Liquid−Liquid Coexistence Curves for Binary Systems: Methanol + Cyclohexane and + Several Isomers of Hexane

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Experimental liquid−liquid miscibility temperatures as a function of mole fraction are reported for binary systems formed by methanol as common component with hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, and cyclohexane. All the studied coexistence curves present an upper critical solution temperature (UCST). The UCST of the binary systems presents a clear dependence with the molecular shape of the hydrocarbons (e.g., the solubility of the alkanes in methanol increases as branching increases in the structural isomers); hence, 2,2-dimethylbutane shows the lowest UCST with methanol. Cyclohexane presents the highest UCST with methanol (i.e., it shows the lowest mutual miscibility for the six studied systems). Values of the UCST have been calculated with the Weimer−Prausnitz modification for polar components of Hildebrand's Regular Solutions Theory. The predicted UCSTs compare well with those obtained experimentally.

Introduction

Methanol (methyl alcohol) is a versatile chemical widely used in research laboratories and in many industries. For example, in the petroleum industry methanol can be used in several stages of natural gas processing (e.g., in dehydration plants and gas sweetening processes). In the dehydration process, for temperatures lower than about 277 K, glycol injection is impractical because of the high viscosity of glycol solutions; then methanol is the best option as solvent.[1] Gas purification processes use methanol as an option for sweetening sour gas streams, and in fact it was the first commercial process to use a physical organic solvent. Methanol reduces acid gases (e.g., hydrogen sulfide and carbon dioxide) so that they appear in concentrations of just a few parts per million (i.e., mg/kg) in the treated hydrocarbon-rich gas.[1] Methanol is still widely used as a hydrate inhibitor in very low temperature applications such as in turbo expanders for gas refrigeration plants of LPG recovery. Methanol can be easily produced from natural gas. Additionally, methanol is a raw material for the production of *tert*-butyl methyl ether, the latter being an oxygenated compound that is extensively used in several countries to be blended with gasoline to enhance the octane number. Furthermore, methanol has been used as a gasoline substitute in cars and also as an oxygenated compound in the reformulation of gasoline. Methanol as a fuel for fuel cells is a subject of great interest; hence, large efforts are devoted to applications in transport and portable electronics applications due to the clear advantages for the protection of the environment.[2−4]

Owing to the evident importance of methanol in both the scientific and technological fields, it is necessary to carry out systematic studies on the thermodynamic properties of pure methanol and its mixtures with other selected compounds as well as phase equilibria for systems in which methanol is one of the components. Liquid−liquid phase equilibria and the miscibility behavior for methanol + hydrocarbon systems at 0.1 MPa have been studied extensively for binary, ternary, and multicomponent systems. After a comprehensive bibliographic search, we found that the following systems have been reported: methanol + hexane, + nonane, + decane;[5] methanol + hexane;[6−8] methanol + cyclohexane;[7−18] methanol + heptane, + octane;[8,19] methanol + 2-methylpentane, + 2,2-dimethylbutane, + 2,3-dimethylbutane, + 3-methylheptane, + 2,2,4-trimethylpentane, + nonane, + 2,3,5-trimethylhexane, + decane, + cyclopentane, + methylcyclopentane, + methylcyclohexane;[8] methanol + pentane, + heptane, + nonane, + undecane;[20] methanol + butane, + pentane;[21] methanol + pentane, + hexane, + heptane, + octane;[22] methanol + water + hexane;[23] methanol + 2,2,4-trimethylpentane + *o*-xylene, + *m*-xylene, + ethylbenzene;[24] methanol + cyclohexane + hexane;[7] methanol + water + 2,2,4-trimethylpentane + benzene.[25]

