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CHANGE IN THE DROP OF POTENTIAL AT THE AIR/SOLUTION INTERFACE AS RELATED TO THE AGE OF THE LATTER

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A paper by Klein and Lange (¹) recently published deals with the time variation of the potential drop at the interface air/solution. According to the experimental data of the authors referred to, the drop of potential in the case of salt-solutions of medium and high concentrations varies with time from negative values to positive ones. In the case of a 5.46 N KBr-solution the drop of potential changes by over 300 millivolts in 100 min. Klein and Lange believe themselves to have discovered an effect of interface «maturing» due to a slow reorientation of water molecules or to some superficial process of crystallization. That the drop of potential at an air/solution interface varies with time has already been reported in literature, as for instance, in a paper by A. Frumkin (²), where it is pointed out, however, that a gradual contamination of the surface in question with surface-active materials from the surrounding air must be regarded as the principal cause of this change.

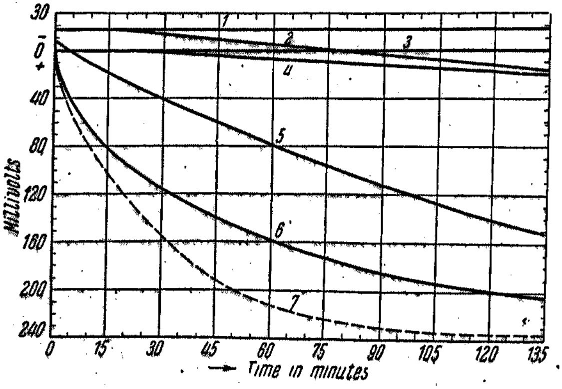
From studying the capacity of the electric double layer at the solution/metal interface, M. Proskurnin and A. Frumkin (³) arrived at a conclusion that traces of surface-active materials present in salts might be the principal source of contamination of the interface in the case of inorganic salt-solutions. These materials could be eliminated by a preliminary calcining of the salt. Adam ⁴) likewise pays attention to this circumstance. Therefore apart from protection of the interface under investigation from air contaminations due care should be taken to prepare solutions free from any surface-active materials in order to obtain proper results from measuring the drops of potential at the air/solution interface. The importance of this circumstance received added evidence from our own studies (⁵) of the mechanical and electrical properties of monomolecular layers on the surface of concentrated salt-solutions.

The present investigation suggested by A. Frumkin had for object definitely to establish the causes of the phenomenon observed by Klein and Lange; measurements of the drop of potential at the air/solution interface have been effected by the method of Guyot-Frumkin.

Schering's KBr was taken for the experiments. Three portions of 2 N KBr solution were prepared: one was obtained directly from commercial (uncalcined) salt and the other two from a heated salt; the latter two solutions were filtered through a glass filter. The salt was calcined till fusion in a platinum crucible. The water used for preparation of the first and second solutions was twice distilled, the middle fraction only being collected during the second distillation. Water distilled with potassium permanganate was used for preparation of the third solution.

While checking constancy of the potential drop at the surface of the disc covered with polonium, use was always made of a freshly renewed surface of a 0.01 *N* KCl solution prepared from a calcined salt.

The experiment was run simultaneously with the first and second KBr solutions. The initial values of the potential drop for the first and second solutions were checked by renewing their surfaces repeatedly. Then the surfaces of both solutions were allowed to rest for 135 min. During this interval drops of potential at the surface of both solutions were measured (at first every 1—2 min. and afterwards every 10—15 min.). Throughout the experiment the surfaces of both solutions were not altogether inaccessible to the laboratory air in so far as the Faraday cage which protected the apparatus was not hermetically closed. Mean values from several series of measurements are given in Fig. 1 in the form of curves where curve *6* and *2* show the change of the drop of potential at the interface between air and solutions prepared from uncalcined or calcined salt respectively.*



The drop of potential at the interface between the air and a solution prepared from calcined salt dissolved in water distilled with potassium permanganate was investigated in an analogous manner. These experiments were performed in such a way either to protect the surface of the solutions from the air dust as far as possible or, as it was the case in the preceding experiment, to leave it open to some extent to the action of dust.

Mean values of the drop of potential obtained in the latter case, fit in with the data obtained in the previous experiment and may therefore be represented graphically by curve *2* in Fig. 1. However, when the surface of the solution under investigation was carefully protected from dust, there was no change whatever in the drop of potential at the air/solution interface; the results of these measurements are represented by curve *1* in Fig. 1. To ascertain whether the drop of potential is liable to change under these conditions if they are upheld for a much longer time, we have carried out two experiments observing the behaviour of the surface during 4 hours in both cases; the drop of potential, however, remained constant and coincided within 0.3 millivolts with the value obtained with the same solution in a few seconds after the renewal of the surface. The straight line *3* and curve *4* in Fig. 1 represent the results of measurements at the air/0.01*N* KCl solution interface

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* The zero point on the ordinate axis in Fig. 1 is the value of the drop of potentia at the interface air/0.01 *N* KCl solution when the surface of the latter is freshly renewed

in the cases of protected and unprotected surface, respectively, Curve *5* in Fig. 1 was obtained with a KBr solution prepared from uncalcined salt, after 30 hours from the first experiment with the same solution (curve *6*) have passed. A somewhat higher course of curve *5* is accounted for by the fact that the experiment was brought about with a less contaminated solution, part of the surface-active materials being adsorbed at the surface of the solution. The latter was contained in a separate reservoir and the construction of the apparatus did not allow the surface-active materials adsorbed at the surface to get into the vessel, where the surface of the solution investigated was obtained. The dotted curve *7* represents the data of Klein and Lange (^{1}) which they obtained in studying a 1.93 *N* KBr solution.

Conclusions

From the data obtained in studying the time variation of the potential drop at an air/solution interface, we arrive at the following conclusion: if the conditions of the experiment prevent an accumulation of surface-active materials at the surface of the solution, there is no change in the drop of potential during comparatively large intervals of time (lines *1* and *3* in Fig. 1). If not, the drop of potential changes to more positive values owing to a gradual accumulation of surface-active materials at the surface; these contaminations penetrate to the surface mainly from the solution and partly as a result of dust settling from the air which is in contact with the surface under investigation. The influence of both factors in the course of 135 min. effected, in our case, a change of 210 millivolts in the drop of potential of a 2 *N* KBr solution (curve *6*). The influence of the second factor alone changed the drop of potential by 35 millivolts (curve *2*) only. In the case of a 0.01 *N* KCl solution this change amounted to 20 millivolts (curve *4*). A smaller value of the change in the drop of potential for a 0.01 *N* KCl solution compared with a 2 *N* KBr solution is in agreement with our results of the studies of properties of monolayers on the salt-solutions, according to which the presence of KBr in the solution facilitates the spreading of monolayers over the surface. The surface-active contaminations which affect the drop of potential get into the solution with the dissolved salt and can be eliminated by a preliminary calcining of the latter. The degree of purification of distilled water had in our case no influence upon the change in the drop of potential.

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