

THE SOLUBILITIES OF THE NORMAL SATURATED FATTY ACIDS IN WATER

D. N. EGGENBERGER, F. K. BROOME, A. W. RALSTON, AND H. J. HARWOOD

Received May 27, 1949

Solubilities of saturated fatty acids in water reported by John and McBain (1) are one-fifth to one-tenth of those reported by Ralston and Hoerr (2). As a result of these discrepancies, it was decided to reopen the study.

EXPERIMENTAL

Preparation of Materials. The fatty acids used in this work were highly purified samples prepared by Mr. R. S. Sedgwick. Freezing points of the acids were as follows: octanoic, 16.63°; nonanoic, 12.52°; decanoic, 31.49°; hendecanoic, 28.59°; dodecanoic, 44.16°; tetradecanoic, 54.25°. Water with a conductivity of 1 micromho was used in making up all solutions.

Procedure. Most of the determinations were made on fatty-acid solutions saturated by heating to 100°, shaking, then placing in a constant-temperature bath with a regulation range of $\pm 0.05^\circ$. In several cases, saturation was also approached from a lower temperature, and in all such runs identical values were obtained. The minimum saturation time at the desired temperature was 16 hours. This time was checked in some cases by starting from an over- or under-saturated state, and was found to be adequate. During the saturation period, the solution was stirred by bubbling purified nitrogen through it. The nitrogen had previously been led through soda-lime and then water.

To measure a volume of solution for analysis, a pipet of 149.4 cc. capacity was built into the constant-temperature bath in such a way that most of the path for transporting the solution from the saturation flask to the pipet was in the water-bath. This system was so arranged that the solution was exposed only to the purified-nitrogen atmosphere.

The cell consisted of unplatized platinum electrodes built into a 300-cc. round flask. The constant was approximately 0.07.

Titration were performed in a separate water-bath. To prevent possible precipitation in moving the cell, 50 cc. of water was placed in the cell before the solution was added, and the titration bath was always at the saturation temperature or higher. To remove any remaining carbon dioxide from the solution in the cell, nitrogen, freed from carbon dioxide and saturated with water vapor at the titration temperature, was bubbled through the solution for 1 hour before titration. This passage of nitrogen was also used to stir the solution during the titration. The titrations of decanoic and longer-chain acids were run conductometrically. After preliminary trials, using various procedures with a known concentration of dodecanoic acid, it was concluded that by adding an excess of NaOH solution and back-titrating with HCl, the sharpest end-point was obtained. It was found that an excess of at least 1 cc. of 0.02 *N* base was necessary to give correct results. Lesser excesses of base did not remove all adsorbed acid from the cell walls. Octanoic and nonanoic acids were titrated directly with 0.1 *N* and 0.02 *N* NaOH, respectively, at 100°, using phenolphthalein as an indicator.

RESULTS AND DISCUSSION

The solubilities of the fatty acids at several temperatures are shown in Table I and temperature-solubility curves are shown in Figure 1. Attempts to measure the solubility of hexadecanoic and octadecanoic acids yielded values which were

not considered reliable. This is also true of dodecanoic and tetradecanoic acids at the lower temperatures (40° and 30°). Values for the solubility of octanoic acid are in agreement with those previously reported (2).

It is to be noted that alternation in the solubilities of even- and odd-chain-length acids does not occur although it might be expected from the alternation exhibited in melting points and latent heats of fusion. This may be due to the non-ideal nature of the solutions.

At comparable experimental points, our values are of the same magnitude as those of John and McBain (1). We believe that our values are more nearly correct

TABLE I
SOLUBILITIES OF NORMAL SATURATED FATTY ACIDS IN WATER

NO. OF C ATOMS	SOLUBILITY IN G./100 CC. OF SOLUTION			
	30°	40°	50°	60°
8	0.0789	0.0843	0.0943	0.1071
9	.0212	.0222	.0264	.0299
10	.0064	.0072	.0081	.0100
11	.00198	.0023	.0026	.0032
12		.00077	.00092	.00116
14			.00042	.00056

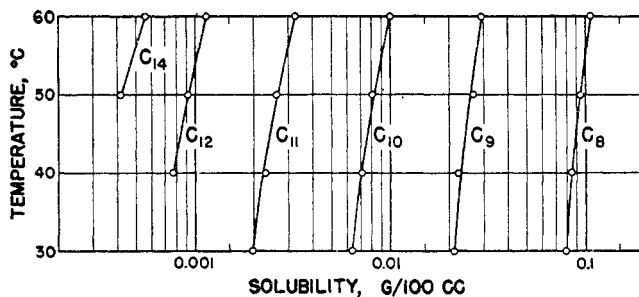


FIGURE 1. SOLUBILITIES OF THE FATTY ACIDS IN WATER

for the reasons following. John and McBain, using a conductivity method, took readings after fifteen minutes even though the resistance was changing owing probably to adsorption. The fact that material was adsorbed would lead to erroneous results. The assumption that their impurity was entirely carbon dioxide may be questioned. The equation $C_{H^+} = C_{P^-} = 4.26 \times 2.35 \times 10^{-12} = 3.16 \times 10^{-6} M$ is also not justified. In our work, acid adsorbed on the walls was removed by a proper excess of NaOH. Carbon dioxide was also removed, and the method is in general a more direct one.

Acknowledgment. The authors wish to acknowledge valuable suggestions made by Dr. I. M. Kolthoff in the course of this work.

SUMMARY

The solubilities of octanoic, nonanoic, decanoic, and hendecanoic acids were determined in water at 30°, 40°, 50°, and 60°; of dodecanoic acid at 40°, 50°, and 60°, and of tetradecanoic acid at 50° and 60°.

CHICAGO, ILLINOIS

REFERENCES

- (1) JOHN AND MCBAIN, *J. Am. Oil Chemists' Soc.*, **25**, 40 (1948).
- (2) RALSTON AND HOERR, *J. Org. Chem.*, **7**, 546 (1942).