DETERMINATION OF THE COMPOSITION OF THE COMPLEX OF ZINC IN ZINCATE SOLUTIONS OF KOH

B. N. Kabanov, T. I. Popova,
A. I. Oshe, and Ya. Ya. Kulyavik

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There are diverse opinions concerning the participation of water in the anodic dissolution of zinc in alkali, which can be written in general as:

$$Zn + 4OH^- + xH_2O = [Zn(OH)_4xH_2O]^{2-} + 2e^- \qquad (1)$$

According to [1], water is the reaction product and x = —2, while according to [2] water is the reagent and three to four molecules of it are contained in the complex. It should be kept in mind that the composition of the complex may depend on the concentration of alkali. In [1, 2] the measurements were conducted in solutions of KOH no higher than 7 M. A determination of the composition of the complex in concentrated solutions (up to 14 M), chiefly a determination of the coefficient x, was the purpose of the present investigation.

We determined the equilibrium potential of zinc in solutions of KOH with various concentrations (3.8, 7.6, 9.3, and 13.8 M) with a constant low concentration of zincate (0.004 M). The low zincate concentration was selected considering the fact that it did not significantly influence the activity of the solution, which was determined in our experiments chiefly by the alkali concentration. Moreover, a low zincate concentration made it possible to neglect the diffusion potential arising between the investigated solution and the solution in the reference electrode. The reference electrode was a Hg/HgO electrode, containing alkali of the same concentration as the working solution but containing no zincate. The potential was measured with a cathodic voltmeter with an imput resistance of 10^{11} Ω. The experiments were conducted in a hermetically sealed glass cell in an atmosphere of argon (with O_2 content ≤ 0.003%), additionally purified by passing over heated activated copper. The cell and reference electrode were thermostatically controlled; the experiments were conducted at 25± 0.1°C. The cell had a special adaptation permitting additional purification of the electrode in an atmosphere of argon without its removal from the cell. The volume of the working solution in the cell was equal to 200 cm^3 (Fig. 1).

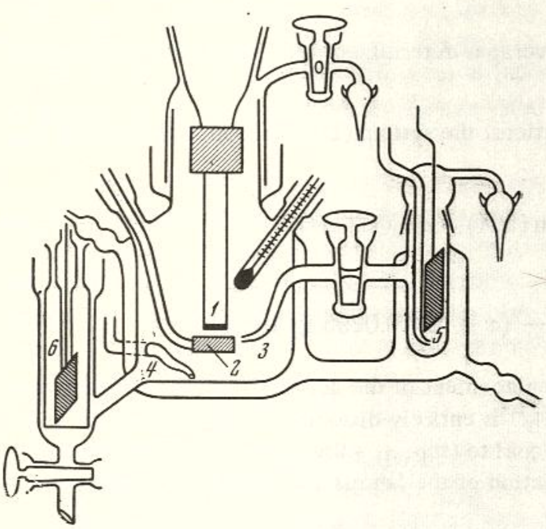

Fig. 1. Construction of the cell: 1) disc electrode; 2) polishing disc; 3) Luggin capillary; 4) outlet of argon; 5) reference electrode; 6) auxiliary electrode.

The reagents used in the work, KOH and ZnO, were very pure grade, while the other reagents were cp grade. The solutions were prepared in double-distilled water. The zincate solutions were prepared by dissolving a weighed sample of zinc oxide in a solution of alkali of the set concentration. The zincate concentration in solution was monitored polarographically (in 1 N solutions of KOH). The concentration of free and total alkali was determined by titration with a 1 N solution of H_2SO_4, with phenolphthalein and methyl orange. The specific gravity of the alkaline solutions was determined by precise weighing of a calcined glass weight (with lead inside) in the solution and without it.

