CXXXIII.—*Studies of the Constitution of Soap Solutions. Sodium Behenate and Sodium Nonoate.*

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PREVIOUS communications * have been devoted to the study of solutions of salts of the saturated fatty acids containing an even number of carbon atoms, from the acetate up to the stearate. Data are now presented for sodium nonoate, as representing soaps with an uneven number of carbon atoms, and for sodium behenate with its twenty-two carbon atoms, lying almost beyond the range of the soaps proper.

Nonoic acid was chosen because it is the only acid containing an uneven number of carbon atoms which can readily be obtained in a state approaching purity. The numerical data for sodium nonoate are here found to lie between those of the octoate and the decoate, showing that the soaps of uneven carbon number

* For references, see McBain, Laing, and Taylor, this vol., p. 621.

fall regularly into the series and are intermediate in properties between the neighbouring even soaps. This is what might have been expected from the properties of such a synthetic acid as margaric acid (L. Schneider, *Dissert.*, München, 1913).

The properties of the solutions of sodium behenate present interesting and only partly investigated problems, due on the one hand to the very great possibilities of undercooling, and, on the other, to the tendency of behenate to separate from solution. The equilibria involved are, however, of the same general type as those in the ordinary soap solutions. The amount of ionic micelle in concentrated solution does not differ greatly from that in the other soaps, but neutral colloid is much more largely developed and, like the ionic micelle, persists in more dilute solution.

The data in the present paper include conductivities, osmotic activities, and densities of solutions of both soaps in addition to observations on physical behaviour.

EXPERIMENTAL.

The behenic acid was obtained through the kindness of Messrs. Crosfield and Sons, who made it specially by hardening Kahlbaum's erucic acid. It was purified by recrystallisation from 80 per cent. alcohol, its molecular weight as ascertained by titration before and after treatment being 343.2 and 340.0 (theory 340.3). The melting point of the recrystallised material was 81.0–82.0°. Meyer, Brod, and Soyka (*Monatsh.*, 1913, **34**, 1113) give the melting point of the purest acid they could obtain as 82–84°, but they state that if it is prepared from impure acid or left too long in contact with the catalyst, impurities, which lower the melting point but cannot be detected analytically, are obstinately retained.

Pure nonoic acid was obtained from Kahlbaum.

The experimental method for the determination of the conductivity was that used by McBain and Taylor (*Z. physikal. Chem.*, 1911, **76**, 179) using glass cells in every case but that of the half-normal solution.

Owing to the high viscosity of the sodium behenate solutions, it was found impossible to determine the conductivity of solutions of concentrations higher than half-normal. Even in the case of this solution (half-normal) the difficulty of forcing the dipping-electrode vessel into the liquid, and the entrapping of air bubbles which could not be removed, may have led to results which are lower than the true conductivity values. On the other hand, all solutions of sodium behenate showed a tendency to separate, even at 90°, into two distinct phases, a stringy curd and a thin, alkaline liquid

(approximately $N/20$). This ready separation and the frothing of dilute solutions may account for the deviations in molar conductivity of dilute solutions of identical strength.

The densities were determined as in previous communications; each value given is the mean of two independent measurements.

The sodium nonoate solutions were made up in silver tubes according to the method previously described (T., 1914, **105**, 418), using nonoic acid "Kahlbaum." All measurements were carried out in Jena-glass vessels. All the solutions were clear at the high temperature, although on cooling or long standing a fine sediment always settled. This is in accordance with the observations of Bunbury and Martin (*loc. cit.*) with solutions of octoates and hexoate and is presumably due to acid soap.

Conductivity and Osmotic Data.

The conductivity results for behenates and nonoates are collected in Tables I and II, and the lowering of dew point for the nonoates in Table III. All concentrations are expressed in weight normality. Several independent solutions were studied in each case. The corresponding determinations of osmotic activity for the behenates were made and recorded by McBain and Salmon (*J. Amer. Chem. Soc.*, 1920, **42**, 426; *Proc. Roy. Soc.*, 1920, [A], **97**, 44).

TABLE I.
Conductivity of Solutions of Sodium Behenate at 90°.

