140. *Specific Heats of Aqueous Solutions of Potassium* n-*Octoate at* 15°.

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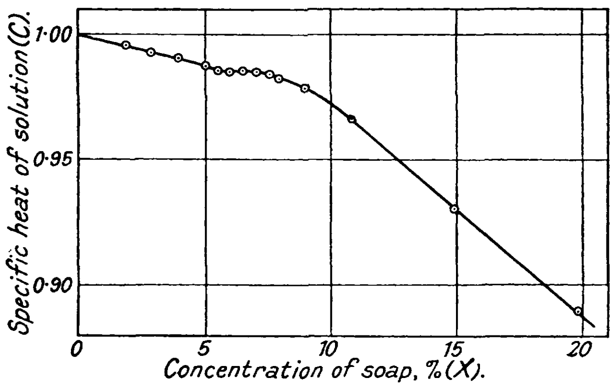
In a previous paper (Bury and Davies, J., 1932, 2413) it was pointed out that the specific heat–concentration curves of aqueous solutions afford evidence of the existence of micelles in such solutions. It seemed of interest, therefore, to investigate the corresponding curve for an aqueous solution of a soap, and the specific heats of solutions of potassium *n*-octoate in water have accordingly been measured, this particular soap being selected for reasons already given by Davies and Bury (J., 1930, 2263).

The solutions were prepared, and their concns. determined, as described by Davies and Bury (*ibid.*). The sp. heats were measured with an accuracy of 0·1% by the differential method described by Bury and Davies (*loc. cit.*).



The results are in the table, and sp. heats (C) are plotted against concns. (X = g. of soap per 100 g. of solution) in the fig. The sp. heats are mean values over a range 13·5—16·5° relative to H_2O (= 1) over the same range of temp.

X, %	19·86	14·88	10·83	8·936	7·897	7·535	7·000
C	0·8901	0·9305	0·9666	0·9787	0·9825	0·9844	0·9853
X, %	6·489	5·940	5·492	5·000	3·927	2·842	1·864
C	0·9857	0·9852	0·9857	0·9877	0·9908	0·9930	0·9957

In the earlier paper it was indicated that the shape of the specific heat–concentration curve might be affected by micelle formation in two distinct ways: (1) if the contribution of the micelles to the total specific heat is less than that of the simple molecules which compose it, the specific heat–concentration curve will exhibit a sudden change of slope at the critical concentration for micelles (see Fig. 3A, J., 1932, 2416); (2) if heat is absorbed or evolved when micelles are formed there will be a sudden increase in the specific heat at the critical concentration for micelles (see Fig. 3B, *ibid.*). If the heat of micelle formation at the temperature of the specific-heat determinations is very small, the second effect may be absent, as was found with aqueous butyric acid solutions. On the other hand, if the heat of micelle formation is sufficiently great, the two effects may occur together.

It is clear from the figure that both these effects occur in aqueous solutions of potassium *n*-octoate at 15°. The specific heat–concentration curve is almost linear up to a concentration of about 6% of soap, where an increase in the specific heat occurs which results in the graph becoming nearly parallel to the axis of concentration over the range 6—8%. The last portion of the curve, from 10 to 20%, is again linear, but has a greater slope than the first part. Moreover, these effects occur in the neighbourhood of 7·5% of soap, a value for the critical concentration for micelles in agreement with those deduced from freezing-point measurements (McBain, Laing, and Titley, J., 1919, **115**, 1279), dew-point measurements (see Randall, McBain, and White, *J. Amer. Chem. Soc.*, 1926, **48**, 2517), and the density determinations of Davies and Bury. Although for butyric acid the specific heat–concentration curve showed only an abrupt change of slope in the neighbourhood of the critical concentration for micelles, the presence of the two effects discussed above is to be expected in the case of the soap solutions considered here, since the critical concentration for micelles is more markedly dependent on the temperature in the case of the soaps than in that of butyric acid.

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