CCLXXXIX.—*The Partial Specific Volume of Potassium* n-*Octoate in Aqueous Solution.*

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In a previous paper (Grindley and Bury, J., 1929, 679) it was shown that in solutions, one component of which can associate to form micelles, there must be a certain concentration below which micelles can only be present in infinitesimal quantities, while above this concentration the number of micelles will increase rapidly. This concentration will be called the critical concentration for micelles.

The existence of such a critical concentration was supported by work on the densities of mixtures of butyric acid and water. It was shown that the slope of the contraction–composition curve and the magnitude of the partial specific volumes changed abruptly, but not discontinuously, at a concentration which is indicated by freezing points (Jones and Bury, *Phil. Mag.*, 1927, 4, 841) to be the concentration at which micelle formation begins.

It seemed important to investigate whether soap solutions show the same sudden change of partial specific volume that was observed with butyric acid solutions, and we have therefore investigated the densities of aqueous solutions of potassium octoate. A potassium, rather than a sodium, soap was chosen as the subject of this research because sodium soaps are generally less soluble than, and do not tend to form micelles so readily as, the potassium soaps. It also seemed desirable to use a soap derived from an acid containing a relatively small number of carbon atoms, for with those derived from the higher fatty acids the critical concentration for micelles seems to lie in very dilute solution, which would increase the experimental difficulties. The formation of acid soap, which is favoured by dilution and lengthening of the carbon chain, would be an added complication. Lastly, the relatively low solubility of the higher soaps would probably necessitate working at a higher temperature.

The procedure adopted was to prepare and analyse a solution of potassium hydroxide (2—3 mols. per 1000 g. of water) and to add the required weight of this to a weighed quantity of octoic acid. After the density of this soap solution had been determined, a known weight of it was diluted with a suitable weight of water, the density was determined again, and so on. Whilst this method was the best that could be devised, taking into consideration the nature of potassium octoate, it has two disadvantages. There is the difficulty of adding the correct quantity of alkali in the synthesis of the original solution; owing to unavoidable errors of analysis of the potassium hydroxide solution there may be a small error in calculating the quantity of it that is required to neutralise the acid, and owing to the impossibility of adding less than a drop of it to the acid there may be a difference between the quantity required and the quantity added. Preliminary experiments in which insufficient or excess alkali was deliberately added showed that this uncertainty in the composition of the solution might lead to an error of 0·0001 in the density of a 2·0*N*-solution. This error will affect each member of a series of determinations proportionately.

The second disadvantage of the method is the possible accumulation of errors at the end of a long series of dilutions. This source of error seems to have affected some of the preliminary series but to have been eliminated, by practice in manipulation, from the final series.

Octoic acid was purified by conversion into its methyl ester, which was fractionally distilled twice in a vacuum and then hydrolysed. The resulting acid was fractionally distilled in a vacuum and it then froze at 15·7°. Freezing points were determined by the Beckmann method, samples of about 20 c.c. being used, and a standardised thermometer graduated in tenths of a degree. Fractional crystallisation is valueless as a method of purification, for five recrystallisations of the crude product did not raise the freezing point by more than 0·1°. Fractional distillation of the crude acid also is valueless, but fractional distillation of the purified acid appears to remove a small amount of impurity introduced by esterification and subsequent hydrolysis, possibly water or alcohol.

Potassium hydroxide solution was prepared by washing sticks of the pure solid three times in order to remove the outer layers, which are contaminated by carbonate and possibly silica, and dissolving the remaining cores. The entire operation was carried out in a closed vessel of resistance glass and in an atmosphere of nitrogen. Conductivity water was used. The resulting solution was shown to be free from carbonate by Winkler's method (Treadwell's "Analytical Chemistry," English translation, 1919, vol. II, p. 563) and was standardised by determining the weight necessary to neutralise a known weight of pure succinic acid, phenolphthalein being used as indicator.

The procedure recommended by Hartley and Barrett (J., 1911, **99**, 1072) was used in determining the densities at 25°. The results are in Table I. If densities are plotted against concentrations, the resulting graph is almost a straight line from 0 to 6% of soap, then bends slightly and becomes straight again over the range 9 to 28% of soap. Bunbury and Martin ("International Critical Tables," vol. V, p. 447) have determined the density of this soap at three concentrations at 90°, and found the density to be a linear function of the concentration. Whilst more accurate and more numerous determinations might reveal deviations from this, these results show that the abrupt change of slope, which we attribute to the existence of a critical concentration for micelles at this point, is far less marked at higher temperatures, which is in agreement with the work of McBain, all of which shows that the tendency to form micelles decreases with rise of temperature.

