.852 06

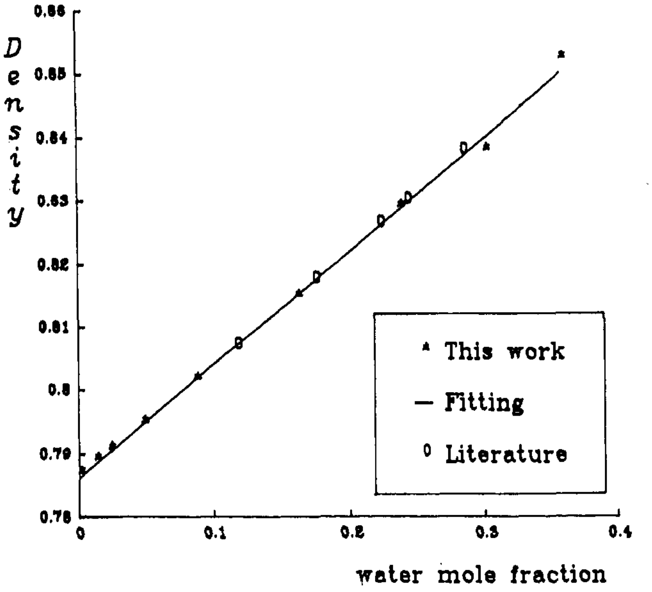

Figure 1. Density (g/cm^3) versus water composition plot for water–methanol system at 298.15 K: comparison with literature data.

difference in density between water and methanol. Table I reports the experimental densities and compositions at 298.15 K and 0.1 MPa measured in this work. All the data, in the methanol-rich region, are measured by preparing synthetic mixtures of water–methanol starting from high-purity components.

Figure 1 reports, as a comparison, data obtained in this work and those of Patel and Sandler (*5*), who determined the density for the same binary mixture in the whole concentration range. The comparison can be performed only over a limited composition range and it is satisfactory: in the composition range investigated by Patel and Sandler there is no effect of the impurity present in the methanol used. They report a density of the purchased methanol of 0.786 846 g/cm^3 that corresponds, on the basis of data here reported, to a purity of 99.9%. This is also in agreement with the original purity of the chemical claimed by Ott et al. (*1*), who investigated LLE for mixtures of hydrocarbons with methanol.

Data of Table I were used to determine the density of purchased methanol (face value 99.9%); the density corresponds to a purity of 99.7%, showing that, even with careful handling, the purity cannot be retained for a long time.

In order to consider the effect of water on the binary system *n*-hexane–methanol, the miscibility gap for this mixture has been determined. Table II reports temperatures and compositions determined by cloud-point determinations. The compositions obtained via GLC analysis of the samples are indicated by footnote *b*: these determinations were performed with the same equilibrium cells employed for studying the ternary mixtures.

Figure 2 shows the experimental data obtained; the agreement among the data from different techniques employed in this work is very good. From these data an upper critical solution temperature of 308.15 K is evaluated. For the sake of comparison, literature data are also reported in Figure 2. The data obtained in the present investigation are in good agreement with those of Kiser (*6*) and with those of Radice (*7*) but only for the solubility of *n*-hexane in methanol. On the other hand, they are in total disagreement with those of Rothmund (*8*), which predict an upper critical solution temperature of 316.5 K, and with those of Radice regarding the solubility of methanol in *n*-hexane. For a better understanding, Figure 2 reports also the data obtained at 293.15 and 298.15 K using methanol to which water (2.67 and 5.32 wt %) has been added. It is very interesting to compare these values with the values of Rothmund: such comparison let us suspect about 2% (weight) water content of the methanol used by this author.

Table II. Experimental Data for the System *n*-Hexane (1)–Methanol (2)

T, K	S_{21}[a]	S_{12}[a]
278.15		12.61
284.15[b]	14.22	14.21
287.15		14.77
288.15[b]	18.44	15.32
290.65	20.46	
293.15[b]	22.91	17.81
295.15		18.48
298.15[b]	29.47	20.97
302.15	34.57	
303.15	36.40	26.50
304.15	38.10	
306.15	48.06	
307.15		44.78

[a] Solubility in mol %. [b] Data measured with the equilibrium cell.

