

Table III. Thermal Conductivities for Methane-Nitrogen ($x_{\text{CH}_4} = 0.5102$)

T_0 , K	P , atm	ρ , mol/L	λ_0 , mW/(m K)
221.32	61.47	4.085	30.39
227.95	64.73	4.114	31.02
237.78	71.93	4.314	32.70
246.34	76.13	4.331	33.41
253.19	79.84	4.367	34.22
266.58	85.92	4.361	34.47
271.76	86.24	4.254	36.39
246.14	23.58	1.223	27.18
238.19	4.32	0.223	25.04
229.97	2.90	0.155	24.63
248.42	3.07	0.151	26.66

in addition contains a few results for ethane. The deviation between the results of this work and the correlation by Hanley et al. is in no case larger than 3%.

Tables II and III show the measured thermal conductivities for the gaseous mixtures methane-carbon dioxide ($x_{\text{CH}_4} = 0.5061$) and methane-nitrogen ($x_{\text{CH}_4} = 0.5102$).

In Tables I, II, and III, the densities are calculated by using the highly accurate corresponding states correlation by Mollerup (6).

Acknowledgment

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Solubility of α -HgI₂ in Dimethyl Sulfoxide-Methanol and Dimethyl Sulfoxide-Ethyl Acetate Mixtures

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The solubility of α -HgI₂ in dimethyl sulfoxide-methanol mixtures was determined in the range of 0.6–0.8 dimethyl sulfoxide mole fractions from 25 to 40 °C (for 35 °C it was determined in the full range of mole fractions). The solubility of α -HgI₂ in ethyl acetate and in dimethyl sulfoxide-ethyl acetate mixtures was determined up to 0.1287 dimethyl sulfoxide mole fraction in the range 40–60 °C.

Introduction

We have recently developed a new method of growing single crystals of α -HgI₂ in solution using HgI₂-Me₂SO (dimethyl sulfoxide) molecular complexes (5).

To better understand and control the crystallization process of α -HgI₂ by means of its molecular complexes, we have previously studied the donor-acceptor type interaction between HgI₂ and various basic solvents (2) and we now study the solubility of α -HgI₂ in Me₂SO-MeOH (methanol) and Me₂SO-EA (ethyl acetate) mixtures. As we have found formerly, Me₂SO acts as a complexing agent against HgI₂. The ranges of temperatures and concentrations investigated have been restricted to those useful for growing single crystals of α -HgI₂.

Experimental Section

Materials. Analytical grade α -HgI₂ from Merck was further purified by three successive recrystallizations in solution of Me₂SO-MeOH (5). Analytical grade dried Me₂SO from Merck and analytical grade EA from Carlo Erba have been used without further purification. Analytical grade MeOH from Prolabo was further rectified on a packed column to eliminate its water content.

Procedure. For measuring the HgI₂ concentration of saturated solutions, a straight-forward gravimetric analysis was

chosen. Different Me₂SO-solvent mixtures, in volumes of about 100 mL, were prepared by weighing in bottles of 200 mL, tightly stopped by screwing on plastic stoppers supplied with Teflon gaskets. α -HgI₂ in excess was then introduced and the bottles were kept in a thermostated bath for 2 weeks to reach saturation, stirring the mixture twice a day. The temperature was controlled within ± 0.01 °C. Samples of 5 mL of saturated solution have been pipetted out from the bottles and kept in closed weighing bottles. The samples were evaporated to dryness in a drying chamber under vacuum for a few hours at room temperature to evaporate the most volatile solvent (MeOH or EA) and then 12 h at 50 °C to evaporate Me₂SO. The samples were accurately weighed before and after solvent evaporation. New samples of saturated solution were again pipetted out from the bottles after 2 weeks and worked out as above. The data listed in tables are averages among many close values obtained from many samples. The experimental values do not differ from these data more than 1% for the Me₂SO-EA mixtures and more than 0.5% for the Me₂SO-MeOH mixtures.

Results

The solubility of α -HgI₂ in Me₂SO-MeOH mixtures was investigated in the range of 0.6–0.8 Me₂SO mole fractions, $X_{\text{Me}_2\text{SO}} = n_{\text{Me}_2\text{SO}}/(n_{\text{Me}_2\text{SO}} + n_{\text{MeOH}})$, from 25 to 40 °C and in the full range of Me₂SO mole fractions at 35 °C.

