

The Properties and Structures of Aqueous Sodium Caprylate Solutions

VI. Measurements of the Activity of Sodium Ions

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The sodium ion activity in sodium caprylate solutions has been measured with glass electrodes responsive to sodium ions. The activity rises linearly up to the c.m.c., and continues to rise above this concentration, too, but at a slower rate. Also between c.m.c. and up to 1.0–1.2 m the activity curve is almost linear, after which there is a steady but slight decrease in the slope. In the 3.5 m caprylate solution the activity reaches a value of about 1.0.

The sodium ion activity of sodium caprylate solutions was measured with glass electrodes responsive to sodium ions.

The electrodes were of type "GNA 33" of Electronic Instruments Ltd. and the measurements were performed in a vessel immersed in an oil thermostat at 20°C. The reference was a silver/silver chloride electrode in 3.5 m potassium chloride solution saturated with silver chloride and connected to the measuring vessel by means of a bridge with saturated potassium nitrate solution. The silver/silver chloride electrode was made as specified by Brown.¹ The electromotive force was determined with the Radiometer PHM 4 c tube potentiometer, which has a reproducibility of about 0.2 mV.

The sodium caprylate and water were weighed directly in the measuring vessel which was flushed with nitrogen. When the glass electrode had stood in the solution for about 40 min the emf of the electrode system was measured. The procedure was repeated for each particular concentration (point measurements). Later on in the study a titration procedure was developed in which, after the emf for the original solution had been measured, water was added to the measuring vessel from a calibrated burette directly; the solution was shaken and left to stand for 20 min, after which the emf for this new concentration was measured. In this way it was possible to perform measurements

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at extremely small intervals of concentration. The accuracy of the concentrations was $\pm 0.05\%$. The values obtained with the two methods were in good agreement.

The E° of the electrode system was determined by measurement in sodium formate solutions. The total E° for the system (including the emf of the reference electrode) was obtained by inserting the mean ion activity of sodium formate in the following expression:

$$E = E^\circ + 0.0582 \log a_{\text{NaFo}} \quad (1)$$

Robinson's values for the mean ionic activity coefficients for sodium formate were used² and it was assumed that the sodium ion activity of the formate solutions could be calculated from them. Measurements were carried out at the three formate concentrations, 0.3, 1.0, and 1.6 m. All three gave the same value of E° , to an accuracy of 0.5 mV. As the reproducibility of the electrode is about 0.5 mV it is evident that the diffusion potentials with formate solutions in the measuring vessel are negligibly small. E° was checked with formate solutions before and after the measurements in caprylate solutions; the variation in E° was 0.5–0.8 mV, with no systematic trend; this implies that the value of E° for the sodium ion glass electrode was not affected significantly by the caprylate. A mean value of E° for the electrode system obtained by measurements in formate solutions before and after the measurement in caprylate solution was therefore used as the E° of the caprylate solution. That value of E° varied from one measuring series to another, because the E° -value of the glass electrode was not constant for a longer time, but had usually values between 420 and 430 mV.

From the emf values measured the sodium ion activity of the caprylate solutions was obtained in accordance with the expression:

$$E = E^\circ + 0.0582 \log a_{\text{Na}^+} \quad (2)$$

By combining the measurements obtained as above with those obtained by the system in which a second silver/silver chloride electrode was dipped in the actual experimental solution and small known amounts of sodium chloride were added, it was found that the diffusion potential for the original electrode combination was negligibly small, even when the cell contained micellar caprylate solutions.

The course of the reasoning was as follows: If there is a noticeable diffusion potential at the bridge/caprylate solution interface, this ought to be altered by a change of the chloride ion content of the solution because the mobility of the chloride ions probably is greater than that of the caprylate micelles. If one at constant sodium concentration adds chloride ions to the solution, that effect must be seen as different changes of the emf when the chloride ion content is measured by a silver/silver chloride electrode in the solution and a) the sodium glass electrode in the solution or b) the outer silver/silver chloride electrode is used as a reference electrode. In the case a) we have a cell without, and in the case b) a cell with transference. The emf-changes of these two cells showed no differences which were greater than the experimental uncertainty of the sodium glass electrode.

