Solubility of Stearic Acid in Some Halofluorocarbons, Chlorocarbons, Ethanol, and Their Azeotropes

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The solubility of stearic acid in each of the solvents CCl_2FCClF_2, CCl_3CF_3, CH_3CCl_3, CCl_2FCCl_2F, CF_2BrCF_2Br, CCl_4, CH_2Cl_2, CH_3CH_2OH, and the azeotropes of CCl_2FCClF_2 with CH_3CH_2OH, CH_2Cl_2, $CHCl_3$, $(CH_3)_2CO$, and $(CH_3)_2CHOH$ was determined as a function of temperature in the range from 20–50° C by the phase disappearance method.

Stearic acid is a monocarboxylic acid of great interest in both industry and science. Careful solubility studies of this compound in a variety of organic solvents were carried out by Ralston and Hoerr (*6, 7*), Ralston et al. (*8*), Preckshot and Nouri (*5*), and by Brown and co-workers (*2, 3*). In this work we have extended the range of solvents to include an important class of halofluorocarbons well-known for their nonflammability and low toxicity.

These data are particularly pertinent to cleaning operations inasmuch as stearic acid is a common contaminant on many metal and plastic surfaces owing to its use as a metal-working lubricant and its occurrence in human sebum. Since gross contamination—i.e., more than a monomolecular layer—is commonly removed by immersing the contaminated object in a bath of solvent, it is of interest to study the solubility of a typical long-chain fatty acid, such as stearic acid, in a variety of chlorofluorocarbon solvents and in their associated azeotropes with other industrially important solvents such as acetone, ethanol, methylene dichloride, and chloroform.

The method used to determine the solubility of stearic acid in these solvents was the phase disappearance method, also known as the plethostatic or synthetic method (*1, 11*). This method involves determining the temperature at which the last trace of a known quantity of the solid solute disappears when the temperature of the solute/solvent system is raised very slowly.

Comparison with the data of Ralston and Hoerr (*7*) for stearic acid in carbon tetrachloride showed agreement within 10% up to 38° C. It is not known how much of the difference can be ascribed to purity differences and how much to technique and bias. We believe the purity of the stearic acid used in this work was higher than that used by previous workers inasmuch as high-purity vacuum distilled material was used here with the purity of the stearic acid being checked by gas-liquid chromatography. Much of the previously published stearic acid solubility data was carried out over 20 years ago when high-purity stearic acid was not available commercially and purity was not so readily verified. Another factor often neglected is the water content of the solvent. In some cases, such as the system ethanol–stearic acid, the influence of trace water is marked. Water determinations were run routinely on the solvents in this work using the Karl Fischer method.

The stearic acid used in this work was Lachat Chemicals, Inc., 99.5% stearic acid with a melting point of 70.0° C determined with a Kofler hot stage as compared to a value of 69° C determined by differential thermal analysis. This stearic acid was used because ordinary reagent grades were shown by gas-liquid chromatography to contain several percent homologs difficult to remove adequately by fractional crystallization. A Varian column, with 5 wt % Carbowax 20*M* and terephthalic acid on 40/60-mesh Fluoropak 80, was used on an Aerograph 1520 with hydrogen flame detector using 1 μl. samples of 5 wt % solutions in benzene, column temperature of 230° C, and a helium flow of 25–30 cc/min. The solvents were distilled and dried with Davison 3A Molecular Sieve prior to use. The solvents CCl_2FCClF_2, CCl_2FCCl_2F, and CF_2BrCF_2Br were Du Pont Freon 113, Freon 112, and Freon 114B2, respectively. The CH_3CCl_3 was Dow Dowclene WR, and the other solvents were all reagent-grade materials.

Gas-liquid chromatography was used as the principal means of checking purity, but in the case of 1,2-difluorotetrachloroethane, the 1,1-isomer was not separated by the column, so isomer content was determined by infrared absorption spectroscopy.

Table I gives the boiling points and compositions of the trichlorotrifluoroethane azeotropes as determined by ebulliometry and gas-liquid chromatography.

Table II shows the measured density values of the solvents and azeotropes. Densities were measured with a 10-ml pycnometer calibrated with water.

The apparatus and procedure have been described previously (*1*). A sample of the stearic acid was weighed into a heavy-wall 35-ml glass bottle closed with a precision-ground Teflon stopper. After the added solvent was weighed, a Teflon-coated stirring bar was dropped into the container, and it was stoppered. As an added precaution, the top of the bottle and the Teflon stopper were covered with a tight-fitting rubber cap. The bottle was then immersed in a water bath whose temperature was uniformly raised at 1–2° C/hr, the sample being continuously agitated by the magnetic stirrer. Karl Fischer water analyses, run on samples of several of these solvent samples in the sealed bottles, after six hours immersion showed less than 10 ppm water, so it was concluded that water leakage was not a problem. The temperature at which the last trace of solid disappeared was measured with a thermometer calibrated against a Hewlett-Packard quartz crystal thermometer calibrated at the manufacturer's to within 0.02° C absolute accuracy using NBS techniques. This was further checked by a field calibration at the ice point.

