275. *Specific Heats of* iso*Butyric Acid–Water Mixtures at* 15°.

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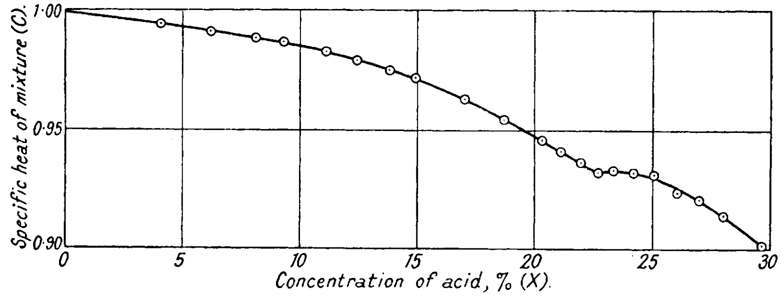
In previous papers (Bury and Davies, J., 1932, 2413; Davies, J., 1933, 551) it has been noted that the specific heat–concentration curves of aqueous solutions show characteristic features if micelles are present. In particular, the curve for aqueous solutions of *n*-butyric acid at 15° (Bury and Davies, *loc. cit.*) exhibited an abrupt change of slope at about 13% of acid, showing a critical concentration for micelles in agreement with that deduced from density measurements (Grindley and Bury, J., 1929, 679). It was considered probable that a similar study of *iso*butyric acid–water mixtures would present some points of interest. This acid is not completely miscible with water at 15°, a two-phase system being formed when the concentration of acid has risen to about 20%. *n*-Butyric acid resembles the *iso*-acid in that its mixtures with water are likewise homogeneous up to a certain concentration (the critical concentration for micelles), a second phase then being formed. However, although the second phase is colloidal for the *n*-acid, separation into two liquid layers occurs with the *iso*-acid, and the specific heat–concentration curve at 15° for aqueous mixtures of this acid, carried into the region where two phases appear, thus allows a comparison between formation of micelles and of a second phase. The results afford evidence as to whether *iso*butyric acid behaves similarly to the *n*-acid in forming micelles in aqueous solution, and also allow a comparison of the magnitudes of the specific heats of aqueous solutions of the *n*- and the *iso*-acid at the same concentrations.



The specific heats were measured by the differential method (Bury and Davies, *loc. cit.*) with an accuracy of 0·1% for the homogeneous systems. The experimental error is somewhat greater (0·2%) for the measurements in the two-phase systems, owing to the difficulty of complete attainment of equilibrium between the two phases in the comparatively short duration of an experiment, in spite of the efficient stirring.

*iso*Butyric acid was three times fractionally distilled; its concentration in the mixtures was determined by titration with baryta, phenolphthalein being the indicator. In the case of the two-phase systems, the mixture was first warmed slightly until homogeneous (the most concentrated mixture examined—about 30% of acid—becomes homogeneous at about 24°), the samples for analysis removed, and the requisite quantity introduced into the calorimeter. When the solutions were cool, the necessary weighings were carried out.

The results are given in the table, and the specific heats (C; mean values over a range 13·5—16·5°, relative to water as unity over the same range of temperature) are plotted against concentrations (X = g. of acid per 100 g. of solution) in the fig.

X (%)	29·69	28·05	27·06	26·08	25·11	24·22	23·38	22·73	21·98	21·15	20·34
C	0·9008	0·9137	0·9200	0·9231	0·9307	0·9319	0·9328	0·9317	0·9360	0·9407	0·9453
X (%)	18·71	17·03	14·94	13·84	12·45	11·12	9·305	8·111	6·214	4·080	
C	0·9539	0·9627	0·9715	0·9748	0·9789	0·9825	0·9867	0·9883	0·9911	0·9942	

The shape of the curve resembles that obtained for aqueous solutions of potassium *n*-octoate (Davies, *loc. cit.*) rather than that given by *n*-butyric acid (Bury and Davies, *loc. cit.*). There is a sudden increase in the specific heat at a concentration of about 22% of acid, the curve becoming nearly parallel to the axis of concentration over a range of concentrations of about 2%. The concentration at which the increase first becomes appreciable is rather higher than that corresponding to the solubility of *iso*butyric acid in water at 15° quoted in the literature. This solubility has been determined by several workers by observation of the temperature at which a clear solution becomes cloudy, or *vice versa*, but this method, although accurate for measurements near the critical solution temperature, is known to be inaccurate at temperatures considerably removed from it. International Critical Tables (Vol. III, 1928, p. 388) give 19·4% as the value of the solubility at 15°, but a determination made by allowing the mixture to settle in a vessel immersed in a thermostat at 15° ± 0·04°, and analysis of the lower layer, gave 21·92%, a value close to the concentration at which the increase of specific heat first becomes appreciable.

Besides the analogy between the curves obtained for the acid (which forms a second phase) and the soap (which forms micelles), a second point of interest is the close agreement between the specific heats of aqueous solutions of the *n*- and the *iso*-acid at the same concentration up to the critical concentration for micelles (about 13%) for the *n*-acid. At the same concentration the values of the specific heat for the two acids are identical within the limits of experimental error. When this concentration is exceeded, however, the values of the specific heat for the *n*-acid lie below those for the *iso*-acid, the contribution to the specific heat of a given weight of acid being smaller when the acid is in the form of micelles than when it is present as simple molecules.

Further, there is no sign of a sudden change of slope in the specific heat–concentration curve for the *iso*-acid in the homogeneous region, the slope changing gradually until a second phase appears. This indicates that *iso*- differs from *n*-butyric acid in not forming micelles, an observation which may be correlated with the smaller lateral cohesion between the chains of *iso*- as compared with *n*-acids, deduced from studies on soluble films (Schofield and Rideal, *Proc. Roy. Soc.*, 1925, *A*, **109**, 58).

I thank Mr. C. R. Bury for suggesting this work and for valuable advice.

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