[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The Systems Ammonium Sulfamate–Sodium Sulfamate and Sodium Sulfamate–Sodium Nitrate

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The present paper describes the binary systems ammonium sulfamate–sodium sulfamate and sodium sulfamate–sodium nitrate.

Preparation and Purification of Materials.—The method used in the purification of ammonium sulfamate was described in the previous paper.

Merck sodium nitrate C. P. was crystallized twice from distilled water and dried under vacuum with phosphorus pentoxide.

Sodium sulfamate was prepared by the method described by Laning and van der Meulen.[2]

The Binary System Ammonium Sulfamate–Sodium Sulfamate.—Mixtures of weighed quantities of the components were prepared and placed in the melting point apparatus described in the previous paper. They were melted and allowed to crystallize slowly. The initial freezing point was taken, and then the melt was slowly warmed and the temperature at which the last crystals disappeared was also taken. In most cases the two temperatures were not more than a half degree apart. The mean of the temperatures at which crystals were just formed and at which the last crystal disappeared was taken as the freezing point. This procedure was necessary because the high viscosity of most of the melts led to extensive supercooling and exceedingly slow crystallization even when the melt was seeded.

The results of these determinations are given in Table I, and represented graphically in Fig. 1.

TABLE I

FREEZING POINTS OF MIXTURES OF AMMONIUM SULFAMATE (B) AND SODIUM SULFAMATE (C)

$NaSO_3NH_2$ (C), % by wt.	F. p., °C.	Eutectic point, °C.	Solid phase
0.0	132.85		B
5.0	128.80		
10.0	124.75		
15.0	120.70	118.7	
16.2	119.80	118.8	
16.8	119.20	118.8	
17.0	119.0	118.8	B_2C_5
17.5	121.0	118.8	
18.0	122.9	118.8	
20.0	130.2		
25.0	144.7		
30.0	157.9		
35.0	168.5		
40.0	177.0		
50.0	193.0		
60.0	204.4		
65.0	209.0		
70.0	212.3		
72.5	212.9		
73.0	212.6		C
75.0	215.0		
77.5	218.0		
80.0	221.5		
100.0	250.5		

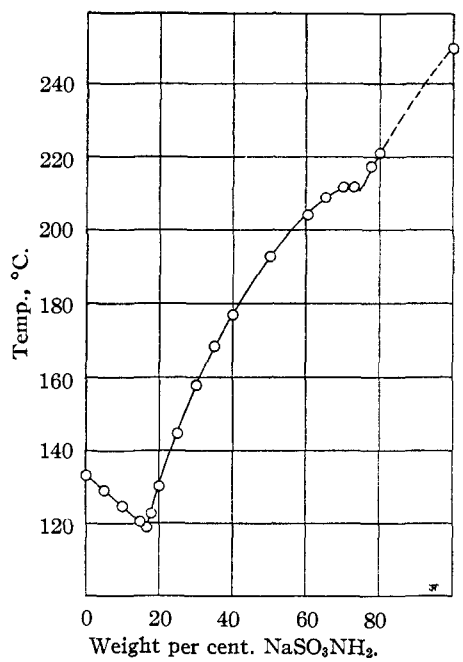

Fig. 1.—Freezing points of mixtures of $NH_4SO_3NH_2$ and $NaSO_3NH_2$.

The curve shows two eutectics. The lower occurs at a composition of 16.95% sodium sulfamate, and a temperature of 118.8°. The solid phases at this point are ammonium sulfamate and a compound $2NH_4SO_3NH_2 \cdot 5NaSO_3NH_2$. The latter compound melts congruently at 213 ± 1°. Since at temperatures above 170° decomposition of ammonium sulfamate occurs, it was necessary to work rapidly, especially at temperatures above 200°. An accurate determination of the upper eutectic point was not possible, but it lies near a temperature of 212° and a composition of 73.0% sodium sulfamate. From melts containing more sodium sulfamate, the solid which separates is pure sodium sulfamate.

The Binary System Sodium Sulfamate–Sodium Nitrate.—A preliminary investigation indicated that only a limited range of compositions could be studied. Mixtures containing

(1) Based on a thesis submitted by Stephen H. Laning to the graduate faculty of Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Laning and van der Meulen, THIS JOURNAL, **69**, 1828 (1947).

less that 15% or more than 60% of sodium nitrate have melting points at which decomposition is sufficiently rapid to prevent accurate determinations of melting points.

The melting points of mixtures in the range in which decomposition does not occur are given in Table II and are shown graphically in Fig. 2.

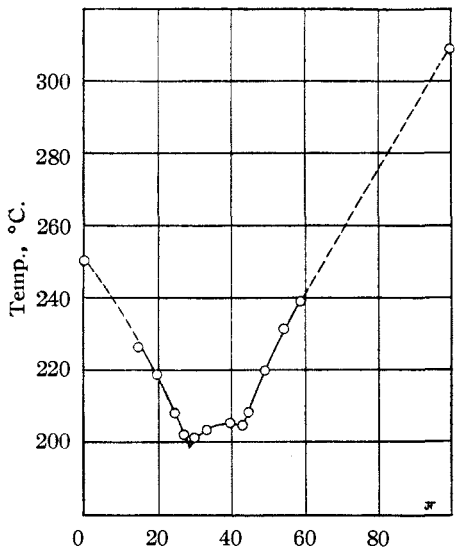

Fig. 2.—Freezing point of mixtures of $NaSO_3NH_2$ and $NaNO_3$.

From melts containing less than 28.5% sodium nitrate, the first crystals which separate are sodium sulfamate. The lower eutectic mixture contains 28.5% sodium nitrate, and melts at 199°. The other eutectic mixture contains 43.4% sodium nitrate and melts at a temperature of 205.0°. There is a compound $NaSO_3NH_2 \cdot NaNO_3$ with a melting point of 205.7°. It contains 41.68% sodium nitrate. From melts containing more than 43.4% sodium nitrate, the first crystals which separate on cooling are sodium nitrate.

TABLE II

FREEZING POINTS OF MIXTURES OF SODIUM SULFAMATE (C) AND SODIUM NITRATE (D)

$NaSO_3NH_2$ % (D) by wt.	F. p., °C.	Eutectic point, °C.	Solid phase
0.0	250.0		C
15.0	226.5		
20.0	219.0		
25.0	208.3	198.3	
27.5	202.5	198.8	
30.0	201.6	199.0	
33.3	203.8		
35.0	204.7		
40.0	205.3		
41.65	205.7		CD
41.67	205.3		
42.50	205.2		
43.33	205.2	205.0	
45.0	208.6	205.0	D
50.0	220.0		
55.0	231.6		
55.6	232.0		
59.8	238.8		
100.0	307.5		

Summary

1. Ammonium sulfamate and sodium sulfamate form a compound, $2NH_4SO_3NH_2 \cdot 5NaSO_3NH_2$, which melts congruently at 213 ± 1°.

2. The eutectic point between ammonium sulfamate and the 2:5 compound is at 118.8° with a melt containing 16.95% sodium sulfamate; the eutectic point between sodium sulfamate and the 2:5 compound is at a temperature near 212° with a melt containing 73.0% sodium sulfamate.

3. Sodium sulfamate and sodium nitrate form a compound $NaSO_3NH_2 \cdot NaNO_3$ with a melting point of 205.7°.

4. The eutectic point between sodium sulfamate and the 1:1 compound is at 199° with a melt containing 28.5% sodium nitrate; the eutectic point between sodium nitrate and the 1:1 compound is at 205° with a melt containing 43.4% so dium nitrate.

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