353. *Specific Heats of Aqueous Solutions of Formic, Acetic, Propionic, and* n-*Butyric Acids.*

By Charles R. Bury and D. Gwynne Davies.

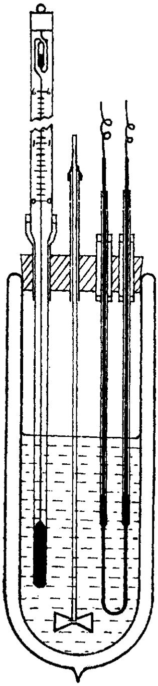
This work was undertaken as a continuation of the study of the physical properties of aqueous solutions of *n*-butyric acid that is being pursued in these laboratories (Jones and Bury, *Phil. Mag.*, 1927, **4**, 841; Bury, *ibid.*, p. 980; Grindley and Bury, J., 1929, 679; 1930, 1665). Measurements were extended to acetic acid solutions in order to test the experimental methods used by comparison of the results with those of Richards and Gucker (*J. Amer. Chem. Soc.*, 1925, **47**, 1876), and it then seemed desirable to complete the work by including the two other soluble acids of this series.

Experimental.

The substitution method of Richards and Gucker was used, two identical calorimeters being employed, each fitted with a thermometer, stirrer, and an electrical heating coil. The first calorimeter, or " tare," contains a suitable amount of H_2O which is kept const. throughout the research; while the second, or variable, calorimeter contains either H_2O or the liquid under investigation, the amount of which is varied until equal rises of temp. are registered by the thermometers of the two calorimeters when a current is passed through the two coils in series. Any two masses of liquid in the variable calorimeter which produce equal rises of temp. in the tare and variable calorimeter are thermally equiv., and it is therefore possible to calculate the relative specific heats of the two liquids. The method is probably the most accurate for comparing sp. heats, and it has the advantage of working over a relatively small temp. range, which was desirable in this, as in most other researches. A further advantage, particularly for the chemist, is that no accurate measurements of electrical quantities are involved.

For reasons of economy, a simplified apparatus (Fig. 1) was devised. Dewar flasks of 350-c.c. capacity were used as calorimeters, these being placed side by side in a large closed box and surrounded by cotton wool. Temp. rises were measured by Beckmann thermometers. Considerable difficulty was experienced in finding suitable heating coils, the insulation of which would withstand the solutions used. Ultimately glass capillary tubes containing Hg were employed; these were drawn from ¼-in. tubing and bent in the form of a U; two such "coils" having almost identical resistances (*ca.* 5 ohms each) were chosen. It was also desirable to employ some device by which the calorimeters could be cooled between runs. The best of the three methods tried was the evaporation by a current of dry air of a few c.c. of Et_2O which was placed in long closed tubes dipping into the calorimeters. (These tubes are omitted from Fig. 1 for the sake of clarity.)

FIG. 1.



In performing an expt., exactly 180 g. of H_2O were weighed into the tare, and a suitable wt. of the liquid under examination placed in the variable calorimeter. The temp. of the room was maintained const. at 16—17° during a run. The calorimeters were first cooled to about 13°, allowed to stand for about ½ hr., and then heated individually to 13·5°. After thorough stirring, the initial temps. were read, and both calorimeters were then heated together to about 16·5° by the passage for about 15 mins. of a current of 0·7 amp. through the coils in series. After stirring, the final temps. were read, and the ratio of the temp. rises calculated. After confirming this ratio by two further expts., a small amount of the liquid under examination was added from a weight pipette to the variable calorimeter, and the expt. repeated.

Temp. rise ratios were plotted against wts. of liquid in the variable calorimeter, the points lying on a straight line. From this graph, the wt. of liquid that would cause a temp. rise ratio of unity was obtained by interpolation.

Careful consideration of the various sources of error leads to the conclusion that the accuracy of the method is determined by the errors in reading the thermometer. Possible errors due to this cause may affect the final result by ± 0·1%. Other sources of error appear to be unimportant: heat leakages are negligible provided the expts. are performed near to room temp. Errors in the calibration of the thermometers are practically without effect on the final result provided that the same range of temps. be used consistently. Wts. were not corr. for buoyancy, since this was shown to be without effect on the final result.

An A.R. sample of formic acid was dehydrated with anhyd. $CuSO_4$, fractionally distilled, and then fractionally frozen five times. Acetic acid was purified by distillation from CrO_3 (Orton and Bradfield, J., 1927, 983). Propionic acid was twice fractionally distilled. Butyric acid was fractionally frozen ten times in a current of dry air, the f.p. of the final fraction being — 7·1°. Concns. of the solutions were determined by titration with $Ba(OH)_2$.

Formic acid.

X, %	5·767	11·10	16·83	21·61	28·02	31·65
C	0·9656	0·9352	0·9043	0·8745	0·8386	0·8187

Acetic acid.

