# The Effect of Water On the Solidification Points of Fatty Acids. Solubility of Water in Fatty Acids

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## Introduction

Water is miscible with the first four normal saturated fatty acids, but the higher homologs dissolve water to a very slight extent. The solidification points of the low molecular weight acids are greatly depressed by the addition of water (1,2,3,4,5,6,7). Thus, in the case of acetic acid, the maximum depression of the solidification point by water is 44°C., while that of normal propionic acid is 7°C. Since there are no accurate data concerning the effect of water on the solidification points of acids containing more than five carbon atoms, it was considered desirable to determine this effect because of the wide use of this constant as a criterion of purity. In the course of this investigation it was found advisable to determine the solubility of water in several of the acids at temperatures up to 100°C. Due to a limited supply of the pure acids, only a few such measurements could be made. However, the data obtained were considered sufficient to permit the construction by interpolation of approximate solubility curves for the acids not investigated. This paper presents a study of the effect of water in lowering the solidification points of the normal saturated fatty acids from caproic to stearic, inclusive, and a preliminary report of the solubility of water in these acids from their solidification points to 100°C.

## Apparatus and Materials

The solidification points of the acids and solutions were determined on five-gram samples contained in 1 x 15 cm. test tubes partially immersed in an oil (or acetone) bath. The thermometer, which was used for measurements above 0°C., was graduated in one-tenth degree intervals, and had been calibrated at 0°, 32°, and 61°C. by measuring the transition temperatures of water, sodium sulfate decahydrate (8), and strontium chloride hexahydrate (9). Temperatures below 0°C. were measured with an iron-constantan thermocouple which had been checked against the temperature of an ice-water mixture. Solidification points could be duplicated within ± 0.02°C., and the results presented are probably accurate to ± 0.05°C.

The solubility determinations were carried out in a water bath consisting of a two-liter beaker heated electrically by means of a coil of "Chromel" wire wound on the outside of the beaker. The temperature of the bath was controlled by means of a rheostat in series with the coil, and was measured with the calibrated thermometer. The temperatures thus obtained are probably accurate to ± 0.5°C.

The acids were obtained from the following sources: Armour and Company, Carbide and Carbon Chemicals Corporation, and Eastman Kodak Company. Tridecylic, pentadecylic, and heptadecylic acids were synthesized from their next lower homologs. Each acid was purified by one or more of the following methods: crystallization from suitable solvents, fractionation under vacuum in a Stedman-packed column, and fractional crystallization without a solvent. The purity of a given acid was considered sufficient when its freezing point was in satisfactory agreement with, or was higher than, the best value reported in the literature.

The water used in these experiments was distilled from an alkaline potassium permanganate solution in an all-Pyrex glass still, and was cooled without access to the atmosphere. Since its specific conductance was 1 x $10^{-6}$ mhos at 25°C., its impurities were, therefore, at a minimum.

## Experimental Procedure

In the determination of the solidification point the test tube containing the sample was partially immersed in the oil (acetone was used for sub-zero temperatures) bath held at a temperature slightly higher than the melting point of the sample. The temperature of the bath was slowly lowered while the sample was agitated with a small "Chromel" wire stirrer. Above room temperature, air surrounded the bath. Between this temperature and 0°C., the bath was partially immersed in ice-water, and below 0°C., the bath was cooled with solid carbon dioxide in acetone. At the moment of crystallization of the sample, the temperature of the bath was never more than two degrees below that of the sample. In general, supercooling did not occur.

After the solidification point of an acid had been determined, a small weighed amount of water was added to a known weight of the acid, and the solidification point of the solution was determined. This procedure was repeated with further additions of water until the solidification point of the solution reached a constant value, indicating that an isothermal transition had been attained. This system is shown diagrammatically in Fig. 1. The isothermal transition is represented by PC. The line BP is the solubility curve of water in acid from 100°C. to the solidification point, and AP represents the lowering of the solidification point of the acid upon addition of water. By plotting the solidification temperatures against the percentage of water, the composition of the point P was ascertained. It was found that the intersection of lines AP and PC could be located more accurately by plotting the logarithms of the percentage of water against the amount of depression of the solidification temperature.

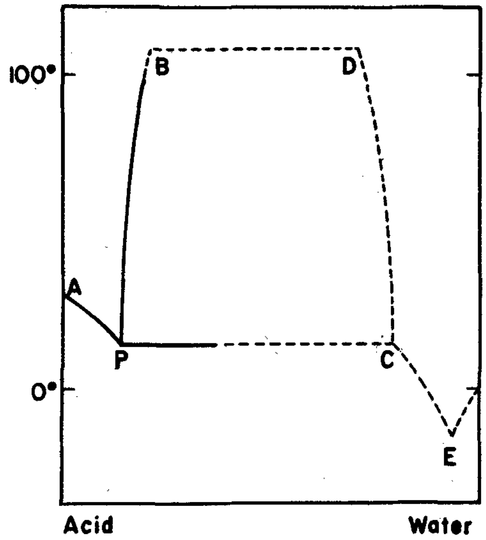

FIG. 1. Schematic Diagram of the Fatty Acid-Water Systems. The solid lines represent the part of the system investigated in this report.

