CCXVII.—*The Electrical Conductivity of Butyric Acid–Water Mixtures.*

By JOHN GRINDLEY and CHARLES R. BURY.

THE work recorded in this paper, the measurement of the electrical conductivity of butyric acid–water mixtures, is a continuation of an investigation of the physical properties of this system that is being carried out in these laboratories (Jones and Bury, *Phil. Mag.*, 1927, **4**, 841; Bury, *ibid.*, p. 980; Grindley and Bury, J., 1929, 679). While several investigators have measured the conductivity of dilute solutions, the only previous measurements for concentrated solutions are those of Otten (Diss., Munchen, 1887) at 18°. In view of the complexity of the conductivity–concentration curve and of the fact that Otten measured the conductivities of only nine mixtures, a fuller investigation seemed desirable. Conductivities have therefore been measured at over 30 different concentrations, and at two temperatures, 0° and 25°.

EXPERIMENTAL.

Butyric acid was purified by fractional crystallisation, the final product melting at — 6·5°. Conductivity water was prepared in a Bourdillon still (J., 1913, **103**, 791) and had a conductivity of about $0{\cdot}2 \times 10^{-6}$ mho. Concentrations were determined by titration with baryta, phenolphthalein being used as indicator.

The electrical assembly used has been fully described elsewhere (Grindley and Davies, *Trans. Faraday Soc.*, 1929, **25**, 133). The resistance box had been calibrated at the National Physical Laboratory and the bridge was also calibrated. A correction was made for the resistance of the leads.

The cell, of the type described by Hartley and Barrett (J., 1913, **103**, 786), consisted of a silica bulb with cap and electrode-supports made of borosilicate glass. The cell constant was determined by measurement of the conductivity of dilute potassium chloride solutions at 18°: it can be shown from the temperature coefficients of expansion of glass and platinum that the change of cell constant with temperature is negligible over the range used (Grindley and Davies, *loc. cit.*).

About 200 c.c. of the pure acid were placed in the cell, and its conductivity at 0° and 25° determined. A suitable quantity of water was then added and, after determining the conductivities, a sample of the mixture was withdrawn for analysis, after which a further addition of water was made, and so on. In measuring the conductivity of the more dilute solutions, the cell was filled with water and successive additions of acid were made, concentrations being determined, as before, by analysis. During additions of one of the components or withdrawals of samples for analysis, entry of carbon dioxide from the air was prevented by a current of pure air. For measurements at 0°, the cell was surrounded by melting ice, while at 25° it was placed in a thermostat constant to ± 0·03°. Two hours were found necessary, and three were allowed, for the attainment of temperature equilibrium before taking any measurements.

No solvent correction was applied, since the conductivity of water is almost entirely due to dissolved carbon dioxide, the ionisation of which is strongly repressed on addition of acid.

Three independent series of measurements were made, the results of which are given in the table. In Col. 1 is the concentration of acid as g. per 100 g. of solution; and in Cols. 2 and 3 are the specific conductivities, κ, at 0° and 25° respectively in reciprocal ohms $\times 10^4$. In the figure, specific conductivities are plotted against concentrations.

Acid,	κ, ohms^{-1} $\times 10^4$.		Acid,	κ, ohms^{-1} $\times 10^4$.		Acid,	κ, ohms^{-1} $\times 10^4$.	
%.	0°.	25°.	%.	0°.	25°.	%.	0°.	25°.
1·212	3·459	5·374	26·42	5·056	8·655	67·25	0·4465	0·8170
2·982	5·055	7·934	30·48	4·422	7·694	69·21	0·3253	0·6555
4·749	5·918	9·364	34·25	3·875	6·692	70·92	0·2809	0·5251
6·246	6·355	10·154	37·73	3·373	5·872	73·65	0·1780	0·3778
6·878	6·530	10·371	41·01	2·932	5·132	75·75	0·1457	0·2769
8·403	6·681	10·741	44·54	2·501	4·362	78·88	0·0851	0·1692
10·48	6·780	10·984	47·61	2·121	—	82·02	0·04862	0·0948
13·00	6·700	10·929	51·13	1·724	3·076	86·17	0·01885	0·03787
15·12	6·512	10·742	54·87	1·3485	2·386	90·58	0·00547	0·01126
17·58	6·237	10·338	58·44	1·0281	1·8424	95·63	0·00058	0·00105
19·37	6·027	10·073	61·20	0·8059	1·4495	100	0·00018	0·00039
22·08	5·685	9·656	64·32	0·5901	1·1000			

