

# Solubility of Some *n*-Alkanes (C<sub>23</sub>, C<sub>25</sub>, C<sub>26</sub>, C<sub>28</sub>) in Heptane, Methylcyclohexane, and Toluene

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Solubilities of four heavy *n*-alkanes (tricosane, pentacosane, hexacosane, and octacosane) in a solvent containing seven atoms of carbon (heptane, methylcyclohexane, and toluene) are determined by simple thermal analysis. It is shown that the nature of the solvent has no major influence on the solubility and that, in a same solvent, the solubility decreases when the carbon number of the alkane chain increases. Simple expressions are applied to represent the solubility lines, which reveals that the binary mixtures are not ideal.

## Introduction

Accumulation of waxy deposits is a commonly occurring problem during the exploitation and the transformation of paraffinic crude oils. Removal of these undesirable solids increases production cost. An adequate thermodynamic model to describe liquid–solid equilibrium would be helpful to predict the solid deposition conditions. In recent years, more effort has been spent on the development of such a model (Couthino, 1995; Lira-Galeana et al., 1996). However, experimental data are necessary to validate it, first on simple and well-defined systems, such as binary or ternary systems. For these reasons, our laboratory has studied the following:

(i) The thermodynamic properties and structural states of pure alkanes (Barbillon et al., 1991) and binary (Dirand et al., 1996) and ternary mixtures of consecutive alkanes (Nouar et al., 1998), differing by one or two carbon atoms.

(ii) The solubility of heavy pure alkanes (Ghogomu et al., 1997a) and their binary mixtures in organic solvents (Ghogomu et al., 1989, 1997b). Their results have been recently confirmed by Flöter et al., 1997.

The aim of this work is to determine the solubility of tricosane (denoted C<sub>23</sub>), pentacosane (denoted C<sub>25</sub>), hexacosane (denoted C<sub>26</sub>), and octacosane (denoted C<sub>28</sub>) in heptane, methylcyclohexane, and toluene.

## Experimental Section

**Material.** Heptane, methylcyclohexane, and toluene were purchased from S.D.S. (99+% purity), and the solid *n*-alkanes were from Aldrich Chemical Co., with a purity grade of 99%, as determined by gas chromatography and mass spectrometry analyses. All the materials were used without additional purification.

**Technique.** Solubilities were determined with a simple thermal analysis (S.T.A.) device constructed in our laboratory. It is made from a stainless steel crucible (inner diameter, 8 mm; outer diameter, 10 mm) closed by a screwed stopper. The weighed amounts of solid *n*-alkane and solvent are placed in the crucible (a Sartorius mi-

crobalance-type A200G is used, giving an accuracy of  $\pm 0.001$  in mole fraction for the composition of the sample). A thermocouple hermetically sealed through a hole in the stopper is in contact with the sample. The crucible is introduced in a programmable furnace equipped with cooling and heating elements based on the Peltier effect, allowing it to work from 240 K to 373 K. The thermocouple is a T-type one (copper/copper–nickel) whose best sensitivity temperature range is 173 K to 673 K. The cold junction is realized by a same type thermocouple, connected in opposition and immersed in a {water + ice} bath at 273 K. The temperature signal is recorded on a SEFRAM 8201 recorder. A sketch of the apparatus is presented in Figure 1.

The sample is first heated until melting and then slowly cooled. The actual measurement then begins, by heating the sample at a temperature rate of 1 K/min. The plot of the heating curve versus time gives the solid-state transition temperature (when it exists) and the melting temperature.

All measurements were carried out at thermodynamic equilibrium with increasing temperature, to avoid a supercooling phenomenon. Figure 2 shows the typical heating curve of a mixture, with one deviation, corresponding to a phase transformation. The following procedure was adopted to determine the temperature of the transformation: three changes in slope points were observed on the curve, denoted by A, B, and C in Figure 2. Point A characterizes the beginning of the transformation of the material in contact with the crucible face: the temperature on the face was higher than the temperature on the thermocouple because of the temperature gradient existing between the face and the center of the crucible. Point B shows the end of the transformation, and C the returning to linear heating. Point B is the interesting point; it corresponds to the transformation temperature of the last crystal in contact with the thermocouple. The tangents to the curve are traced at this point; their intersection indicates the real temperature of transformation end as shown in Figure 2. For a pure component, this value is the transformation temperature; for a mixture, it is the final transformation temperature. This procedure has been