The composition at the point P gives the solubility of water in a given acid at one temperature. The solubility of water in some of the acids was determined at several higher temperatures by the method of Alexejeff (10). In this synthetic method, weighed amounts of the two components were sealed in small glass tubes and observed visually as the tubes were rotated in a bath while the temperature was changed gradually. After the samples had been heated until clear solution was obtained, the temperature of the bath was lowered very slowly (about one degree per half hour) and the temperature at which water droplets separated from the solution was recorded. It was found that the temperatures at which the two liquids separated were more readily reproducible than those at which solution occurred. In this way the solubility of water in caproic, heptylic, undecylic, lauric, pentadecylic, and stearic acids was measured. The few determinations which were made allowed the construction of temperature-solubility curves for these acids. Since the appropriate point P was known for each of the other acids, interpolated curves could be plotted for the other acids. Thus, a rough approximation of the solubility of water in caprylic, nonylic, capric, tridecylic, myristic, palmitic, and heptadecylic acids has been obtained. These solubilities are probably accurate to ± 1%.

## Results

The results of the solidification point experiments are listed in Table I, and are shown graphically in Fig. 2 as the weight per cent of water in each acid against the depression of the solidification point of the pure acid.

TABLE I

Solidification Points of Fatty Acids Containing Water

| % $H_2O$ | °C. | % $H_2O$ | °C. | % $H_2O$ | °C. |
|---|---|---|---|---|---|
| Caproic | | Undecylic | | Pentadecylic | |
| 0.000 | —3.24 | 0.000 | 28.13 | 0.000 | 52.49 |
| 0.910 | —4.61 | 0.301 | 27.65 | 0.191 | 52.28 |
| 1.94 | —5.28 | 0.698 | 27.29 | 0.408 | 52.09 |
| 2.70 | —5.38 | 1.41 | 26.98 | 0.708 | 51.95 |
| 4.74 | —5.38 | 1.82 | 26.89 | 1.13 | 51.82 |
| Heptylic | | 2.41 | 26.80 | 1.29 | 51.79 |
| 0.000 | —6.26 | 3.33 | 26.77 | 1.45 | 51.77 |
| 1.78 | —8.02 | 3.97 | 26.77 | 1.74 | 51.77 |
| 2.63 | —8.20 | Lauric | | 2.02 | 51.77 |
| 4.30 | —8.32 | 0.000 | 43.86 | Palmitic | |
| Caprylic | | 0.224 | 43.50 | 0.000 | 62.41 |
| 0.000 | 16.30 | 0.627 | 43.16 | 0.204 | 62.19 |
| 0.680 | 15.32 | 1.12 | 43.01 | 0.499 | 62.01 |
| 1.10 | 14.99 | 1.64 | 42.82 | 0.763 | 61.90 |
| 1.77 | 14.70 | 2.01 | 42.76 | 1.09 | 61.82 |
| 2.46 | 14.53 | 2.44 | 42.72 | 1.31 | 61.79 |
| 3.02 | 14.43 | 2.88 | 42.72 | 1.50 | 61.79 |
| 3.39 | 14.39 | Tridecylic | | Heptadecylic | |
| 4.06 | 14.35 | 0.000 | 41.76 | 0.000 | 60.94 |
| 4.89 | 14.35 | 0.277 | 41.39 | 0.158 | 60.78 |
| Nonylic | | 0.591 | 41.15 | 0.329 | 60.68 |
| 0.000 | 12.24 | 0.887 | 41.03 | 0.564 | 60.57 |
| 0.437 | 11.49 | 1.38 | 40.89 | 0.836 | 60.49 |
| 1.04 | 11.01 | 1.77 | 40.80 | 1.09 | 60.42 |
| 1.58 | 10.80 | 2.17 | 40.76 | 1.29 | 60.42 |
| 2.33 | 10.63 | 2.54 | 40.76 | Stearic | |
| 3.12 | 10.53 | Myristic | | 0.000 | 69.20 |
| 3.88 | 10.51 | 0.000 | 54.01 | 0.149 | 69.07 |
| 5.02 | 10.51 | 0.398 | 53.57 | 0.309 | 68.96 |
| Capric | | 0.701 | 53.41 | 0.445 | 68.89 |
| 0.000 | 30.92 | 1.04 | 53.29 | 0.507 | 68.86 |
| 0.584 | 30.17 | 1.30 | 53.26 | 0.698 | 68.79 |
| 1.04 | 29.81 | 1.56 | 53.20 | 1.02 | 68.74 |
| 1.88 | 29.55 | 1.82 | 53.18 | 1.28 | 68.74 |
| 2.54 | 29.44 | 2.12 | 53.18 | | |
| 3.25 | 29.39 | | | | |
| 3.82 | 29.39 | | | | |

The curves in Fig. 2 terminate at the concentration represented by the point P for each acid. Thus caproic acid containing 2.2% water solidifies approximately 2°C. below the solidification point of the pure acid. This solution has the composition of the point P, and an increase in the amount of water present in the acid does not further depress the solidification point until the composition represented by C is reached. The maximum depression for any given acid is greater than that for the next higher member of the series. Stearic acid saturated with water solidifies only 0.5°C. lower than does the anhydrous acid. A given percentage of water, if below the amount represented by P, is more effective in depressing the solidification point of any acid than that of the next higher homolog.

