The Properties and Structures of Aqueous Sodium Caprylate Solutions

IV. The Vapour Pressure of the Solutions and the Osmotic Coefficient of the Sodium Caprylate

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The vapour pressure of sodium caprylate solutions has been measured by an isopiestic and a thermistor method, and from the values obtained the osmotic coefficient of sodium caprylate was calculated. The coefficient was found to change with concentration in a manner characteristic of association colloid solutions, with a sharp drop in the concentration range above the c.m.c. and a weak minimum at relatively high concentrations.

The vapour pressure decreases more slowly from the c.m.c., at 0.38 m, up to about 1.1 m than at lower and higher concentrations, and it is largely in this range that there is an extremely rapid fall in the osmotic coefficient. Above 1.1 m the osmotic coefficient falls more slowly and at this concentration the plot of $(1 - \Phi)\sqrt{m}$ *versus* m passes through a well defined maximum. At about the same strength (1.15—1.4 molal and 1.0—1.2 molar) a change in the micellar structure of the solution was disclosed by our earlier determinations of the partial specific volume and the viscosity of sodium caprylate. This structural change is thus reflected also in the osmotic behaviour of the solutions. In addition, the change which was disclosed by the two methods at rather high concentrations (about 2.5—2.7 molal, 1.8—2.8 molar) and which, according to the viscosity measurements, indicates a transformation of the spherical micelles to anisometric ones, can be traced, if weakly, in the variation of the vapour pressure and osmotic coefficient with concentration: the drop in vapour pressure accelerates slightly and the osmotic coefficient begins to increase in this concentration range.

The vapour pressures of sodium caprylate solutions have been measured at 90°C by McBain and Salmon[1] in concentrations from 0.01 to 1.0 m by the dewpoint method and at 25° by Smith and Robinson[2] in concentrations up to 3.0 m by an isopiestic method. We have now measured the vapour pressures

of the caprylate solutions at 20 and 25° over the range from *ca.* 0.1 to 4.0 m. The measurements were performed at the Institute of Physical Chemistry at the Åbo Akademi; they were first carried out by an isopiestic method and checked some years later by a thermistor method.[3]

The apparatus for isopiestic measurements, which has been described earlier in connection with vapour pressure studies at the abovementioned laboratory,[4] included a copper block with holes for four or six gold-plated silver crucibles, two or three of them containing the solution to be examined, and the others standard solutions of potassium chloride. The copper block and the crucibles were placed in a vacuum desiccator, which was then evacuated. By rocking the desiccator constantly in a thermostat at 20°C by means of a motor, the solutions were thus mixed continuously *in vacuo;* water then passed from the solutions of higher vapour pressure to those of lower. The concentrations were determined by weighing the crucibles. Equilibrium was normally reached in 3—4 days, but in some cases 8—10 days were required, depending on the initial concentrations.

The measurements by the thermistor method were carried out with a Mechrolab Vapor Pressure Osmometer at 25°. They confirmed the results received by the isopiestic method and will therefore only be mentioned briefly.

The sodium caprylate and the aqueous caprylate solutions were prepared as described previously.[5]

Table 1. Vapour pressure and osmotic coefficient of the sodium caprylate solutions. Measurements by the isopiestic method; 20°C.

