

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, THE UNIVERSITY OF NEBRASKA]

THE SOLUBILITY OF BARIUM PROPIONATE

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In 1887 Sedlitzky¹ determined the solubilities of the calcium salts of *isovaleric*, *isobutyric*, and *methylacetic* acids. Renard,² in the same year, states that a monohydrate, a trihydrate and a hexahydrate of barium propionate can be prepared. A short time later Krasnicki³ published results upon the solubilities of the barium and calcium salts of formic, acetic and propionic acids. He also determined the solubilities of the "waterfree salt" of barium propionate which, from his calculation, was the monohydrate. He expressed his results in a smooth curve concave to the temperature axis.

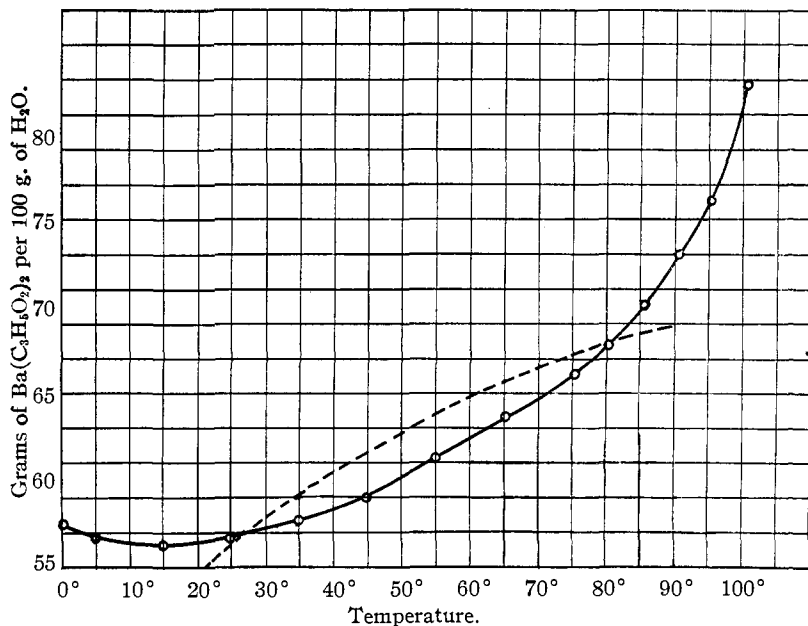


Fig. 1.—Solubility of barium propionate.

In 1902 Lumsden⁴ determined the solubilities of the calcium salts of a number of the acids of the acetic acid series. His results are quite different from those of Krasnicki. Furthermore, a year later Walker and Fyffe⁵ studied the solubilities of barium acetate and also found a wide deviation from the results of Krasnicki.

¹ Sedlitzky, *Monatsh.*, **8**, 563 (1887).² Renard, *Compt. rend.*, **104**, 913 (1887).³ Krasnicki, *Monatsh.*, **8**, 595 (1887).⁴ Lumsden, *J. Chem. Soc.*, **81**, 350 (1902).⁵ Walker and Fyffe, *ibid.*, **83**, 173 (1903).

Since the work of Lumsden and of Walker and Fyffe has shown that the curves of the solubilities of the salts of the fatty acids they investigated are convex to the temperature axis, it was believed that the curve of barium propionate should also be convex and not concave. It has developed that such is the case. Fig. 1 shows Krasnicki's curve as a dotted line and the curve of the solubility of barium propionate monohydrate. This curve resembles closely the solubility curve of calcium propionate monohydrate as determined by Lumsden. This is the first of a series of investigations upon the solubilities of the metallic salts of the fatty acids.

Experimental Part

Preparation of the Salt.—The barium propionate was prepared by treating c. p. barium hydroxide with a slight excess of propionic acid. The solution was decolorized with charcoal and evaporated to crystallization. At first the crystals were washed with water to remove the mother liquor. It was found that the salt is quite soluble in water, but practically insoluble in 95% ethyl alcohol. Consequently, the material used in these determinations was prepared by washing the crystals with alcohol, and recrystallizing twice from water.

The determination of the effect of the alcohol washing was made by drying at room temperature, a sample of the crystals washed with water, while another sample was washed with alcohol and dried in the usual way. Analysis showed that the two samples had the same composition.

Determination of the Form of Hydrate.—Since Renard² had reported two forms of barium propionate at ordinary temperatures, considerable time was consumed trying to determine the transition point by means of a dilatometer. However, no transition point could be located between 0° and 100°.

The composition of the salt was determined by analysis. Samples of the salt in equilibrium with water at various temperatures were analyzed, and the barium was weighed as barium sulfate. Table I shows that over the entire temperature range the salt in equilibrium with the solution is the monohydrate. This accounts for the fact that the dilatometer determinations did not show a transition point.

TABLE I
DETERMINATION OF FORM OF SALT

Temp., °C.	0	15	50	100
BaSO ₄ , found, g.	0.7560	0.8867	0.4398	0.3905
calcd., g.	.7532	.8831	.4363	.3874

Determination of the Solubility.—The solubilities were determined first by the method of Lumsden.⁴ Since the salt exists in the same form at all temperatures it was but necessary to place the salt and water in a flask and stir until equilibrium was established. This stirring was continued for eight hours at the lower temperatures and for only two to three hours at the higher temperatures. Three samples were stirred simultaneously. The liquid was filtered by suction as suggested by Lumsden⁴

and then portions of the filtrate were placed in tared platinum crucibles and weighed.

Since the barium propionate is hydrolyzed by water to such an extent that the warm solutions all smelled strongly of propionic acid, no attempt was made to weigh the barium propionate as such, but the propionate was converted in the crucible to barium sulfate, and the amount of the barium propionate originally taken was calculated from the barium sulfate obtained.

In repeating the determinations, a boiling saturated solution was made in a flask and this was then closed by a rubber stopper carrying two tubes. The flask was placed in a thermostat at the required temperature and shaken vigorously until the temperature equilibrium was established. The liquid was filtered by forcing it through a plug of cotton in a wide tube which had been sealed to a capillary tube. After several cubic centimeters had run out, the liquid was caught and weighed in the platinum crucibles. The rest of the procedure was the same as in the first method.

The results of the supersaturation method as well as the undersaturation method were in close agreement with themselves, the maximum deviation being less than ± 0.1 g. of barium propionate in 100 g. of solution. In addition, the results of the two methods (undersaturation and supersaturation) agree closely. For example, by the undersaturation method at 85.3° the test portion contained 40.9 g. of barium propionate in 100 g. of solution, whereas at 85.6° by the supersaturation method 41.2 was found in 100 g. of solution.

TABLE II
SOLUBILITY

Temp., $^\circ\text{C}$.	0.3	5.1	15.0	24.8	34.8	44.8	55.0
BaPr ₂ in 100 g. of soln., g.	36.5	36.2	36.0	36.2	36.6	37.1	38.0
in 100 g. of water, g.	57.5	56.7	56.3	56.7	57.7	59.0	61.3
Temp., $^\circ\text{C}$.	65.3	75.6	80.4	85.6	90.5	95.4	100.7
BaPr ₂ in 100 g. of soln., g.	38.9	39.8	40.2	41.2	42.2	43.2	44.7
in 100 g. of water, g.	63.7	66.1	67.8	70.1	73.0	76.1	82.7

Summary

1. The solubility of barium propionate is a minimum at about 10° .
2. Over the entire temperature range the salt in equilibrium with the solution is the monohydrate.
3. The solubility curve of barium propionate is convex to the temperature axis, and not concave as Krasnicki believed.

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