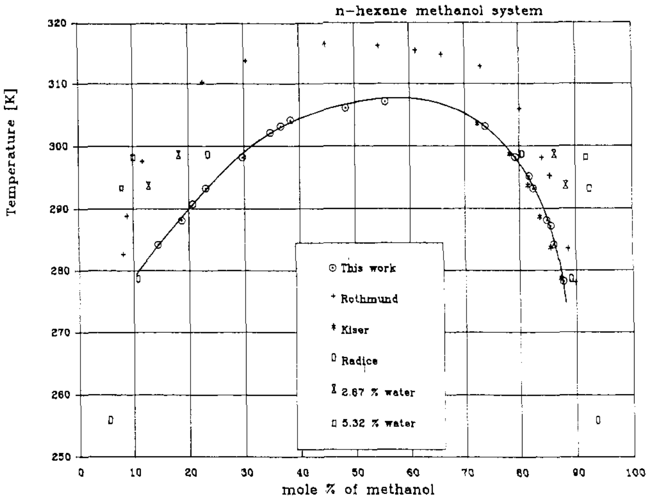

Figure 2. Binary LLE data for the *n*-hexane–methanol system as a function of temperature: comparison with literature data.

A comparison among the data with and without water allows us to conclude that the solubility of *n*-hexane in methanol is less influenced by water with respect to the solubility of methanol in *n*-hexane.

The system cyclohexane–methanol is less sensitive to water content of methanol, as it can be also derived from the good agreement of different sets of data reported in the literature (*9*). Nevertheless, mutual solubility data have been measured for this system and the agreement with literature data was good; the experimental data are reported in Table III.

From the analysis of the binary systems one can conclude that the water present as an impurity in methanol will influence the selectivity of the methanol solvent in the ternary system.

Ternary System. The system was measured at temperatures of 284.15, 288.15, 293.15, and 298.15 K and a pressure of 0.1 MPa. A graphical representation of the experimental data is given in the ternary diagrams of Figures 3–6. The compositions of the measured tie lines are reported in Table III. Table IV reports the LLE data obtained for the same system with the addition of 2.67 and 5.32 wt % water. In

Table III. Ternary LLE Data for the System Cyclohexane (1)-*n*-Hexane (2)-Methanol (3) at Different Temperatures[a]

x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	T, K
0.0000	0.8578	0.0000	0.1421	284.15
0.2611	0.6008	0.0502	0.1037	
0.4754	0.3814	0.0960	0.0565	
0.5583	0.3112	0.1007	0.0484	
0.6333	0.2501	0.1136	0.0339	
0.7398	0.1556	0.1131	0.0256	
0.9113	0.0000	0.1325	0.0000	
0.0000	0.8156	0.0000	0.1532	288.15
0.2365	0.5819	0.0573	0.1020	
0.4612	0.3897	0.1062	0.0660	
0.5483	0.3076	0.1189	0.0490	
0.6106	0.2522	0.1283	0.0401	
0.7197	0.1542	0.1452	0.0233	
0.9034	0.0000	0.1640	0.0000	
0.0000	0.7709	0.0000	0.1781	293.15
0.2251	0.5507	0.0637	0.1064	
0.4286	0.3619	0.1120	0.0668	
0.5228	0.2874	0.1332	0.0509	
0.5924	0.2259	0.1465	0.0393	
0.6851	0.1420	0.1580	0.0231	
0.8926	0.0000	0.1676	0.0000	
0.0000	0.7053	0.0000	0.2097	298.15
0.2107	0.5114	0.0661	0.1271	
0.4116	0.3422	0.1191	0.0813	
0.4878	0.2744	0.1362	0.0612	
0.5394	0.2286	0.1447	0.0497	
0.6489	0.1395	0.1570	0.0269	
0.8703	0.0000	0.1825	0.0000	

[a] Data in mole fraction.

