XCVII.—*The Densities of Butyric Acid–Water Mixtures.*

By John Grindley and Charles R. Bury.

In a previous communication from this laboratory (Jones and Bury, *Phil. Mag.*, 1927, **4**, 841), it was suggested that aqueous solutions of butyric acid contain micelles resembling those that exist in soap solutions (McBain and Salmon, *J. Amer. Chem. Soc.*, 1920, **42**, 426). This conclusion was based on a study of freezing points; in particular, the " A plot," used in the graphical evaluation of activities (Lewis and Randall, " Thermodynamics," 1923, p. 287), is related to that of the lower fatty acids in exactly the same manner as the " A plots " of the soaps are related to those of the sodium salts of the lower fatty acids (Randall, McBain, and White, *J. Amer. Chem. Soc.*, 1926, **48**, 2517). Further, the hypothesis is not improbable from a structural point of view: butyric acid belongs to that class of substances the molecules of which consist of a hydrocarbon chain combined with a polar group and tend to form unimolecular layers on the surface of water and micelles in water, when they are soluble in it. Since the soaps are strong electrolytes, the formation of micelles—or aggregates of anions—must involve considerable work against the electrical forces; it would therefore be expected that weaker electrolytes should form micelles more readily. Butyric acid is a weak electrolyte, so it is not improbable that it should form micelles even though its hydrocarbon chain contains far fewer carbon atoms than are present in typical colloidal soaps.

In order to test the above suggestion, we have relied on the following considerations. Micelle formation can be regarded thermodynamically as an extreme case of association (complicated, in the case of soaps, by ionisation; with butyric acid, however, ionisation can be neglected except in very dilute solutions, with which this work is not concerned). Micelle formation can be represented by the equation $nC_3H_7{\cdot}CO_2H \rightleftharpoons (C_3H_7{\cdot}CO_2H)_n$, where n is the number of simple molecules in a micelle. If s and m are the concentrations of butyric acid as simple molecules and as micelles, respectively, and if the equilibrium constant be written in the form K^n (K being the Haber form of the constant), then, assuming as a first approximation that the activity coefficients of the two molecular species are unity, we have $s^n/m = K^n$ or $(s/K)^n = m$. Since n is a relatively large number, it follows that, if s/K is appreciably smaller than unity, m will be negligibly small, *i.e.*, the concentration of micelles will be negligible until the total concentration approaches the value K. In the neighbourhood of this point the concentration of micelles will first become appreciable, and will rapidly increase as the total concentration increases. Consequently, if any physical property of aqueous butyric acid solutions be plotted against the concentration, the slope of the curve will change abruptly * near this point : in other words, partial molal (or specific) quantities will change abruptly when the concentration has the value K. From freezing-point data, this concentration should be approximately 15% of acid.

None of the physical properties of butyric acid–water mixtures has been measured with sufficient thoroughness to test this conclusion, and we have therefore determined their densities and thence calculated the partial specific volumes of the two constituents. In order to find the effect of temperature on the concentration at which the slope changes abruptly, determinations have been made at five temperatures.

EXPERIMENTAL.

The procedure recommended by Hartley and Barrett (J., 1911, **99**, 1072) for the determination of densities was followed, with two exceptions. First, their formula requires modification when applied to a liquid of which the temperature coefficient of expansion is much greater than that of water (Grindley, J., 1928, 3297); and secondly, a small flask with restricted neck, of the type used by Baxter and Wallace (*J. Amer. Chem. Soc.*, 1916, **38**, 70), was used.

---

* Some observers have claimed that the slopes of certain property–composition curves change discontinuously at certain points (*e.g.*, Mendeléeff, " Principles of Chemistry," 1891, vol. 2, p. 237). With micelle formation, the greater the value of n, the more abrupt the change of slope will be, but only in the limiting case, when n is infinite, could it become discontinuous.

This was found more convenient than the pyknometers of Hartley and Barrett when carrying out a series of determinations on the same liquid at temperatures extending from 0° to 35°. The flask was blown from a test-tube and had a capacity of about 28 c.c.: a counterpoise of similar form, and made from the same glass, was used. The weight of the flask, when filled with water at any given temperature and weighed against the counterpoise, was reproducible to ± 0·1 mg. Weights were standardised by the method of Richards (*J. Amer. Chem. Soc.*, 1900, **22**, 144).

As starting point for the preparation of pure butyric acid, British Drug Houses' "normal butyric acid" (freezing point — 10°) and Kahlbaum's "normal (purest) butyric acid" (freezing point — 12°) were used: no other samples examined could be made to freeze above — 21°. By fractionally freezing ten times, care being taken to avoid the introduction of moisture, the freezing point was raised to — 7·1°. The purified acid apparently still contained traces of water, for, after shaking with phosphoric oxide in the cold, the freezing point was raised to — 6·70° ± 0·05° (mean of determinations with two independently purified samples): when about half the material was frozen the freezing point was 0·15° lower, from which it is probable that the freezing point of the pure acid is about — 6·55°.* The freezing points were determined by the Beckmann method with a standardised thermometer, graduated to 0·1°.