Furthermore to the experimental results that each paper reports on the liquid−liquid behavior of the particular systems considered, some of the above works include useful tabulations to carry out comparisons with data from previous work, which contributes to, in some cases, a relatively large set of results to establish if more results are necessary for some systems. Unfortunately, some works include comparisons between experimental results only in figures, which are not the most adequate mean to establish the reproducibility of the data among different workers. Also, some works performed extrapolations of pressure−temperature isopleths through the use of empirical correlations to obtain liquid−liquid phase equilibria data at 0.1 MPa from experimental results that were obtained at higher values of pressure. Some comparisons that were carried out in tables are given by the following: Hölscher et al.[5] include values of the critical solution temperature T_c at 0.1 MPa for methanol + hexane, + heptane, + octane, + nonane, and + decane from different works published before 1986; some of those reports go back to the end of the nineteenth century and the first half of the twentieth century. Kiser et al.[8] give a comparison of T_c for eight different hydrocarbons with methanol. It is important to underscore that in this comparison, apart from the values reported by Kiser et al., no previous data were included for the binaries of methanol + 3-methylpentane, + 2,2-dimethylbutane,

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and 2,3-dimethylbutane. Singh and Van Hook[9] summarized 14 values of T_c for methanol + cyclohexane from 1926 up to 1986. Aizpiri et al.[15] include in their work a summary of 16 reported critical mole fraction x_c values for the latter system from 1930 up to 1988.

From the analysis of the different systems studied in the open literature, it is observed that the lineal saturated hydrocarbons are the most studied compounds in binary systems with methanol. This result could lead to think that there are quite a lot of results that fully define the liquid−liquid phase diagrams for all the reported systems, particularly for binary systems; however, some works only report a few tie-lines or a few points of coexistence temperature−mole fraction results since their main objective was the study of thermodynamic properties above the partial miscibility region or the phase diagram of ternary or multicomponent systems. Consequently, in some works the phase diagram for the binary systems is not completely defined, and no values of T_c are reported.

One of the systems whose liquid−liquid phase diagram has been extensively studied is methanol + cyclohexane. This is mainly due to its very special properties as discussed by Aizpiri et al.,[15] which make this system very adequate to test the concept of critical point universality on binary liquid mixtures. This system has even been considered to be a very adequate example for the study of phase diagrams by students in a teaching laboratory.[16]

The bibliographic search on liquid−liquid phase diagrams also revealed that up to now very few system have been studied that include as one of the components a saturated branched hydrocarbon. The only report found that includes experimental results for the coexistence temperature of methanol + a branched hydrocarbon is that by Kiser et al.[8] Among several different hydrocarbons, six branched hydrocarbons were individually studied with methanol, including 2-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane, which are studied in the present work. It is however rather unfortunate that these authors present all their experimental T, x results in plots that do not allow the values to be obtained with the accuracy that the authors reported: ± 0.2 K for the unmixing temperatures and ± 2 % for the solubilities. The results that Kiser et al. present in a table are a limited number of solubility values of the different studied hydrocarbons in the methanol-rich phase at rounded values of temperature in the range (278 to 313) K, which seem to have been interpolated from a set of experimental results.

From the analysis of the T, x values for the liquid−liquid phase behavior of the systems already mentioned, it has been concluded that there is lack of reproducibility among the results from different laboratories for a given system, and as noted by Singh and Van Hook,[9] even batch-to-batch results from the same laboratory often do not agree to any better than ± 0.1 K. This statement overestimates the reproducibility of T_c for some systems as will be shown below. Therefore, to contribute with T, x results for binary system for which no numerical results are available, we have studied the systems composed of methanol as the common component with the structural isomers of hexane: 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane. We have also studied the systems methanol + hexane and + cyclohexane in order to have a set of internally consistent experimental results.