Weight normality.	Grams of soap to 100 grams of water.	Spec. cond.	Mean.	α_{40}^{90} .	μ^{90} .
0.500	18.12	0.03469 0.03112	0.03291	0.96	80.96
0.200	7.249	0.011110 0.011325 0.01091 0.01119	0.01113	0.96312	61.99
0.100	3.624	0.005806 0.006625 0.006230	0.006244	0.9644	67.09
0.050	1.812	0.003975 0.003681 0.003528	0.003728	0.9657	78.58
0.010	0.3624	0.001184 0.001384 0.001413 0.001469	0.001363	0.96534 *	141.7

* Taken equal to that of water.

TABLE II.

Conductivity of Solutions of Sodium Nonoate at 90°.

Weight normality.	Grams of soap to 100 grams of water.	Spec. cond.	Mean.	d_{40}^{90} .	μ^{90} .
1.000	18.018	0.08794 0.08919	0.8897	0.98216	106.9
(0.500					127.5)
0.200	3.6036	0.02807 0.02826	0.02817	0.96955	150.44
0.100	1.8018	0.01582 0.01577	0.01580	0.9672 *	166.42
0.020	0.3604	0.003716 0.003664	0.003690	0.9653 *	191.82
0.010	0.1802	0.001955 0.001891	0.001923	0.9653 *	199.8

* Taken equal to that of water.

TABLE III.

Osmotic Activity of Solutions of Sodium Nonoate at 90°

Weight normality.	$\Delta_0 C.$	Osmotic activity.
0.2	0.165	1.71
0.5	0.36	1.49
1.00	0.52	1.08

It should be noted that the osmotic activities of the nonoate solutions are intermediate between those of the octoate and the decoate (compare the diagrams of McBain and Salmon, *loc. cit.*). The conductivities are about 83 to 88 per cent. as great as those of sodium acetate and thus fall into their expected places. The conductivity increases regularly with dilution.

The conductivity of the behenate exhibits a very decided minimum at $0.2N_w$. The minimum is more pronounced and occurs at a slightly higher concentration than in the case of the ordinary soaps, although the general form resembles that of sodium palmitate. Owing to the impossibility of extending the observations to high concentrations it cannot be decided whether or not the conductivity would again fall off in very high concentration.

At room temperature, especially after long standing, all the nonoate solutions deposited a slight sediment, although the fresh $0.1N_w$ -solution was clear when hot and freshly made; the N_w -solution was clear even in the cold. The sediment is presumably acid soap.

The Constituents of the Solutions.

Using the methods previously described (McBain, Taylor, and Laing, *loc. cit.*) it is possible to deduce the concentrations of each of the constituents present in these solutions. The results, as calculated by Miss M. H. Norris, are shown in Tables IV and V and Figs. 1 and 2. Fig. 3 contains for comparison the results of similar measurements and calculations for solutions of potassium laurate (C_{12}).

TABLE IV.*

Concentrations in Relative Proportions of the Constituents of Solutions of Sodium Behenate at 90°.

Weight nor- mality.	Total cryst.	Na'.	Be'.	NaBe.	Ionic micelle.	Neutral colloid.	Acid soap.
0.01		0.005206	0.004506	0.003394	0.00	0.00	0.0021
		52.06 %	45.06 %	33.94 %			21 %
0.05		0.01508	0.013580	0.03192	0.00	0.00	0.0045
		30.16 %	27.16 %	63.85 %			9.0 %
0.2	0.19	0.047	0.028	0.115	0.019	0.035	0.003
		23.5 %	14 %	57.5 %	9.5 %	17.5 %	1.5 %
0.5	0.23	0.148	0.010	0.072	0.138	0.274	0.006
		29.6 %	2.0 %	14.4 %	27.6 %	54.8 %	1.2 %

* Acid soap is expressed in terms of behenate radicle. The allotment of total colloid between ionic micelle and neutral colloid, and of crystalloid between behenate ion and simple sodium behenate, is made in accordance with the conductivity data for 0.05N_w-solution ($K = 0.05224$); had the conductivity for 0.01N_w-solution been used instead, the alteration would have affected dilute solutions only, increasing neutral colloid at the expense of ionic micelle and causing it to persist in more dilute solutions. The acid soap is presumed to be similar to that of the palmitate.

TABLE V.†

Concentrations in Relative Proportions of the Constituents of Solutions of Sodium Nonoate at 90°.