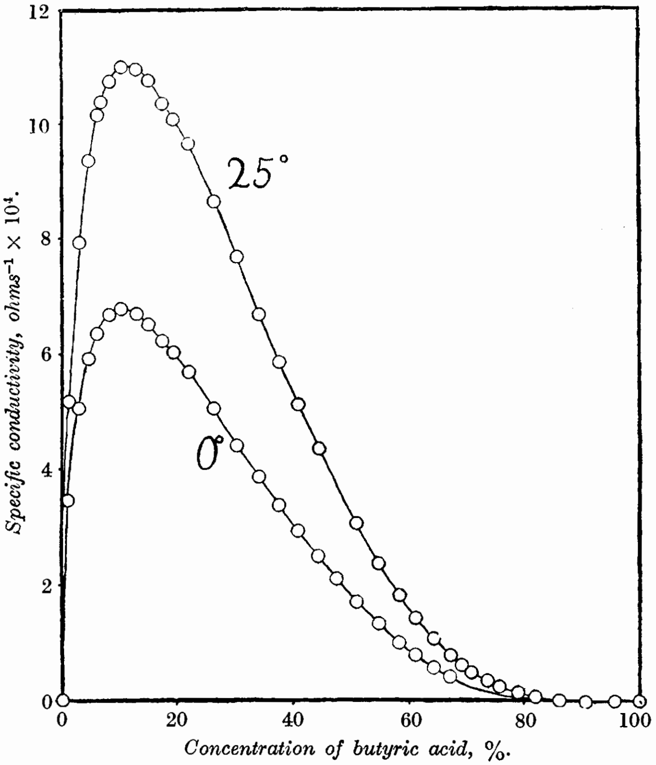
Discussion.

Over the range 0—12% of acid the conductivity increases rapidly, as demanded by the dilution law, which, however, is only obeyed quantitatively at concentrations lower than any that we have used (see, *e.g.*, Wilsdon and Sidgwick, J., 1913, **103**, 1959).

The most noticeable feature of the curves is the sharp maximum in the conductivity at a concentration of about 12% of acid. Abrupt changes in the slope of the freezing point–composition curve (Jones and Bury, *loc. cit.*), and in the contraction–composition curves (Grindley and Bury, *loc. cit.*), have been found at about the same concentration, which have been attributed to micelle formation, and the question arises as to whether there is any connexion between the maximum in the conductivity curve and micelle formation.

On the one hand, although micelle formation exerts a profound influence on the form of the conductivity-concentration curves of the soaps (see, *e.g.*, McBain, Laing, and Titley, J., 1919, **115**, 1279), there is no reason to believe that it should exercise a corresponding influence in the case of weak electrolytes. The conductivity of butyric acid is mainly due to the hydrogen ions, since their mobility is so great, and it should therefore be little affected by the association of un-ionised molecules and anions to form micelles. Again, there is always a maximum in the conductivity of mixtures of acids and water, and no particular significance has hitherto been attached to this.

FIG. 1.



On the other hand, the maximum is singularly sharp, and the slope of the curve therefore changes very rapidly in its neighbourhood. As has been emphasised before, it is this abrupt change of slope (which may, or may not, coincide with a maximum) that is the significant feature of solutions in which micellar association occurs. Further, this abrupt change of slope occurs at about the same concentration as those in the freezing-point curve (13—16%) and in the contraction curves (12—15%).

We incline to the view that this work affords no evidence of the existence of micelles in butyric acid–water mixtures, and that it could hardly be expected to afford any evidence on this point, though, in view of the success of the conductivity method as applied to the soaps, it was obviously necessary to investigate the conductivity of butyric acid solutions.

A second feature of the curves is the very low conductivity of mixtures containing less than 15% of water; the conductivity only begins to increase rapidly when the concentration of water exceeds 25%. Similar curves, in which, however, this phenomenon is not so strongly developed, are shown by propionic and acetic acids, but not by formic acid (Otten, *op. cit.*).

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UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

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