ACTA CHEMICA SCANDINAVICA 21 (1967) 1639–1642

The Properties and Structures of Aqueous Sodium Caprylate Solutions

V. The Activity of Water and Sodium Caprylate

PER EKWALL, HENRIK EIKREM and PER STENIUS

Laboratory for Surface Chemistry (Ytkemiska Laboratoriet), the Royal Swedish Academy of Engineering Sciences, Stockholm, Sweden

The activity of water and the mean activity of sodium caprylate at 20 and 25°C in aqueous solutions of this soap has been calculated from previously published data for the vapour pressure and the osmotic coefficient. The dependence of concentration below c.m.c. is analogous with that of a typical 1—1 electrolyte, whereas above c.m.c. the activities in an intermediate region are altered to a rather small extent with the concentration and become at somewhat higher concentrations again more dependent on the concentration.

ACTIVITY OF WATER

The vapour pressure determinations in sodium caprylate solutions published earlier [4] give directly the activity of water in these solutions. The activity values at 20° and 25°C, respectively, are given in Tables 1A and B and in Figs. 1a and 2a. The two series are practically identical.

Throughout the concentration region examined the activity of water is fairly high. After an initial steep fall with concentration it changes little over an intermediate range, and then beings to fall more rapidly. The slowest decrease, from about 0.985 to 0.981, occurs between 0.5 and 1.1 m. Above the latter value and particularly from about 2.5—3.0 m upwards the dependence on concentration gradually increases. In the 4 m solution the water activity is about 0.944.

It is thus slightly above the c.m.c., at 0.38 m, — at the beginning of the micellar region — that the water activity is least dependent on the caprylate concentration. The small change in activity between 0.5 and 1.1 m is probably due chiefly to the rise in concentration of free counter ions, which is known to continue above the c.m.c. The activity of water thus seems not to be affected appreciably by the increase in the number of caprylate micelles that occurs in this region. Nor it is likely therefore that the slightly more rapid decrease

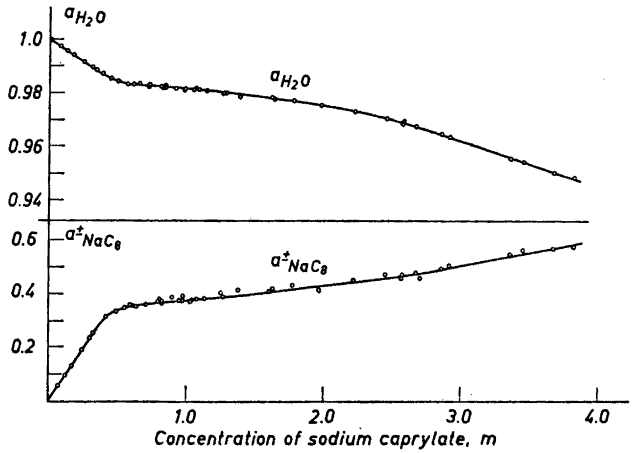

Fig. 1. Sodium caprylate solutions. 20°C. a. The activity of water; b. Mean activity of sodium caprylate.

Table 1. The activities of water and of sodium caprylate in sodium caprylate solutions. A. According to measurements by the isopiestic method; 20°C.

NaC_8 m	Activity of water	Mean activity coefficient for NaC_8	NaC_8 m	Activity of water	Mean activity coefficient for NaC_8
0.0730	0.9976	0.820	1.0898	0.98152	0.3525
0.1232	0.99584	0.790	1.1448	0.98090	0.335
0.1706	0.99418	0.784	1.2660	0.97998	0.321
0.2460	0.99179	0.775	1.2820	0.98044	0.305
0.3050	0.98968	0.774	1.3890	0.97873	0.301
0.3360	0.98871	0.764	1.620	0.97839	0.255
0.3897	0.98717		1.634	0.97793	0.258
0.4429	0.98574	0.719	1.789	0.97707	0.244
0.4943	0.98489	0.677	1.979	0.97548	0.211
0.5640	0.98380	0.6195	2.231	0.97308	0.204
0.6023		0.595	2.461	0.97035	0.190
0.6062	0.98352	0.588	2.579	0.96874	0.180
0.6496	0.98352	0.547	2.5900	0.96977	0.184
0.7179	0.98226	0.529	2.6832	0.96727	0.181
0.7210	0.98306	0.5055	2.7063		0.171
0.8102	0.98238	0.461	2.870	0.96481	0.173
0.8206	0.98204	0.464	2.9275	0.96362	0.174
0.8346	0.98232	0.449	3.3700	0.95535	0.164
0.8400	0.98283	0.436	3.4650	0.95438	0.161
0.9134	0.98152	0.427	3.6940	0.95061	0.155
0.9660		0.393	3.8396	0.94850	0.152
0.9837	0.98135	0.400	3.9390	0.94679	0.150
0.9853	0.98186	0.383	4.097	0.94423	0.145
1.0478	0.98221	0.356			
1.059	0.98198	0.3545			

Table 1. Continued.
B. According to measurements with Mechrolab Vapour Pressure Osmometer 25°C.