Several determinations of the disappearance temperature were made for each point and an average value for each such set was used. The reproducibility of individual determinations fell within a range of 0.1° C for the heating rates used. Since significant errors often arise due to supercooling when the equilibrium is approached from the other side, only disappearance temperatures were measured.

An error analysis was run to estimate the accuracy of the solubility determinations. It showed that the measured values do not differ from the true values by more than 2%.

Melting point determinations of the Lachat stearic acid in the as-received state and as recrystallized from the solvents used here were run on a Kofler hot stage as well as by differential thermal analysis. The Kofler melting

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points obtained with a calibrated thermometer which can be read to the nearest 0.1° C were regarded as being more accurate than the DTA melting points since temperatures were not resolved more closely than the nearest 1° C on the DTA apparatus. Table III presents the results of these melting point determinations.

The general trend of values reported for the melting point of stearic acid has been upward toward 70° C over the years (*12*). This trend is very likely due to the higher purity stearic acid resulting from better separation methods and means for monitoring purity. Francis et al. (*4*) pointed out, for example, that 1% palmitic acid in stearic acid lowers the melting point of stearic acid from 69.9-69.3° C.

Table I. Compositions and Boiling Points of Chlorofluorocarbon Azeotropes

System	Composition, wt % chlorofluorocarbon	Normal bp, ° C
$CCl_2FCClF_2 + CH_3CH_2OH$	96.0	44.5
$CCl_2FCClF_2 + CHCl_3$	92.8	47.4
$CCl_2FCClF_2 + CH_2Cl_2$	50.1	36.5
$CCl_2FCClF_2 + (CH_3)_2CO$	88.4	43.6
$CCl_2FCClF_2 + (CH_3)_2CHOH$	96.0	46.3

Table II. Density of Solvents at 25° C

Solvent	Density, g/cc
CCl_2FCClF_2	1.564
CCl_3CF_3	1.566
CH_3CCl_3	1.319
CCl_2FCCl_2F	1.647
CF_2BrCF_2Br	2.164
CH_2Cl_2	1.316
CCl_4	1.587
CH_3CH_2OH	0.785
$CCl_2FCClF_2 + CH_3CH_2OH$ azeotrope	1.499
$CCl_2FCClF_2 + CHCl_3$ azeotrope	1.554
$CCl_2FCClF_2 + CH_2Cl_2$ azeotrope	1.423

Table III. Melting Points of Stearic Acid in the As-Received State and After Recrystallization from Various Solvents

Solvent	Melting point, DTA, ° C[a]	
	T_i[b]	T_p[c]
As-received	66	69
CCl_4	63	68
$CCl_2FCClF_2 + CH_3CH_2OH$ azeotrope	64	69
$CCl_2FCClF_2 + CHCl_3$ azeotrope	66	69
CCl_2FCClF_2	64	69
$CCl_2FCClF_2 + CH_2Cl_2$	64	69
$CCl_2FCClF_2 + (CH_3)_3CO$	65	69
CCl_2FCCl_2F	66	69

[a] Heating rate 15° C/min on Du Pont Model 900 differential thermal analyzer (DTA). [b] Start of melting. [c] Temperature at which peak occurs.

Samples of stearic acid recrystallized in the same way for the solubility determinations—i.e., rapidly cooling the solution from about 55° C to about 15° C with ice—were submitted for X-ray and infrared analyses. Singleton et al. (*10*) state that mixtures of polymorphs occur when crystallization occurs in the range 35-53° C. The X-ray diffraction patterns, obtained by using the powder method, confirmed that a mixture of *B*- and *C*-forms was present, whereas comparison with the infrared spectra of von Sydow (*13*) showed that the *C*-form, the stable form at these conditions, was definitely present, and that the unstable *B*-form might be.

The solubility data were fitted with an Antoine-type vapor pressure equation of the form

$$S = 10 \exp ([D + AT]/[T - C]) \qquad (1)$$

where S is solubility in grams solute per 100 grams solvent, and T is temperature in degrees centigrade.

The least-squares criterion for best fit was used resulting in nonlinear equations for determination of the constants (Table IV; A, C, D). These equations were solved using a method described by Scarborough (*9*). The values of the constants, the standard deviation of the points from the fitted curves, and the experimental range covered are given in Table IV.

Table V gives smoothed values calculated from Equation 1 for the solubilities at intervals of 5 degrees centigrade in the experimental range.

Consideration of these data leads to several observations: (1) Of the chlorinated solvents, chloroform exhibits the highest solvency for stearic acid. This fact is in agreement with the observation by Zellhoffer et al. (*14*) that solvents which contain donor atoms (oxygen or nitrogen) dissolve the halogenated hydrocarbons which have at least one hydrogen atom in the molecule much more readily than do solvents without atoms readily donating electrons. (2) The extra chlorine atom in CCl_2FCCl_2F (compared to $CClF_2CCl_2F$) confers higher solvency for stearic acid on that compound.