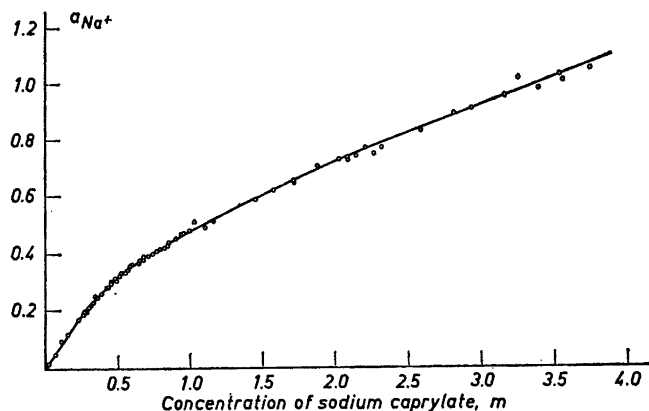


Fig. 1.

A method was developed for calculating the sodium ion activity of the solution from the emf measurements for the glass electrode and the silver/silver chloride electrode in the measuring cell. This gave the same result as the direct measurements.

Table 1. Activity of sodium ions in sodium caprylate solutions at 20°C.

NaC_8 m	a_{Na^+}	NaC_8 m	a_{Na^+}	NaC_8 m	a_{Na^+}
0.0202	0.0188	0.5173	0.328	1.5720	0.622
0.0606	0.0462	0.5477	0.334	1.7130	0.654
0.1005	0.0940	0.5680	0.340	1.7139	0.647
0.1485	0.116	0.5737	0.356	1.879	0.706
0.2181	0.171	0.5978	0.360	2.029	0.731
0.2534	0.182	0.6407	0.366	2.087	0.738
0.2694	0.197	0.6478	0.375	2.088	0.728
0.2754	0.196	0.6723	0.389	2.142	0.743
0.2986	0.210	0.6784	0.389	2.207	0.772
0.3089	0.213	0.7088	0.390	2.315	0.774
0.3230	0.223	0.7370	0.399	2.593	0.836
0.3279	0.226	0.7695	0.408	2.847	0.894
0.3296	0.226	0.7891	0.414	2.947	0.912
0.3384	0.247	0.8162	0.423	3.166	0.955
0.3540	0.240	0.8414	0.426	3.267	1.014
0.3741	0.258	0.8491	0.438	3.395	0.978
0.3840	0.259	0.8925	0.451	3.547	1.021
0.4183	0.279	0.8969	0.443	3.573	1.010
0.4203	0.279	0.9401	0.468	3.729	1.046
0.4446	0.298	0.9650	0.471		
0.4485	0.292	0.9923	0.483		
0.4743	0.311	1.095	0.489		
0.4807	0.303	1.160	0.511		
0.5080	0.321	1.453	0.589		

The purity of the initial material, the preparation of the sodium caprylate and the preparation of the experimental solutions were the same as has been described earlier.³ The sodium content of the sodium caprylate was always controlled.

RESULTS

Sodium caprylate preparations with different amounts of sodium gave slightly different values for the sodium ion activity. The observed variations were, however, never greater than $\pm 0.01-0.02$. The tables contain only the results for preparations whose sodium content was closest to the theoretical value. The dependence of the sodium ion activity on concentration is illustrated in Fig. 1; the curve rises linearly below the c.m.c, but in this region of concentration the increase slows down; the activity continues to rise, however, even above the c.m.c., and up to 1.0–1.1 m the curve is nearly linear after which there is a steady slight decrease in the slope. In the 3.5 m caprylate solution the sodium ion activity reaches about 1.0.

The measurements were performed in 1962–63 at the Institute of Physical Chemistry, Åbo Akademi, Åbo, Finland.

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