139. *The Densities of Aqueous Solutions of Potassium Acetate and Laurate.*

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THE work described here is a continuation of previous work (Davies and Bury, J., 1930, 2263) on the densities of soap solutions. Data for solutions of potassium acetate at 25° and for potassium laurate at 25° and 35° are presented, and it is shown that irregularities in the partial specific volumes of potassium acetate (Davies and Bury, *loc. cit.*) are due to experimental errors in the densities from which they were calculated. Further, an abrupt change in the density–composition curve of the laurate is discussed.

EXPERIMENTAL.

Acetic acid was distilled from chromium trioxide (Orton and Bradfield, J., 1924, **125**. 960), fractionally frozen three times, and then neutralised with pure potassium hydroxide. The resulting salt was twice recrystallised. A concentrated solution was prepared, and its strength determined by evaporation and conversion into the chloride. The more dilute solutions were prepared by dilution of this concentrated solution. A different preparation of the salt was used for each of the three series of density determinations.

Lauric acid was purified by two fractional distillations of its methyl ester under low pressure. Solutions of the potassium soap were prepared by treating a known weight of acid with the required quantity of carbon dioxide-free potassium hydroxide solution. This was prepared by washing sticks of caustic potash with water to remove the outer layers and then dissolving the cores. The entire operation was performed in resistance-glass vessels and in an atmosphere of nitrogen. The absence of carbonate in the alkali was proved by analysis by Winkler's method (Treadwell and Hall, "Analytical Chemistry," 1919, Vol. ii, 563). The strength of the most concentrated solution of each series was thus determined by synthesis, and the more dilute solutions were obtained from this by dilution. In making up the laurate solutions, analysing the acetate solutions, and diluting solutions, weights were corrected for buoyancy.

Dilute solutions of potassium laurate show a tendency to deposit acid soap: this tendency increases with the age and dilution of the solution and is favoured by low temperatures. No results are quoted for solutions which were cloudy or showed any other sign of the formation of acid soap.

In determining densities, Hartley and Barrett's procedure (J., 1911, **99**, 1072) was followed, except that flask-shaped pyknometers were used. Weights were standardised by Richards's method (*J. Amer. Chem. Soc.*, 1900, **22**, 144). The correction to which attention has been

Potassium acetate.

Series.	c, %.	$d_{4°}^{25°}$.	Series.	c, %.	$d_{4°}^{25°}$.	Series.	c, %.	$d_{4°}^{25°}$.
2	62·30	1·3453	1	44·67	1·2401	3	12·84	1·06150
1	61·56	1·3417	2	41·71	1·2220	3	11·03	1·05233
3	60·82	1·3373	3	39·78	1·2110	2	9·930	1·04649
2	57·25	1·3149	1	35·26	1·1846	3	8·930	1·04148
3	55·68	1·3060	2	29·89	1·1536	3	8·102	1·03733
3	54·51	1·2992	1	29·01	1·1491	3	6·418	1·02883
1	53·13	1·2909	2	25·02	1·1264	1	4·870	1·02111
2	50·59	1·2749	3	24·86	1·1260	3	3·787	1·01575
2	49·05	1·2655	1	18·60	1·09181	3	2·005	1·00686
3	46·91	1·2533	2	15·01	1·07270	3	1·005	1·00204

Potassium laurate.

Series.	c, %.	$d_{4^\circ}^{25^\circ}$.	$d_{4^\circ}^{35^\circ}$.	Series.	c, %.	$d_{4^\circ}^{25^\circ}$.	$d_{4^\circ}^{35^\circ}$.
1	20·21	1·01514	1·01057	2	3·001	1·00016	0·99684
2	18·21	1·01351	1·00907	3	2·987	1·00015	0·99683
1	17·03	1·01247	1·00814	1	2·001	0·99927	0·99604
1	14·05	1·01000	1·00587	2	2·000	0·99927	0·99601
2	12·52	1·00861	1·00458	1	1·505	0·99883	0·99563
1	11·02	1·00740	1·00351	2	1·501	0·99881	0·99560
2	9·000	1·00550	1·00174	2	1·000	0·99835	0·99517
1	8·002	1·00470	1·00104	3	0·797	0·99813	0·99500
1	5·998	1·00289	0·99939	3	0·718	—	0·99491
1	4·006	1·00110	0·99774	3	0·643	—	0·99482
2	4·001	1·00105	0·99767	3	0·595	0·99789	0·99478
1	3·042	1·00021	0·99693	3	0·300	0·99749	0·99442

called by Grindley (J., **1928**, **3297**) was found negligible. The results obtained are in the tables, concentrations (*c*) being expressed as g. of salt per 100 g. of solution.

The error in determining densities is probably negligible in comparison with the uncertainty in the concentration of the solutions, except in the most dilute solutions. The uncertainty in the determination of the acetate solutions is probably about 0·05%. In the laurate solutions, the weight of lauric acid is known with accuracy; the uncertainty lies in the addition of the correct amount of alkali. Though all densities were determined to the fifth place, this fifth place is of no absolute value for the more concentrated solutions of potassium acetate owing to this uncertainty in the composition, and is therefore omitted from the tables. With potassium laurate the change of density with concentration is much smaller, and the measurements cover a smaller range of concentrations; consequently, the fifth place is probably significant even at the highest concentration studied.

DISCUSSION.

Our densities of potassium acetate solutions are slightly lower than those given in International Critical Tables (1928, Vol. iii, 90), based on determinations of previous investigators. The difference is 0·0007 at a concentration of 60%, and decreases with concentration, but not quite regularly. Partial specific volumes of potassium acetate calculated from the densities in the International Critical Tables had revealed some small irregularities (Davies and Bury, *loc. cit.*, figure). The present work shows that these were due to small experimental errors, and that the density–composition and partial specific volume–composition graphs are smooth curves that show no sign of any abrupt change of slope or other irregularity.

The densities of a few solutions of potassium laurate were determined at 90° by Bunbury and Martin (J., 1914, **105**, 433), but these are not comparable with our results owing to difference of temperatures. Our results show that there is an abrupt change of slope in the density–composition graph similar to that found for potassium *n*-octoate. This graph consists of two almost straight lines which meet at a concentration of about 1%. It is not suggested that the slope of the curve changes discontinuously at this point (*i.e.*, that the graph consists of two intersecting straight lines) but only that the slope changes rapidly over a narrow range of concentrations. The concentration at which the abrupt change of slope (the critical concentration for micelles) occurs is thus a somewhat ill-defined quantity, and various methods of plotting indicate slightly different values. It is, however, quite clear that the concentration at which the change occurs is lower at 35° than it is at 25°, the approximate concentrations being 0·8 and 0·9% respectively. From the measurements of McBain, Laing, and Titley (J., 1919, **115**, 1290; see also Randall, McBain, and White, *J. Amer. Chem. Soc.*, 1926, **48**, 2517), there appears to be an abrupt change in the slope of the freezing point–composition curve at about the same concentration, but the data in this region are too scanty to fix the concentration with any accuracy.

Another feature of importance is the magnitude of the change of slope at this point. If concentrations are expressed as percentages, the slope of the density–composition curve for potassium laurate at 25° is 0·00133 in the range 0—0·8%, and 0·00090 for the range 1·0—4·0%. The change of slope in the neighbourhood of 0·9% is therefore 0·00043. At 35° the change of slope is appreciably smaller (0·00035), and at higher temperatures the abrupt change of slope may be expected to become too small to be detectable.

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