Solubilities of Some Long-Chain *n*-Alkanes in Dipropyl Ether, Dibutyl Ether, 1-Chlorobutane, and 1-Chlorooctane as Functions of Temperature

Jolanta Rolińska and Tadeusz Hofman*

Division of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, ul. Noakowskiego 3, 00-664 Warszawa, Poland

Solubilities of *n*-octadecane, *n*-nonadecane, *n*-eicosane, and *n*-tetracosane in dipropyl ether, dibutyl ether, 1-chlorobutane, and 1-chlorooctane have been measured by the synthetic method as functions of temperature from near 0 °C to the melting point of the alkane. All systems exhibit small deviations from ideal solubility, positive at lower solute compositions and, for some systems, slightly negative at higher solute compositions.

Introduction

This work is a part of the systematic study on the thermodynamics of mixtures containing chain components. In this paper, solubilities of four solid high *n*-alkanes (octadecane, nonadecane, eicosane, and *n*-tetracosane) dissolved in a linear monoether (dipropyl ether, dibutyl ether) and a 1-chloroalkane (1-chlorobutane, 1-chlorooctane) are presented. The special significance of this kind of data results from the temperature dependence that the compounds exhibit. The majority of the other thermodynamic properties have been measured at a single temperature only.

The only solubility data on *n*-alkanes with similar solvents, which have been reported in the literature, are the scarce data sets for C_8, C_{12}, C_{16}, C_{17}, and C_{32} *n*-alkanes dissolved in diethyl ether.[1,2]

Experimental Section

Purities of solutes octadecane (Fluka, ≥99%), nonadecane (Fluka, ≥98%), eicosane (Fluka, >98%), and tetracosane (Fluka, >99%) have been confirmed by the flame ionization detector gas chromatography and found to be at least 99.9% for all the compounds. The measured melting-point temperatures are given in Table 1. The actual purities of the solvents, dipropyl ether (Fluka, ≥99.5%), dibutyl ether (Aldrich, 99+%), 1-chlorobutane (Fluka, ≥99.5%), and 1-chlorooctane (Fluka, ≥99.5%), were determined to be 99.9, 99.5, 99.8, and 99.9%, respectively. The solvents were dried with the molecular sieves (4A, BDH, Poole, UK) prior to the measurements.

The alkane solubilities were determined by the synthetic method. Mixtures were prepared by mass, placed in a glass cell that was immersed in a thermostated bath, and continuously stirred. The first sample was a pure solute, and then successive portions of the solvent were added. The temperature was increased slowly with the rate (0.03−0.05) K·min^{-1}, and the crystal disappearance was observed visually. The temperature was measured by the calibrated Anschutz mercury thermometer (TGL 11996, H. Schlegel, Ilmenau, GDR) subdivided in 0.1 K and enabling a direct reading with the precision of ±0.05 K. The uncertainty of the mole fractions due to weighing varied between $\pm 1 \times 10^{-4}$ for the lowest concentrations of the solute up to about $\pm 2 \times 10^{-3}$ for the solubilities at temperatures close to that of the melting point. It resulted from the balance precision equal to $\pm 5 \times 10^{-5}$ g and the amounts of components added. It should be slightly increased because of possible small evaporation of the solvent and losses of the solute during stirring.

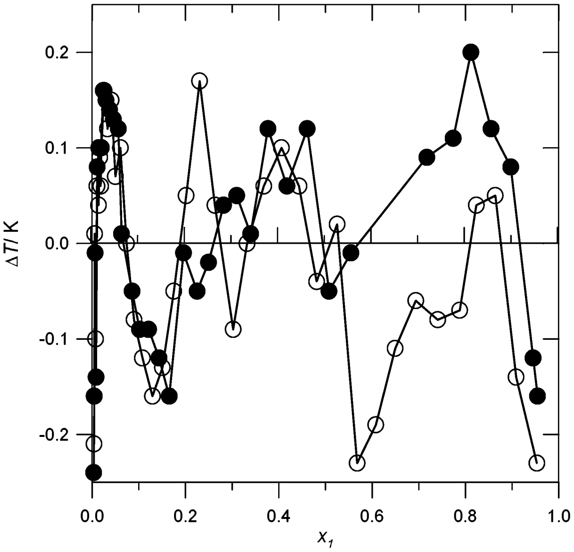

Figure 1. The residuals ΔT for the tetracosane + 1-chlorobutane system between the smoothed solubility temperatures calculated with the help of the Redlich−Kister equation and the experimental ones. ○, run 1 (the heating rate 0.04 K·min^{-1}); ●, run 2 (the heating rate 0.025 K·min^{-1})

The maximum uncertainty of the solubility temperature is difficult to estimate as it results mainly from the dynamic character of the method and can be assigned only in an indirect way.

The original synthetic method consists of two steps, heating of a sample and then cooling, with the temperatures of the crystal disappearance and appearance being noted. The solubility temperature has been taken as an arithmetic mean of temperatures. Our experience has shown, however, that such a procedure can lead to errone-

---

* Corresponding author. E-mail: hof@chemix.ch.pw.edu.pl. Fax: + 48 22 628 27 41.