| Isopiestic solutions		Vapour pressure mm Hg	Osmotic coefficient of NaC$_8$ Φ	Isopiestic solutions		Vapour pressure mm Hg	Osmotic coefficient of NaC$_8$ Φ
NaC$_8$ m	KCl m			NaC$_8$ m	KCl m		
0	0	17.535	—	1.059	0.566	17.219	0.476
0.0730	0.0742	17.492	0.935	1.090	0.581	17.211	0.473
0.1232	0.1258	17.462	0.939	1.145	0.5895	17.206	0.468
0.1706	0.1772	17.433	0.934	1.266	0.6295	17.184	0.443
0.2460	0.2590	17.391	0.941	1.282	0.6144	17.192	0.428
0.3050	0.3250	17.354	0.945	1.389	0.667	17.162	0.429
0.3360	0.3550	17.337	0.940	1.620	0.681	17.156	0.374
0.3847	0.4047	17.310	0.931	1.634	0.695	17.148	0.379
0.4429	0.4492	17.285	0.901	1.789	0.723	17.133	0.358
0.4943	0.4752	17.270	0.855	1.979	0.7716	17.105	0.348
0.5640	0.5008	17.251	0.804	2.231	0.8500	17.063	0.339
0.606	0.518	17.246	0.761	2.461	0.9383	17.015	0.339
0.650	0.517	17.246	0.710	2.579	0.988	16.987	0.330
0.718	0.557	17.224	0.692	2.590	0.958	17.005	0.339
0.721	0.532	17.238	0.658	2.683	1.035	16.961	0.347
0.810	0.554	17.226	0.609	2.870	1.1145	16.918	0.345
0.821	0.565	17.220	0.619	2.927	1.1462	16.897	0.351
0.835	0.556	17.225	0.594	3.370	1.409	16.752	0.376
0.840	0.541	17.234	0.572	3.465	1.443	16.735	0.374
0.914	0.581	17.211	0.567	3.694	1.557	16.669	0.380
0.984	0.587	17.208	0.531	3.839	1.626	16.632	0.383
0.985	0.569	17.217	0.516	3.939	1.679	16.602	0.385
1.048	0.562	17.223	0.476	4.097	1.724	16.557	0.389
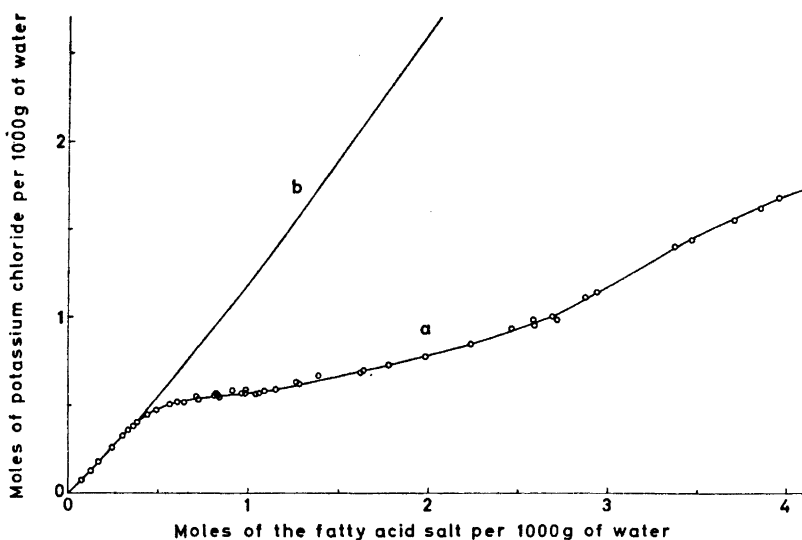
Fig. 1. (a) Curve showing the concentrations of isopiestic solutions for potassium chloride and sodium caprylate solutions at 20°. (b) Curve showing the concentrations for iso-piestic potassium chloride and sodium heptylate, capronate, valerate, and butyrate solutions (according to measurements by Smith and Robinson at 25°).

VAPOUR PRESSURE OF THE SOLUTIONS

The results of the isopiestic measurements and the values calculated from the findings are presented in Table 1. The concentrations of isopiestic solutions of sodium caprylate and potassium chloride, which are given in columns 1 and 2 of the table are plotted against one another in Fig. 1 (curve a). So long as the vapour pressure of the solutions of the two salts alters at the same rate with concentration the slope of the curve is 45°; any deviation from this thus indicates a disparity between the solutions. As Fig. 1a shows, at low concentrations up to about 0.3 m caprylate the potassium chloride-sodium caprylate curve is linear with an angle of about 45°. Above this concentration, however, the curve turns off towards the concentration axis and assumes an extremely flat course, showing that the vapour pressure of the caprylate solutions decreases here at a much slower rate with concentration than does the vapour pressure of the potassium chloride solutions. Above 1.1—1.2 m caprylate the curve becomes steeper, and at 2.6—2.9 m it again tends upwards slightly, indicating that at higher concentrations the vapour pressure is again somewhat more dependent on concentration than at the intermediate strengths between about 0.4 and 1.2 m.