This work is a continuation of a research program carried out in our laboratory on the behavior of the phase equilibria of highly nonideal systems. A part of the program has considered the study of polar organic solvents to be used for the efficient and selective separation of multicomponent mixtures by absorption and by liquid extraction. In the latter case, it has included the experimental study of liquid−liquid coexistence curves and the liquid−liquid equilibrium for systems composed of polar and nonpolar components of scientific and industrial interest.[20,24−29] In this report, measurements of liquid−liquid miscibility temperatures as a function of mole fraction are presented to define the corresponding coexistence curve for several binaries of the type methanol + hexane isomer, where the studied structural isomers are hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane. We have also included cyclohexane in the study in order to study the influence of molecular shape of the hydrocarbons on their miscibility behavior in methanol. All the binary systems formed by methanol as common component individually with each of five isomers of hexane and with cyclohexane show a liquid−liquid coexistence curve with upper critical solution temperature (UCST), which defines the minimum temperature at which a system achieves total miscibility in the whole concentration range. Since the UCST is a point of particular interest, we have used the Weimer−Prausnitz version of the Regular Solution Theory using pure component property data and one binary parameter to calculate the UCST values for the six systems studied in this work.

Experimental Procedures

Methanol was obtained from Baker (HPLC grade) with mole fraction purity higher than 99 %. The hydrocarbons were obtained from different sources with the following mole fractions: hexane (*n*-C6) > 99.0 % was obtained from Merck; 2-methylpentane (2-MP) 99+ % and 2,2-dimethylbutane (2,2-DMB) 98 % were from Aldrich; 3-methylpentane (3-MP) 99+ % and 2,3-dimethylbutane (2,3-DMB) 97 % were from Phillips; and cyclohexane (*c*-C6) 99.5 % was from Baker.

Due to the fact that the water is the most likely impurity and the one most difficult to remove from methanol, the latter was twice distilled in an all-glass apparatus with high reflux ratio and stored over a molecular sieve. Furthermore, the water content in methanol was monitored along the study using a Karl Fischer titration apparatus, Photovolt Aquatest 8. The maximum water content in mass fraction found in methanol was 3×10^{-3} %. All hydrocarbons were used without further purification other than storing over sodium to remove any possible traces of moisture. Chromatographic analyses were carried out on each sample of hydrocarbon, and only one peak was detected for each sample using a thermal conductivity detector.

Binary systems of known mole fraction were prepared by mass in an analytical balance with a precision and accuracy of ± 0.0001 g; hence, the uncertainty in mole fraction is ± 0.0001. Liquid−liquid miscibility temperature−concentration values were determined using sealed all-glass cells. All the samples were thoroughly degassed by freeze−pump−thaw cycles in a high vacuum manifold. Full details of the experimental method together with dimensions of the different cells have been reported earlier in several of the cited works from our laboratory.[20,28,32] Miscibility temperatures were determined visually as the temperature slowly increased in the water bath (i.e., the systems were studied from the two-liquid phase region up to the transition to observe complete miscibility). Near the solubility temperature, the heating rate was about 0.03 K·min^{-1} in order to clearly observe the onset of mixing, which was marked by the well-known phenomenon of critical opalescence. Two stainless steel ball-bearings were placed inside each glass cell for stirring of the system during measurements. A minimum of

Table 1. Experimental Coexistence Temperature−Mole Fraction Results for the Binaries x_1 Methanol + (1 − x_1) Hydrocarbon Systems, at 0.1 MPa