10.1021/je030206q CCC: $27.50

Table 1. Temperatures and Enthalpies of Fusion and Solid−Solid Transition

	fusion				transition		
	T_{fus}/K				T_{tr}/K		
solute, $C_nH_{2n+,2}$ n	this work	literature	$\Delta_{\mathrm{fus}}H$/kJ·mol^{-1}	$\Delta_{\mathrm{fus}}c_p$/J·K^{-1}·mol^{-1}	this work	literature	$\Delta_{\mathrm{tr}}H$/kJ·mol^{-1}
18	301.7	301.35[a] 301.32[b] 301.5[c] 301.64[d]	61.71[g]	80.84[g]	(300.5 ± 0.5)[i]	299.95[b]	-
19	305.55	305.15[a] 305.15[b] 305.1[c] 305.02[d]	43.75[c]	56.72[h]	(295.5 ± 0.5) (304.1 ± 0.5)	295.95[a] 296.1[c] (302.86)[d]	13.75[c]
20	310.35	309.75[a] 309.75[b] 310.0[e] 309.85[d]	69.92[h]	82.59[h]	(309.2 ± 0.5)	309.35[a] 305.15[b] 309.2[e] (309.55)[d]	-
24	323.85	323.75[a] 323.85[f] 323.8[e] 323.5[c] 323.83[d]	54.00[c]		(321.4 ± 0.5)	321.25[a] 321.35[f] 321.0[e] 321.1[c] (320.65)[d]	31.50[c]

[a] Schaerer et al.[3] [b] TRC Thermodynamic Tables.[4] [c] Barbillon et al.[5] [d] Domańska and Venkatesu.[6] [e] Claudy and Letoffe.[7] [f] Company.[8] [g] Messerly et al.[9] [h] van Miltenburg et al.[10] [i] Values in parentheses were determined graphically from the solubility curves.

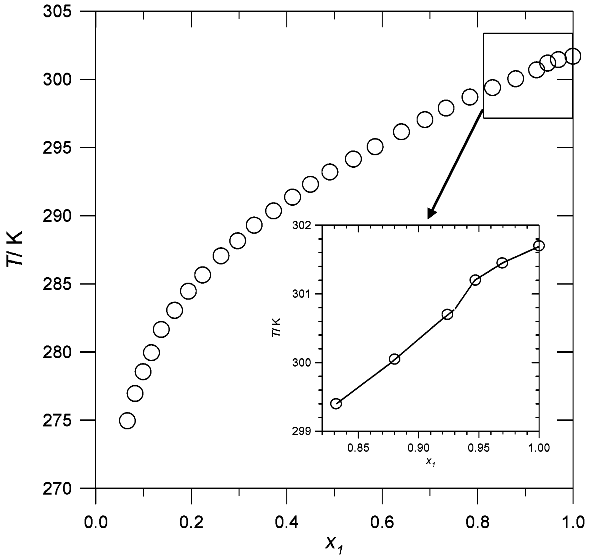

Figure 2. Experimental solubility temperatures for the system octadecane + 1-chlorobutane with respect to the mole fractions of octadecane. Inset: an evidence of the solid−solid transition for octadecane at about 300.5 K

ous results as usually a decrease of temperature due to supercooling is significantly higher than a corresponding increase due to overheating. Hence identifying a temperature at which the crystal disappears with the solubility temperature is more credible provided that the heating rate is sufficiently slow. This conclusion has been commonly recognized since many solubility measurements were performed using the technique based on the crystal disappearance temperatures only.[11−13] The heating rate in the cited papers varied between (0.06 up to 0.4) K·min^{-1}, and a good reproducibility was claimed. Hence the rate used in this experiment, being lower than 0.06 K·min^{-1}, seemed to be sufficiently low.

To test the reproducibility of an experiment, two runs of the measurements for the tetracosane + 1-chlorobutane were performed with the heating rate about 0.04 K·min^{-1} (run 1) and about 0.025 K·min^{-1} (run 2). All the data joined together were correlated by the Redlich−Kister equation, and the deviations between the calculated and experimental temperatures, separate for both runs, are shown in Figure 1. At low concentrations of the solute, the average differences between both data sets are about 0.02 K, although the maximum deviations are higher. They significantly increase with the increase of the concentration up to 0.2 K, probably due to the higher uncertainties of the mole fractions for concentrated solutions. Thus the maximum precision of the data is not worse than ±0.5 K, while the average discrepancy is probably about 10 times lower.

Results and Discussion

The thermodynamic description of the solid−liquid equilibrium is based on the solubility equation which follows from the equality of chemical potentials between components in both coexisting phases. If the solid phase is pure and undergoes the phase transition, the rigorous form of this equation is following

$$-R\ln(x_1\gamma_1) = \int_{T_{\mathrm{fus}}}^{T} \Delta_{\mathrm{fus}}H\,dT^{-1} \quad \text{for} \quad T_{\mathrm{tr}} \le T \le T_{\mathrm{fus}} \tag{1a}$$

$$-R\ln(x_1\gamma_1) = \int_{T_{\mathrm{fus}}}^{T} \Delta_{\mathrm{fus}}H\,dT^{-1} + \int_{T_{\mathrm{tr}}}^{T} \Delta_{\mathrm{tr}}H\,dT^{-1} \quad \text{for} \quad T \le T_{\mathrm{tr}} \tag{1b}$$

where T_{fus} and T_{tr} designate the temperature of fusion and transition, respectively, and $\Delta_{\mathrm{fus}}H$ and $\Delta_{\mathrm{tr}}H$ are the corresponding enthalpy changes, and x_1 and γ_1 are the solute mole fraction and the activity coefficient.