The cause of these differences is to be sought chiefly in the formation of micelles, the associated changes in the counterion binding, and the action of the inter-ionic forces in the caprylate solutions; the water binding to ions and micelles is another significant factor. According to our density measurements

the c.m.c. of sodium caprylate is 0.38 m at 20°.[5] To examine the effect of the micelle formation more clearly the solutions of sodium caprylate were compared with those of fatty acid salts that do not form micelles (curve 1b). In the construction of this curve we relied on isopiestic data published by Smith and Robinson;[2] although these apply at 25°, the relationship between the vapour pressures of solutions of the fatty acid salt and potassium chloride at this temperature probably does not differ essentially from that at 20°. For lower concentrations curve 1b is based on the values obtained by these workers for sodium heptylate (0.26 — 0.50 m), capronate (0.26 — 0.82 m), and valerate (0.58 — 1.2 m), and for higher concentrations on values for sodium butyrate (0.70 — 2.0 m). As the figure shows, this curve coincides with ours for caprylate at the lowest concentrations but diverges from it at about 0.3—0.4 m, that is, at about the point where micelles begin to form in the caprylate solutions. Above this strength, too, the curve for the lower salts continues to rise at nearly 45°, whereas the caprylate curve bends towards the concentration axis.

The vapour pressures of sodium caprylate solutions at 20° were calculated from our own isopiestic findings and published values for the vapour pressure of potassium chloride solutions [6] (Table 1, col. 3; Fig. 2a). The curve in Fig. 2 also shows that at low concentrations below the c.m.c. the vapour pressure falls off with the caprylate concentration as in the case of ordinary electrolytes. Not until 0.3—0.4 m does the drop in vapour pressure slow down; finally, between about 0.6 and 1.1 m, it diminishes by only 0.04 mm Hg. Above 1.1 m,
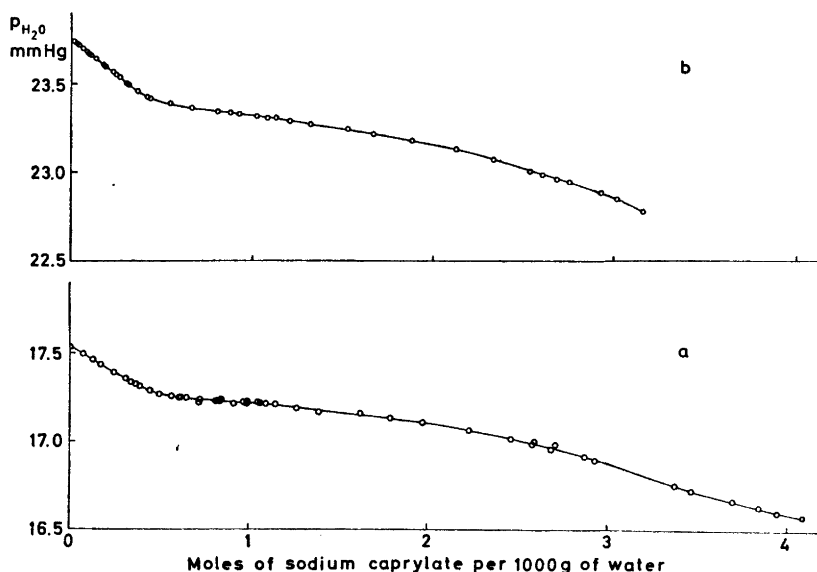

Fig. 2. (a) Vapour pressure of sodium caprylate solutions at 20° measured by the isopiestic method. (b) Vapour pressure of sodium caprylate solutions at 25° measured by the Mechrolab Osmometer method.

however, the fall accelerates again. According to the density measurements there is a change in the structure of the micellar substance at about this concentration:[5] this change would thus seem to be associated with a slightly steeper drop in vapour pressure. It is thus evident from our measurements that the vapour pressure diminishes more slowly with the caprylate concentration between the c.m.c. and about 1.1 m than below and above this range.