x_1	T/K	x_1	T/K	x_1	T/K
hexane		2-methylpentane		3-methylpentane	
0.1403	294.39	0.1516	291.88	0.1620	290.60
0.2119	305.03	0.2554	300.87	0.2492	303.24
0.3009	312.03	0.2852	303.57	0.2854	300.85
0.3539	312.15	0.3613	302.45	0.3451	305.35
0.3947	314.86	0.4052	304.06	0.3994	307.83
0.4091	314.39	0.4946	305.76	0.4344	305.04
0.4355	313.09	0.5442	303.69	0.4930	305.38
0.4509	311.83	0.5993	302.99	0.5457	304.31
0.4907	313.41	0.6462	302.89	0.5943	304.07
0.4941	314.41	0.7042	300.86	0.6991	300.99
0.5532	311.05	0.7995	292.46	0.8001	291.46
0.5498	310.96				
0.6545	310.27				
0.7545	305.63				
2,2-dimethylbutane		2,3-dimethylbutane		cyclohexane	
0.1516	289.49	0.1552	296.68	0.1471	308.36
0.2372	290.26	0.2529	295.43	0.2503	317.36
0.3128	292.07	0.2905	298.42	0.3018	319.24
0.3536	295.80	0.3470	298.74	0.3553	320.86
0.3967	293.04	0.4030	298.87	0.4040	322.22
0.4010	291.37	0.4494	296.86	0.4578	321.53
0.4429	292.81	0.4988	298.89	0.5082	321.64
0.5046	291.76	0.5507	297.38	0.5582	321.36
0.5487	291.26	0.6050	297.33	0.6008	321.30
0.5982	290.98	0.6410	296.16	0.7015	319.09
0.6502	289.23	0.7015	294.54	0.8019	306.28
0.8036	274.70	0.8051	283.42		

10 binary systems of known concentration were studied to define the liquid−liquid coexistence curves of each pair of components. The measurement of temperature was carried out with a Systemteknik AB digital thermometer and a platinum resistance probe with a precision of ± 0.001 K. Readings from this thermometer in the studied temperature range were compared with those from a calibrated thermometer of Automatic System Laboratories (ASL) whose accuracy is ± 0.005 K, traceable to the U.S. National Institute of Standards and Technology. The reproducibility of the mixing temperatures was ± 0.01 K, which we take as the total uncertainty for the mixing temperatures. Furthermore, the reported miscibility temperatures are an average of four determinations carried out on each studied binary system of known mole fraction.

Results and Discussion

The experimental miscibility temperature−mole fraction (T, x) results are listed in Table 1 and plotted all together in Figure 1. The different symbols in Figure 1 correspond to the experimental results, and the lines were obtained by correlating the experimental values with eq 1. The coexistence T, x curves also contain the experimentally derived UCST of each system, which is indicated with the same symbol as the rest of the experimental values in each system although larger.

As discussed above, the methanol + cyclohexane system has been studied previously by several workers.[7−18] In most of those works, the main emphasis has been given to the study of the coexistence curve very close, within a few degrees, to the liquid−liquid critical temperature T_c to describe the critical region using the parametric equation of state. Also, several works have studied with great detail the effect of dissolved gas and liquid impurities on T_c of methanol + cyclohexane.[9,30,31] The effect of pressure on the coexistence curve of methanol + cyclohexane has also been studied[15,17,18] in a relative large range of pressure. The dependence of T_c on isotopic dilution of each of the components of the system methanol + cyclohexane has also been studied.[18] A summary[9] of T_c values at 0.1 MPa reported for the methanol + cyclohexane system up to 1986 shows a wide range of values; hence, the authors concluded that reproducibility among different works had not been adequate.

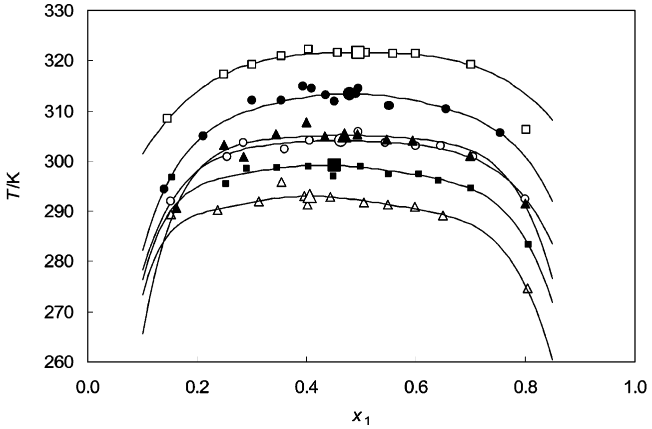

Figure 1. Liquid−liquid miscibility behavior for six x_1 methanol + (1 − x_1) hydrocarbon systems. Symbols represent experimental T, x values; curves are calculated with eq 1 and the coefficients in Table 4. The UCST of each system is indicated with a larger symbol: ●, hexane; ○, 2-methylpentane; ▲, 3-methylpentane; △, 2,2-dimethylbutane; ■, 2,3-dimethylbutane; □, cyclohexane.

