POTENTIAL OF ZERO CHARGE ON STREAMING MERCURY ELECTRODE AND INDIVIDUAL ACTIVITY COEFFICIENTS OF IONS

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Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

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A method of measurement of the potential of zero charge on a streaming mercury electrode was elaborated involving correction for the faradaic current. The measurements were performed at various concentrations of potassium chloride and fluoride against S.C.E. Based on potential measurements of the cell Ag | AgCl, KCl(c_1) || sat. KCl, Hg_2Cl_2 | Hg, the potential of zero charge for an infinitely diluted aqueous solution referred to S.H.E. was determined as $-0{\cdot}1901 \pm 0{\cdot}0002$ V. From these measurements, the individual activity coefficients of the Cl^- ion were calculated.

The questions about values of electrode potentials, individual activity coefficients of ions and the "medium effect" constitute an unsolved problem in theoretical electrochemistry, which becomes again important in connection with the development of electrochemistry of nonaqueous solvents. One of the possible ways to solve this problem is the use of an electrode with zero charge, the potential of which is independent of the concentration of nonadsorbable electrolyte. Therefore, it can be used as reference in measurement of electrode potentials eliminating the necessity of estimating the liquid junction potential between solutions of different concentrations from the approximate Henderson equation.This, however, assumes the existence of a nonadsorptive electrolyte, at least one ion of which can depolarize a reversible and well reproducible electrode. Since such electrolyte fulfilling the condition of good reproducibility is not known as yet, we must use two electrolytes such as nonadsorptive KF and adsorptive KCl in the same solvent, the latter giving well reproducible potentials with a silver chloride electrode. The use of the Henderson equation is then limited to the estimation of small differences between the liquid junction potentials for the KCl(c_1) || sat. KCl and KF(c_2) || sat. KCl junctions (for $c_1 = c_2$).

To determine correctly the potential of zero charge, we made use of certain phenomena characteristic for the streaming mercury electrode; these were on the basis of the observations of Heyrovský and coworkers[1] studied by Valenta[2]. The charging current on the mentioned electrode drops to zero under certain conditions in a certain potential range making it possible to measure exactly the faradaic current and eventually, in contrast to other similar methods[3-6], to introduce a correction for nonideal polarizability of the electrode.

EXPERIMENTAL

In a series of measurements of the charging current on a streaming mercury electrode the base electrolyte was $5 . 10^{-4}$ – 0·1M-KCl. The salt (Lachema, Brno) was of analytical grade, triply recrystallized from redistilled water and heated for several hours at 180°C. In another series of measurements the base electrolyte was 0·001–0·1M-KF of analytical grade (Merck, Darmstadt), prepared analogously. The solution was closely before measurement purified by active carbon (3–5 mg per 10 ml) which had been washed many times with hot redistilled water and dried. After 10 min the suspension was centrifuged. The solution was deaerated by bubbling nitrogen (for up to 1 hour) purified by means of a copper catalyst and washed with water. Mercury was of analytical grade and was doubly distilled.

In recording polarographic curves the electrolytic cell shown in Fig. 1 was used. In space 1 streaming mercury electrode 2 was placed the outlet orifice of which was under the solution level. The level height in the cell was controlled by mercury reservoir 3. Nitrogen was led through inlet 4 and outlet 5 connected to a water siphon. Stopcock 6 served both for outlet of solution from space 1 and to produce a sharp and reproducible interface between the measured solution and the electrolyte of saturated calomel electrode 7. Platinum contact 8 was free from contamination with electrolyte owing to favourable design. Reference electrodes 7 were two of the same type and were joined with the cell by an Y tube located at 9; both were provided with electrolyte reservoir 10. The cell shown in Fig. 1 was used also in potentiometric measurements, the streaming electrode being replaced by several silver chloride electrodes.

Of several types of *streaming mercury electrodes*, the electrode according to Zikmund[7] was chosep (2, Fig. 1) after preliminary tests. It was made from a glass tube drawn out to a thin capillary. The inner diameter of its orifice was 0·14 mm, outer 0·35 mm, rate of flow of mercury 170 mg/s at a height of mercury column 175 cm. The mercury streamed out at an angle of about 60° with respect to the solution level and disintegrated on the wall of the cell. The electrolyte level was initially kept about 1 mm above the capillary orifice, and gradually elevated in further measurements until the whole stream of mercury was submerged. With the given capillary and height of mercury column, the length of the continuous stream of mercury was about 5 mm at the potential of zero charge.