Weight nor- mality.	Total cryst.	Na'.	Non'.	NaNON.	Ionic micelle.	Neutral colloid.
0.01		0.00862	0.00862	0.00138	0.00	0.00
		86.2 %	86.2 %	13.8 %		
0.02		0.0165	0.0165	0.0035	0.00	0.00
		82.5 %	82.5 %	17.5 %		
0.2	0.342	0.130	0.130	0.082	0.00	— 0.012
		65 %	65 %	41 %		— 6 %
0.5	0.7453	0.272	0.253	0.220	0.019	0.008
		54.4 %	50.6 %	44.0 %	3.8 %	1.6 %
1.0	1.076	0.438	0.307	0.331	0.131	0.231
		43.8 %	30.7 %	33.1 %	13.1 %	23.1 %

† The small amount of acid soap is not included in the table or the corresponding diagram. The constant used for allotting crystalloid was $K = 0.596$.

Comparison of Figs. 1 and 2 in the light of the intermediate member shown in Fig. 3 shows clearly that the difference between

FIG. 1.

The relative proportions of the various constituents of solutions of pure sodium behenate at 90°. (The asterisk * marks the field showing the proportion of acid soap, $2\text{NaBe}, \text{HBe}$, present).

FIG. 2.

The relative proportions of the various constituents of solutions of pure sodium nonoate at 90°.

the highest and lowest salts in this homologous series is merely one of degree, exhibiting steady transition. The chief difference

is that highly concentrated solutions of the lower members correspond with moderately dilute solutions of the highest soaps. The diagrams for the highest soaps are compressed towards the left-hand side as compared with the lower soaps, but the type remains the same.

Sodium acetate is not so highly dissociated as sodium chloride. This weakness is rapidly accentuated as the homologous series is ascended, until in the behenate the greater proportion of the crystalloidal matter is undissociated.

FIG. 3.

*The relative proportions of the various constituents of solution of pure potassium laurate at 90°. (The asterisk * marks the field showing the proportions of acid soap, 2KL,HL, present.)*

There appears to be no such great difference in the amount of ionic micelle attained in concentrated solutions, although the dissociation of colloidal electrolyte into ionic micelle is unmistakably least in the highest soaps.

The most prominent effect of these relationships is that the amount of neutral colloid in ordinary solutions increases rapidly with each step in ascending the homologous series, so that, for instance, in a half-normal behenate solution the amount of neutral colloid is twice as great as in the same concentration of the palmitate (C₁₆).

There is still no very satisfactory information with regard to the effect of extremely high concentration on a soap which in moderate concentration consists entirely of neutral colloid and

ionic micelle. It is surprising that further concentration does not appear to drive back the dissociation of the colloidal electrolyte. The approximate constancy of the proportion of ionic micelle depends of course on the assumption that its mobility is likewise nearly constant. The proportion of ionic micelle becomes constant at about 40 per cent. in the laurate, at 30 per cent. in the palmitate, and at about 38 per cent. in the behenate, the remainder being neutral colloid in each case.

Appearance of Solutions of Sodium Behenate.

The curding temperature of the more concentrated solutions appears to be above 90° , although $0.5N_w$ -solution can be prepared as a clear, stiff jelly at this temperature. The liquid separating from the curd is alkaline. Hydrolysis would appear to be very much greater than has been observed in the case of any soap, and quantitative work is necessary. The solutions were increasingly opalescent on dilution, and oily drops were observed on the surface of $0.01N$ -solutions at 90° .

Remarkable behaviour is observed on rapid cooling of behenate solutions. Whereas the ordinary stable form of all except the $N_w/100$ -solution is a hard, white curd at room temperature, on sudden cooling a mobile, slightly milky liquid is obtained. For instance, the slightly viscous, almost gelatinous $0.2N_w$ -solution at 90° becomes quite mobile, and this thin, cloudy, alkaline liquid may be kept for many hours before solidification occurs*; shaking causes separation of a stringy, membranous curd. A quantitative investigation of these solutions is being undertaken. Even the jellies which so readily form in these solutions have a tendency to segregate, particularly when they are agitated.

Summary.

1. Sodium behenate solutions (C_{22}) exhibit the same type of dissociation as the higher soaps such as palmitate and stearate. Although in very high concentrations of any of the soaps there is but little difference in the amounts of neutral colloid and ionic micelle, which constitute almost the whole of the solution, these persist in much more dilute solution in the case of the behenate.

2. The nonoate, as representative of fatty acids with an uneven number of carbon atoms, exhibits properties intermediate between those of the adjacent members with even number of carbon atoms.

* This observation was made by Mr. S. E. Wiltshire.

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