The UCST of the methanol + hexane system has been reported by several workers. The 13 different values that had been reported up to 1986 were included in Table 4 of the paper by Hölscher et al.[5] The reported values of the UCST are in the range (301.3 to 315.8) K, altogether those values give a mean of 310.6 K with a standard deviation of 4.9 K. The comparison of UCST values in the work of Kiser et al.[8] for methanol + hexane included 11 values from different authors; five of these values were not included in the review of Hölscher et al.[5] The mean of the 11 values is 310.6 K with a standard deviation of 4.4 K. These two examples show, as mentioned above, that the lack of reproducibility of experimental results from different laboratories is much larger than ± 0.1 K, indeed it is of several degrees.

A profuse number of works have also been published in the open literature in which the liquid−liquid solubility behavior of binary systems that present an UCST is analyzed as a function of the molecular size of the nonpolar component of the studied systems. Hence, the different members of a homologous series of nonpolar compounds (e.g., saturated unbranched chain hydrocarbons) are always most adequate to obtain conclusions on the aforementioned functionality. The behavior of systems that contain methanol + an unbranched chain hydrocarbon has also been discussed in terms of the chain length of the nonpolar component.[5,19−21,27,29] In this work, to investigate the influence of the molecular structure of the saturated hydrocarbon on the liquid−liquid solubility of binary systems, we have studied several binaries of the type methanol + cyclohexane and + hexane structural isomers.

It is well-known that the nature of the pure components that constitute a mixture has a clear influence on the mixture properties. The liquid−liquid miscibility phenomenon is not the exception; therefore, the miscibility in methanol of a linear alkane (e.g., hexane) is different with respect to the miscibility observed for a cyclic hydrocarbon with an equal number of carbon atoms in its molecule (i.e., cyclohexane). The experimental results in Table 1 and Figure 1 show that the miscibility of hexane in methanol is higher than that of cyclohexane;

Table 2. Molar Volume V, Enthalpy of Vaporization $\Delta_{vap}H$, and Total δ, Nonpolar λ, and Polar τ Solubility Parameters Values for Methanol and Saturated Hydrocarbons at 298.15 K

	V^a	$10^{-3}\,\Delta_{vap}H^a$	δ	λ	τ
substance	$cm^3 \cdot mol^{-1}$	$J \cdot mol^{-1}$	$J^{1/2} \cdot cm^{-3/2}$	$J^{1/2} \cdot cm^{-3/2}$	$J^{1/2} \cdot cm^{-3/2}$
CH_3OH	40.733	37.430	29.71[b]	16.38[b]	24.79[b]
n-C6	131.598	31.551	14.87[c]		
c-C6	108.752	33.045	16.77[c]		
2-MP	132.884	29.865	14.36[c]		
3-MP	130.620	30.275	14.58[c]		
2,2-DMB	133.721	30.422	14.46[c]		
2,3-DMB	131.165	29.125	14.26[c]		

[a] Riddick and Bunger.[35] [b] Weimer and Prausnitz.[33] [c] Calculated with $\delta = \sqrt{\Delta H^V - RT/V}$.

therefore, the UCST (see Table 3) for the first system is lower than that for the second system. Also, the position of a methyl group in the main skeleton of the paraffinic hydrocarbon changes the hydrocarbon mutual solubility with methanol. The higher degree of branching in a structural hydrocarbon isomer increases its solubility with respect to other isomers. It can be observed from the experimental T, x values in Table 1 and the coexistence curves in Figure 1 that the solubility of 2,2-dimethylbutane and 2,3-dimethylbutane, hydrocarbons isomers with two methyl groups, is greater than that for the two methylpentanes considered here (i.e., 2-methylpentane and 3-methylpentane); therefore the two dimethylbutanes present lower UCST with methanol than the linear isomer and than the other two studied structural isomers with one methyl group in their chain.

