[CONTRIBUTION FROM THE CHEMICAL LABORATORY, SOUTH DAKOTA STATE COLLEGE]

THE SOLUBILITY OF BARIUM *n*-BUTYRATE[1,2]

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In 1887 Sedlitzky[3] determined the solubilities of the calcium salts of *iso*valeric, *iso*butyric and methylacetic acids. In 1902 Lumsden[4] determined the solubilities of a number of calcium salts of the acetic acid series. In 1903 Walker and Fyffe[5] studied the solubility of barium acetate. In 1926 the solubility of barium propionate was reported.[6] Since some of these later determinations are at variance with those of the earlier investigators, the determination of the solubility of barium *n*-butyrate was undertaken, although it had been reported by Deszáthy in 1893.[7]

While Deszáthy's curve for the solubility of barium *n*-butyrate, as shown by the dotted line in Fig. 1, is somewhat similar to that obtained in this investigation, yet there is a distinct difference in the values obtained.

Experimental Part

Preparation of the Salt.—The barium *n*-butyrate was prepared by treating c. p. barium hydroxide with a slight excess of *n*-butyric acid (Eastman's, *n*-Butyric acid No. 60) and evaporating the solution to crystallization. The crystals were washed with alcohol and dried. The analyses in Table I show that the alcohol washing had no effect on the composition of the salt.

Determination of the Composition of the Hydrate.—Deszáthy reported that the salt in contact with solution was the dihydrate over the entire temperature range.[7]

The salt crystallizes slowly from the solution in beautiful star-shaped clusters of slender crystals. Some individuals over two centimeters in length were obtained. As shown in Table I the salt is in the water-free form at 20° and washing with alcohol and drying at 60° have no effect on its composition. The analysis of the salt at 0° indicates that it is also anhydrous. A microscopic examination of these latter crystals showed them to be identical with those at 20°.

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[1] This is the second of a series of determinations of the solubilities of the barium salts of the fatty acids.

[2] The early completion of this study was accomplished only by the assistance of one of our senior students, Mr. C. W. Eddy, which assistance it gives me great pleasure to acknowledge.

[3] Sedlitzky, *Monatsh.*, **8**, 563 (1887).

[4] Lumsden, *J. Chem. Soc.*, **81**, 350 (1902).

[5] Walker and Fyffe, *ibid.*, **83**, 173 (1903).

[6] Wing and Thompson, THIS JOURNAL, **48**, 104 (1926).

[7] Deszáthy, *Monatsh.*, **14**, 245 (1893).

TABLE I

DETERMINATION OF FORM OF SALT

Type of sample	Wt. of sample, g.	$BaCrO_4$ found	$BaCrO_4$ calcd. from $Ba(but.)_2$	$BaCrO_4$ calcd. from $Ba(but.)_2.H_2O$
Large crystals, H_2O washed, air dried at 20°	0.8609	0.6963	0.7003	0.6620
Small crystals, alc. washed, oven dried at 60°	.5500	.4452	.4474	.4229
Crystals at 20°, H_2O washed, air dried, 1 hour	.7737	.6205	.6294	.5950
Crystals at 0.3° for 60 hours, filtered and air dried, 1/2 hour	.5728	.5530	.5471	.5173

Determination of the Solubility.—The solubilities were determined by making up the solutions, with an excess of salt, in two large tubes. These were placed in a thermostat equipped with a thermo-regulator in which the mercury contact did not foul, although the current through the regulator was about one-half ampere.[8] The regulation was within a 0.02° over the entire temperature range.

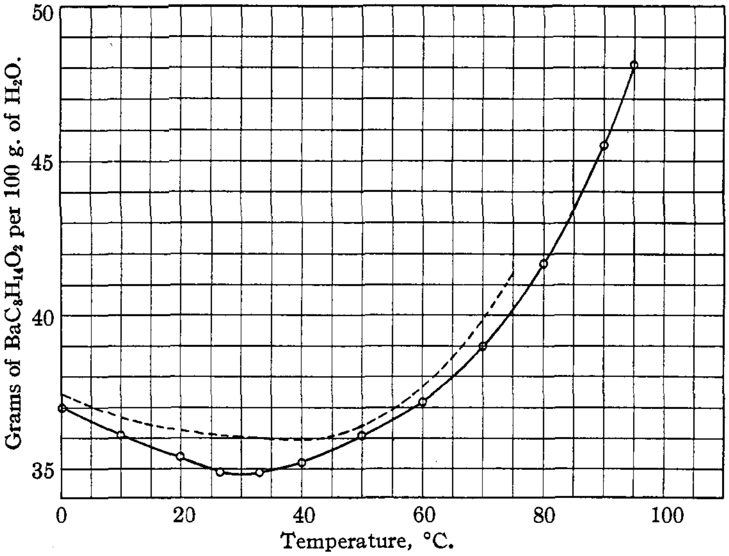

Fig. 1.

The solution in one tube was kept for half an hour at a temperature of from ten to twenty degrees above that of the observation and was then placed in the bath. The solution in the other tube was kept at a temperature below that of the observation until the experiment was ready to be carried out. The two solutions, placed in the bath at the required temperature, were stirred continuously for several hours, two to five, depend-

[8] Wing and Thompson, *Ind. Eng. Chem.*, **17**, 1242 (1925).

ing upon the temperature. Samples were then withdrawn by forcing the liquid through a filter and capillary tube into tared weighing bottles. The barium was precipitated in the form of the chromate and the amount of barium *n*-butyrate present was determined from this. Table II shows the results of these determinations and they are shown graphically by the solid line in Fig. 1.

The results of the determinations made by the supersaturation method and the undersaturation method were in very close agreement. In the average, the agreement was better than 0.2%. For example, by the undersaturation method, at 50.05° the test portion contained 26.50 g. of barium butyrate in 100 g. of solution, while at the same temperature, 26.53 g. of barium butyrate was found in 100 g. of solution by the supersaturation method. The values given in Table II are for the mean solubility at the various temperatures.

TABLE II

SOLUBILITY OF BARIUM BUTYRATE

Temp., °C.	0.06	9.92	19.86	26.50	33.00	39.98
$Ba(but.)_2$ in 100 g. of soln., g.	27.0	26.5	26.1	25.9	25.9	26.0
$Ba(but.)_2$ in 100 g. of water, g.	37.0	36.1	35.4	34.9	34.9	35.2
Temp., °C.	50.05	59.97	70.08	80.05	90.27	94.96
$Ba(but.)_2$ in 100 g. of soln., g.	26.5	27.1	28.0	29.5	31.3	32.5
$Ba(but.)_2$ in 100 g. of water, g.	36.1	37.2	39.0	41.7	45.5	48.1

Summary

1. The solubility of barium *n*-butyrate is a minimum at about 30°.
2. Over the entire temperature range, the salt in equilibrium with the solution is the water-free salt.
3. The solubility curve of barium *n*-butyrate is convex to the temperature axis.

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