If the heat capacities of fusion ($\Delta_{\mathrm{fus}}c_p$) and transition ($\Delta_{\mathrm{tr}}c_p$) are assumed to be independent of temperature, these equations can be integrated into the forms for $T_{\mathrm{tr}} \le T \le T_{\mathrm{fus}}$

$$-R\ln(x_1\gamma_1) = \Delta_{\mathrm{fus}}H\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus}}}\right) - \Delta_{\mathrm{fus}}c_p\left(\frac{T_{\mathrm{fus}}}{T} - 1\right) + \Delta_{\mathrm{fus}}c_p \ln\frac{T_{\mathrm{fus}}}{T} \tag{2a}$$

for $T \le T_{\mathrm{tr}}$

$$-R\ln(x_1\gamma_1) = \Delta_{\mathrm{fus}}H\left(\frac{1}{T} - \frac{1}{T_{\mathrm{fus}}}\right) - \Delta_{\mathrm{fus}}c_p\left(\frac{T_{\mathrm{fus}}}{T} - 1\right) + \Delta_{\mathrm{fus}}c_p \ln\frac{T_{\mathrm{fus}}}{T} + \Delta_{\mathrm{tr}}H\left(\frac{1}{T} - \frac{1}{T_{\mathrm{tr}}}\right) - \Delta_{\mathrm{tr}}c_p\left(\frac{T_{\mathrm{tr}}}{T} - 1\right) + \Delta_{\mathrm{tr}}c_p \ln\frac{T_{\mathrm{tr}}}{T} \tag{2b}$$

Table 2. Experimental Equilibrium Temperatures (T) and Solute Activity Coefficients (γ_1) for a Given Mole Fraction of an Alkane in Saturated Solution (x) in a Mixture with Dipropyl Ether $CH_3(CH_2)_2O(CH_2)_2CH_3$ or Dibutyl Ether $CH_3(CH_2)_3O(CH_2)_3CH_3$