It can be observed in Table 3 that the UCST values are sensitive enough to the position of the methyl substituents in the hydrocarbon molecule since the position of the methyl group in carbon 2 or in carbon 3 of the methylpentanes gives a difference in the corresponding UCST of 1 K. Also, two methyl groups in carbon 2 give an UCST which is 6 K lower than that for the isomer with methyl groups in carbons 2 and 3 in the dimethylbutanes. It is then possible to infer that the branching of the hexane structural isomers allows easier and more intensive molecular interactions with methanol; thus the molecular interactions are more favorable for the dimethylbutanes than for the methylpentanes, and these are in turn greater than those present between molecules of hexane and methanol. The same behavior has also been observed for the same isomers studied here in binary systems with ethanenitrile as the common component.[27]

The experimentally derived values of the UCST included in Table 3 were obtained through a fit of experimental T, x mutual miscibility results to the following expression:[27−29]

$$T/\mathrm{K} = \sum_{i=0}^{3} A_i \left(\frac{\dfrac{x_1}{B} - \dfrac{x_2}{1-B}}{\dfrac{x_1}{B} + \dfrac{x_2}{1-B}} \right)^{2i} \tag{1}$$

where T and x_i are experimental results; A_i and B are adjustable parameters to be determined.

By means of the above equation, it is obtained that for a set of T, x results of a given binary system the value of A_0 is equal to the UCST and B corresponds to the critical mole fraction x_1^c. Values of the parameters determined by the least-squares method are given in Table 4 together with the value of the standard deviation σ of each fit for the six systems studied here. The curves in Figure 1 were calculated with the values of the reported coefficients for each binary.

Table 3. Experimental and Calculated Values of the UCST for Systems Formed by Methanol + Hydrocarbon

	UCST/K		
CH_3OH +	exptl	calcd[a]	calcd[b]
n-C6	313.42	526.3	317.5
2-MP	304.05	535.4	325.9
3-MP	305.09	528.8	320.5
2,2-DMB	293.02	535.0	325.0
2,3-DMB	299.20	534.6	326.1
c-C6	321.62	482.6	287.9

[a] Calculated with eq 2 using $\psi_{12} = 0.396\ \tau_1^2$ from Prausnitz and coworkers.[33,34] [b] Calculated with eq 2 using $\psi_{12} = 0.438\ \tau_1^2$ from the correlation of experimental UCST of four methanol + saturated chain hydrocarbon systems, as discussed in the main text.

Table 4. Adjusted Coefficients of Equation 1 and Standard Deviation of Each Fit

methanol +	no. of points	B	A_0	A_1	A_2	A_3	σ/K
n-C6	7	0.4794	313.42	−25.817	26.610	−108.89	0.32
2-MP	8	0.4628	304.05	−9.7521	−11.390	−74.907	0.48
3-MP	9	0.4684	305.09	−8.1127	1.6709	−160.89	1.04
2,2-DMB	9	0.4057	293.02	−27.036	92.808	−218.57	0.35
2,3-DMB	8	0.4287	299.16	−21.352	59.669	−174.21	0.27
c-C6	9	0.4959	321.62	−8.1050	−42.018	7.7280	0.16

Since the complexity of the molecular interactions present in the liquid phase for systems that exhibit partial miscibility has proved to be a difficult problem for the theories of the liquid state, it is highly desirable to use the present experimental UCST results as a test for one of such theories. Therefore, we have calculated UCST values for the six systems considered here with the well-known modification of Weimer and Prausnitz[33] to the solubility parameter version of the Regular Solution Theory.[34] This theory uses pure component data and only one parameter derived from mixture information, that is, there are no adjustable parameters. The theory has been used successfully in previous works from our laboratory[27,29,32] for the prediction of the UCST of binary systems of the same type as studied here (i.e., polar + nonpolar systems).