The following empirical parabolic relation fits the experimental data within the experimental accuracy ($\pm 0.25\%$):

$$R_{\text{HgI}_2} = -(3.03 \times 10^{-2}) + (5.4 \times 10^{-4})(t - 25) + [(1.735 \times 10^{-1}) + (2 \times 10^{-4})(t - 25)]X_{\text{Me}_2\text{SO}} + (3.95 \times 10^{-1})X_{\text{Me}_2\text{SO}}^2 \quad (1)$$

The temperature t is in °C and the α -HgI₂ mole ratio R_{HgI_2} is $n_{\text{HgI}_2}/(n_{\text{Me}_2\text{SO}} + n_{\text{MeOH}})$. Experimental and calculated data are given in Table I. Figure 1 shows the complete isotherm of

Table I. Experimental α -HgI₂ Solubility Data in Me₂SO-MeOH Mixtures^a

$X_{\text{Me}_2\text{SO}}$	R_{HgI_2}							
	25 °C		30 °C		35 °C		40 °C	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
0.60	0.2165	0.2160	0.2190	0.2193	0.2225	0.2226	0.2260	0.2259
0.65	0.2509	0.2494	0.2522	0.2527	0.2565	0.2561	0.2625	0.2561
0.70	0.2855	0.2847	0.2881	0.2881	0.2920	0.2915	0.2931	0.2949
0.75	0.3203	0.3220	0.3247	0.3254	0.3281	0.3289	0.3320	0.3320
0.80	0.3617	0.3613	0.3655	0.3648	0.3683	0.3689	0.3715	0.3718

$10^3 R_{\text{HgI}_2}$ at 35 °C			
$0.0 X_{\text{Me}_2\text{SO}}$	$0.20 X_{\text{Me}_2\text{SO}}$	$0.40 X_{\text{Me}_2\text{SO}}$	$1.00 X_{\text{Me}_2\text{SO}}$
3.17	27.2	102	518

^a Experimental α -HgI₂ solubility data in Me₂SO-MeOH mixtures expressed as α -HgI₂ mole ratios $R_{\text{HgI}_2} = n_{\text{HgI}_2}/(n_{\text{Me}_2\text{SO}} + n_{\text{MeOH}})$, $X_{\text{Me}_2\text{SO}} = n_{\text{Me}_2\text{SO}}/(n_{\text{Me}_2\text{SO}} + n_{\text{MeOH}})$; calculated data with relation 1.

Table II. Experimental α -HgI₂ Solubility Data in Me₂SO-EA Mixtures^a

$10^3 X_{\text{Me}_2\text{SO}}$	$10^3 R_{\text{HgI}_2}$									
	40 °C		45 °C		50 °C		55 °C		60 °C	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
0.00	2.57	2.58	2.93	2.92	3.30	3.29	3.69	3.70	4.10	4.14
5.394			4.30				5.09			
5.613	3.94				4.73				5.65	
10.03	5.18	5.18			6.00	6.02			6.93	6.86
10.10			5.61	5.55			6.44	6.46		
23.74			9.88	9.93			10.81	10.9		
24.82	9.73	9.78			10.7	10.8			11.6	11.8
47.12			17.9	17.9			19.2	19.1		
49.12	18.0	18.0			19.1	19.3			20.5	20.5
80.20			30.6	30.6			32.5	32.2		
81.13	30.15	30.20			31.7	31.8			33.6	33.3
125.3			50.5	50.5			52.5	52.4		
128.7	50.2	50.1			51.8	52.8			54.3	54.1

^a Experimental α -HgI₂ solubility data in Me₂SO-EA mixtures expressed as α -HgI₂ mole ratios $R_{\text{HgI}_2} = n_{\text{HgI}_2}/(n_{\text{Me}_2\text{SO}} + n_{\text{EA}})$, $X_{\text{Me}_2\text{SO}} = n_{\text{Me}_2\text{SO}}/(n_{\text{Me}_2\text{SO}} + n_{\text{EA}})$; data calculated with relation 2 for Me₂SO-EA mixtures and with relation 3 for pure EA.