x	T/K	γ_1	x	T/K	γ_1	x	T/K	γ_1
n-octadecane + dipropyl ether								
0.0765	274.95	1.14	0.353	289.90	1.03	0.753	298.25	1.00
0.0946	276.75	1.11	0.400	291.10	1.02	0.786	298.80	1.00
0.1175	278.85	1.10	0.444	292.35	1.02	0.821	299.30	1.00
0.1384	280.45	1.09	0.487	293.45	1.02	0.857	299.75	0.99
0.1614	281.75	1.06	0.534	294.30	1.01	0.895	300.30	1.00
0.1922	283.55	1.06	0.574	295.10	1.00	0.938	300.90	1.00
0.2275	285.35	1.06	0.620	296.00	1.00	0.966	301.35	1.01
0.2680	287.00	1.05	0.666	296.85	1.00	1.000	301.70	1
0.313	288.55	1.03	0.708	297.50	1.00			
n-octadecane+ dibutyl ether								
0.0787	274.55	1.07	0.364	290.15	1.02	0.755	298.40	1.01
0.0990	276.75	1.06	0.410	291.45	1.02	0.794	298.95	1.00
0.1190	278.65	1.06	0.452	292.55	1.02	0.826	299.30	0.99
0.1444	280.55	1.06	0.494	293.45	1.01	0.856	299.75	1.00
0.1727	282.25	1.04	0.538	294.45	1.01	0.892	300.20	0.99
0.2050	284.05	1.04	0.581	295.25	1.00	0.934	300.80	1.00
0.2424	285.85	1.04	0.630	296.15	1.00	0.952	301.10	1.00
0.2809	287.40	1.04	0.674	296.85	0.99	0.976	301.40	1.00
0.322	288.85	1.03	0.713	297.65	1.00	1.000	301.70	1
n-nonadecane+ dipropyl ether								
0.0597	274.05	1.41	0.347	290.95	1.09	0.691	299.30	1.00
0.0694	275.55	1.40	0.381	291.95	1.08	0.724	300.05	1.00
0.0847	277.40	1.36	0.415	292.90	1.07	0.756	300.85	1.01
0.1024	279.35	1.35	0.442	293.60	1.06	0.796	301.75	1.01
0.1213	280.65	1.28	0.474	294.30	1.05	0.834	302.40	1.00
0.1411	282.15	1.26	0.502	294.85	1.03	0.874	303.15	0.99
0.1612	283.45	1.23	0.534	295.50	1.02	0.897	303.40	0.98
0.1844	284.65	1.20	0.561	296.20	1.03	0.927	303.95	0.98
0.2122	285.85	1.16	0.594	297.20	1.03	0.954	304.60	0.99
0.2420	287.15	1.13	0.627	298.05	1.03	0.977	305.25	1.00
0.2734	288.40	1.12	0.660	298.75	1.02	1.000	305.65	1
0.312	289.80	1.10						
n-nonadecane + dibutyl ether								
0.0657	274.35	1.33	0.352	290.95	1.08	0.688	299.25	1.01
0.0783	275.95	1.30	0.382	291.90	1.07	0.740	300.15	0.99
0.0951	277.85	1.27	0.416	293.05	1.09	0.770	300.85	0.99
0.1155	279.75	1.25	0.447	293.60	1.06	0.808	301.75	1.00
0.1382	281.65	1.24	0.484	294.55	1.05	0.842	302.45	1.00
0.1645	283.25	1.20	0.515	295.20	1.04	0.877	303.05	0.99
0.1915	284.75	1.17	0.547	295.85	1.04	0.923	303.85	0.98
0.2239	286.35	1.15	0.577	296.60	1.03	0.945	304.30	0.99
0.2558	287.65	1.13	0.609	297.35	1.02	0.973	304.90	0.99
0.2865	288.75	1.10	0.647	298.25	1.01	1.000	305.55	1
0.318	289.85	1.09						
n-eicosane+ dipropyl ether								
0.0263	275.05	1.09	0.2245	294.05	0.98	0.708	305.95	0.96
0.0315	276.45	1.07	0.2635	295.65	0.98	0.744	306.55	0.96
0.0377	278.05	1.08	0.309	297.20	0.97	0.787	307.20	0.97
0.0459	279.85	1.08	0.350	298.45	0.97	0.831	307.85	0.97
0.0559	281.65	1.08	0.390	299.65	0.97	0.874	308.50	0.98
0.0703	283.75	1.08	0.438	300.80	0.97	0.903	308.75	0.97
0.0873	285.55	1.06	0.491	301.95	0.96	0.926	309.10	0.97
0.1084	287.55	1.05	0.534	302.85	0.96	0.954	309.55	0.98
0.1310	289.15	1.03	0.575	303.65	0.96	0.974	310.00	1.00
0.1598	290.95	1.01	0.618	304.45	0.96	1.000	310.30	1
0.1898	292.55	1.00	0.660	305.15	0.96			
n-eicosane+ dibutyl ether								
0.0277	274.95	1.02	0.1750	291.75	1.00	0.651	304.90	0.95
0.0338	276.75	1.03	0.1991	292.90	0.98	0.688	305.55	0.95
0.0412	278.35	1.01	0.2309	294.35	0.98	0.734	306.35	0.96
0.0495	279.85	1.00	0.2670	295.80	0.98	0.781	307.00	0.95
0.0593	281.50	1.00	0.310	297.25	0.97	0.816	307.50	0.95
0.0704	283.15	1.01	0.354	298.60	0.97	0.854	308.10	0.96
0.0843	284.85	1.01	0.403	299.90	0.96	0.901	308.75	0.97
0.0996	286.35	1.00	0.456	301.20	0.96	0.924	308.95	0.97
0.1155	287.75	1.00	0.509	302.30	0.95	0.948	309.25	0.96
0.1336	289.15	1.00	0.555	303.20	0.95	0.974	309.90	0.99
0.1534	290.45	1.00	0.604	304.15	0.95	1.000	310.35	1
n-tetracosane+ dipropyl ether								
0.0025	273.95	1.36	0.0816	300.05	1.09	0.533	316.70	1.01
0.0036	276.65	1.36	0.0968	301.45	1.08	0.579	317.75	1.04
0.0051	279.15	1.34	0.1166	303.00	1.07	0.635	318.65	1.04
0.0075	281.95	1.32	0.1400	304.50	1.05	0.684	319.25	1.02
0.0108	284.75	1.31	0.1665	305.95	1.04	0.739	320.00	1.02
0.0149	287.15	1.28	0.1996	307.55	1.03	0.780	320.50	1.02
0.0180	288.35	1.23	0.2331	309.00	1.03	0.827	321.15	1.02
0.0200	289.35	1.25	0.2701	310.40	1.03	0.872	321.95	1.02
0.0209	289.30	1.19	0.312	311.85	1.04	0.900	322.20	1.00
0.0289	291.75	1.16	0.348	312.75	1.03	0.929	322.75	1.01
0.0380	293.90	1.14	0.391	313.75	1.02	0.965	323.35	1.00
0.0509	296.25	1.13	0.433	314.80	1.02	1.000	323.85	1
0.0647	298.15	1.11	0.476	315.70	1.02			
n-tetracosane+ dibutyl ether								
0.0035	275.45	1.19	0.0764	299.25	1.06	0.518	316.60	1.03
0.0046	277.55	1.20	0.0913	300.75	1.06	0.557	317.40	1.04
0.0063	279.95	1.21	0.1090	302.30	1.05	0.604	318.10	1.03
0.0087	282.45	1.21	0.1287	303.75	1.05	0.646	318.75	1.03
0.0122	284.95	1.19	0.1534	305.25	1.04	0.695	319.40	1.02
0.0170	287.35	1.15	0.1820	306.65	1.02	0.744	320.15	1.03
0.0215	289.35	1.17	0.2161	308.30	1.03	0.773	320.45	1.02
0.0251	290.55	1.16	0.2668	310.35	1.04	0.815	321.10	1.03
0.0271	290.85	1.11	0.311	311.85	1.05	0.862	321.60	1.01
0.0336	292.65	1.11	0.357	313.15	1.05	0.894	322.20	1.01
0.0419	294.35	1.10	0.400	314.05	1.03	0.929	322.80	1.01
0.0517	296.05	1.08	0.435	314.85	1.03	0.963	323.45	1.01
0.0628	297.65	1.08	0.474	315.75	1.03	1.000	323.85	1