UCST/K data were calculated with the following relation given by the mentioned theory:

$$\mathrm{UCST} = 2\left[\frac{(\lambda_1 - \delta_2) + {\tau_1}^2 - 2\psi_{12}}{R}\right]\left[\frac{V_1 V_2}{V_1^{1/2} + V_2^{1/2}}\right]^2 \tag{2}$$

where λ_1 is the nonpolar contribution of the total solubility parameter ($\delta_1 = \lambda_1^2 + \tau_1^2$) for the polar component, τ_1 is the polar contribution of the total solubility parameter δ_1 for the polar component, δ_2 is the total solubility parameter of the nonpolar component, V_i is the molar volume of component i, and ψ_{12} is an induction energy density arising from induction forces between the polar and the nonpolar components. The molar volume,[35] enthalpy of vaporization,[35] and total δ, nonpolar λ, and polar τ solubility parameters[33] values for methanol and the studied hydrocarbons are included in Table 2.

Weimer and Prausnitz studied experimental activity coefficients of saturated hydrocarbons, olefins, and aromatics infinitely diluted in different polar organic solvents and proposed general empirical relations over the temperature range (273 to 373) K for the induction energy density ψ_{12} between the polar and the nonpolar components: $\psi_{12} = 0.396\tau_1^2$ for saturated hydrocarbons (normal paraffins and cycloparaffins), $\psi_{12} = 0.415\tau_1^2$ for olefins (1-pentene), and $\psi_{12} = 450\tau_1^2$ for aromatics (benzene).[21,22] However, there are not reported values of ψ_{12} from systems in which the polar component is methanol. Nonetheless, we obtained calculated values of the UCST with eq 2 for the six binaries studied here using the properties given in Table 2 together with $\psi_{12} = 0.396\tau_1^2$. The calculated UCST values are given in Table 3. It can be observed that the solubility parameter theory overestimates the UCST for all the studied systems. The mean absolute relative error is 71 % for the six calculated values.

To test the theory using a value of ψ_{12}, which were obtained from information that included methanol as one of the components, we have taken experimental UCST values reported in the literature for four binaries that include methanol as the polar component and as nonpolar components members of the saturated hydrocarbon homologue series (pentane, heptane, nonane, and undecane)[20] to obtain in this work the relation $\psi_{12} = 0.438\tau_1^2$. This value reproduced the experimental UCST with a mean absolute relative error of 3.8 %, which is equal to a standard deviation of 16 K for the four systems reported in the literature.[20] Introducing the derived value of ψ_{12} in eq 2, we have obtained a new set of UCST values for the binaries studied here, also included in Table 3. It can now be observed that the theory gives a close quantitative prediction of the experimental UCST values for the six studied systems using pure component parameters and only one mixture parameter, which was obtained from independent measurements. However, it is observed that the theory does not reproduce the observed effect of the position and number of methyl groups in the branched hydrocarbons on the experimental UCST.

Conclusions

In the systems studied here (i.e., methanol + cyclohexane and + isomers with six carbon atoms), the molecular shape of the nonpolar component has an evident effect on the liquid−liquid miscibility behavior. It was observed that the mutual miscibility phenomena are sensitive to the position and number of methyl groups in the paraffin skeleton of the hydrocarbon; therefore, the studied branched alkanes are more soluble in methanol than either linear or cyclic hydrocarbons. The mutual solubility increases as the number of methyl groups increases in the structural isomer. The cyclic structure has an opposite effect on the solubility behavior since cyclohexane is the least soluble component in methanol. The UCST values calculated with the Weimer−Prausnitz version of the Regular Solution Theory using an induction energy density parameter from methanol + saturated chain hydrocarbon systems are in good agreement with the experimental results. The experimental results should be of interest for the study of systems that form methane hydrates with structure type “H”.

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