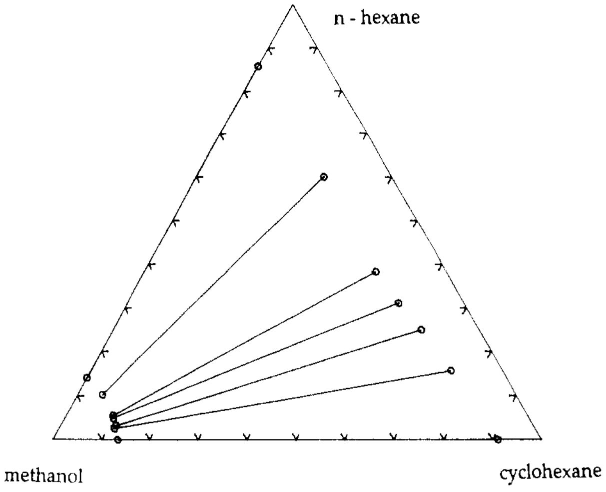

Figure 3. LLE data for the ternary system at 284.15 K.

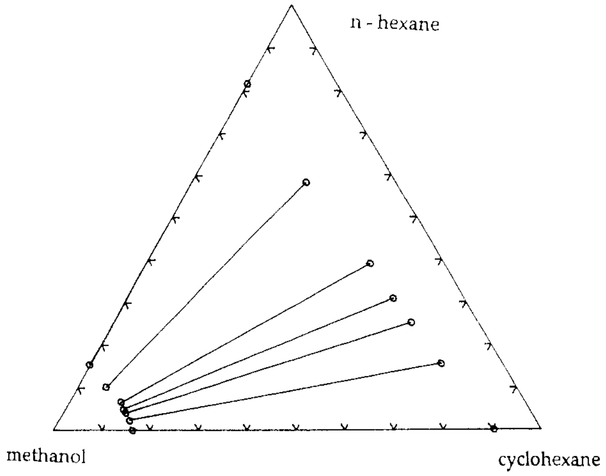

Figure 4. LLE data for the ternary system at 288.15 K.

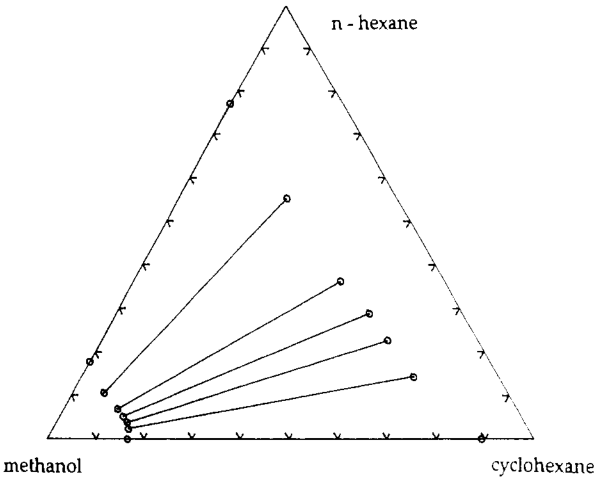

Figure 5. LLE data for the ternary system at 293.15 K.

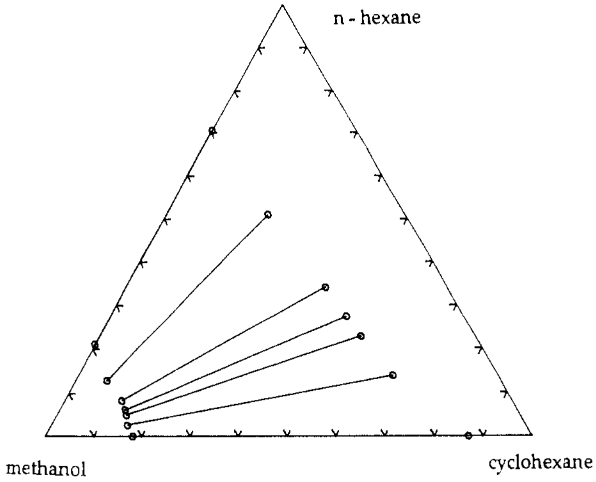

Figure 6. LLE data for the ternary system at 298.15 K.