Unfortunately, the phosphoric oxide cannot be satisfactorily separated from the acid; distillation, even at low pressures, gives rise to the anhydride and to some sweet-smelling impurity. The phosphoric oxide adheres to the walls of the vessel, and most of it is removed by decantation through a filter; the acid so obtained, however, was found by analysis to contain 0·04% P_2O_5, but was used for density determinations of the pure acid only. In preparing the butyric acid–water mixtures, the acid, purified by crystallisation and then distilled in a vacuum, was mixed with a suitable amount of conductivity water, the final concentration being determined by titration with baryta.

The most important sources of error in this work appear to be the analytical error in determining the concentrations of the acid (about 0·1%), and the uncertainty as to the exact temperatures of

---

* Previous determinations of the freezing point of butyric acid are —2° to +2° (Linnemann, *Annalen*, 1871, **160**, 228); —3·12° (Faucon, *Compt. rend.*, 1909, **148**, 1189); —4·5° to —2·0° (Zander, *Annalen*, 1884, **224**, 63); —4·5° (Ballo, *Z. physikal. Chem.*, 1910, **72**, 448); —4·65° to —4·70° (English and Turner, J., 1915, **107**, 779); and —7·9° (Schneider, *Z. physikal. Chem.*, 1897, **22**, 223).

the thermostats. These could be regulated to within 0·02° of the desired temperature, an uncertainty which might lead to an error of 2×10^{-5} in the density of the most expansible (*i.e.*, concentrated) solutions.

TABLE I.

Acid, %.	$D_{4°}^{0°}$.	$D_{4°}^{12°}$.	$D_{4°}^{18°}$.	$D_{4°}^{25°}$.	$D_{4°}^{34·94°}$.
0	0·99987	0·99953	0·99862	0·99707	0·99408
4·905	1·00379	1·00250	1·00122	0·99930	0·99577
7·505	1·00587	1·00408	1·00256	1·00038	0·99657
10·01	1·00785	1·00546	1·00371	1·00127	0·99713
11·74	1·00912	1·00631	1·00436	1·00173	0·99736
13·94	1·01045	1·00707	1·00491	1·00207	0·99745
15·59	1·01124	1·00746	1·00517	1·00214	0·99738
17·39	1·01177	1·00766	1·00522	1·00207	0·99714
19·21	1·01218	1·00777	1·00521	1·00196	0·99688
20·86	1·01240	1·00781	1·00516	1·00179	0·99657
23·85	1·01264	1·00769	1·00489	1·00135	0·99594
26·93	1·01274	1·00748	1·00453	1·00082	0·99520
30·07	1·01277	1·00719	1·00409	1·00021	0·99435
35·05	1·01270	1·00662	1·00327	0·99913	0·99294
40·06	1·01251	1·00591	1·00233	0·99792	0·99138
45·31	1·01221	1·00502	1·00120	0·99651	0·98959
50·13	1·01177	1·00406	0·99996	0·99506	0·98781
54·09	1·01130	1·00314	0·99887	0·99374	0·98622
58·08	1·01066	1·00210	0·99767	0·99234	0·98453
60·23	1·01026	1·00145	0·99692	0·99147	0·98356
61·93	1·00986	1·00090	0·99629	0·99078	0·98272
63·32	1·00954	1·00045	0·99578	0·99016	0·98206
66·00	1·00880	0·99949	0·99465	0·98898	0·98070
70·02	1·00747	0·99774	0·99280	0·98695	0·97845
74·07	1·00573	0·99566	0·99057	0·98452	0·97580
77·90	1·00372	0·99336	0·98812	0·98194	0·97306
81·56	1·00140	0·99080	0·98546	0·97917	0·97010
85·96	0·99801	0·98711	0·98163	0·97521	0·96598
90·95	0·99310	0·98191	0·97626	0·96968	0·96030
95·62	0·98715	0·97561	0·96983	0·96312	0·95351
100	0·97844	0·96642	0·96045	0·95350	0·94367