NaC_8 m	Activity of water	Mean activity coefficient for NaC_8	NaC_8 m	Activity of water	Mean activity coefficient for NaC_8
0.01409	0.9995	—	1.028	0.98149	0.387
0.03260	0.9988	—	1.085	0.98130	0.371
0.04601	0.9983	—	1.127	0.98122	0.353
0.06397	0.9977	—	1.207	0.98050	0.339
0.08828	0.9968	—	1.322	0.97985	0.315
0.09560	0.9966	—	1.526	0.97852	0.279
0.1115	0.9961	0.832	1.673	0.97730	0.261
0.1338	0.99534	0.828	1.883	0.97569	0.248
0.1730	0.99399	0.836	2.123	0.97349	0.218
0.1892	0.99334	0.830	2.336	0.97115	0.208
0.2280	0.99199	0.816	2.533	0.96838	0.194
0.2442	0.99124	0.832	2.604	0.96762	0.188
0.2687	0.99064	0.806	2.687	0.96644	0.183
0.3086	0.98916	0.812	2.754	0.96602	0.181
0.3089	0.98906	0.818	2.929	0.96335	0.178
0.3134	0.98894	0.818	3.016	0.96166	0.176
0.3634	0.98754	0.798	3.171	0.95865	0.171
0.4192	0.98616	0.762			
0.4315	0.98590	0.769			
0.5428	0.98446	0.652			
0.6787	0.98359	0.552			
0.8088	0.98285	0.472			
0.8737	0.98242	0.443			
0.9270	0.98208	0.422			

in the water activity observed above 1.1 m is a consequence of the changes in number of micelles that takes place at higher concentrations; here, too, the cause of the reduction in the water activity is probably to be sought in changes in the actual intermicellar solution. Factors that call for more attention than they have received hitherto are the changes with soap concentration that obviously occur in the water binding of the micelles and as a consequence in the quantity and concentration of the intermicellar solutions.[2,5] It is to be noted that a first slightly more rapid reduction in the activity of water begins above 1.1 m, and a second between 2.5 and 3 m, that is at about the second and third critical concentration, where changes in the micellar structure take place.[1-4]

ACTIVITY OF SODIUM CAPRYLATE

The mean activity coefficients of sodium caprylate were calculated from the expression derived by Sinclair and Robinson [6]

$$\log \gamma_{NaC_8} = \log \gamma_{KCl} + \log R + \frac{2}{2.303} \int_0^{a_{KCl}} \left(\frac{R-1}{\sqrt{a_{KCl}}} \right) d\sqrt{a_{KCl}} \qquad (1)$$

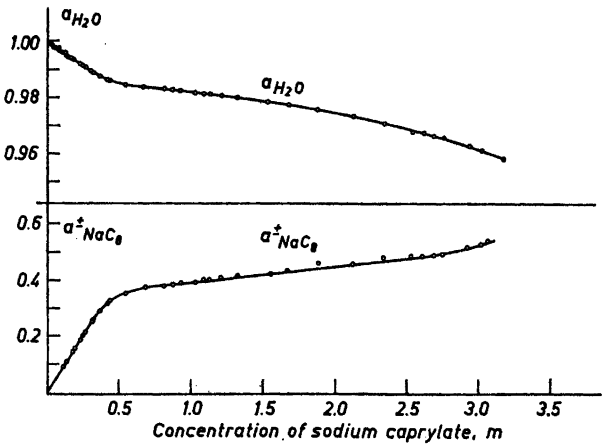

Fig. 2. Sodium caprylate solutions, 25°C. a. The activity of water; b. Mean activity of sodium caprylate.

where R is the ratio between the concentrations of isopiestic potassium chloride and sodium caprylate solutions, a_{KCl} and γ_{KCl} the mean activity and the mean activity coefficient for potassium chloride in aqueous solutions at 20° and 25°, respectively.

The values for the mean activity coefficients of sodium caprylate are given in Tables 1A and B.

Above the c.m.c. the activity coefficient falls off, at first extremely rapidly, and then at a gradually diminishing rate. At the highest concentrations it falls to about 0.15. Unlike the osmotic coefficient it does not pass through a minimum.

The activity coefficients were used in calculating the mean activity for sodium caprylate at various concentrations. (Figs. 1 b and 2 b; the ordinate scale for these curves is only one tenth of that for the water activity). These curves are mirror images of those for the water activity. Up to the c.m.c. the mean activity rises rapidly with concentration, then extremely slowly in an intermediate region, to resume a somewhat more rapid growth again at higher concentrations.

The activity values for 25° are only slightly higher than those for 20°.

REFERENCES

1. Ekwall, P., Eikrem, H. and Mandell, L. *Acta Chem. Scand.* **17** (1963) 117.
2. Ekwall, P. and Holmberg, P. *Acta Chem. Scand.* **19** (1965) 456.
3. Ekwall, P. and Holmberg, P. *Acta Chem. Scand.* **19** (1960) 573.
4. Ekwall, P., Lemström, K.-E. and Eikrem, H. *Acta Chem. Scand. In press.*
5. Ekwall, P. *Wiss. J. Friedrich-Schiller-Univ., Jena, Math.-Naturwiss. Reihe* **14** (1965) 181.
6. Sinclair, D. A. *J. Phys. Chem.* **37** (1933) 495.

Received March 16, 1967.