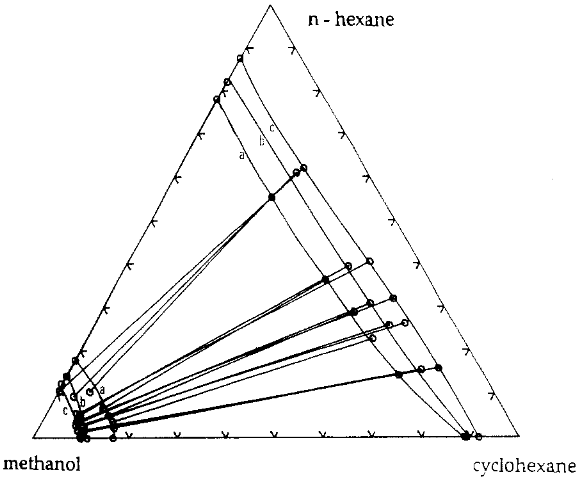

Figure 7. LLE data for the ternary system at 293.15 K: comparison between experimental data at different water content (a = 0.0, b = 2.67, and c = 5.32 wt %).

these cases the quaternary systems are considered as pseudoternary systems and the compositions are given on the water-free basis.

The effect of temperature and of water content (as an impurity in methanol) is investigated in the ternary system. The system (type 2) increases the miscibility region for increasing temperature. Figure 7 shows clearly how water influences the LLE: the effect is particularly evident in that part of the isotherm

Table IV. Ternary LLE Data for the System Cyclohexane (1)-*n*-hexane (2)-Methanol (3) at Different Temperatures and Different Water Content[a]

x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	T, K
		2.67 wt % Water		
0.0000	0.8760	0.0000	0.1220	293.15
0.2571	0.6186	0.0012	0.1070	
0.4977	0.4031	0.0619	0.0571	
0.5870	0.3188	0.0719	0.0391	
0.6382	0.2622	0.0750	0.0275	
0.7593	0.1562	0.0870	0.0142	
0.9178	0.0000	0.0987	0.0000	
0.0000	0.8216	0.0000	0.1420	298.15
0.2471	0.6094	0.0363	0.0960	
0.4594	0.3931	0.0702	0.0548	
0.5458	0.3080	0.0786	0.0379	
0.6096	0.2578	0.0897	0.0289	
0.7255	0.1550	0.0968	0.0158	
0.8898	0.0000	0.1118	0.0000	
		5.32 wt % Water		
0.0000	0.9250	0.0000	0.0788	293.15
0.2739	0.6401	0.0216	0.0599	
0.5116	0.4202	0.0412	0.0402	
0.6001	0.3260	0.0464	0.0247	
0.6720	0.2740	0.0548	0.0200	
0.7787	0.1637	0.0584	0.0076	
0.9447	0.0000	0.0708	0.0000	
0.0000	0.9033	0.0000	0.0842	298.15
0.2930	0.6369	0.0237	0.0611	
0.5037	0.4131	0.0457	0.0352	
0.6012	0.3223	0.0504	0.0222	
0.6681	0.2769	0.0582	0.0169	
0.7672	0.1602	0.0666	0.0097	
0.9387	0.0000	0.0782	0.0000	

[a] Data in mole fraction on a water-free basis.

relative to the hydrocarbon phase. This is perfectly in agreement with what one can expect from the analysis of binary data.