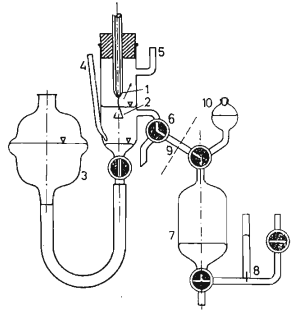

FIG. 1

Measuring Cell with Streaming and Calomel Electrodes

1 Space for measured solution; 2 streaming electrode; 3 mercury reservoir to control the level height; 4 nitrogen inlet; 5 nitrogen outlet; 6 stopcock to produce liquid junction; 7 reference electrode (S.C.E.); 8 electric contact; 9 location of Y tube; 10 reservoir of saturated KCl.

The reference electrode used in measurement of *i–E* curves was saturated calomel electrode with excess KCl crystals. Analytical grade calomel was ground with mercury, saturated KCl and excess KCl crystals. The electrolyte was in equilibrium with air. The electrodes thus prepared reached their equilibrium potential after 48 hours and differed among themselves by not more than 20 µV provided that their temperature was constant after their preparation.

Silver chloride electrodes were prepared by electrolytic silver coating of a platinum wire sealed in glass; a silver chloride layer was formed by electrolysis in 0·1M-KCl. Their potentials after 24 hours did not differ by more than 70 µV (largest difference in 0·001M-KCl).

Polarization curves were recorded with an LP-60 type polarograph and EZ-2 type pen recorder without damping (Laboratorní přístroje, Prague). Potentials were measured with a compensation voltmeter ("Cambridge portable potentiometer"), the EZ-2 pen recorder serving as a null indicator (sensitivity 1 . 10^{-10} A per scale division). Thus it was possible to measure voltage with a sensitivity of 10 µV. All measurements were made in a room thermostated at 25 ± 0·2°C.

RESULTS

In Fig. 2 are shown typical *i–E* curves in 0·1M-KF, the height of electrolyte level above the capillary orifice increasing from curve *1* (about 1 mm) to *4* (the whole mercury stream under electrolyte). Curves *1*–*3* show at potentials more positive than the electrocapillary zero a discontinuous drop of charging current or its discontinuous changes (curves *2* and *3*) ending by a decrease to zero. At negative potentials the charging current changes from zero to higher values, rises discontinuously and then monotonously. Whereas the potentials of the discontinuities are irreproducible (*cf.* curve *3* with several discontinuities), the potential range of zero current is well reproducible. At higher charging current, either positive or negative, the stream of mercury is

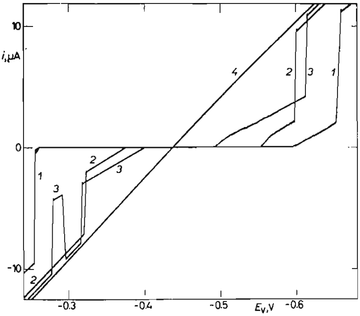

FIG. 2

Dependence of Charging Current of Streaming Electrode on Polarization

Curves *1*–*4* with increasing length of the mercury stream in 0·1M-KF.

wetted by the solution, whereas at low or zero current the stream of mercury emerges dry (*cf.*[1,2]). The potential region of zero current becomes definitely narrower with increasing length of the submerged mercury stream; it is equal to zero with curve *4* (Fig. 2), where the charging current changes monotonously and the curve intersects the potential axis in a single point. This point denotes obviously the potential of zero charge, the faradaic current and hence the correction for nonideal polarization being entirely negligible.