The above equations, in a simplified form with the heat capacity terms neglected, probably were for the first time shown by Weimer and Prausnitz.[14]

If the activity coefficient in eqs 1 and 2 may be neglected, the so-called ideal solubility equation is derived. Otherwise its explicit dependence on concentration and eventually temperature must be given. For correlational purposes, the Redlich−Kister expansion of the excess Gibbs energy has been used frequently. It gives the following expression for the solute activity coefficient

$$RT \ln \gamma_1 = x_2{}^2[a_0 + \sum_{i=1}^{n-1} a_i(x_1 - x_2)^{i-1}(x_1 - x_2 + 2ix_1)] \quad (3)$$

with the parameters $a_0, a_1, ..., a_{n-1}$ being adjusted to the solubility data.

The parameters of the Redlich−Kister equation were assumed to be independent of temperature. This is equivalent to the neglecting of the nonideal entropic effects. Such a simplification can be questioned but seems to be meaningless as far as only correlation is concerned. For this case, the final solubility equation may be also interpreted as based directly on eq 3 without referring to the excess Gibbs energy.

In all systems, the transition points between two solid phases have been observed. They can be noticed as a change of the slope of the solubility curve (Figure 2). The data suggest an appearance of the second transition point for nonadecane, which was not confirmed previously. Pentacosane is the first odd-numbered *n*-alkane in which existence of the two transition points is not questioned.[15] The accuracy and the number of data do not justify a more refined determination of the transition points parameters, e.g., based on the regression equation. The values shown may be considered merely as the crude estimates. Nevertheless, the coincidence with the literature data is worth noting (Table 1).

The experimental data, i.e., the *n*-alkane mole fractions in a liquid phase and the corresponding equilibrium temperatures, are shown in Tables 2 and 3. The literature

Table 3. Experimental Equilibrium Temperatures (T) and Solute Activity Coefficients (γ_1) for a Given Mole Fraction of an Alkane in Saturated Solution (x) in a Mixture with 1-Chlorobutane $Cl(CH_2)_3CH_3$ or 1-Chlorooctane $Cl(CH_2)_7CH_3$