Data Treatment

The experimental data are correlated with NRTL (*10*) and UNIQUAC (*11*) models by using a computer program developed by Sørensen and described elsewhere (*12*). Both models are based on the local composition concept and have been applied so far for describing liquid–liquid equilibrium data. They contain two adjustable parameters per binary which can be determined either from binary data or from ternary data.

In this case the data correlation is performed on ternary data by an objective function written in terms of concentrations in the two phases. A penalty function is included in order to prevent unreasonably high numerical values of the parameters. Table V reports the parameters and the standard deviations obtained in the fitting.

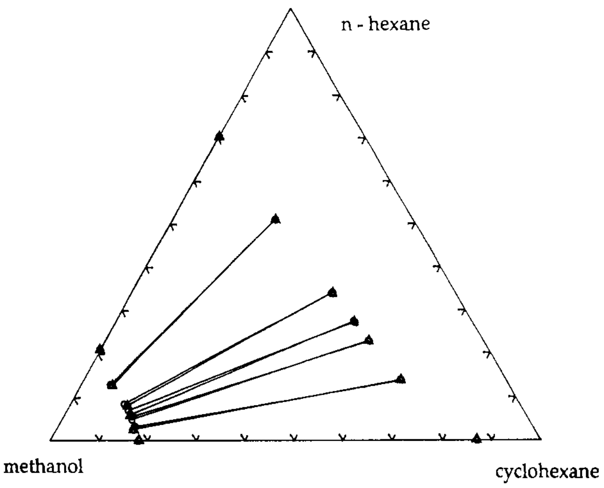

Figure 8. Comparison between experimental (O) and calculated (Δ) data by NRTL model for the ternary system at 298.15 K.

The results are compared on the basis of the root-mean-square deviations (rmsd) defined as

$$\text{rmsd} = [\textstyle\sum_k \min \sum_i \sum_j (x_{ijk}{}^{\text{calcd}} - x_{ijk}{}^{\text{exptl}})^2/6M]^{1/2} \qquad (1)$$

$$i = 1, 2, 3; \quad j = \text{I}, \text{II}; \quad k = 1, ..., M$$

A small value of rmsd assures a good correlation of mole fraction and a good representation of the binodal curve; the slope of the tie lines is also given with a satisfactory degree of accuracy. An example of graphical comparison between the calculated (NRTL model) and experimental tie lines and miscibility gap is reported in Figure 8.

The rmsd values are substantially lower when individual fitting is performed. This means that the intrinsic temperature dependence of the model is not sufficient to take into account the strong temperature effect in the equilibrium data. Better results could be obtained by using an explicit temperature dependence of the parameters.

It is not surprising that the parameters obtained in the individual fitting are in some cases different from the ones obtained in the global fitting. In fact, it is well-known that different sets of model parameters give more or less the same rmsd and a local minimum is reached rather than another depending upon the minimization procedure.

Conclusions

Ternary data for the system cyclohexane–*n*-hexane–methanol and mutual solubility data for the binary systems *n*-hexane–methanol and cyclohexane–methanol have been measured in the temperature range 284.15–298.15 K at atmospheric

Table V. Root-Mean-Square Deviation (rmsd) and Model Parameters from Experimental Data Fitting

		model parameters, K					
T, K	rmsd	$CyC_6/n\text{-}C_6$		$CyC_6/MeOH$		$n\text{-}C_6/MeOH$	
				NRTL			
284.15	0.541	−305.9	500.45	535.3	353.69	421.62	447.04
288.15	0.367	−564.6	1303.4	537.34	310.61	547.25	456.66
293.15	0.455	−554.9	1122.7	470.14	348.34	447.61	496.96
298.15	0.415	67.29	0.062	409.95	406.41	220.20	567.98
a	1.498	−515.9	1452.4	451.22	364.70	527.08	504.25
				UNIQUAC			
284.15	0.489	338.64	−235.5	678.68	−235.5	604.51	10.988
288.15	0.400	15.228	−11.30	640.02	1.8262	554.91	19.517
293.15	0.499	−41.26	53.852	593.87	7.1449	530.17	27.587
298.15	0.489	848.00	−436.7	898.32	−29.63	508.74	22.410
a	1.324	956.69	−420.8	966.14	−16.22	529.54	20.418

[a] Results obtained by fitting all isotherms together.

pressure. Particular attention has been given to the effect of water as an impurity in methanol, and evidence is given on how a small amount of water strongly influences LLE data for both binary and ternary systems.