In Fig. 3 are shown polarization curves for various lengths of the submerged mercury stream in the potential range from −0·4 to −0·475 V (S.C.E.) in 0·005M-KF. Again the potential range of zero charging current diminishes with increasing length of the mercury stream. With more diluted solutions, the faradaic current ceases to be negligible. Curve *4* intersects the horizontal portion of curve *3* at a potential differing from the potential of zero charge only by ohmic polarization, which was calculated from the corresponding current and resistance. The latter was determined from the shift of the potential of the intersection caused by an intentional increase of the faradaic current of oxygen reduction. The correction for ohmic polarization reached a value of 10 mV in most diluted solutions. Taking into account the mentioned corrections, we obtained values of potential E_1 of an ideally polarizable mercury electrode with zero charge, referred to S.C.E. (including the liquid junction potential). Analogous measurements were made with $5 . 10^{-4}$–0·1M-KCl solutions. The form of the polarographic curves was analogous to those in fluoride solutions of the same concentrations.

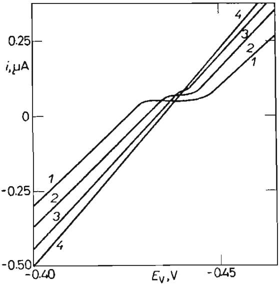

FIG. 3

Polarization Curves Close to Zero Charge Potential

Curves *1*–*4* with increasing length of the mercury stream in $5 . 10^{-3}$M-KF.

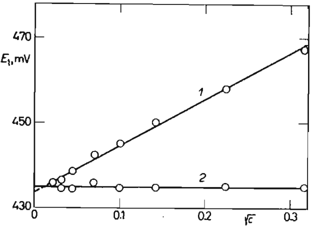

FIG. 4

Dependence of Zero Charge Potential of Streaming Electrode on Square Root of Electrolyte Concentration

1 KCl; *2* KF; against S.C.E.

The E_1 values for chloride (E_1^{KCl}) and fluoride (E_1^{KF}) solutions were plotted as function of the square root of concentration (Fig. 4). The points lie on a straight line intersecting in a point on the potential axis with a deviation of about 1 mV. Whereas the E_1 value decreases linearly in chloride solutions (curve *1*), it is practically independent of the concentration of fluoride.

Further, we measured the electromotive force E_2 of the cell Ag | AgCl, KCl(c_1) || || sat. KCl, Hg_2Cl_2 | Hg, where $c_1 = 0{\cdot}001 - 0{\cdot}5$ mol/l. The probable error in measuring the value of E_2 was $\pm 0{\cdot}05$ mV, whereas with E_1 it was $\pm 0{\cdot}5$ mV. To diminish the error in E_1, we proceed as follows: The weighed arithmetic mean of the E_1 values for different concentrations of KF is $\bar{E}_1 = -434{\cdot}9 \pm 0{\cdot}2$ mV. This value includes the mean value of diffusion potentials of the liquid junction KF(c_2) || sat. KCl. According to the Henderson equation, the diffusion potential is directly proportional to $\log c_2$, hence the mean diffusion potential included in the value of $\bar{E}_1$ corresponds to the arithmetic mean of $\log c_2$, *i.e.* in our case to $c_2 = 0{\cdot}01$ mol/l. Therefore we calculated from the Henderson equation the difference between the potentials of the liquid junctions 0·01M-KCl || sat. KCl and 0·01M-KF || sat. KCl. This difference, $-0{\cdot}08$ mV, was subtracted from $\bar{E}_1$ to obtain $-434{\cdot}8 \pm 0{\cdot}2$ mV which corresponds to a hypothetical cell consisting of a mercury electrode with zero charge in 0·01M-KCl and of a saturated calomel electrode, provided that the potential of mercury is not shifted by specific adsorption of anions. Analogous values for other KCl concentrations (E_1') were obtained by introducing corrections for the change of the diffusion potential with respect to that of the liquid junction 0·01M-KCl || || sat. KCl according to the Henderson equation. These corrections were in the range from 0·59 to $-1{\cdot}00$ mV for 0·001–0·5M-KCl. The E_1' values thus obtained were better comparable with E_2 as to their accuracy than E_1. To find the potential of zero charge of mercury against S.H.E, $E_{Hg}^{q=0}$, we introduce the function