The solubility data are given in Table II, and are shown graphically in Fig. 3.

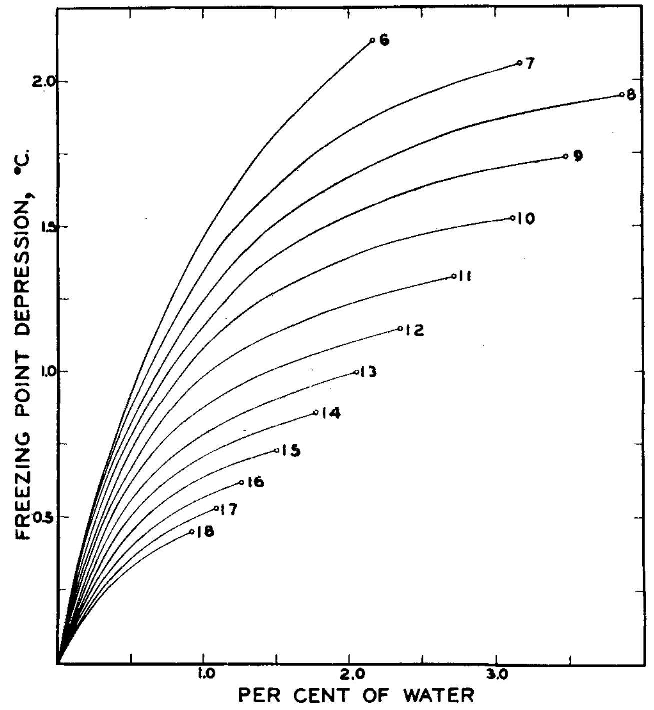

FIG. 2. Depression of the Solidification Points of Fatty Acids by the Addition of Water. The numbers refer to the number of carbon atoms in the acids.

TABLE II

Solubility of Water in Fatty Acids

| | % $H_2O$ | Solution Temp., °C. | | % $H_2O$ | Solution Temp., °C. |
|---|---|---|---|---|---|
| Caproic | 2.21<br>4.73<br>7.57<br>9.70 | —5.4<br>12.3<br>31.7<br>46.3 | Lauric | 2.35<br>2.70<br>2.85 | 42.7<br>75.0<br>90.5 |
| Heptylic | 2.98<br>8.98 | —8.3<br>42.5 | Tridecylic | 2.00 | 40.8 |
| Caprylic | 3.88 | 14.4 | Myristic | 1.70 | 53.2 |
| Nonylic | 3.45 | 10.5 | Pentadecylic | 1.46<br>1.62 | 51.8<br>90.0 |
| Capric | 3.12 | 29.4 | Palmitic | 1.25 | 61.8 |
| Undecylic | 2.72<br>4.21 | 26.8<br>57.5 | Heptadecylic | 1.06 | 60.4 |
| | | | Stearic | 0.92<br>1.02 | 68.7<br>92.4 |

The lower end of the curves in Fig. 3 represents the solidification point of the composition at P for each acid. Of the group of acids investigated, any one is capable of dissolving more water than will its next higher homolog. The only exception to this generalization is the fact that water is less soluble in caproic acid than in heptylic acid. The temperature coefficients of solubility of water in the acids become increasingly smaller as the series is ascended.

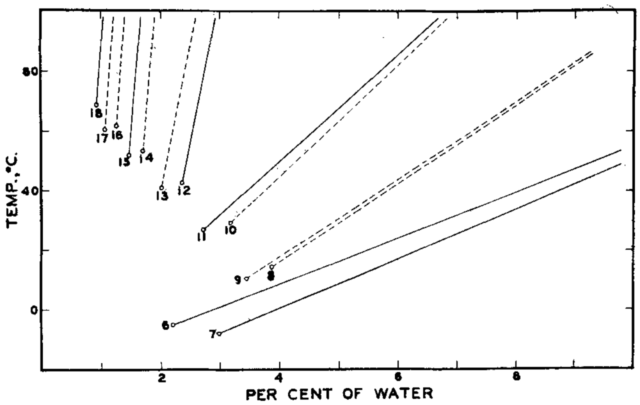

FIG. 3. Solubility of Water in the Fatty Acids. The solid lines represent the solubilities which were measured (see Table II), while the broken lines indicate the probable solubility of water in the other acids.

## Summary

The effect of water on the solidification points of the normal saturated fatty acids from caproic to stearic, inclusive, has been investigated, and the depressions caused by given amounts of water in each of these acids has been presented. The solubility of water in six of the acids above their solidification points has been determined, and these data have been reported, together with rough approximations of the solubility of water in the other acids of this series.

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