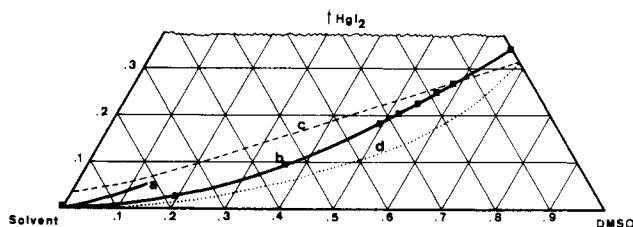


Figure 1. Solubility isotherms of α -HgI₂ in various Me₂SO-solvent mixtures, in mole fractions: (a) Me₂SO-EA at 40 °C, (b) Me₂SO-MeOH at 35 °C, (c) Me₂SO-xylene at 22 °C, (d) Me₂SO-water at 22 °C. Isotherms c and d are from ref. 1.

α -HgI₂ solubility in Me₂SO-MeOH mixtures plotted in mole fractions for 35 °C.

The solubility of α -HgI₂ in Me₂SO-EA mixtures was investigated up to 0.1287 Me₂SO mole ratio $X_{\text{Me}_2\text{SO}} = (n_{\text{Me}_2\text{SO}}/(n_{\text{Me}_2\text{SO}} + n_{\text{EA}}))$, in the range of 40–60 °C. The following parabolic relation fits the experimental data within the experimental accuracy ($\pm 1\%$) in the range of 10^{-2} – 1.287×10^{-1} Me₂SO mole fractions:

$$R_{\text{HgI}_2} = (2.24 \times 10^{-3}) + (7.4 \times 10^{-5})(t - 40) + [(2.86 \times 10^{-1}) + 10^{-3}(t - 40)]X_{\text{Me}_2\text{SO}} + (7.25 \times 10^{-1})X_{\text{Me}_2\text{SO}}^2 \quad (2)$$

The temperature t is in °C and the α -HgI₂ mole ratio $R_{\text{HgI}_2} = n_{\text{HgI}_2}/(n_{\text{Me}_2\text{SO}} + n_{\text{EA}})$. Experimental and calculated data are given in Table II. The temperature variation of the α -HgI₂ solubility in pure EA is compatible with an ordinary exponential relation

$$R_{\text{HgI}_2} = 6.89 \exp(-\Delta G/RT) \quad (3)$$

ΔG being 4.90 kcal mol⁻¹.

The α -HgI₂ concentrations have been expressed in mole ratios in order to be directly useful for the crystal grower in the

graphical calculation of supersaturation. Indeed, if one plots R_{HgI_2} vs. $X_{\text{Me}_2\text{SO}}$ for different temperatures, cooling is represented by vertical lines and isothermal solvent evaporation or solvent addition by lines passing through the origin. Alternatively, if we plot R_{HgI_2} vs. temperature for different $X_{\text{Me}_2\text{SO}}$, cooling is represented by horizontal lines and isothermal solvent evaporation or solvent addition by vertical lines.

Discussion

Within the range of temperatures and concentrations investigated, the single solid phase in equilibrium with the saturated solution is α -HgI₂, as was proved by chemical analysis and by X-ray diffraction of the solid phase.

The solubility of α -HgI₂ increases largely with the Me₂SO mole fraction but weakly with the temperature. The temperature coefficient of solubility is positive and increases with the Me₂SO mole fraction; thus saturated solutions become supersaturated by cooling.

Up to a certain Me₂SO mole fraction, dependent on the temperature, e.g., 0.056 for 40 °C, saturated solutions become supersaturated by EA evaporation. Above this mole fraction, saturated solutions become supersaturated by dilution with EA. The solutions of α -HgI₂ in Me₂SO-MeOH mixtures show the same behavior as regards the ways to reach supersaturation.

The solubility of α -HgI₂ in pure Me₂SO is very large, the mole ratio of α -HgI₂ slightly exceeding 0.5 due to the formation of HgI₂·2Me₂SO and (HgI₂)₂·2Me₂SO molecular complexes (2). The solubility decrease of HgI₂-Me₂SO solutions by solvent addition is enhanced along the row of solvents: xylene \leq EA < MeOH < water. The solubility decrease is larger for the protic solvents as compared to the aprotic ones. The addition of protic solvents involves the formation of Me₂SO solvent molecular complexes (3, 4), the formation of HgI₂·Me₂SO molecular complexes being

repressed. A more detailed discussion of the chemical equilibria involved in these complex solutions will be given elsewhere (5).