The vapour pressures measured by the Mechrolab Osmometer at 25° are given in Fig. 2b; this curve has the same course as that in 2a.

OSMOTIC COEFFICIENT OF THE SODIUM CAPRYLATE

The vapour pressures obtained experimentally were applied in the calculation of the osmotic coefficient, Φ, of sodium caprylate (Table 1, col. 4; Fig. 3a). After an interval below c.m.c. in which there are a slight increase and decrease in Φ, there is a sharp drop between 0.38 and 1.1 m; above the latter value the downward trend continues, but at a much slower rate; at $2.0-2.7$ m Φ passes through a minimum and begins to increase — at first fairly rapidly and then more slowly at the highest concentrations.

This general behaviour of the osmotic coefficient, namely, a rapid fall in Φ above the c.m.c. and then a minimum at higher concentrations, is familiar from earlier studies of various association colloids.[2] Our curve for the caprylate
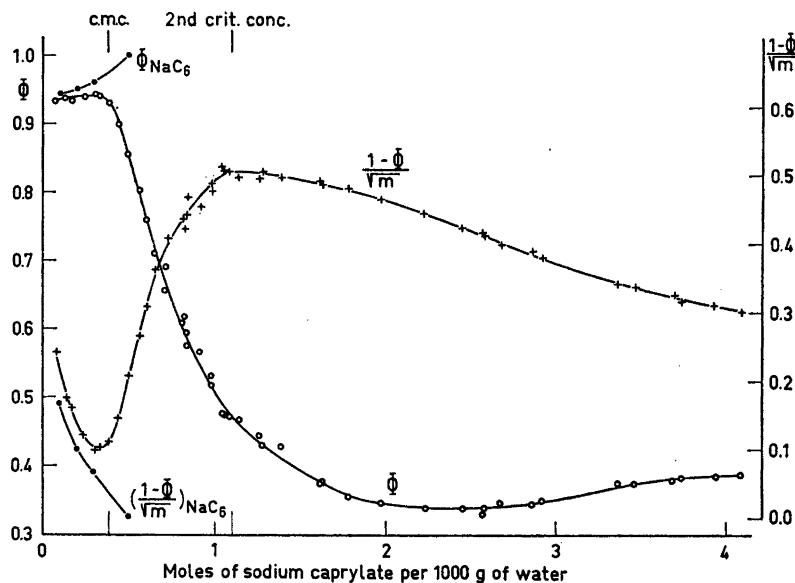

Fig. 3. (a) Osmotic coefficient of sodium caprylate at 20°. (b) Dependence of $(1-\Phi)/\sqrt{m}$ on concentration for sodium caprylate solutions at 20°.

solutions, however, displays some new features. One of these is brought out more clearly if $(1-\Phi)/\sqrt{m}$ is plotted against the molal concentration (Fig. 3b). From a well defined minimum below the c.m.c. this curve rises steeply from 0.38 m up to 1.1 m, where it passes through a well defined maximum.* This lies at the concentration for which our earlier measurements of the partial specific volume of the caprylate and the viscosity values of the solutions indicated a change in the micellar structure of the caprylate solution, a level that we have accordingly termed the 'second critical concentration' of sodium caprylate (1.15—1.4 molal, 1.0—1.2 molar).[5,7-10] Thus, this structural change is reflected also in the osmotic behaviour of the solutions. In addition to the density and viscosity measurements, we have in the determination of the vapour pressure, the calculation of Φ and plotting of $(1-\Phi)/\sqrt{m}$ against m or $\sqrt{m}$, a third experimental method for finding the point at which the changes begin — that is for determining the position of the second critical concentration.

At 25° the curves have a similar course as at 20° (Figs. 4 a and b); also at this temperature there is a well defined maximum in the curve for $(1-\Phi)/\sqrt{m}$ versus m at 1.05—1.15 m sodium caprylate.