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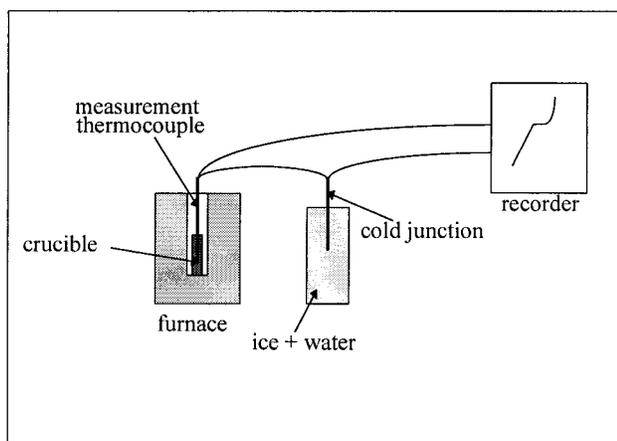


Figure 1. Sketch of the simple thermal analysis device.

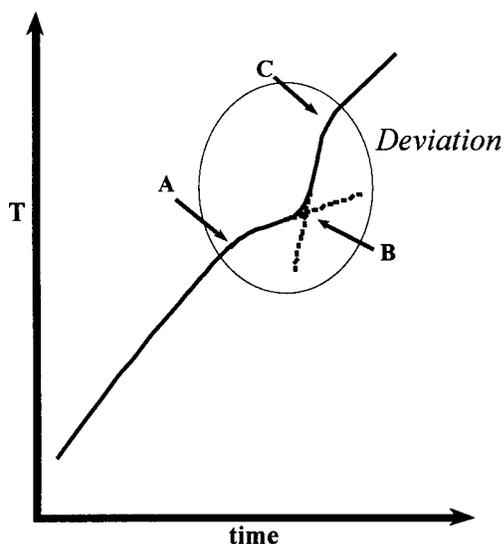


Figure 2. Typical heating curve of a mixture of *n*-alkane + solvent.

Table 1. Thermodynamic Properties of C<sub>23</sub>, C<sub>25</sub>, C<sub>26</sub>, and C<sub>28</sub><sup>a</sup>

	$T_{tr}/K$	$T_m/K$	$\Delta_{tr}H/J\cdot mol^{-1}$	$\Delta_m H/J\cdot mol^{-1}$
C <sub>23</sub>	313.5 (this work)	320.0 (this work)	21 500 (2)	52 250 (2)
	313.5 (2)	320.6 (2)		
	313.15 (3)	320.15 (3)		
C <sub>25</sub>	319.8 (this work)	326.2 (this work)	26 500 (2)	56 750 (2)
	320.0 (2)	326.3 (2)		
	319.85 (3)	326.25 (3)		
C <sub>26</sub>	325.9 (this work)	329.5 (this work)	32 900 (5)	58 700 (5)
	325.5 (1)	329.25 (1)		
	325.6 (2)	329.2 (2)		
C <sub>28</sub>	330.6 (this work)	334.0 (this work)	33 400 (5)	62 900 (5)
	330.75 (3)	333.95 (3)		
	330.40 (4)	333.98 (4)		

<sup>a</sup> Comparison with literature values of the transition temperature ( $T_{tr}$ ) and the melting temperature ( $T_m$ ). References: (1) Andon, 1976; (2) Barbillon et al., 1991; (3) Broadhurst, 1962; (4) Domanska and Wyrzikowska, 1991; (5) Provost, 1997.

applied to the determination of the solid–solid transition and melting temperatures of pure hexacosane and pure octacosane. Experimental results are in good agreement with the literature data (Table 1). The accuracy of the measurements is  $\pm 0.5$  K.

## Results

Experimental values of solubility are given in Tables 2–5. In all the binaries,  $x$  is the mole fraction of heavy *n*-alkane. The results of the octacosane + heptane system