The pronounced effect of water concentration on stearic acid solubility in ethanol is shown in Table VI where smoothed values from these experiments for 760-ppm water–ethanol are compared with the data of Ralston and Hoerr (*6*) for 95.0 and 99.6 wt % ethanol. When very dry ethanol (<100 ppm) was used as the solvent, we were not able to obtain reproducible solubility values because the solution exhibited turbidity which decreased so imperceptibly with increasing temperature that accurate estimates of solid phase disappearance could not be made.

Table IV. Values of Constants, Range of Validity, and Standard Deviation for Function $S = 10 \text{ Exp } ([D + AT]/[T - C])$ Used to Fit Stearic Acid Solubility Data

System	Range, ° C	A	C	D	σ, ° C
CCl_2FCClF_2	24-49	−26.512	372.976	851.779	0.15
CF_2BrCF_2Br	24-37	−9.622	−90.715	−300.957	0.15
CCl_2FCCl_2F	28-48	−72.599	1211.276	1685.540	0.21
CCl_3CF_3	28-43	−10.459	178.513	337.214	0.17
CCl_4	24-41	4.567	−36.413	−68.824	0.13
CH_3CH_2OH	12-40	−2.592	80.585	45.412	0.34
CH_3CCl_3	24-36	−7.856	195.699	80.238	0.23
CH_2Cl_2	23-35	4.192	−16.264	−81.943	0.29
$CCl_2FCClF_2 + CH_2Cl_2$	8-37	7.360	−78.457	−118.137	0.27
$CCl_2FCClF_2 + (CH_3)_2CH_2OH$	18-38	−14.492	394.083	223.029	0.30
$CCl_2FCClF_2 + CHCl_3$	19-38	19.027	−222.869	−537.052	0.03
$CCl_2FCClF_2 + CH_3CH_2OH$	22-42	−55.308	1287.201	741.442	0.22
$CCl_2FCClF_2 + (CH_3)_2CO$	20-40	−10.861	245.852	231.045	0.25

Table V. Smoothed Values of Stearic Acid in Various Solvents

(Temperature, ° C. Solubility, g/100 g solvent)

CH_2Cl_2	
25	3.58
30	8.85
35	18.3

$CCl_2FCClF_2 + (CH_3)_2CHOH$	
20	1.50
25	2.38
30	3.81
35	6.18

$CCl_2FCClF_2 + CH_2Cl_2$	
10	0.31
15	0.82
20	1.97
25	4.33
30	8.84
35	17.0

CCl_2FCCl_2F	
30	2.61
35	5.33
40	11.0
45	22.7

CCl_3CF_3	
30	0.69
35	1.58
40	3.85

$CCl_2FCClF_2 + (CH_3)_2CO$	
20	0.86
25	1.52
30	2.74
35	5.09
40	9.72

CCl_4	
25	5.47
30	10.6
35	18.8
40	30.9

CH_3CCl_3	
25	4.79
30	8.67
35	16.3

$CCl_2FCClF_2 + CHCl_3$	
20	0.22
25	0.56
30	1.35
35	3.16

$CCl_2FCClF_2 + CH_3CH_2OH$	
25	3.22
30	5.37
35	8.99
40	15.1

CH_3CH_2OH (760 ppm H_2O)	
15	0.79
20	1.27
25	2.23
30	4.35
35	9.86
40	27.3

CCl_2FCClF_2	
25	0.28
30	0.68
35	1.67
40	4.23
45	11.0

CF_2BrCF_2Br	
25	0.30
30	0.79
35	1.92

Table VI. Effect of Water Concentration on Stearic Acid Solubility in Ethanol

	Solubility, g/100 g solvent		
	This work,	Ralston and Hoerr (*6*)	
Temp, ° C	760 ppm H_2O	50,000 ppm	6000 ppm
20	1.27	1.13	2.24
30	4.35	3.42	5.43
40	27.3	17.1	22.7

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Pore-Size Distributions of Copper Oxide–Alumina Catalysts

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Six copper oxide–alumina catalysts were prepared using cupric chloride, bromide, nitrate, or sulfate in conjunction with sodium or potassium hydroxide, with wet or dry alumina as the carrier. The pore-size distributions were determined by the Cranston-Inkley method, based on adsorption isotherms. The resulting distributions, unimodal or multimodal, were adequately represented by simple or complex Weibull distributions. The surface areas based on the Cranston-Inkley method were compared with the BET areas.

In recent years copper oxide–alumina catalysts assumed increased importance because of their effectiveness in the removal of carbon monoxide, hydrocarbons, and nitrogen oxides which exist in the automobile exhaust emissions. (See, for example, refs. *1*, *3*, and *11*.) Copper oxide catalysts prepared in different ways showed different catalytic activities. In an attempt partially to explain the variation in catalyst performance, the pore-size distributions of six copper oxide–alumina catalysts with approximately the same chemical composition but prepared with different raw materials were determined. It is expected that differences in the pore structure of the catalysts may affect catalyst effectiveness, reaction selectivity, surface stability, susceptibility to poisoning, as well as heat transfer characteristics (*8*).

The pore-size distributions of a large family of silica gels were found by Wheeler (*10*) to follow approximately a normal distribution. Debaun et al. (*5*) reported that

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