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A Correlation between the Solubility of Aromatic Hydrocarbons in Water and Micellar Solutions, with Their Normal Boiling Points

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A linear correlation between the logarithm of the solubility in water of aromatic hydrocarbons and their normal boiling points is shown. Similarly, the logarithm of the distribution ratio of aromatic hydrocarbons in aqueous micellar solution is shown to be linearly related to the boiling points of the hydrocarbons.

Introduction

In previous studies on the water solubility of various groups of sparingly soluble hydrocarbons, e.g., alkanes or aromatics, attempts have been made to correlate the solubility with some property of the hydrocarbons. Possibly the most successful has been the linear correlation between either the partial molar volume¹ or the cavity surface area of the hydrocarbons^{2,3} and the logarithm of their solubility in water.

A useful aspect of such correlations is that they provide a means of estimating the solubility of other hydrocarbons with sufficient accuracy for a number of purposes, e.g., solubility values in environmental studies.

We show in this note that there is a linear correlation between the logarithm of the water solubility of aromatic hydrocarbons and their boiling point. A similar correlation is also found for the solubilization of aromatic hydrocarbons in several micellar systems.

Experimental Section

There is a large amount of reliable data available in the literature⁴⁻⁹ on the solubility of various hydrocarbons in water. We have used these data to obtain the plot shown in Figure 1.

The solubility of the aromatic hydrocarbons in micellar solutions was measured by using the technique described in detail elsewhere.¹⁰ Briefly, it involves the saturation of a micelle solution with the hydrocarbon, usually equilibrated for several days, and measurement of the total concentration in the solution by absorption spectrometry.

The data for the solubilization of aromatic hydrocarbons in cetyltrimethylammonium bromide (CTAB) and sodium lauryl sulfate (NaLS) solutions are taken from ref 10. These data are compared with solubilization in the bile surfactants sodium taurocholate (Calbiochem, >96% (TLC)) and sodium cholate (Calbiochem, >97% (TLC)). With the latter two surfactants some solubilization measurements were made with concentrations below the critical micelle concentration¹¹ (cmc). Below the cmc the additive was found to be only slightly more soluble than in pure water. However, above the cmc, the solubilization in-

creased linearly with an increase in the micelle concentration. This indicates that there is no specific binding of the arene with a monomer unit but that a micelle environment is required for solubilization.

The solubilization of naphthalene in Brij-35 (polyoxyethylene lauryl ether, Pierce Chemical Co. (specially purified)), and in a vesicle solution of didodecylammonium bromide (DDAB, Eastman Chemical) was also measured to compare with the other surfactant systems.

The source and quality of all chemicals used that have not been listed here are given in ref 10.

Discussion

In Figure 1, the logarithm of the water solubility of a variety of aromatic hydrocarbons has been plotted as a function of their normal boiling points.¹² Where there is a large discrepancy in the values reported in the literature, both values are shown, otherwise a single value is plotted, generally from the most recent measurement. The references cited in the previous section give a list of all the original data. A linear least-squares analysis of the plot gives

$$\log S = 0.0138T_b + 0.76 \quad (1)$$

with a correlation coefficient of 0.97.

S is the solubility in water in mol dm⁻³ and T_b the normal boiling point of the arene in °C. Similar relationships also exist for most of the alkanes, alkenes, alkynes, and cyclic hydrocarbons; all these groups have similar slopes but different constant values. The relationship in these cases is only useful in extrapolating to longer chain lengths, since at small carbon numbers and on addition of various substituent groups to the basic hydrocarbon unit a marked deviation from the linear trend is observed.

With the aromatic hydrocarbons, addition of a substituent such as a halogen or small alkyl groups to the basic ring structure does not appear to cause a large deviation from the general trend. A marked exception to this is anthracene, chrysene, and the butylbenzenes. These compounds were not included in the least-squares plot. For most other aromatics eq 1 is a reasonable description of the water solubility of the hydrocarbons. It allows one to estimate how the solubility of an aromatic will change with either the addition of a functional group to the basic ring or an alteration in the position of a side group.

The reason for the empirical relationship of the water solubilities with the boiling point of the aromatic hydrocarbons can be understood, qualitatively, from the discussions by Hermann,² Harris et al.,³ and Tanford et al.¹³ of the correlations between