The experimental data have been successfully correlated by NRTL and UNIQUAC models, and the interaction parameters were found to be temperature dependent.

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Glossary

rmsd	root-mean-square deviation defined in eq 1
x	liquid composition mole fraction
M	number of tie lines
T	temperature, K
S_{ij}	Solubility of component i in component j, mol %
δ	density, g/cm^3

Registry No. MeOH, 67-56-1; hexane, 110-54-3; cyclohexane, 110-82-7.

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Measurement of γ^∞ Using Gas–Liquid Chromatography. 3. Results for the Stationary Phases 10-Nonadecanone, *N*-Formylmorpholine, 1-Pentanol, *m*-Xylene, and Toluene

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In order to extend the range in which gas–liquid chromatography (GLC) can be used to measure activity coefficients at infinite dilution (γ^∞) to include more volatile stationary phases, we have constructed a modified gas chromatograph. Transport of solvent out of the column, which is the most significant error in the determination of γ^∞ by the GLC method, has been minimized by including thermostatic control accurate to 0.05 K, as complete as possible a saturation of the carrier gas with solvent, and a reduction of the pressure drop across the chromatographic separation column. The efficiency of the apparatus has been determined by comparison of our own measurements using the stationary phases 10-nonadecanone and *N*-formylmorpholine (NFM) with data from the literature. Results with the lighter solvents 1-pentanol, *m*-xylene, and toluene (at three temperatures in each case) are also reported. The vapor pressures of these solvents at measuring conditions lie between ca. 5 and ca. 80 mbar. The error in γ^∞ increases with increasing solvent volatility from 3% for nonvolatile stationary phases to ca. 10% for volatile solvents.

Introduction

Activity coefficients at infinite dilution are of interest for the development of liquid theories and are of great importance for the development and simulation of thermal separation processes. It is possible to estimate the variation of the activity coefficients across the complete concentration range with the help of a suitable thermodynamic model when only information on both boundary activity coefficients of a binary system is available: thus the vapor–liquid equilibrium (VLE) can be predicted.

The boundary activity coefficients γ^∞ (*1*), as well as VLE (*2*) and mixing enthalpy (*3*) data, serve as a database for the further development of liquid theories (in particular group contribution methods (*4*, *5*)). Activity coefficients at infinite dilution are of practical importance in the design of thermal separation plants for the production of very pure products. In particular the removal of the last traces of an impurity often requires a considerable amount of separation effort. Apart from ebulliometry, dilutor technique, and liquid–liquid chromatography, gas–liquid chromatography (GLC) is a rapid and exact method for the experimental determination of activity coefficients at infinite dilution. The calculation of these values by extrapolation from VLE measurements is subject to considerable errors. The GLC method normally involves the measurement of the retention of a sample of high vapor pressure at quasi-infinite dilution (solute) on a stationary phase (solvent) of very low vapor pressure.

In continuation of work carried out by Weidlich et al. (*6*, *7*) the present article deals with measurement of solutes on the technically more interesting, more volatile solvents using a gas chromatograph constructed by us.

The design of the gas chromatograph requires that the various elements be chosen on the basis of the tolerable degree of error. We were able to refer to an extensive literature dealing with gas chromatography in the measurement of thermodynamic quantities (*8*–*11*). Another apparatus also constructed specially for the requirements of the measurement of more volatile solvents has been described by Eckert et al. (*12*).

The number of systems whose activity coefficients at infinite dilution can be determined by using this modified technique is

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