Table 2. Solubility of C<sub>23</sub> in Heptane, Methylcyclohexane, and Toluene

heptane		methylcyclohexane		toluene	
$x$	$T/K$	$x$	$T/K$	$x$	$T/K$
1.000	320.0	1.000	320.0	1.000	320.0
0.849	319.7	0.927	319.8	0.943	319.8
0.816	319.5	0.883	319.5	0.905	319.3
0.797	318.6	0.836	318.9	0.885	319.2
0.754	317.1	0.781	317.6	0.821	318.0
0.725	317.1	0.742	317.2	0.775	316.7
0.668	316.1	0.721	316.5	0.729	316.2
0.622	313.3	0.680	317.0	0.700	315.5
0.576	312.4	0.641	313.3	0.623	314.8
0.525	312.2	0.581	313.0	0.555	312.5
0.481	311.8	0.526	312.3	0.500	310.3
0.459	310.5	0.468	310.6	0.446	309.8
0.430	309.8	0.414	307.6	0.400	307.8
0.410	309.5	0.368	306.4	0.349	306.5
0.367	308.3	0.322	303.9	0.302	305.2
0.327	307.1	0.277	302.2	0.247	302.5
0.308	306.7	0.226	301.7	0.199	300.6
0.268	305.2	0.198	299.3	0.149	297.4
0.252	304.5	0.141	294.6	0.101	294.8
0.235	304.3	0.071	286.6	0.050	289.0
0.200	301.3				
0.171	300.9				
0.142	298.8				
0.117	297.2				
0.093	294.2				
0.072	292.6				
0.052	286.5				
0.033	281.7				
0.016	274.7				

Table 3. Solubility of C<sub>25</sub> in Heptane, Methylcyclohexane, and Toluene

heptane		methylcyclohexane		toluene	
$x$	$T/K$	$x$	$T/K$	$x$	$T/K$
1.000	326.2	1.000	326.2	1.000	326.2
0.937	326.0	0.911	326.0	0.951	325.8
0.902	325.9	0.875	325.6	0.909	325.7
0.888	325.9	0.842	325.5	0.838	325.7
0.866	325.7	0.827	325.5	0.806	324.4
0.866	325.4	0.742	324.2	0.784	325.4
0.843	324.8	0.699	321.6	0.745	324.7
0.840	325.4	0.645	322.2	0.710	323.7
0.828	325.1	0.637	321.5	0.651	322.8
0.804	324.6	0.566	320.2	0.593	319.6
0.783	324.7	0.521	318.4	0.568	320.6
0.731	323.7	0.513	318.2	0.530	318.3
0.659	322.7	0.408	315.6	0.458	318.0
0.633	321.4	0.350	313.4	0.444	317.1
0.568	319.8	0.305	312.2	0.390	315.5
0.559	319.7	0.204	307.5	0.330	313.4
0.502	317.3	0.151	304.4	0.310	314.3
0.469	317.3	0.105	299.4	0.292	313.4
0.391	315.8			0.241	311.2
0.376	315.4			0.214	309.7
0.356	314.2			0.159	306.8
0.257	310.9			0.103	302.1
0.223	310.4			0.050	296.1
0.104	301.5				
0.098	300.7				

are compared with the measurements of Domanska (1987) and Madsen and Boistelle (1976) in Figure 3. As for the results on pure C<sub>26</sub> and C<sub>28</sub>, our data show good agreement with these literature values.

The heavy pure *n*-alkanes present several crystalline phases (Heyding et al., 1990; Doucet et al., 1981). To simplify, the “low-temperature” structures are called “crystal” phases, and the “high-temperature phases”, which are observed a few degrees below the melting point, are called “rotator” phases (Ungar and Masic, 1985). The solid–solid

**Table 4. Solubility of C<sub>26</sub> in Heptane, Methylcyclohexane, and Toluene**

heptane		methylcyclohexane		toluene	
<i>x</i>	<i>T</i> /K	<i>x</i>	<i>T</i> /K	<i>x</i>	<i>T</i> /K
1.000	329.5	1.000	329.5	1.000	329.5
0.886	329.2	0.960	329.3	0.923	329.3
0.867	329.1	0.920	329.1	0.880	329.1
0.843	328.7	0.804	327.7	0.830	328.6
0.804	328.2	0.784	327.9	0.760	327.5
0.720	326.9	0.733	326.6	0.690	326.7
0.684	326.2	0.618	325.7	0.630	326.3
0.643	326.0	0.570	325.0	0.610	325.5
0.596	324.4	0.473	323.4	0.600	324.7
0.595	325.2	0.398	321.7	0.550	324.7
0.573	323.9	0.340	318.3	0.540	323.7
0.507	323.2	0.304	316.2	0.430	321.5
0.450	322.4	0.269	314.4	0.290	318.1
0.436	320.8	0.224	312.7	0.250	316.3
0.402	320.1	0.207	311.9	0.190	312.2
0.337	318.4	0.170	308.7	0.112	305.7
0.302	317.0	0.100	303.1		
0.220	313.6				
0.147	309.3				
0.103	303.3				