x	T/K	γ_1	x	T/K	γ_1	x	T/K	γ_1
n-octadecane+ 1-chlorobutane								
0.0662	274.95	1.32	0.2974	288.15	1.05	0.690	297.05	0.99
0.0824	276.95	1.30	0.332	289.30	1.04	0.734	297.90	0.99
0.0991	278.55	1.27	0.373	290.35	1.02	0.784	298.70	1.00
0.1168	279.95	1.23	0.412	291.35	1.01	0.832	299.40	1.00
0.1373	281.65	1.24	0.450	292.30	1.00	0.880	300.05	0.99
0.1652	283.05	1.17	0.491	293.20	1.00	0.924	300.70	1.00
0.1941	284.45	1.14	0.540	294.15	0.98	0.947	301.20	1.01
0.2240	285.65	1.10	0.586	295.05	0.98	0.970	301.45	1.01
0.2626	287.05	1.07	0.641	296.15	0.98	1.000	301.70	1
n-octadecane+ 1-chlorooctane								
0.0636	273.85	1.23	0.360	290.50	1.07	0.737	298.05	1.00
0.0714	275.05	1.24	0.393	291.45	1.07	0.764	298.55	1.01
0.0965	277.85	1.21	0.427	292.35	1.06	0.797	298.95	1.00
0.1238	280.25	1.20	0.464	293.30	1.06	0.832	299.45	1.00
0.1534	282.35	1.18	0.502	294.05	1.05	0.870	299.95	1.00
0.1825	284.00	1.16	0.546	294.95	1.04	0.910	300.55	1.00
0.2131	285.45	1.14	0.586	295.65	1.03	0.953	301.15	1.00
0.2519	287.05	1.12	0.625	296.30	1.02	0.977	301.40	1.00
0.2880	288.35	1.10	0.660	296.90	1.02	1.000	301.70	1
0.324	289.45	1.08	0.698	297.45	1.01			
n-nonadecane + 1-chlorobutane								
0.0559	274.85	1.63	0.329	290.75	1.13	0.689	299.45	1.02
0.0776	277.55	1.51	0.361	291.65	1.11	0.730	300.30	1.01
0.0882	278.95	1.51	0.390	292.45	1.10	0.775	301.30	1.01
0.1076	280.65	1.45	0.432	293.50	1.08	0.816	302.25	1.01
0.1304	282.35	1.39	0.464	294.35	1.08	0.846	302.85	1.01
0.1594	284.05	1.32	0.504	295.20	1.06	0.883	303.25	0.99
0.1939	285.80	1.26	0.540	295.85	1.04	0.914	303.85	0.99
0.2333	287.55	1.22	0.578	296.85	1.04	0.953	304.65	0.99
0.2698	288.75	1.17	0.621	297.95	1.03	1.000	305.60	1
0.2967	289.75	1.16	0.653	298.70	1.03			
n-nonadecane+ 1-chlorooctane								
0.0575	274.95	1.56	0.342	291.50	1.15	0.699	299.70	1.02
0.0732	277.15	1.54	0.380	292.40	1.12	0.730	300.15	1.00
0.0922	279.35	1.50	0.414	293.30	1.11	0.762	300.90	1.00
0.1141	281.20	1.43	0.448	294.15	1.10	0.801	301.75	1.00
0.1399	283.15	1.39	0.483	294.95	1.08	0.843	302.65	1.00
0.1667	284.65	1.33	0.515	295.55	1.07	0.885	303.50	1.00
0.1971	286.25	1.29	0.552	296.25	1.05	0.910	303.90	1.00
0.2295	287.55	1.24	0.583	297.15	1.05	0.939	304.45	1.00
0.2662	289.05	1.21	0.617	298.00	1.04	0.969	304.95	0.99
0.302	290.25	1.18	0.655	298.90	1.03	1.000	305.65	1
n-eicosane+ 1-chlorobutane								
0.0245	275.95	1.29	0.2321	294.85	1.01	0.638	304.90	0.96
0.0313	277.85	1.25	0.2631	296.10	1.01	0.688	305.75	0.96
0.0394	279.85	1.24	0.2948	297.05	1.00	0.746	306.75	0.97
0.0488	281.75	1.24	0.334	298.30	0.99	0.784	307.35	0.97
0.0618	283.65	1.20	0.380	299.60	0.98	0.834	308.20	0.98
0.0848	285.65	1.08	0.431	300.85	0.97	0.881	308.65	0.97
0.0962	287.15	1.12	0.475	301.85	0.97	0.911	309.00	0.97
0.1182	288.95	1.10	0.517	302.75	0.97	0.940	309.50	0.98
0.1428	290.45	1.06	0.558	303.55	0.97	0.971	310.05	1.00
0.1686	291.95	1.05	0.597	304.15	0.96	1.000	310.45	1
0.1981	293.45	1.03						
n-eicosane+ 1-chlorooctane								
0.0238	274.95	1.19	0.2155	294.65	1.08	0.693	305.85	0.97
0.0312	277.25	1.18	0.2482	295.95	1.07	0.725	306.35	0.97
0.0407	279.85	1.21	0.2852	297.20	1.05	0.758	306.85	0.97
0.0533	282.25	1.21	0.329	298.60	1.04	0.792	307.35	0.97
0.0663	283.95	1.17	0.384	300.15	1.03	0.828	307.75	0.96
0.0776	285.65	1.20	0.441	301.45	1.02	0.868	308.35	0.97
0.0886	286.55	1.15	0.499	302.60	1.00	0.892	308.60	0.96
0.1065	288.25	1.14	0.544	303.40	0.99	0.918	308.95	0.96
0.1263	289.75	1.13	0.579	304.05	0.98	0.944	309.30	0.97
0.1459	290.95	1.10	0.621	304.75	0.98	0.973	309.85	0.98
0.1665	292.25	1.10	0.654	305.25	0.97	1.000	310.35	1
0.1889	293.45	1.09						
n-tetracosane+ 1-chlorobutane[a]								
0.0027	275.35	1.52	*0.0630*	*298.25*	*1.15*	*0.417*	*314.70*	*1.05*
0.0032	*276.35*	*1.47*	0.0737	299.45	1.13	0.443	315.25	1.05
0.0039	277.75	1.46	*0.0855*	*300.65*	*1.12*	*0.461*	*315.55*	*1.04*
0.0045	*278.75*	*1.44*	0.0896	301.05	1.11	0.481	316.10	1.05
0.0055	280.05	1.40	*0.1015*	*302.05*	*1.10*	*0.508*	*316.60*	*1.05*
0.0062	*280.95*	*1.40*	0.1075	302.55	1.10	0.525	316.85	1.04
0.0074	282.35	1.40	*0.1211*	*303.50*	*1.09*	*0.555*	*317.40*	*1.05*
0.0082	*283.15*	*1.40*	0.1291	304.10	1.09	0.568	317.85	1.07
0.0103	284.65	1.35	*0.1432*	*304.95*	*1.08*	*0.608*	*318.50*	*1.07*
0.0109	*285.05*	*1.35*	0.1506	305.40	1.08	0.650	319.10	1.06
0.0136	286.75	1.34	*0.1652*	*306.25*	*1.08*	*0.694*	*319.75*	*1.06*
0.0140	*286.90*	*1.32*	0.1749	306.65	1.07	0.717	319.95	1.05
0.0164	288.10	1.31	*0.1958*	*307.65*	*1.06*	*0.741*	*320.45*	*1.07*
0.0183	*288.95*	*1.30*	0.2014	307.85	1.05	0.774	320.70	1.05
0.0184	288.95	1.30	*0.2250*	*309.00*	*1.07*	*0.788*	*321.05*	*1.06*
0.0198	*289.50*	*1.29*	0.2303	309.00	1.04	0.812	321.15	1.04
0.0239	290.85	1.26	*0.2493*	*309.95*	*1.07*	*0.824*	*321.50*	*1.05*
0.0254	*291.30*	*1.25*	0.2631	310.40	1.06	0.855	321.90	1.04
0.0296	292.45	1.24	*0.2817*	*311.05*	*1.06*	*0.864*	*322.10*	*1.04*
0.0328	*293.25*	*1.23*	0.302	311.85	1.08	0.897	322.50	1.03
0.0371	294.15	1.21	*0.310*	*311.95*	*1.06*	*0.909*	*322.85*	*1.03*
0.0408	*294.85*	*1.19*	0.332	312.65	1.07	0.945	323.25	1.02
0.0456	295.70	1.18	*0.340*	*312.85*	*1.07*	*0.953*	*323.45*	*1.02*
0.0497	*296.40*	*1.18*	0.368	313.55	1.06	0.955	323.40	1.02
0.0560	297.25	1.15	*0.377*	*313.70*	*1.06*	*1.000*	*323.85*	*1*
0.0605	297.85	1.14	0.406	314.40	1.05			
n-tetracosane+ 1-chlorooctane								
0.0031	275.75	1.40	0.0777	300.45	1.20	0.486	316.40	1.08
0.0044	277.95	1.33	0.0965	302.35	1.20	0.521	317.05	1.07
0.0064	281.15	1.39	0.1160	303.75	1.17	0.564	317.65	1.06
0.0093	283.95	1.37	0.1369	296.25	1.17	0.616	318.50	1.05
0.0130	286.35	1.33	0.1611	306.55	1.14	0.665	319.10	1.04
0.0172	288.55	1.32	0.1866	307.95	1.15	0.719	319.70	1.02
0.0218	290.45	1.32	0.2155	309.25	1.15	0.778	320.45	1.01
0.0252	291.45	1.29	0.2474	310.45	1.14	0.820	321.00	1.02
0.0274	291.95	1.26	0.2804	311.55	1.13	0.850	321.40	1.01
0.0330	293.45	1.25	0.320	312.75	1.12	0.881	321.85	1.00
0.0413	295.20	1.23	0.363	313.90	1.11	0.918	322.50	1.00
0.0507	296.85	1.21	0.405	314.85	1.10	0.954	323.10	1.00
0.0631	298.65	1.20	0.446	315.65	1.09	1.000	323.85	1

