

Short communication

TEMPERATURE DEPENDENCE OF THE POTENTIAL OF ZERO CHARGE AT THE MERCURY/POTASSIUM IODIDE AQUEOUS SOLUTION INTERFACE

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Most published works aim mostly at the determination of the effect of electrolyte concentration on the potential of zero charge, E_z , while little information is presently available concerning its temperature dependence. Anderson and Parsons [1] performed electrocapillary surface measurements of the KI aqueous solutions at 5, 25 and 45°C. Similar studies have been carried out with sulphonate anions by Parry and Parsons [2]. Grahame [3] measured the thermal coefficients of E_z in NaF solutions in the 0–85°C temperature range by the capacity method. Randles and Whiteley [4] made similar measurements with 0.1 M solutions of KCl, NaOH and K_2SO_4 in the 15–35°C range. Hills and Payne [5] have also analyzed the temperature and pressure effect on double-layer parameters for 0.1 M aqueous solutions of $NaNO_3$, NaF, Na_2SO_4 and NaCl at 20°C and 30°C. Minc and Jastrzebska [6] measured the minimum capacity in dilute concentrations of KBr, KCl and KF aqueous solutions. All these measurements, except Grahame's, were carried out keeping both the reference and tested solution at the same temperature. Paik et al. [7] have also studied the temperature effect on 0.1 M and 1 M aqueous solutions of KI, KCl, KBr and NaF, keeping the reference electrode at 25°C. These authors found that E_z increases negatively in the order: $F^- < Cl^- < Br^- < I^-$ for 0.1 M solutions in accordance with the increasing adsorbability of the anions. However, for 1 M solutions, they found that this trend is reversed for Br^- and I^- ions [7]. In the course of a thorough study of the temperature behaviour of I^- ion adsorption on mercury [8], the temperature coefficient of E_z was measured covering a wide range of electrolyte concentrations and, in this case, results were at variance with those of ref. 7.

The streaming mercury electrode technique described by Grahame [3] was used to measure the potential of zero charge (pzc). The solutions were made up in alkaline permanganate bidistilled water from Baker Reagent salts and were deaerated by bubbling nitrogen in the cell before each run. Experimental details have been reported elsewhere [8]. In order to check the experimental behaviour of the system, a 0.1 M solution of KCl was measured at 25°C, and a discrepancy of only ± 0.001 V with Grahame's results was found [3].

TABLE 1

Potential of zero charge at 25°C

Concentration/ <i>M</i>	$-E_z/V^a$	$-E_z/V^b$
0.010	0.612	0.615 ± 0.002
0.025	0.638	0.638 ± 0.002
0.050	0.664	0.663 ± 0.002
0.100	0.687	0.688 ± 0.001
0.200	0.715	0.716 ± 0.002
0.500	0.740	0.742 ± 0.001

^a Back-integration method.^b Streaming mercury electrode method.

The emf of the isothermal cell:



was measured for six concentrations in the 0.005–0.75 *M* range and three temperatures (5°C, 25°C, 45°C). A smoothed E_z vs. $\ln a$ curve was drawn through known values at each temperature and E_z values were read off for intermediate concentrations. The pzc was also determined by the back-integration method from capacity curves [8] using -1.500 V (vs. SCE) as the starting point. These values are compared with the experimental E_z values in Table 1, being in good agreement. The E_z values obtained by back integration for 12 concentrations in the above-mentioned range at three temperature are given in Table 2. Using these values, linearly dependent E_z vs. T plots are obtained. For suitable comparison with published data, the E_z value was referred to a reference electrode kept at 25°C. Neglecting the effect due to the thermal gradient in solution, the difference between E_z , referred to an electrode kept at the same temperature T as the tested solution and E_z^0 referred to an electrode kept

TABLE 2

Potential of zero charge at different temperatures

Concentration/ <i>M</i>	$-E_z(5^\circ\text{C})/V$	$-E_z(25^\circ\text{C})/V$	$-E_z(45^\circ\text{C})/V$
0.005	0.591	0.580	0.577
0.010	0.626	0.612	0.593
0.015	0.633	0.620	0.607
0.025	0.645	0.638	0.620
0.035	0.665	0.650	0.632
0.050	0.673	0.663	0.643
0.075	0.691	0.678	0.658
0.100	0.700	0.689	0.675
0.200	0.737	0.716	0.687
0.350	0.750	0.730	0.709
0.500	0.762	0.742	0.722
0.750	0.780	0.756	0.733

TABLE 3

Thermal coefficient of the pzc at 25°C

Concentration/ <i>M</i>	(dE_z^0/dT)/mV deg ⁻¹
0.750	1.040
0.500	0.835
0.350	0.835
0.200	0.885
0.100	0.785
0.075	0.735
0.050	0.635
0.035	0.585
0.025	0.521
0.015	0.485
0.010	0.535
0.005	0.485

at 25°C, is simply due to the entropy change at the reference electrode. Hence, the change of E_z^0 with temperature T has been evaluated from:

$$dE_z^0/dT = dE_z/dT + dE_{ref}/dT \quad (1)$$

the thermal coefficient of the reference electrode dE_{ref}/dT being equal to the entropy variation accompanying the electrode reaction ($\Delta S/F$). The thermal coefficient of the saturated calomel electrode (0.165 mV deg⁻¹) was obtained from deBethune's tables [9]. In Table 3 temperature coefficients of the E_z^0 are shown for different concentrations at 25°C. It is clear that dE_z^0/dT increases with concentration for all the solutions tested. These results when compared with results for other salts [3,5] show that the temperature coefficient of the pzc increases with adsorbability at any concentration. On the other hand, Paik et al. [7] had found that the halide anion adsorbability trend appears not to be valid, as can be seen by comparing their dE_z^0/dT data for some 1 *M* potassium halide aqueous solutions. They found that the value for potassium iodide is smaller than that of potassium bromide and attempted an explanation of that trend in terms of thermal deorientation of dipoles. The values of dE_z^0/dT given in Table 3 as well as the value extrapolated to 1 *M* potassium iodide when compared to results of other authors [3-5] are in agreement with the adsorbability trend $F^- < Cl^- < Br^- < I^-$. Therefore, it appears that the temperature coefficient of E_z^0 follows the well-known adsorbability trend of anions in the whole concentration range.

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