$$Y = -E_1' + E_2 + (RT/F) \ln [KCl] - 2{\cdot}303(RT/F)[0{\cdot}5115[KCl]^{1/2}/(1 + 0{\cdot}5[KCl]^{1/2})] - E^0(Ag \mid AgCl) = -E_{Hg}^{q=0} - 2{\cdot}303(RT/F)\,C[KCl]\,, \qquad (1)$$

where E^0(Ag | AgCl) was set equal to[8] 0·22239 − 0·00015 = 0·2222 V (based on the molarity scale). The terms $[KCl]^{1/2}$ and C[KCl] correspond to the generalized Debye–Hückel equation with an empirical coefficient 0·5 which suits best the rectification of the extrapolation curve. The Y function was used in extrapolation to zero concentration (Fig. 5). The deviations from the straight line are largest at very low concentrations and do not exceed about 0·3 mV.

According to Eq. (*1*) the section on the vertical axis in Fig. 5 taken with opposite sign is equal to the potential of zero charge of mercury, $E_{Hg}^{q=0} = -190{\cdot}1 \pm 0{\cdot}2$ mV (S.H.E.) (based on the molarity scale). This value was used in calculating the molar individual activity coefficients of Cl^- ions from the equation

$$\ln y_{\mathrm{Cl}^-} = (F/RT)\left(E^0(\mathrm{Ag} \mid \mathrm{AgCl}) - E_{\mathrm{Hg}}^{q=0} + E_1' - E_2\right) - \ln\left[\mathrm{KCl}\right]. \qquad (2)$$

The results are shown in Table I (second column) and their graphical evaluation based on the generalized Debye–Hückel equation in Fig. 6. The largest deviation of the individual points from the straight line passing through the origin of coordinates corresponds to a relative error in y_{Cl} of about 1%.

DISCUSSION

Potentials of Zero Charge in KCl *and* KF *Solutions*

The values of the potentials of zero charge, E_1^{KCl}, were treated as shifts of the potential of zero charge due to specific adsorption of Cl^- ions, the K^+ and F^- ions being considered as nonadsorbable: $\varphi^{(m)} = E_1^{\mathrm{KCl}} - E_1^{\mathrm{KF}}$, where E_1^{KF} was set equal to its average value, 434·9 mV. The term $\log(-\varphi^{(m)}/a_{\mathrm{Cl}^-})$ was plotted as a function of $-\varphi^{(m)}$ (Fig. 7, curve *1*). This dependence should be a straight line according to the equation

$$\varphi^{(m)} = -K'(a_{\mathrm{Cl}^-}) \exp\left(K''\varphi^{(m)}\right) \qquad (3)$$

derived for the specific adsorption of anions[9]. The activity of chloride ions, a_{Cl^-}, was calculated from the activity coefficients y_{Cl^-} (Table I), K' and K'' are constants. Curves *2* and *3* in Fig. 7 show the course of deviations in the dependent variable corresponding to an error in the determination of $-\varphi^{(m)}$ of 0·5 mV or $-0·5$ mV. Except

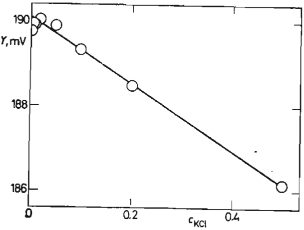

FIG. 5

Extrapolation of the Y Function to Zero Concentration of KCl

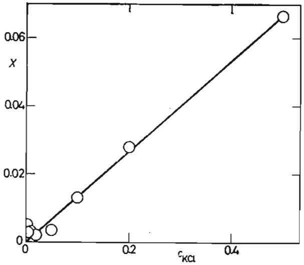

FIG. 6

Dependence of the Rectification Function $X = \log y_{\mathrm{Cl}^-} + A[\mathrm{KCl}]^{1/2}/(1 + 0{\cdot}5[\mathrm{KCl}]^{1/2})$ on Concentration of KCl