[a] Two runs of the measurements performed with the heating rates equal approximately to 0.04 K·min^{-1} (normal face) and to 0.025 K·min^{-1} (italic).

Table 4. Values of the Redlich–Kister Parameters (a_i) and the Root-Mean-Squared Deviations between Experimental and Calculated Solubility Temperatures

solute, C_nH_{2n+2}				a_i/J·mol^{-1}				
n	solvent	m[a]	RMSD/K	a_0	a_1	a_2	a_3	a_4
18	$(C_3H_7)_2O$	25	0.06	226.3	−85.57	14.90	−159.1	
	$(C_4H_9)_2O$	26	0.06	148.8	−39.96			
	1-ClC_4H_9	26	0.08	371.5	−494.9			
	1-ClC_8H_{17}	28	0.06	488.7	−90.00			
19	$(C_3H_7)_2O$	33	0.12	622.4	−216.3	81.48	−225.9	
	$(C_4H_9)_2O$	30	0.10	573.6	−143.1	−56.07	−271.4	
	1-ClC_4H_9	28	0.08	844.8	−278.4	193.9	−153.6	
	1-ClC_8H_{17}	29	0.07	913.1	−220.0	81.06	−262.5	
20	$(C_3H_7)_2O$	31	0.12	−79.77	−423.6	−117.0		
	$(C_4H_9)_2O$	32	0.13	−119.6	−382.3	−485.1	−314.8	
	1-ClC_4H_9	30	0.13	84.10	−403.9	−215.5	−453.6	
	1-ClC_8H_{17}	33	0.11	268.8	−228.5	−208.9	−620.5	−484.0
24	$(C_3H_7)_2O$	37	0.12	225.7	27.34	0.500	144.2	638.2
	$(C_4H_9)_2O$	38	0.09	223.9	118.5	47.61	142.1	442.2
	1-ClC_4H_9	76	0.12	372.4	118.4	130.9	560.8	1027
	1-ClC_8H_{17}	38	0.09	623.0	139.4	−156.2	−75.19	346.1

[a] The number of experimental points.

values of the enthalpies of the solid−solid phase transition from Table 1, together with the temperatures of transition experimentally determined in this work, were used in the calculations. As for octadecane and eicosane, such enthalpies have not been determined yet; an existence of the transition points has been ignored in the calculations for these compounds. If the heat capacities of fusion or transition were not available (see Table 1), they were assumed to equal zero.

The typical experimental solubility curve, for the system *n*-octadecane + 1-chlorobutane, is shown in Figure 2.

In Tables 2 and 3, also the solute activity coefficients calculated by means of eqs 2a and 2b are included. It should be noted that an uncertainty in the determination of the enthalpy of melting can lead to the systematic deviations of the activity coefficients and hence the latter values cannot be recognized as the strictly experimental ones. If the absolute uncertainty of the enthalpy of melting is taken to be ±2 $\text{kJ}\cdot\text{mol}^{-1}$, the maximum relative error in the solute activity coefficient, which corresponds to the lowest mole fraction (about 0.0025), has been estimated to be about 12% for the systems without the transition point. The contribution resulting from the uncertainty of the enthalpy of fusion is responsible for 10%, while the remaining 2% can merely be attributed to the direct experimental errors. For the systems with the transition points or when the heat capacity data are not available, the systematic deviations can be even greater.