The results are given in Table I; in the first column is given the concentration of acid in g. per 100 g. of solution, and in the remaining columns are given the densities ($D_{4°}^{t°}$) at 0°, 12°, 18°, 25°, and 34·94°. The density of pure butyric acid, over the range studied, is given by the formula

$$D_{4°}^{t°} = 0·97844 - 0·001004t + 2·5 \times 10^{-7}t^2.$$

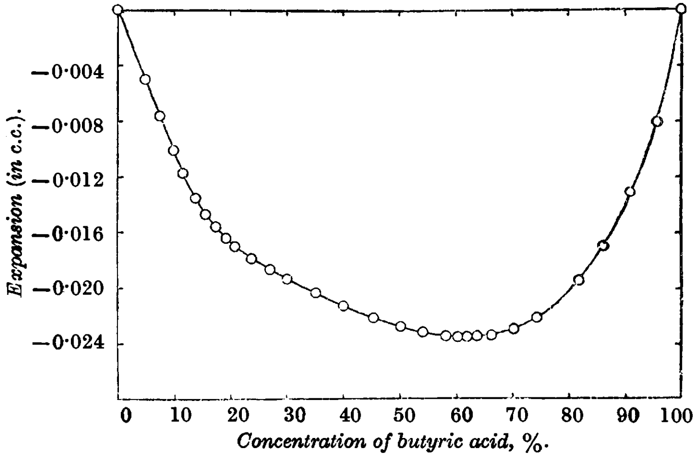
Values calculated from this formula are in good agreement with the determinations of Brühl (*Annalen*, 1880, **203**, 80) and Eijkman (*Rec. trav. chim.*, 1893, **12**, 157). The densities of solutions shown in the table are in fair agreement with measurements at 25° and 35° by Drucker (*Z. physikal. Chem.*, 1905, **52**, 649), whose work refers mainly to dilute solution, and at 25° by Ludeking (*Ann. Physik*, 1886, **27**, 72), whose results cover the whole range of concentrations but are not accurate enough for the purpose in view.

The change of density with concentration is unsuitable for illustration in a small-scale graph; we have therefore plotted in Fig. 1 the expansion on formation of 1 g. of solution from its constituents (ΔV) at 0° against the percentage composition of the solution. If d is the density of a solution containing x% of acid, and d' and d'' are the densities of the pure acid and water respectively at the same temperature,

$$\begin{aligned}\Delta V &= 1/d - x/100d' - (100 - x)/100d'' \\ &= 1/d - 1/d'' + x(1/d'' - 1/d')/100,\end{aligned}$$

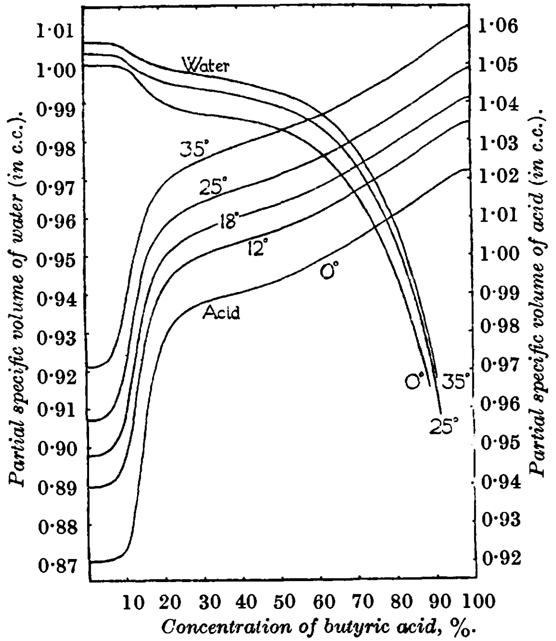
the second form of the equation being more suitable for numerical calculations. An abrupt change in the slope of the curve, such as we had been led to expect, is noticeable at a concentration of about 15% of acid. At higher temperatures the curves obtained are of the same general form.

FIG. 1.



Partial specific volumes of water and acid have been evaluated by a graphical method described by Hildebrand ("Solubility," American Chemical Society Monograph, 1924, p. 64) and are shown in Fig. 2 (for the sake of clearness the values for water at 12° and 18° are omitted). The partial specific volume of water changes very rapidly when its concentration is low, and it is impossible to calculate its limiting value (in pure acid) from our data. The limiting value given for the partial specific volume of butyric acid in pure water is also doubtful, since we have not made a special study of extremely dilute solutions, where the effect of ionisation would become appreciable. Fig. 2 shows that the partial specific volumes of both constituents change very rapidly when the concentration is about 12—15% of acid; that, as the temperature is raised, the change tends to become less abrupt; and that the concentration at which the change is greatest decreases with rise of temperature, being 15·0% of acid at 0°, 13·7% at 12°, 13·0% at 18°, 12·3% at 25°, and 12·0% at 35°. The results of this work confirm, therefore, the existence of micelles in butyric acid solutions.

FIG. 2.



Summary.

It is argued that micelle formation must lead to abrupt changes in the slope of physical property–composition curves.

The densities of butyric acid–water mixtures at 0°, 12°, 18°, 25°, and 35° have been measured and partial specific volumes calculated. The results obtained support the contention of Jones and Bury that micelle formation occurs in these solutions.

EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

[*Received, November 6th,* 1928.]