TABLE I

Ionic and Mean Activity Coefficients of Cl^- and KCl

[KCl]	y_{Cl^-}	γ_{Cl^-}	$\gamma_{\pm}^{a}$	$\Delta\gamma$, %	$\gamma_{Cl^-}^{c}$
0·5	0·630	0·624	0·654	−4·1	0·631
0·2	0·694	0·690	0·719	−4·0	0·704
0·1	0·749	0·746	0·769	−3·0	0·755
0·05	0·795	0·794	0·815	−2·6	0·786
0·02	0·860	0·860	—	—	—
0·01	0·901	0·901	0·901	0·0	—
0·005	0·929	0·929	0·927	+0·2	—
0·002	0·963	0·963	—	—	—
0·001	0·966	0·966	$0·965^{b}$	+0·1	—

[a] Harned and Owen[21]; [b] Harned[22]; [c] Komar and Musailov[12].

for the extreme right point (for 0·1M-KCl), the distance of the points from the straight line is smaller than the difference of the functions depicted by curves *2* and *3* showing good agreement between the experiments and the theoretical dependence (*3*) in the interval $5 \cdot 10^{-4} - 5 \cdot 10^{-2}$M-KCl. Since the function (*3*) is not suitable for extrapolation to zero concentration of KCl, we used to this purpose an empirical function shown in Fig. 4. The straight lines for KCl and KF intersect on the potential axis, an evidence that this method of extrapolation is justified.

The potential of zero charge in 0·1M-KCl was compared with literature data. The results of Grahame and coworkers[10] referred to 0·1N calomel electrode or to N.C.E. were recalculated against S.C.E. based on the data recommended by Ives and Janz[11] (including the liquid junction potential) to obtain −0·4697 or −0·4675 V respectively in accord with our value of −0·4675 V. Similarly, the E_1^{KF} value for 0·1M-KF recalculated from the work[10] is −0·4358 V (originally referred to N.C.E.), our value being −0·4350 V.

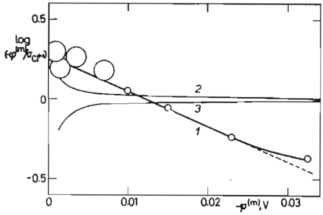

FIG. 7

Dependence of the Rectification Function $\log(-\varphi^{(m)}/a_{Cl^-})$ (Curve *1*) and its Deviation Due to Error in $-\varphi^{(m)}$ of +0·5 mV (Curve *2*) or −0·5 mV (Curve *3*) on Potential Shift $-\varphi^{(m)}$

It is seen that the agreement is good, especially when we consider the uncertainty in determining the liquid junction potentials in the case of the recommended values of potentials of calomel electrodes. The influence of the ohmic potential drop (iR) could not be determined in the cited work[10], a circumstance which does not play an important role in this comparison. According to our work the iR correction for the faradaic current is negligible in well purified solutions of 0·1M-KCl or KF but not in more diluted solutions.

Activity Coefficients of Cl^- *Ions in Aqueous Solution*

The calculated individual molar and molal activity coefficients, y_{Cl^-} and γ_{Cl^-} are compared with literature data in Table I, where the first column gives the KCl concentrations in mol/l for y_{Cl^-} and in mol/kg H_2O for γ_{Cl^-} (the numerical values being the same). In the fourth column are the mean molal activity coefficients $\gamma_\pm$ and in the fifth the differences $\Delta\gamma = \gamma_{Cl^-} - \gamma_\pm$ in %. These do not exceed the experimental errors foı $[KCl] \leqq 0{\cdot}05$M but are considerable at higher concentrations and cannot be attributed entirely to experimental errors. It is seen that the values of γ_{Cl^-} obtained by Komar and Musailov[12] (sixth column) are in a comparatively good agreement with ours. Our method enables to obtain individual activity coefficients of ions both in aque ous and nonaqueous solutions.