The systems studied exhibit medium deviations from ideality which apparently may be split into two parts: a positive enthalpic contribution and a negative entropic one. The latter is due to considerable differences between volumes of unlike molecules. The summation of the both contributions makes the solute activity coefficients less than 1 at the higher solute concentrations.

The experimental data were correlated by means of the Redlich−Kister equations, which parameters were adjusted to minimize the sum of squares of the residuals between experimental equilibrium temperatures and those calculated with the help of eqs 2 and 3. The number of parameters were determined in the usual way. The results of the correlation are shown in Table 4. They include values of the adjusted parameters and the root-mean-square deviations associated with them. The latter values may be recognized as an additional estimate of the reproducibility of data. It agrees with the analysis performed in the previous section.

Literature Cited

(1) Ralston, A. W.; Hoerr, C. W.; Crews, L. T. Solubilities of Some Normal Saturated Aliphatic Hydrocarbons. *J. Org. Chem.* **1944**, *9*, 319−328.

(2) Hildebrand, J. H.; Watcher, A. Solubility of Dotriacontane (Bicetyl). *J. Phys. Chem.* **1949**, *53*, 886−890.

(3) Schaerer, A. A.; Busso, C. J.; Smith, A. E.; Skinner, L. B. Properties of Pure Normal Alkanes in the C_{17}−C_{36} Range. *J. Am. Chem. Soc.* **1955**, *77*, 2017−2019.

(4) *TRC Thermodynamic Tables*−*Hydrocarbons*; Thermodynamic Research Center, The Texas A&M University System: College Station, TX, 973; p d1014.

(5) Barbillon, P.; Schuffenecker, L.; Dellacherie, L.; Balesdent, D.; Dirand, M. Enthalpy Change from 260 K to 340 K for All Normal Paraffins from Octadecane (*n*-C_{18}) to Hexacosane (*n*-C_{26}). *J. Chim. Phys. Phys.*−*Chim. Biol.* **1991**, *88*, 91−113.

(6) Domańska, U.; Venkatesu, P. Solubility of *n*-Alkanes in Ethyl *tert*-Butyl Ether. *Pol. J. Chem.* **1998**, *72*, 1981−1993.

(7) Claudy, P.; Letoffe, J. M. Phase Transitions in Even *n*-Alkanes C_nH_{2n+2}, $n = 16$−28. Characterization by Diffrerential Calorimetric Analysis. Effect of Deuteration. *Calorim. Anal. Therm.* **1991**, *22*, 281−290.

(8) Company, J. C. Measurement and Interpretation of Crystallization Equilibriums of Heavy Paraffin and Aromatic Hydrocarbon Solutions. *Chem. Eng. Ser.* **1973**, *28*, 318−323.

(9) Messerly, J. F.; Guthrie, G. B.; Todd, S. S.; Finke, H. L. Low-Temperature Thermal Data for Pentane, *n*-Heptadecane, and *n*-Octadecane. Revised Thermodynamic Functions for the *n*-Alkanes C_5−C_{18}. *J. Chem. Eng. Data* **1967**, *12*, 338−346.

(10) van Miltenburg, J. C.; Oonk, H. A. J.; Metivaud, V. Heat Capacities and Derived Thermodynamic Functions of *n*-Nonadecane and *n*-Eicosane between 10 K and 390 K. *J. Chem. Eng. Data* **1999**, *44*, 715−720.

(11) Kehiaian, H. V.; Guieu, R.; Faradjzadeh, A.; Carbonnel, L. Solid−Liquid Equilibria in *n*-Alkylbenzene + *n*-Alkane Mixtures. A Group Contribution Study of Phase Diagrams. *Ber. Bunsen*−*Ges. Phys. Chem.* **1981**, *85*, 132−139.

(12) Proust, P. C.; Fernandez, J. C. Experimental Solid−Liquid Equilibria of Binary Mixtures of Organic Compounds. *Fluid Phase Equilib.* **1986**, *29*, 265−272.

(13) Coon, J. E.; Auwaerter, J. E.; McLaughlin, E. A. Comparison of Solid−Liquid Equilibrium with Vapor−Liquid Equilibrium for Prediction of Activity Coefficients in Systems Containing Polynuclear Aromatics. *Fluid Phase Equilib.* **1989**, *44*, 305−345.

(14) Weimer, R. F.; Prausnitz, J. M. Complex Formation between Carbon Tetrachloride and Aromatic Hydrocarbons. *J. Chem. Phys.* **1965**, *42*, 3643−3644.

(15) Maroncelli, M.; Qi, S. P.; Strauss, H. L.; Snyder, R. G. Nonplanar Conformers and the Phase Behavior of Solid *n*-Alkanes. *J. Am. Chem. Soc.* **1982**, *104*, 6237−6247.

Received for review July 23, 2003. Accepted January 27, 2004.

JE030206Q