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Solubilities of Higher Normal Alkanes in *m*-Xylene

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The solubilities of *n*-octacosane (*n*-$C_{28}H_{58}$), *n*-dotriacontane (*n*-$C_{32}H_{66}$), and *n*-hexatriacontane (*n*-$C_{36}H_{74}$) in *m*-xylene have been measured over the temperature range 11.7–38.6 °C. Although the entropies and enthalpies of dissolution are higher than the corresponding values for short-chain alkane solvents, the present data are still well described by the parametric van't Hoff equation.

Introduction

The crystallization of higher normal alkanes (waxes) from hydrocarbon fuel oils at low temperatures poses a constantly recurring problem in the petroleum industry (*1*), e.g., the fouling the fuel lines and filters of diesel engine vehicles by wax crystal cakes.

As a first step toward a fundamental study of wax nucleation and crystal growth, the present work provides solubility data for a "model" fuel-oil system, i.e., one incorporating a typical higher normal alkane as solute dissolved in a well-characterized hydrocarbon solvent.

For a saturated solution in equilibrium with pure solid solute at a given temperature, the chemical potential of the solute in the saturated solution is identical with that of the pure solid solute at that temperature. In the case of an ideal solution, i.e., one obeying Raoult's law

$$\left[\frac{\partial \ln x}{\partial(1/T)}\right]_P = -\frac{\Delta H_f}{R} \tag{1}$$

or, in parametric form

$$\ln x = -\frac{\Delta H_f}{RT} + \frac{\Delta S_f}{R} \tag{2}$$

where x is the mole fraction of solute in solution and ΔH_f and ΔS_f its enthalpy and entropy of fusion, respectively.

In practice, even though a plot of ln x vs. T^{-1} may give a straight line, the slope of the line may differ from $-\Delta H_f/R$ if the solution exhibits nonideal behavior. In such cases, the excess enthalpy and entropy of mixing, resulting from the interaction of molecules of different shape and size, must be taken into consideration (*2*). Equation 2 may thus be rewritten (*3*), replacing ΔH_f by the enthalpy of dissolution ΔH_d, which incorporates the excess enthalpy of mixing, and ΔS_f by ΔS_d:

$$\ln x = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R} \tag{3}$$

Experimental Section

The solvent used was AnalaR grade *m*-xylene (BDH Chemicals Ltd.) with a minimum assay of 99.5% as determined by gas–liquid chromatography. The chosen normal alkanes (Aldrich Chemical Co. Ltd.) were *n*-octacosane (*n*-$C_{28}H_{58}$) of 97% purity and melting point range 61–63 °C, *n*-dotriacontane (*n*-$C_{32}H_{66}$) of 97% purity and melting point range 68–70 °C, and *n*-hexatriacontane (*n*-$C_{36}H_{74}$) of 98% purity and melting point range 74–76 °C. The impurities in the *n*-alkanes were made up of neighboring homologues, the last traces of which are very difficult to remove by recrystallization due to solid-solution formation.

Table I. Solubility of *n*-Octacosane in *m*-Xylene

	concentration	
T, °C	g/100 g solvent	mole fracn in soln, ×10^3
11.7	1.0	2.683
16.8	2.0	5.352
18.7	3.0	8.006
22.4	5.0	13.27
25.1	7.0	18.48
27.0	10.0	26.20
30.2	15.0	38.79

Parameters of the Solubility Curve

$\Delta H_d = 1.05 \times 10^5$ J mol^{-1}

$\Delta H_f = 1.00 \times 10^5$ J mol^{-1} (ref *2*)

$\Delta S_d = 3.19 \times 10^2$ J mol^{-1} K^{-1}

$\Delta S_f = 3.00 \times 10^2$ J mol^{-1} K^{-1} (ref *2*)

Table II. Solubility of *n*-Dotriacontane in *m*-Xylene

	concentration	
T, °C	g/100 g solvent	mole fracn in soln, ×10^3
14.1	0.25	0.5887
17.2	0.50	1.177
21.5	1.0	2.351
25.7	2.0	4.691
31.4	5.0	11.64
38.6	15.0	34.14

Parameters of the Solubility Curve

$\Delta H_d = 1.22 \times 10^5$ J mol^{-1}

$\Delta H_f = 1.18 \times 10^5$ J mol^{-1} (ref *2*)

$\Delta S_d = 3.62 \times 10^2$ J mol^{-1} K^{-1}

$\Delta S_f = 3.46 \times 10^2$ J mol^{-1} K^{-1} (ref *2*)

The apparatus used for the solubility measurements (*4*) was a 30-mL glass cell fitted with a 2-bladed stirrer, with the vessel and stirrer shaft made airtight with a glycerol seal. The cell was immersed in a thermostat water bath connected to a EUROTHERM 103 temperature controller which could activate either a heating element or a cooling coil immersed in the bath. The temperature controller was also connected to a drive unit so that its set-point could be varied at any given rate between 1 and 40 °C/h. The water bath temperature was measured with a 0–50 °C mercury in glass thermometer, with a BSI certificate of calibration, giving an accuracy of ±0.05 °C.