X, %	5·205	10·21	15·01	19·76	24·40	29·67	34·22
C	0·9801	0·9602	0·9399	0·9194	0·8946	0·8686	0·8432

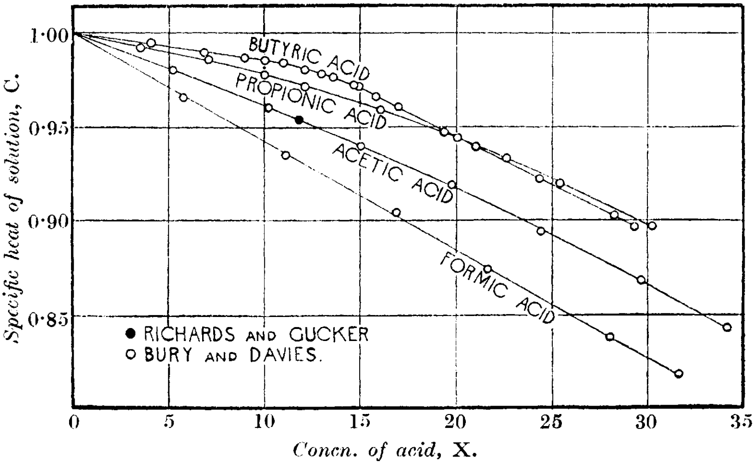
Propionic acid.

X, %	3·534	7·072	10·00	12·08	16·03	19·33	22·59
C	0·9922	0·9855	0·9776	0·9713	0·9590	0·9474	0·9336
X, %	25·38	30·21					
C	0·9199	0·8971					

n-*Butyric acid.*

X, %	4·065	6·857	8·998	10·03	10·95	12·05	12·95
C	0·9945	0·9893	0·9864	0·9853	0·9838	0·9803	0·9781
X, %	13·56	14·66	14·92	15·74	16·95	20·03	20·98
C	0·9764	0·9723	0·9714	0·9660	0·9608	0·9443	0·9397
X, %	24·30	28·26	29·29				
C	0·9226	0·9029	0·8968				

FIG. 2.



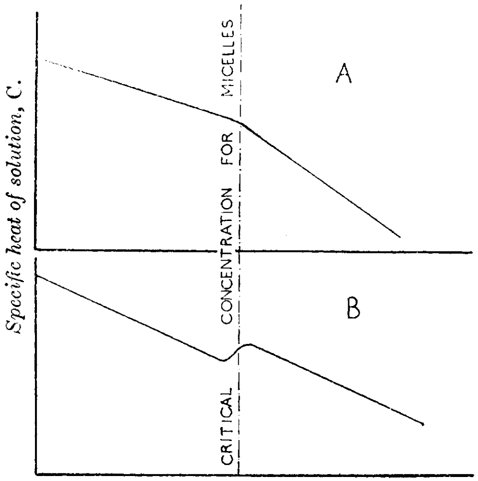
The results obtained are given in the table, concns. (X) being expressed as g. of acid per 100 g. of solution. The sp. heats (C) are mean sp. heats over the range 13·5—16·5° relative to H_2O (= 1) over the same range. The results are also plotted in Fig. 2.

Richards and Gucker have determined the sp. heats of an 11·77% AcOH solution at 16°, 18°, and 20°. Extrapolation of their figures gives the sp. heat at 15° as 0·9539, while interpolation from our results gives it as 0·954. No other data by previous investigators are directly comparable with our results.

Discussion.

In previous papers evidence has been given that butyric acid is associated, with the formation of micelles similar to those that exist in soap solutions, and that there is a critical concentration for micelles in such solutions below which the amount of association is negligible, while above it the number of micelles will increase rapidly.

FIG. 3.



Concn. of acid, X.

These facts may influence the form of the specific heat–concentration curve in two distinct ways. First, if the contribution of the micelles to the total specific heat is different from that of the sum of the simple molecules of which it is composed, there will be an abrupt change of slope of the curve at the critical concentration. Taking into consideration the facts that the specific heats of most aqueous solutions decrease with concentration, and that those of most complex substances are smaller than the sum of the specific heats of their components, a curve of the form shown in Fig. 3A is to be expected.

Secondly, if association is accompanied by emission or absorption of heat, the specific heat of solutions containing micelles will be abnormally great and a curve of the form shown in Fig. 3B will be given. The rise of specific heat at the critical concentration will be proportional to the heat of association and to the change in the degree of association with temperature.

It is obvious from Fig. 2 that the specific heat–concentration curve of butyric acid belongs to the type shown in Fig. 3A, and that it is entirely different from those of the lower aliphatic acids. There is an abrupt change of slope in the curve at about 13% of acid, in agreement with the fact that density determinations show that the critical concentration for micelles is about 13%. The fact that the curve is not of the type shown in Fig. 3B indicates that the heat of micelle formation is small, and this conclusion is in agreement with the fact that density determinations show that the critical concentration for micelles is almost independent of temperature.

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UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

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