The investigated electrode was a wire or disc of brand TsO zinc, pressed into a Teflon holder. The working surface of the electrode was 0.25 cm^2. Before the experiment the electrode was cleaned with fine moist glass powder and was subjected to cathodic reduction at a potential of —1.4 V for 20 min in a solution of pure alkali. The measurements of potential in each solution were conducted with time up to

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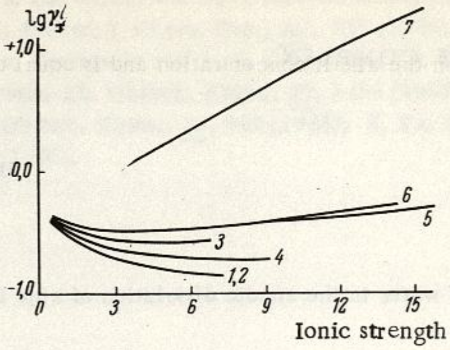

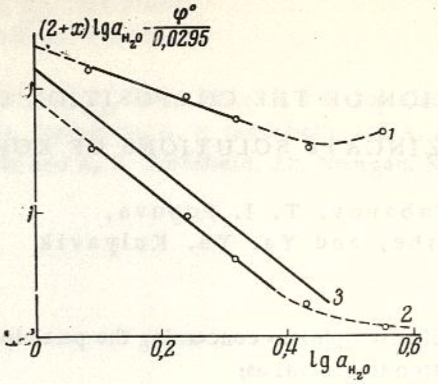

Fig. 2

Fig. 3

Fig. 2. Dependence of the quantity γ_{salt} on the ionic strength of various solutions: 1) $NaSO_4$; 2) K_2SO_4; 3) Li_2SO_4; 4) K_2CrO_4; 5) $Ca(NO_3)_2$; 6) K_2CO_3; 7) KOH.

Fig. 3. Graphical determination of the coefficient n. Curve 1 was calculated on the assumption that $\gamma_{K_2Z} = \gamma_{K_2CO_3}$, curve 2 on the assumption that $\gamma_{K_2Z} = \gamma_{OH^-}$. The following are plotted along the Y axis from the bottom up: 42.5, 43.5, 44.5.

TABLE 1. Results of Calculations According to Eq. (4)

	m_{KOH}, mole/kg	m_{ZnO}, mole/kg	$I = m_{KOH} + 3m_{ZnO}$	φ_{meas} in relative o.r.e. in the same solution	$\lg\gamma_{KOH}$ for a given I	$\lg\gamma_{K_2Z}$		$(2+x)\lg a_{H_2O}-\frac{\varphi^0}{0,0295}$	
						I	II	I	II
1	3,80	0,042	3,92	—1,354	0,12	0,12	—0,48	44,6	44,0
2	7,60	0,044	7,73	—1,372	0,54	0,54	—0,44	44,4	43,5
3	9,30	0,038	9,41	—1,376	0,75	0,75	—0,39	44,2	43,1
4	13,80	0,044	13,93	—1,394	1,25	1,25	—0,26	44,0	42,6

the establishment of a stable (within 0.05 mV/min) value. The averages determined from five to six experiments were taken for the calculations.

In order to introduce the average activities into the calculations, the system (1) is conveniently related to a hydrogen electrode in the same solution:

$$Zn + 2KOH + (x+2)H_2O = K_2Zn(OH)_4\cdot xH_2O + H_2\cdot \tag{2}$$

Its equilibrium potential at atmospheric pressure is equal to:

$$\varphi = \varphi^0 + 0.0295\lg a_{K_2Z} - 0.059\lg a_{KOH} - (x+2)\cdot 0.0295\lg a_{H_2O}, \tag{3}$$

where the subscript K_2Z pertains to the zincate complex. After replacement of the activities in (3) by molarities and activity coefficients, considering that the salt $K_2Zn(OH)_4\cdot xH_2O$ is entirely dissociated into the ions K^+ and $Zn(OH)_4\cdot xH_2O^{2-}$, i.e., the concentration of the first of them is equal to $(m_{KOH} + 2m_{ZnO})$, while that of the second is m_{ZnO} (m_{KOH} is the molarity of free alkali), and after isolation of the factors containing the activity of water and the standard potential, we obtain:

$$-\frac{\varphi\ \text{meas}}{0,0295} + \lg\gamma_{K_2Z} - 2\lg\gamma_{KOH} + \frac{1}{3}\lg m_{ZnO} - \lg m_{KOH}$$

$$-\frac{1}{3}\lg(m_{KOH}+2m_{ZnO}) = (x+2)\lg a_{H_2O} - \frac{\varphi^0}{0.0295}. \tag{4}$$

