

tility was condensed in the dry-ice trap. The remainder of this preparation was oxidized by the method of Thiele. The product consisted entirely of a high-boiling liquid; apparently no azomethane was formed. During a distillation of this liquid to another trap an explosion occurred which demolished the purification train. The cause of this explosion is not known; at the time the system was completely closed off from mercury manometers and the diffusion pump. It seems highly improbable that azomethane should be explosive in these circumstances.<sup>1b</sup> On the basis of these facts it is suggested that azomethane is not responsible for this and other explosions; rather it is the high boiling liquid which is explosive. This latter seems to arise upon oxidation of dimethylhydrazine dihydrochloride which has been kept in a vacuum desiccator over calcium chloride for long periods of time. The 29% yield quoted above lends credence to the conclusion that the hydrazine derivative is perhaps oxidized in the desiccator. The identity of the liquid product has not been determined conclusively, but it is suggested that it may be methyl nitrate. It must be pointed out that Burton and Davis using an equally old preparation of dimethylhydrazine dihydrochloride which had been stored over sulfuric acid found that little high boiling liquid was formed upon oxidation by Thiele's method.

The product resulting by oxidation with cupric chloride has a molecular weight ranging from 57.5 for the first fraction to about 59 for the end fraction, as determined by means of a gas density balance. The writer contemplates preparation of pure azomethane by the use of an all-glass low temperature fractionating column of the Podbielniak type.

The writer acknowledges with appreciation a suggestion by Dr. T. W. Davis which led to the development of this method.

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### Improved Methods of Conditioning Surfaces for Adsorption

BY IRVING LANGMUIR AND VINCENT J. SCHAEFER

In a previous communication<sup>1</sup> a method was described for conditioning the surface of a built-up

(1) I. Langmuir and V. J. Schaefer, *THIS JOURNAL*, **59**, 1406(1937).

barium stearate film so that visible adsorbed monolayers of organic and inorganic substances could be taken up from solution.

We now find that thorium nitrate can be used as well as aluminum chloride and that a barium stearate Y-multilayer can be conditioned by immersion into a  $1 \times 10^{-3}$  molar aqueous solution of either salt. The fact that a B-layer can be conditioned in this manner is evidence of the overturning of barium stearate molecules. Such a surface when conditioned is hydrophilic but when dried becomes hydrophobic.

When sodium silicate is added to a hydrous multilayer conditioned with thorium and then washed and dried, an increment of 10 Å. is observed. This surface after drying is hydrophilic and oleophilic. Successive layers of thorium and silicate may be added, five alternate layers of each giving a thickness of about 52 Å.

A film of pure stearic acid covered by five such layers retains 60% of its thickness after soaking in benzene for ten minutes although it instantly dissolves in its normal state. This coating also provides complete protection from water injury.

When a barium stearate film is conditioned with aluminum, its thickness increases 3.2 Å. If some sodium silicate is placed on the wet surface it causes the water to peel back suddenly and removes not only the aluminum but also 8 Å. of the underlying film. This loss is the equivalent of one-third of the molecules in a monolayer and possibly measures those which turned around. When the aluminum conditioning is followed by thorium conditioning, the peeling back does not occur upon the addition of the silicate, although the increment is removed with no injury to the underlying film.

Better adsorption of protein from solution is found when thorium is used instead of aluminum. Using a 1% solution of egg albumin in water the thickness on thorium was 48 Å., on aluminum 33 Å., and on thorium silicate 35 Å.

The use of a small 60-cycle solenoid vibrator replaces manual stirring and greatly facilitates uniform monolayer adsorption.

A monolayer of desoxycholate may be applied by bringing sodium desoxycholate in contact with a hydrous thorium conditioned surface. When washed the increase due to desoxycholate is 17 Å. The resulting dehydrated surface is hydrophobic and highly oleophilic.

When vapors of decane and tetradecane were

brought into contact with this surface an increase of 3.3 Å. was observed which disappeared, however, within five minutes. This increment would indicate a lengthwise adsorption independent of length of chain.

The ability of a thorium nitrate or aluminum chloride solution to condition the surface of a multilayer depends upon the composition of the built-up film. A mixed barium stearate-stearic acid film containing 50% or more of stearate is conditioned more readily than a film of pure stearic acid. Films of copper stearate from water containing  $1 \times 10^{-5} M$  copper chloride or a barium stearate layer covered by an A-X monolayer of oleic acid do not react at all with either the thorium or aluminum solution.