**Table 5. Solubility of C<sub>28</sub> in Heptane, Methylcyclohexane, and Toluene**

heptane		methylcyclohexane		toluene	
<i>x</i>	<i>T</i> /K	<i>x</i>	<i>T</i> /K	<i>x</i>	<i>T</i> /K
1.000	334.0	1.000	334.0	1.000	334.0
0.928	333.9	0.933	333.8	0.918	333.6
0.909	333.8	0.903	333.7	0.874	333.1
0.821	332.9	0.867	332.9	0.856	333.5
0.760	332.4	0.853	333.0	0.791	332.5
0.717	331.9	0.836	332.3	0.782	332.0
0.548	329.3	0.828	333.0	0.745	331.7
0.518	328.6	0.759	332.6	0.734	331.2
0.399	325.8	0.738	331.8	0.687	330.0
0.266	321.2	0.689	330.5	0.673	330.5
0.160	315.7	0.641	330.1	0.602	329.1
0.125	312.8	0.623	329.9	0.533	327.7
0.025	298.2	0.601	329.8	0.492	327.3
		0.526	328.9	0.425	326.3
		0.448	326.7	0.419	325.5
		0.368	324.3	0.339	322.9
		0.321	321.9	0.297	320.8
		0.248	318.9	0.245	319.5
		0.208	315.7	0.200	315.9
		0.151	313.0	0.157	314.2
		0.100	308.0	0.100	310.7
		0.099	308.5	0.071	307.9
		0.051	301.9	0.062	306.5
		0.049	301.2		

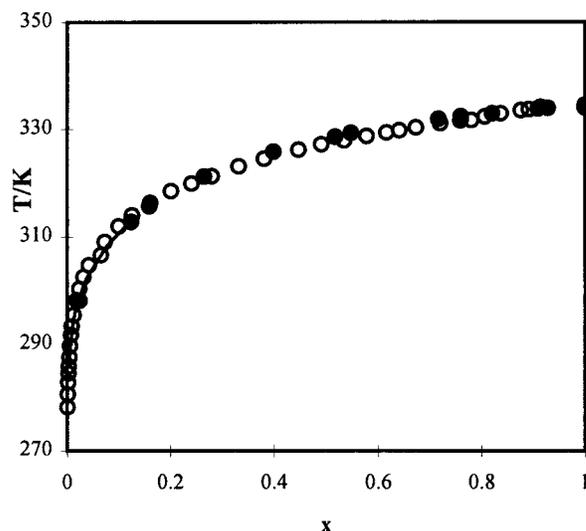
transformation corresponds to the crystal–rotator transition.

## Discussion

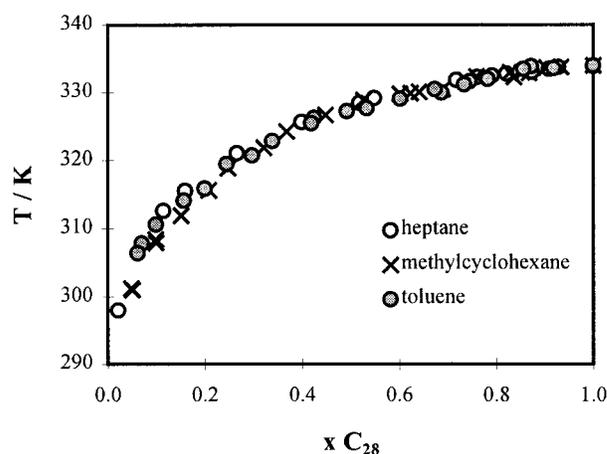
**Influence of the Solvent Concentration.** Whatever the solvent or the heavy *n*-alkane, two behaviors are observed, depending on the solvent concentration.

For low solvent concentrations, two deviations appear on the heating curve; they characterize the following transitions:

(i) The first occurs at a constant temperature *T* for the same solute, respectively, 312.8 K, 319.1 K, 325.9 K, and 330.6 K for the mixtures containing C<sub>23</sub>, C<sub>25</sub>, C<sub>26</sub>, and C<sub>28</sub>. These temperatures correspond to the crystal–rotator transition temperatures observed in the pure *n*-alkanes (see Table 1 for references). This result indicates that the solid in equilibrium with the liquid is the rhombohedral rotator phase  $\alpha$ -R-II ( $R\bar{3}m$ ) of the pure *n*-alkane.



**Figure 3.** Solid–liquid equilibria in the system octacosane + heptane. Key: (●) this work; (○) Domanska (1987); (○) Madsen and Boistelle (1976).