Potential of Zero Charge and "Medium Effect"

The quantity $E_{Hg}^{q=0}$ has the physical meaning of electromotive force of a hypothetical cell consisting of an ideally polarizable mercury electrode without charge and standard hydrogen electrode without liquid junction. Hence, $E_{Hg}^{q=0} = \Delta\varphi + \delta\chi - \chi(H_2O) - E^0(H/H^+, H_2O)$, where $\Delta\varphi$ means the sum of all potential differences independent of the solvent (*e.g.* contact potential between Pt and Hg), $\delta\chi$ interaction potential due to oriented adsorption of water dipoles, $\chi(H_2O)$ surface potential of water and $E^0(H/H^+, H_2O)$ standard potential of aqueous hydrogen electrode, which is set conventionally equal to zero. If the quantity $E_{Hg}^{q=0}(S)$ in a different solvent, S, is measured analogously, then $E_{Hg}^{q=0}(H_2O) - E_{Hg}^{q=0}(S) = E^0(H/H^+, S) + \Delta\chi = (RT/F) \,.\, \ln ({}_m\gamma_{H^+}) + \Delta\chi$, where $E^0(H/H^+, S)$ denotes standard potential of hydrogen electrode in the solvent S, ${}_m\gamma_{H^+}$ "medium effect" in the same solvent, both values referred to water as standard, and $\Delta\chi = \delta\chi(H_2O) - \chi(H_2O) + \chi(S) - \delta\chi(S)$. The values χ and $\Delta\chi$ are up to now not directly measurable; $\delta\chi(H_2O)$, as mentioned by Bockris and Argade[13], is after Randles[14] equal to 0·27 V (0·26 V after Frumkin[15]), $\chi(H_2O)$ was calculated[13] from the preceding quantity and thermodynamic data as $0{\cdot}20 \pm 0{\cdot}11$ V, so that $\delta\chi(H_2O) - \chi(H_2O) = 0{\cdot}07 \pm 0{\cdot}11$ V. Hence the zero value of this difference lies within the range of the error. Other authors[16-20] estimated $\chi(H_2O)$ differently, in some cases even with different signs, $\chi(H_2O)$ lying in the range from

$-0{\cdot}48$ to $+0{\cdot}29$ V. It follows that the influence of the orientation of dipoles on the potential of zero charge has not been proved as yet and can be negligible in some solvents. Therefore, further attention should be paid to the mentioned problems.

REFERENCES

1. Heyrovský J., Šorm F., Forejt J.: This Journal *12*, 11 (1947).
2. Valenta P.: Chem. listy *45*, 249 (1951).
3. Paschen F.: Ann. Physik *43*, 568 (1891).
4. Erdey-Grúz T., Szarvas P.: Z. Physik. Chem. *A 177*, 277 (1936).
5. Smith S. W., Moss H.: Phil. Mag. *15*, 478 (1908).
6. Grahame D. C., Larsen R. P., Poth M. A.: J. Am. Chem. Soc. *71*, 2978 (1949).
7. Heyrovský J., Kalvoda R.: *Oszillographische Polarographie mit Wechselstrom*, p. 81. Akad. Verlag, Berlin 1960.
8. Harned H. S., Paxton T. R.: J. Phys. Chem. *57*, 531 (1953).
9. Eršler B. V.: Ž. Fiz. Chim. *20*, 679 (1946).
10. Grahame D. C., Coffin E. M., Cummings J. I., Poth M. A.: J. Am. Chem. Soc. *74*, 1207 (1952).
11. Ives D. J. G., Janz G. J.: *Reference Electrodes*, p. 160. Academic Press, New York, London 1961.
12. Komar N. P., Musailov O. S.: Ž. Fiz. Chim. *47*, 2947 (1968).
13. Bockris J. O'M., Argade S. D.: J. Chem. Phys. *49*, 5133 (1968).
14. Randles J. E. B.: Trans. Faraday Soc. *52*, 1573 (1956).
15. Frumkin A. N.: Svensk Kem. Tidskr. *77*, 300 (1965).
16. Verwey E. J. W.: Rec. Trav. Chim. *61*, 564 (1942).
17. Passoth G.: Z. Physik Chem. (Leipzig) *203*, 275 (1954).
18. Hush N. S.: Australian J. Sci. Res. *A 1*, 480 (1948).
19. Strehlow H. Z. Elektrochem. *56*, 119 (1952).
20. Fletcher N. H.: Phil. Mag. *18*, 1287 (1968).
21. Harned H. S., Owen B. B.: *The Physical Chemistry of Electrolytic Solutions*, p. 369. Reinhold, New York 1943.
22. Harned H. S.: J. Am. Chem. Soc. *51*, 416 (1929).

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