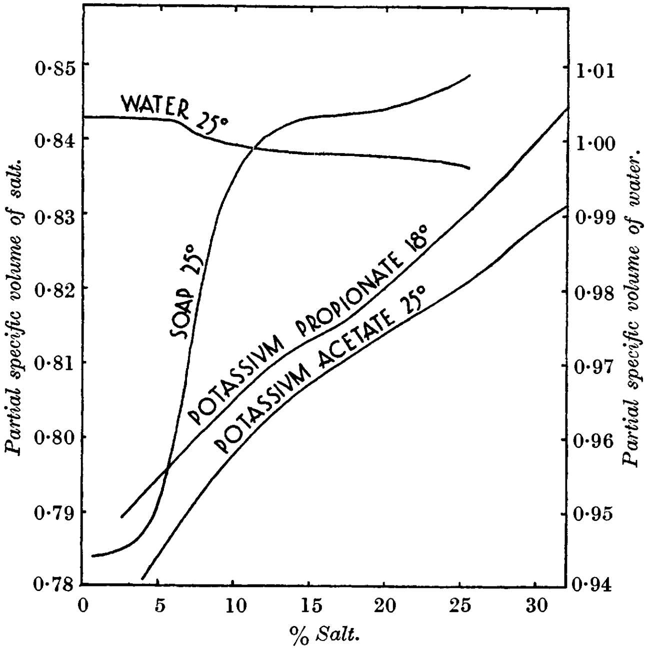
TABLE I.

Series I.			Series II.		
Conc. of soap.			Conc. of soap.		
%.	Mols. per 1000 g. water.	Density, $D^{25^\circ}_{4^\circ}$.	%.	Mols. per 1000 g. water.	Density, $D^{25^\circ}_{4^\circ}$.
28·73	2·213	1·04806	15·94	1·041	1·02727
22·39	1·582	1·03796	13·86	0·8831	1·02388
13·57	0·8616	1·02345	12·14	0·7582	1·02102
10·69	0·6569	1·01867	9·983	0·6085	1·01741
8·516	0·5109	1·01494	7·763	0·4619	1·01351
6·744	0·3969	1·01163	5·562	0·3232	1·00912
5·626	0·3272	1·00935	3·610	0·2055	1·00493
2·888	0·1632	1·00340	1·640	0·0915	1·00065
0	0	0·99707			

Partial specific volumes have been calculated by the method of Hildebrand ("Solubility," 1924, p. 64) and are shown in Table II and graphically in the figure. The curves resemble very closely those obtained with butyric acid (Grindley and Bury, *loc. cit.*, Fig. 2) : in each case there is the same rapid rise which indicates the critical concentration for micelles. With potassium octoate this rise occurs at a concentration of about 7·5 to 8·0% of soap, or about 0·47*N*. Freezing points (McBain, Laing, and Titley, J., 1919, **115**,

TABLE II.

Conc. of soap.		Partial specific volumes.	
%.	Mols. per 1000 g. water.	Water.	Soap.
0	0	1·00294	0·784
2	0·112	1·0029	0·785
4	0·229	1·0028	0·788
5	0·289	1·0027	0·791
6	0·350	1·0024	0·800
7	0·413	1·0012	0·811
8	0·477	1·0004	0·823
9	0·543	1·000	0·830
10	0·610	0·999	0·835
12	0·748	0·999	0·840
15	0·969	0·998	0·843
20	1·372	0·998	0·845
24	1·733	0·997	0·847



1279) indicate that micelle formation first becomes appreciable at 0·5*N*, and at 90° dew-point measurements (see Randall, McBain, and White, *J. Amer. Chem. Soc.*, 1926, **48**, 2517) indicate that micelles are first formed at about 0·4*N*. As with butyric acid, the critical concentration for micelles decreases with rise of temperature.

Further evidence that this rapid rise of the partial specific volume is due to micelle formation is afforded by the fact that it is not shown by the alkali salts of the lower fatty acids, for which, within the limits of experimental error, the curves are smooth. To illustrate this the partial specific volumes of potassium acetate (+0·26) and potassium propionate (+0·215), calculated from the data given in

"International Critical Tables" (vol. III, p. 90), are also plotted in the figure: the constants given in parentheses have been added to bring them on the same graph. Hexoic acid is the lowest fatty acid whose salts exhibit colloidal behaviour, and hence abrupt changes of partial specific volume are not to be expected with salts of lower acids.

We wish to thank Professor F. E. Francis for advice on the purification of octoic acid.

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[*Received, July* 17*th*, 1930.]