In (4), m_{ZnO} and m_{KOH} are set experimentally; φ_{meas} is measured experimentally; $\log \gamma_{KOH}$ and $\log a_{H_2O}$ for solutions of a given ionic strength can be determined from the experimental data for pure KOH, obtained in the work of Akerlof and Bender [3]. The main difficulty lies in finding $\log \gamma_{K_2Z}$. In the work of Dirkse [2] it was assumed that the activity coefficient of zincate does not depend on the alkali concentration and is equal to one. This assumption seems insufficiently correct, since in the region of alkali concentrations used by the authors the ionic strength is extremely high and approximately an order of magnitude greater than the ionic strength of the hypothetical 0.05 m solution of zincate without alkali. However, as is well known, the influence of the ionic strength of the surrounding electrolyte upon the activity coefficient of ions present in low concentrations cannot be neglected [4].

In view of the absence of a complete theory of concentrated mixed solutions of electrolytes, the activity coefficient of zincate ions in concentrated alkali cannot be calculated exactly. To estimate this quantity, we used two possible assumptions in our calculations. In one calculation (I) it was assumed that the activity coefficient of zincate is equal to the activity coefficient of alkali. In the other calculation (II) it was assumed that the activity coefficient of zincate is determined only by the ionic strength of the solution, or, which is close to this, it is equal to the activity coefficient of a typical mono-di-charged salt at an ionic strength equal to the ionic strength of the alkali. According to the literature data, the activity coefficients of various mono-di-charged salts (K_2SO_4, K_2CrO_4, K_2CO_3, Li_2SO_4, etc.) in the region of ionic strengths from 1 to 12 do not differ too greatly from one another and depend weakly on the ionic strength of the solution (Fig. 2). In this case we assumed the activity coefficient of zincate to be equal to the activity coefficient of K_2CO_3 for solutions with ionic strength up to 12.

Table 1 presents the experimentally determined equilibrium potentials of system (2) for various KOH concentrations at a zincate concentration of 0.04 m and the values of $(x + 2) \log a_{H_2O} - \dfrac{\varphi^0}{0.0295}$ calculated according to Eq. (4) for the above-mentioned two (I and II) assumptions on the value of the activity coefficient of zincate in these solutions. In Fig. 3 the value of $(x + 2) \log a_{H_2O} - \varphi^0/0.0295$ obtained in Table 1 is plotted against the values of $\log a_{H_2O}$, calculated according to the data of [3] for solutions of KOH with ionic strength J equal to the ionic strength of our solutions. From the figure it is evident that the experimental points, within the limits of accuracy of the experiments, in both cases lie satisfactorily on a straight line, with the exception of the points obtained for a 13.8 m solution, deviating from a linear dependence. This indicates that the composition of the complex is unchanged within a broad range of alkali concentrations. The deviation of the last point may be due to a decrease in the amount of water in the complex of the zincate ion in concentrated alkali solutions. From the slope of the straight lines in Fig. 3 we find x. In the calculation I, when it was assumed that at the same ionic strength $\log \gamma_{K_2Z} = \log \gamma_{KOH}$, x proves equal to zero, i.e., water does not participate in the formation of the complex. In calculation II, when we assumed $\log \gamma_{K_2Z} = \log \gamma_{K_2CO_3}$, we obtain $x = 2$. Extrapolating the straight lines to intersection with the Y axis, we find $\varphi^0/0.0295$, from which we shall calculate the value of the standard potential of system (2). We obtain $\varphi_0 = -1.219$ V for the first calculation and -1.207 V for the second (the second is closer to the literature data).

In [5], where the kinetics of the anodic dissolution of zinc in concentrated alkali was investigated with the aid of the method of the rotating disc electrode, it was concluded that in the anodic dissolution of zinc according to Eq. (I), two molecules of water participate as a reagent. In addition, comparison with other known crystal hydates of zinc salts, for example, with a number of zinc sulfates, also supports a complex containing two other molecules. On the basis of all these considerations, we arrived at the conclusion that a composition of the zinc complex with two molecules of water is more probable.

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