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### Compound Formation in the Binary Systems $\text{Ba}(\text{NO}_3)_2\text{-KNO}_3$ and $\text{Ba}(\text{NO}_3)_2\text{-NaNO}_3$

BY JOHN E. RICCI

In connection with a discussion appearing in a subsequent note,<sup>1</sup> the existing data on the binary systems  $\text{Ba}(\text{NO}_3)_2\text{-KNO}_3$  and  $\text{Ba}(\text{NO}_3)_2\text{-NaNO}_3$  have been re-examined critically, with the conclusion that whereas both systems have heretofore been represented as of the simple eutectic type, the data actually indicate definite compound formation in both cases.

Aside from incidental measurements by Maumené<sup>2</sup> and by Guthrie,<sup>3</sup> the only phase rule studies of the binary systems  $\text{Ba}(\text{NO}_3)_2\text{-KNO}_3$  and  $\text{Ba}(\text{NO}_3)_2\text{-NaNO}_3$  appear to have been made by Harkins and Clark<sup>4</sup> and by Laybourn, Madgin and Freeman.<sup>5</sup> No double salt formation was reported in either of these latter investigations. The summaries, edited by Amadori, given in the "International Critical Tables,"<sup>6</sup> are those of Harkins and Clark, so that the same statements appear there too. Of these two studies, the earlier, that of Harkins and Clark, is more nearly complete in data, although no inferences at all were drawn as to the phases present. The later work of Laybourn, Madgin and Freeman, which ap-

parently verified the system to be simple, must, in the writer's opinion, however, be considered inconclusive both in the light of a careful inspection of the data of Harkins and Clark, and because of the incomplete range of composition covered: only 0-47 mole %  $\text{Ba}(\text{NO}_3)_2$  in the potassium system, and only 0-40 mole %  $\text{Ba}(\text{NO}_3)_2$  in the sodium system.

The data of Harkins and Clark, recalculated into mole percentages, as listed in the "International Critical Tables,"<sup>6</sup> are used in plotting the freezing point diagrams for the two systems shown in Fig. 1.

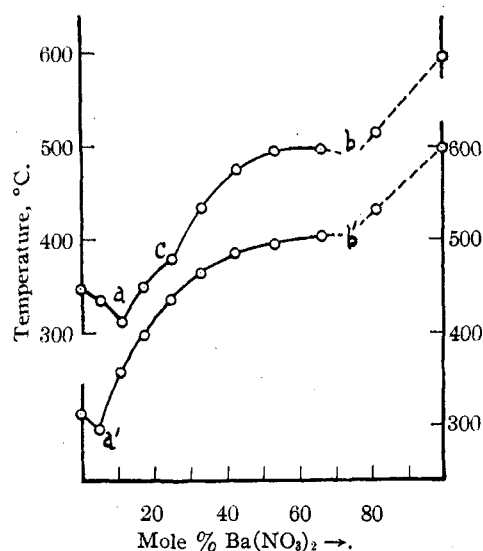


Fig. 1.—Freezing point diagrams for systems  $\text{Ba}(\text{NO}_3)_2\text{-KNO}_3$  (upper curve) and  $\text{Ba}(\text{NO}_3)_2\text{-NaNO}_3$  (lower curve) from data of Harkins and Clark.

The evidence of compound formation is unmistakable. From the configuration of the respective curves a-b and a'-b' of the two systems, the probable formulas of the compounds involved may be given as  $2\text{Ba}(\text{NO}_3)_2\text{-KNO}_3$  and  $2\text{Ba}(\text{NO}_3)_2\text{-NaNO}_3$ . The single point c of the potassium nitrate system, unless due to experimental error, seems to show a further break in the curve of the compound; if this is real, it points to a second compound in the system with the probable formula  $\text{Ba}(\text{NO}_3)_2\text{-2KNO}_3$ . Although a single point can hardly be considered sufficient ground for such an inference, it must be mentioned that the existence of the latter compound in the ternary system  $\text{Ba}(\text{NO}_3)_2\text{-KNO}_3\text{-H}_2\text{O}$  is well established.<sup>7</sup>

In conclusion, although the measurements of Harkins and Clark, which were not performed with

(1) Ricci, *THIS JOURNAL*, **59**, 1764 (1937).  
(2) Maumené, *Compt. rend.*, **97**, 1215 (1883).  
(3) Guthrie, *Phil. Mag.*, [5] **17**, 462 (1884).  
(4) Harkins and Clark, *THIS JOURNAL*, **37**, 1816 (1915).  
(5) Laybourn, Madgin and Freeman, *J. Chem. Soc.*, 139 (1934).  
(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. IV, 1928, p. 66.

(7) Glasstone and Riggs, *J. Chem. Soc.*, **127**, 2846 (1925).