[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE EFFECT OF SODIUM HYDROXIDE UPON THE SURFACE TENSION OF A SOLUTION OF SODIUM NONYLATE

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Introduction and Discussion

The addition of sodium hydroxide to a solution of sodium nonylate produces truly remarkable results. A 0.1 *M* solution of sodium nonylate at 20° has a surface tension of 20.2 dynes per cm., the lowest value known for any aqueous solution. The addition of sufficient sodium hydroxide to make this solution 0.005 *M* with respect to the base, raises the surface tension to 45.4, and at 0.008 *M*, to 48.8. Further addition of sodium hydroxide causes a linear decrease of the surface tension as plotted against the concentration of the base (Table I and Fig. 1). These results seem to indicate that the extremely low surface tension of 0.1 *M* sodium nonylate solution is due to a surface film of the salt together with nonylic acid formed by its hydrolysis. The addition of a base represses the hydrolysis, and the lowering of surface tension produced by the salt alone is not so great as when the acid is present in the film. Further addition of the base increases the activity of the salt in the solution, and also the concentration of the salt in the film, thus lowering the surface tension.

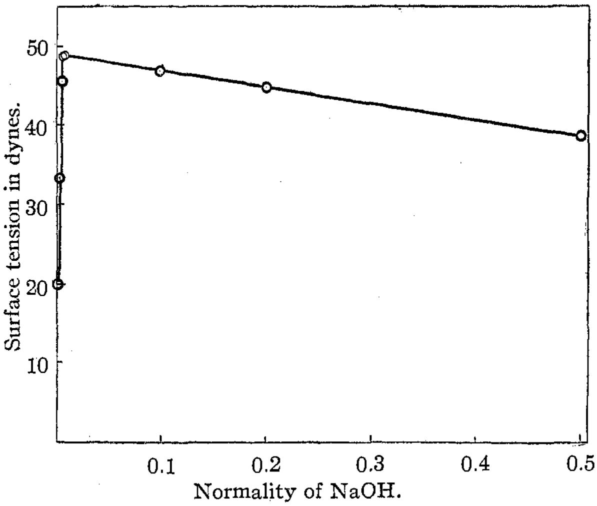

Fig. 1.—The effect of sodium hydroxide upon the surface tension of an aqueous solution of sodium nonylate.

According to McBain[1,2] the amount of colloid and the hydrolysis in an aqueous solution of sodium nonylate should be small at 90° in 0.1 *M* solution. The observations presented in Table I indicate, however, that at 20° the amount of colloid is by no means negligible. From McBain's work it may be assumed that the colloid is an acid salt. It is evident (Col. 3) that the state of the colloid is dependent upon the hydroxyl-ion concentration of the solution.

TABLE I

THE SURFACE TENSION OF SOLUTIONS OF SODIUM NONYLATE IN WATER AT 20° AND THE EFFECT OF SODIUM HYDROXIDE

Moles per liter						
Sodium nonylate	Sodium hydroxide	Hydrolysis cloudiness	Density	Drop-weight × 10^3	Tip	Surface tension
		SODIUM NONYLATE ALONE				
0.000	...	0	....	...	...	72.80
.0001	...	S	0.9984	66.85	1	71.46
.001	...	S	.9985	66.7	1	71.32
.01	...	S	.9986	53.05	1	57.59
.1	...	1 hour	...	21.4	2	20.18
		SODIUM NONYLATE PLUS SODIUM HYDROXIDE				
.1	0.001	R	0.9998	31.27	1	33.37
.1	.005	C	....	41.2	1	45.40
.1	.008	0	....	44.5	1	48.82
.1	.01	0	....	44.5	1	48.82
.1	.1	0	1.0489	49.9	2	46.85
.1	.2	0	1.055	47.2	2	44.44
.1	.5	0	....	34.4	2	38.32
.1	2.0	Formed a gel				

The column marked "Hydrolysis" indicates the cloudiness apparent to the eye. 0 indicates no cloudiness; S indicates appearing slowly; R, rapidly; C, a small amount of cloudiness at the time of measurement. Since the density is involved only in the surface tension correction, it was determined only roughly. Radius of Tip 1 = 0.23052 cm., of Tip 2 = 0.27580 cm.

Preparation of Sodium Nonylate

Pure sodium nonylate was prepared by two methods.

Chemically pure nonylic acid was distilled at 253° and the distillate submitted to crystallization at 12.5°. A boiling solution of pure sodium carbonate was added to an alcoholic solution of the acid, the mixture evaporated to dryness and the residue extracted with absolute alcohol. Inasmuch as the salt is about ten times as soluble in hot absolute alcohol as in cold, the whole mass solidifies upon cooling, enclosing all of the alcohol which was drawn off by suction for 24 hours, and the final drying is accomplished after washing with absolute ether at 50° for three hours. Another portion was prepared by the hydrolysis of ethyl nonylate, made by Kahlbaum, dried over calcium chloride and distilled twice. The following proportions were found best suited to a quantitative

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[1] McBain and Martin, *J. Chem. Soc.*, **105,** 967 (1914).

[2] McBain, "Third Report on Colloid Chemistry," H. M. Stationery Office, London, **1920,** p. 1.

hydrolysis: ethyl nonylate, 10 parts; ethyl alcohol, 40 parts; solid sodium hydroxide, 6 parts; water, 20 parts. This mixture was heated on an electric heater for two hours with a reflux condenser. The two separate layers disappeared after 20 minutes. The yellow solution was evaporated to dryness, and the residue extracted repeatedly with absolute alcohol. Both of the above methods yielded pure white products that gave practically identical results.

Experimental Methods

The determinations of surface tension were made by the drop-weight method, and the precautions and corrections of Harkins and Brown[3] were employed.

Summary

It is found that a 0.1 M solution of sodium nonylate has the lowest surface tension thus far found for a dilute aqueous solution (20.2). The addition of 0.008 M sodium hydroxide more than doubles this value, increasing it to 48.8 dynes per cm. Further addition causes a linear decrease of the surface tension.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

DETERMINATION OF SMALL AMOUNTS OF BORON IN TUNGSTEN

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Some time ago we had occasion to determine boron in tungsten alloys and lamp filaments. In the literature, one method has been described for the analysis of boron in borotungstates[1] wherein the authors precipitate the tungsten with an excess of barium hydroxide, neutralize the solution with hydrochloric acid using methyl orange as an indicator, then titrate the boric acid in a glycerol-alcohol mixture using phenolphthalein as an indicator. The method could not be used as it stands because our samples were alloys of tungsten and boron, and not soluble in water or hydrochloric acid. Some provision had to be made for dissolving the alloys and this, as will be shown later, introduced additional complications in the titration.

Barium hydroxide in neutral solution precipitates tungsten quantitatively. Barium borate also is precipitated, but is soluble in an excess of the hydroxide. The authors in the original method do not provide for the removal of the barium tungstate, or any barium carbonate which is sure to form, but adjust the acidity prior to the addition of glycerol-alcohol mixture and titrate the boron in the presence of the tungsten precipitate.

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[3] Harkins and Brown, THIS JOURNAL, **41**, 499 (1919).

[1] Copaux and Boiteau, *Bull. soc. chim.*, [IV] **5**, 217 (1909).