**Figure 4.** Comparison of the solubility of C<sub>28</sub> in heptane, methylcyclohexane, and toluene.

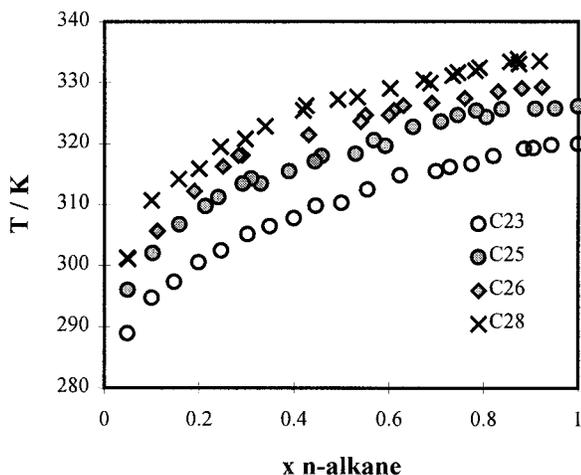
(ii) The second deviation corresponds to the liquidus point temperature of the mixture. This liquidus point characterizes the solubility of the *n*-alkane in the solvent at the considered composition.

When the solvent concentration increases, another behavior appears on the heating curve: only one thermal deviation is observed at a lower temperature than that of the crystal–rotator transition of the heavy pure *n*-alkane. It corresponds to the final melting temperature (liquidus) of the two-phase mixture {crystal of the heavy *n*-alkane + liquid}, and so it indicates the solubility limit point. The structure of the crystal is triclinic or monoclinic for the even numbered *n*-alkanes and orthorhombic for the odd-numbered *n*-alkane.

**Influence of Solvents and Solutes.** The comparison of the solubility curves obtained for the solutions containing the same heavy *n*-alkane in one of the three solvents (heptane, methylcyclohexane, or toluene) leads to the following observations (Figure 4):

(i) For the low solvent concentration, no influence between the three solvents;

(ii) For the very diluted solutions, the solubility is slightly higher in methylcyclohexane, which presents the lower melting point.



**Figure 5.** Comparison of the solubility of C<sub>23</sub>, C<sub>25</sub>, C<sub>26</sub>, and C<sub>28</sub> in toluene.

The solubility decreases in the same solvent when the number of carbon atoms of the alkane chain increases (Figure 5).

**Representation of the Solubility Curves.** The solubility curves have been calculated using two expressions: the ideal solution model and the expression developed by Buchowski to represent the solubility of nonideal solutions (Buchowski et al., 1980).

**(i) Ideal Solution.** If we consider the liquid mixture as an ideal solution, the solubility  $x$  of the pure  $n$ -alkane in the solvent is given by the following expression

$$\ln x = \frac{\Delta_m H}{R} \left( \frac{1}{T} - \frac{1}{T_m} \right) + \frac{\Delta_{tr} H}{R} \left( \frac{1}{T_{tr}} - \frac{1}{T} \right)$$

In the above equation,  $T_m$  is the melting temperature of the solid and  $T_{tr}$  is the temperature of any solid–solid transition that the solute undergoes. Contributions that arise from heat capacity differences between the solid and liquid phases are assumed to be negligible in comparison with terms that arise from the enthalpy of fusion  $\Delta_m H$  and the enthalpy of transition  $\Delta_{tr} H$ .

**(ii) Buchowski Expression.** The solubility  $x$  is given by the following expression

$$\ln \left[ 1 + \lambda \frac{1-x}{x} \right] = \lambda h \left( \frac{1}{T} - \frac{1}{T_m} \right)$$

with

$$\lambda = \frac{a_{\text{solv}}}{1 - a_{\text{solv}}} \cdot \frac{x}{1-x}$$

where  $a_{\text{solv}}$  is the activity of the solvent, and

$$h = [\Delta_m H(T) + H^E/x]/R$$

where  $\Delta_m H(T)$  is the enthalpy of melting at the temperature  $T$ ,  $H^E$  is the excess enthalpy of the mixture, and  $R$  is the gas constant.

