221. *The Viscosity of Butyric Acid–Water Mixtures.*

By C. R. Bury and J. Grindley.

This is one of a series of papers on the physicochemical properties of butyric acid–water mixtures (Jones and Bury, *Phil. Mag.*, 1927, **4**, 841; Bury, *ibid.*, p, 980; Grindley and Bury, J., 1929, 679; 1930, 1665; Davies and Bury, J., 1932, 2413). Viscosities have been thoroughly investigated at five temperatures in the range — 3° to 35°. No abrupt change of slope of the viscosity–concentration curve at the critical concentration for micelles has been detected, but the usual anomaly in the neighbourhood of the critical solution point has been found.

Experimental.

The purification of butyric acid, the preparation of the solutions, and the determination of their densities have been described in previous communications. All measurements recorded in this paper have been made with an Ostwald viscometer, the characteristics and calibration of which have been already described (Bury, J., 1934, 1380), but in a number of cases these have been checked by measurements with two other viscometers of the same type, in one of which the rate of flow was slightly faster and in the other considerably slower.

The procedure adopted was to place in the viscometer a suitable volume of solution, measured at room temperature, and to measure the flow-times at a number of temperatures. A small correction is necessary to compensate for the change in volume of the solution between room temperature and that of the experiment. It can easily be shown that this correction can be made by using a corrected flow-time (T_c) instead of the observed flow-time (T_0), these being connected by the equation $T_c = T_0[1 + k(d' - d'')]$, where d' and d'' are the densities of the solution at the temperature of the experiment and at that of the room respectively. Preliminary experiments showed that the numerical value of the constant (k) was 0·143, and that the formula was valid for far larger changes in volume than were ever encountered. Allowance for the kinetic correction was made in calculating viscosities, though the effect of this correction is often inappreciable, and even in extreme cases does not affect the result by 1%. Values of the absolute viscosity of water were taken from the International Critical Tables (1929, **5**, 10). The results are probably accurate to within 0·2%.

In the first series, the results of which are given in Table I (η = viscosity, in poises), measure-

Table I.

	$\eta \times 10^3$.			
Acid, %.	0°.	12°.	25°.	35°.
0	17·94	12·39	8·95	7·21
3·002	20·20	13·69	9·73	7·77
6·024	22·71	15·12	10·65	8·44
9·07	25·37	16·65	11·52	9·11
12·12	28·15	18·18	12·48	9·79
14·97	30·69	19·66	13·44	10·48
17·49	33·17	21·12	14·40	11·20
20·12	35·69	22·84	15·50	12·01
23·73	39·87	25·21	16·95	13·08
27·93	45·20	28·15	18·81	14·45
31·78	49·66	30·77	20·38	15·63
36·33	55·0	33·61	22·22	16·95
39·81	58·6	35·72	23·65	17·96
42·87	60·9	37·30	24·63	18·73
45·14	62·4	38·44	25·38	19·32
50·1	65·3	40·70	26·99	20·49
55·0	67·1	42·45	28·23	21·50
60·3	69·0	43·94	29·41	22·43
65·2	70·3	45·28	30·39	23·22
69·8	—	46·23	31·21	23·92
73·3	71·0	46·27	31·29	24·15
77·1	70·4	46·12	31·36	24·15
81·4	68·3	45·23	30·95	23·98
84·6	65·4	—	30·32	23·58
85·8	63·8	42·95	—	—
88·8	60·1	40·79	28·61	22·48
90·8	55·2	38·13	27·02	21·42
95·6	42·80	30·60	22·49	18·19
100	25·27	19·46	15·29	12·95

ments were made at four temperatures, 0°, 12°, 25°, and 35°. Flow times were always determined in duplicate; no significant differences were ever observed between the first and second observations except that inconsistent results were obtained for that solution the viscosity of which might be expected to be the highest of the whole series (*i.e.*, 69·8% acid at 0°)—the apparent viscosity varied from one determination to another and was always higher than might be expected. This must have been due to dust in the viscometer, for it was impossible to reproduce the effect with other solutions of similar concentration, but this observation led to a second series of measurements at 0° and at — 3°, covering the range of concentrations where the viscosity is greatest. The measurements at — 3° were extended to a concentration of 33% acid in order to cover the region of the critical solution point. The results of the second series are given in Table II, and both series are plotted in the figure.

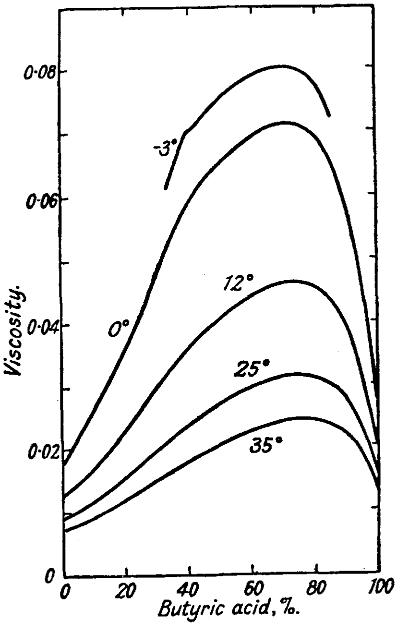

TABLE II.

Acid, %.	$\eta \times 10^3$. −3°.	$\eta \times 10^3$. 0°.
33·92	62·2	
36·88	66·3	
38·98	69·0	
39·99	69·9	
41·45	70·4	
44·91	72·6	
49·95	75·1	
59·8	78·5	
68·1	80·0	70·9
70·2	80·2	71·1
72·3	80·1	71·1
74·5	79·7	70·8
78·9	78·1	69·7
84·6	73·1	65·4

DISCUSSION.

The anomalous viscosity in the neighbourhood of the critical solution point (40% acid, — 3·8°; Faucon, *Compt. rend.*, 1909, **148**, 1189; see also Timmermans, *Z. physikal. Chem.*, 1907, **58**, 129) can be clearly seen in the curve for — 3°, and can also be detected on a large-scale graph in the curve for 0°. These anomalies are similar to those found for other systems in the neighbourhood of the critical solution point (Friedlander, *ibid.*, 1901, **38**, 385).

No abrupt change of slope at about 12% acid can be detected, similar to those found in the density–concentration and the specific heat–concentration curve, which have been attributed to micelle formation. This was not entirely unexpected: the viscosity–concentration curves of the soaps are smooth curves and exhibit no sudden change of slope at the concentration at which micelles begin to be formed. The high viscosity characteristic of many solutions of reversible colloids is generally attributed, not to the existence of colloidal particles, but to a secondary aggregation of these—incipient gel formation (see, *e.g.*, McBain, *J. Physical Chem.*, 1926, **30**, 239).

The most noticeable feature of the curves is the pronounced maxima. Although such maxima are often attributed to the formation of compounds, such an explanation is improbable in this case. There are no other grounds for belief in a compound between butyric acid and water, and the positions of the maxima vary with the temperature, the maxima at 0° and at 35° being at 71 and 76% acid respectively.

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[*Received, April 22nd,* 1936.]