Weighed quantities of solvent and solute were charged into the cell which was agitated and heated to dissolve all the crystals and then held for about 5 min at 10 °C above the saturation temperature. The cell was then transferred to the thermostat bath to equilibrate near the saturation temperature and then momentarily dipped in ice-water to induce nucleation, after which it was replaced in the thermostat bath and then reheated at about 5 °C/h.

Close to the end point, the temperature was increased in steps of 0.05 °C and the cell contents inspected at half-hourly intervals, against a strong back-light, until the last trace of crystalline material had disappeared. The equilibrium saturation temperature could be reproduced to within ±0.05 °C, i.e., the accuracy of the thermometer.

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Table III. Solubility of *n*-Hexatriacontane in *m*-Xylene

	concentration	
T, °C	g/100 g solvent	mole fracn in soln, ×10³
18.2	0.10	0.2094
22.4	0.25	0.5234
25.9	0.50	1.046
29.2	1.0	2.090
38.3	5.0	10.37

Parameters of the Solubility Curve

$\Delta H_d = 1.47 \times 10^5$ J mol^{-1}

$\Delta H_f = 1.29 \times 10^5$ J mol^{-1} (ref *2*)

$\Delta S_d = 4.34 \times 10^2$ J mol^{-1} K^{-1}

$\Delta S_f = 3.71 \times 10^2$ J mol^{-1} K^{-1} (ref *2*)

Results and Discussion

The solubilities over the range 11.7–38.6 °C (Tables I, II, and III) when plotted on a ln x vs. T^{-1} basis (not given here) are shown to be well represented by the parametric eq 3.

Tables I, II, and III compare the entropy and enthalpy of dissolution, ΔS_d and ΔH_d (calculated by a linear regression analysis), with the corresponding fusion parameters ΔS_f and ΔH_f in order to give an indication of the degree of nonideality of the system.

Table IV compares the dissolution parameters calculated by Madsen and Boistelle (*3*, *5*, *6*) with the present data. For a given solute, the entropy of dissolution is highest when *m*-xylene is the solvent rather than a straight-chain solvent belonging to the same homologous series as the solute. This can be explained on the basis of the difference in molecular size and shape of the two components (*2*). For the same reason, the entropy of dissolution in a given solvent increases on increasing the chain length of the solute.

It may be noted here, incidentally, that Madsen and Boistelle (*6*) claim that, for a given solute, the enthalpy and entropy of dissolution both increase when the solvent is changed from an *n*-alkane to petroleum ether, which might be expected since the latter solvent contains both branched-chain and cyclic compounds. A close inspection of their results, however, shows that, although this is true for *n*-hexatriacontane, it is not for the other two solutes used (*n*-octacosane and *n*-dotriacontane).

The main result of the present work, therefore, has been the accurate determination of the entropies and enthalpies of dissolution of higher *n*-alkanes in *m*-xylene. These dissolution parameters are higher than those reported in the literature (*3*, *5*, *6*) for binary alkane mixtures and the excess enthalpies of mixing are also higher. These findings demonstrate that the departure from ideal solution behavior is related to the molecular dissimilarity of solvent and solute. Furthermore, the dissolution parameters for a given solvent increase on increasing the chain length of the solute, a conclusion which agrees with experimental data reported by Lichtenthaler et al. (*7*), for solutions of higher *n*-alkanes of varying chain length in cyclohexane.

Table IV. Comparison of Dissolution Parameters

solute	solvent	ΔH_d, J mol^{-1} × 10³	ΔS_d, J mol^{-1} K^{-1}
n-$C_{28}H_{58}$	dodecane	98.0	295
	decane	97.5	294
	heptane	97.4	295
	pentane	99.5	302
	pet. ether	99.3	301
	m-xylene	105.0	319
n-$C_{32}H_{66}$	heptane	109.7	324
	pentane	111.0	329
	pet. ether	109.0	322
	m-xylene	121.6	362
n-$C_{36}H_{74}$	dodecane	128.9	372
	decane	128.2	371
	octane	125.3	361
	heptane	122.7	354
	hexane	123.0	355
	pentane	124.5	360
	pet. ether	128.5	374
	m-xylene	146.7	433

Finally, it has been demonstrated that the Van't Hoff equation for predicting solubilities (eq 2) is applicable not only to binary alkane mixtures, but also to solutions of *n*-alkanes in aromatic solvents.

Glossary

x	mole fraction of solute in solution
ΔS_d	entropy of dissolution, J mol^{-1} K^{-1}
ΔS_f	entropy of fusion, J mol^{-1} K^{-1}
ΔH_d	enthalpy of dissolution, J mol^{-1}
ΔH_f	enthalpy of fusion, J mol^{-1}
T	absolute temperature, K
R	gas constant, J mol^{-1} K^{-1}
H^E	partial molar excess enthalpy of solute in solution, J mol^{-1}
γ	activity coefficient of solute in solution

Registry No. *n*-$C_{28}H_{58}$, 630-02-4; *n*-$C_{32}H_{66}$, 544-85-4; *n*-$C_{36}H_{74}$, 630-06-8; *m*-xylene, 108-38-3.

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