In this equation,  $\lambda$  and  $h$  are two parameters. We choose to adjust  $\lambda$ , which corresponds approximately to the nonideality of the system, and to calculate  $h$  from the thermodynamic data of the pure heavy  $n$ -alkane (one value of  $h$  per heavy  $n$ -alkane). The mixtures studied are known to behave almost athermally, meaning that  $H^E$  is small. We suppose it is neglected in comparison with the melting term, meaning that  $h$  depends only on the pure heavy

**Table 6.** Mean Composition Deviation between Solubility Calculated with the Ideal Solution Model and the Experimental Values

	$\Delta x$		
	heptane	methylcyclohexane	toluene
C <sub>23</sub>	0.052	0.056	0.032
C <sub>25</sub>	0.078	0.074	0.085
C <sub>26</sub>	0.074	0.071	0.087
C <sub>28</sub>	0.074	0.069	0.058

$n$ -alkane properties. It depends on the temperature. If  $T > T_{tr}$ , it corresponds to the melting of the rotator phase; if  $T < T_{tr}$ , it corresponds to the melting of the crystal phase, and the solid–solid enthalpy of transition has to be considered. Neglecting contribution arising from heat capacity difference between the solid and the liquid phase, we can finally estimate  $h$ :

$$T > T_{tr}: h = \Delta_m H/R$$

$$T < T_{tr}: h = \Delta_{tr} H/R + \Delta_m H/R$$

The fitting of  $\lambda$  is performed with experimental points whose temperature is inferior to the transition temperature. It has not been made for the other part of the curve (from  $T_{tr}$  to  $T_m$ ), because this temperature range is too close, and the number of experimental data points too low, to lead to a good representation of the curve.

The objective function to be minimized is

$$F = \sum_{i=1}^n (x_i^{\text{calc}} - x_i^{\text{exp}})^2$$

where  $x_i^{\text{calc}}$  is the solubility calculated from the Buchowski expression,  $x_i^{\text{exp}}$  the mixture composition that corresponds to the solubility at the measured liquidus temperature, and  $n$  the number of point used for the fitting.

The thermodynamic properties required in the calculations are given in Table 1 together with their sources.

The predictions from the ideal solubility model underestimate the solubility for low solvent composition and slightly overestimate it for high solvent composition. Table 6 presents the mean composition deviation  $\Delta x$  for each system.  $\Delta x$  is defined by the following expressions

$$\Delta x = \frac{1}{n} \sum_{i=1}^n (x_i^{\text{calc}} - x_i^{\text{exp}})$$

where  $x_i^{\text{calc}}$  is the calculated solubility,  $x_i^{\text{exp}}$  the mixture composition that corresponds to the solubility at the measured liquidus temperature, and  $n$  the number of experimental points.

The agreement between experimental and calculated values is not very good, meaning the liquid mixture is not an ideal solution.

The use of the expression of Buchowski gives best agreement between calculation and measurement. The values of  $\Delta x$  are reported in Table 7. They are always lower than 0.045. Table 7 contains also the value of  $h$  and  $\lambda$ .  $\lambda$  is not equal to 1, which confirms that the liquid mixture is not an ideal solution. The nonideality is stronger with methylcyclohexane, where  $\lambda$  is smaller. This result confirms the observation made on the solubility curves.

## Conclusion

The solubility of four  $n$ -alkanes (C<sub>23</sub>, C<sub>25</sub>, C<sub>26</sub> and C<sub>28</sub>) in three solvents containing seven atoms of carbon has been

**Table 7. Mean Composition Deviation between Solubility Calculated with the Buchowski Expression and the Experimental Values**

$\lambda$ $\Delta x$			$\lambda$ $\Delta x$		
$C_{23} \ h = 8870 \text{ K}$			$C_{25} \ h = 10\ 013 \text{ K}$		
heptane	0.918	0.027	heptane	0.758	0.040
methylcyclohexane	0.603	0.036	methylcyclohexane	0.665	0.037
toluene	0.743	0.021	toluene	0.846	0.040
$C_{26} \ h = 11\ 017 \text{ K}$			$C_{28} \ h = 11\ 562 \text{ K}$		
heptane	0.844	0.035	heptane	0.848	0.044
methylcyclohexane	0.761	0.036	methylcyclohexane	0.763	0.034
toluene	0.823	0.045	toluene	0.783	0.027

measured. The results indicate there is no major influence of the nature of the solvent (cyclic, linear, or aromatic). The influence appears only for very diluted solution. In this case, the solubility is slightly higher in methylcyclohexane. As expected, the solubility decreases in the same solvent when the number of carbon atoms of the alkanes chain increases. The solid in equilibrium with the liquid is the pure *n*-alkane. The use of the ideal solution model is not appropriate to represent the experimental results, whereas the application of the expression of Buchowski et al. (1980) gives good results. It shows that these liquid mixtures are not ideal solutions and that mixtures with methylcyclohexane are more strongly nonideal than the mixtures with heptane and toluene.

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