As long ago as 1926 it was pointed out by Randall, McBain and White [12] on basis of dew-point measurements at 90° that the curves of the function
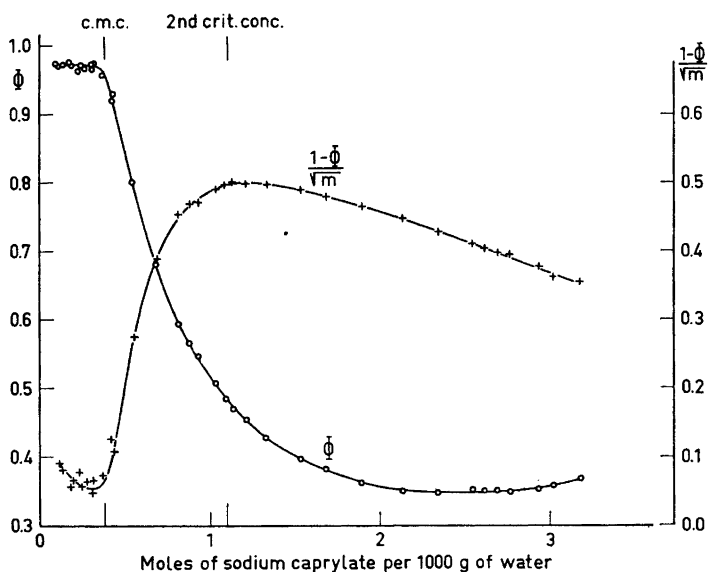

Fig. 4. (a) Osmotic coefficient of sodium caprylate at 25°C. (b) Dependence of $(1-\Phi)/\sqrt{m}$ on concentration for sodium caprylate solutions at 25°C.

* To permit a direct comparison with the Φ—m curves, in Fig. 3b the function $(1-\Phi)/\sqrt{m}$ is plotted against m, not $\sqrt{m}$ as is usual.

$(1-\varPhi)/\sqrt{m}$ *versus* $\sqrt{m}$ for all higher soaps have a pronounced minimum and maximum; but the points at which measurements were made below the maximum were few and unreliable. Later it was noted by Smith and Robinson in fairly large experimental series that a maximum occurred in the curves for a number of fatty acid salts at 25°.[2] On the basis of their measurements we have applied the new method to find the approximate position of the second critical concentration of these salts at 25°; for sodium capronate it is about 3.0—3.5 m, for the heptylate about 2.2—2.5 m, the caprylate about 1.0—1.1 m, the pelargonate about 0.6—0.8 m, and the caprate about 0.5 m. It is notable that in all these cases the minimum value of the osmotic coefficient is still not reached at the second critical concentration, in fact, not until almost twice this concentration.

The structural changes at higher concentrations (at 2.5—2.7 molal and 1.8—2.0 molar; the 'third critical concentration') revealed by viscosity [7,8] and density [5] measurements and attributed to growth of the spherical micelles into cylindrical ones can also be traced in the osmotic properties as a more rapid fall in vapour pressure and an incipient increase in the osmotic coefficient at 2.6—2.9 m, that is to say above the minimum of this coefficient.

The osmotic behaviour below the c.m.c. also merits some attention. Whereas for potassium chloride and many other typical 1—1 inorganic salts the osmotic coefficient decreases steadily between 0.1 and 0.5 m, for sodium salts of intermediate fatty acids it increases in this concentration range; for instance, for sodium capronate and heptylate $\varPhi$ increases from 0.946 to about 0.99—1.00 (Smith and Robinson [2]). In the case of sodium caprylate, however, there is not the same fairly large increase in the osmotic coefficient in this range. The fact that the $\varPhi$ curve for the caprylate begins to level out and approaches the horizontal between 0.1 m and the c.m.c. suggests the presence of a weak association before the true formation of micelles begins. Evidence of a similar phenomenon is found in Smith and Robinson's $\varPhi$ curves for caprylate, heptylate, and capronate, just before they enter on their definitive downward course above the c.m.c.[2]

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