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NOTE ON B. KAMIEŃSKI'S PAPER "THE NATURE OF THE ELECTRIC POTENTIAL AT THE FREE SURFACE OF AQUEOUS SOLUTIONS"*

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Abstract—It is shown that the assumption of Kamieński that the water/air potential difference χ_{H_2O} is a quantity of the order of 1 V, must be rejected, as leading to impossible values for the chemical hydration energies of univalent ions.

Résumé—On démontre que l'hypothèse de Kamienski selon laquelle la différence de potentiel eau/air χ_{H_2O} serait de l'order de grandeur de 1 V doit être rejetée, car elle conduit à des valeurs impossibles pour les énergies d'hydratation chimiques d'ions monoralents.

Zusammenfassung—Es wird dargelegt, dass die Annahme von Kamieński zurückgewiesen werden muss, die Potentialdifferenz Wasser/Luft χ_{H_2O} sei von der Grössenordnung 1 Volt, da sie zu unmöglichen Werten für die chemischen Hydratationsenergieen einwertiger Ionen führt.

WHILE the change of the potential difference at the solution/air interface, which takes place when insoluble monolayers are deposited upon it, has been attracting the attention of many investigators, similar phenomena caused by the adsorption of surface-active compounds have of late been somewhat neglected. The work of Kamieński[1–3] presents an exception, and in this connection its appearance is welcome. The experimental results obtained by Kamieński, as he points out, are in many cases similar to those obtained at our laboratory,[4–7] but there is an essential difference in their interpretation which I wish to consider here.

The quantity which can be directly measured is the change in the compensating e.m.f. which is to be effected in order to bring the potential of the air electrode in a system of the type

air electrode/air/solution/0·1 N KCl, Hg_2Cl_2/Hg/compensating e.m.f./earth

back to the initial value when the composition of the solution is altered, e.g. when a solution containing an addition of a surface-active substance is substituted for 0·1N KCl. In interpreting the results of these measurements, it is assumed that the change in the composition of the solution does not give rise to an appreciable change of the potential difference at the boundary with 0·1 N KCl, or that the latter is accounted for by an appropriate correction. The air electrode must meet the following requirements:

(1) the potential difference at the electrode/air interface must remain constant

(2) the use of an air electrode must secure the complete absence of a potential drop within the air layer. Thus a water jet, a platinum wire on which polonium has been deposited and a vibrating plate according to Yamins and Zisman[8] may be used.† The

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† According to Kamieński, reliable results can be obtained only by the use of the dynamic jet method. In our opinion, the main advantage of a jet electrode is its small sensitivity to the vapours of surface-active substances, which can penetrate through the air layer and exert an influence upon the potential difference at the surface of the air electrode. In the absence of these difficulties, air electrodes of different types give quite similar results. It is to be noted that a horizontal jet can be used to advantage for the measurements of electric potentials of monolayers of insoluble substances.[9]

shifts in the difference of potential between solution and air observed are very considerable, attaining 800 mV (lepidin),[1] 900 mV (hexadecylamine hydrochloride)[10] in the negative direction and 800 (ω-bromohexadecanoic acid[11]), 1000 mV (perfluorodecanoic acid)[12] in the positive direction. In interpreting the values observed, we proceeded in the first place from the assumption that the surface potentials are determined by the orientation of dipoles, the O—C and N—C bonds being oriented towards the air phase usually with their positive (carbon) end, and the H—O and C—halogen bonds with their negative end.

Similar concepts were used with some modifications by other authors also, when they considered the potential differences resulting from the deposition of insoluble monolayers on the surface of water.[13] The quantitative interpretation of the effects observed is, however, impeded by the fact that the effective values of dipole moments in the surface layer differ from those which are obtained from measurements of dipole moments of molecules in the gaseous phase or in non-polar solvents. This circumstance can be explained by the interaction between the dipoles in the surface layer and between them and the water dipoles, by the incomplete orientation of adsorbed molecules,[14] and also by the possibility for the effects resulting from the orientation of different bonds to be compensated.[4,13] Only under certain conditions (dilution of the dipoles in the surface layer by hydrocarbon chains) do the values of the dipole moments computed from surface potentials approach to some extent the theoretical ones.[11]

As the values observed represent in fact not single potential drops, but differences between the potential drop across the surface layers of the solutions of given composition and the potential drop across the surface layer of water, the value we ascribe to this latter quantity is of great importance in the interpretation of the experimental data. Unfortunately, our concepts about the structure of the surface layer of water are still rather hypothetical and there is even no agreement as regards the sign of the potential difference between water and air, χ_{H_2O}. The values of χ_{H_2O} given in the literature vary from $-0{\cdot}48$[15] to $+0{\cdot}29$.[16] It seems to us most likely that the potential difference between water, or rather between dilute aqueous solutions of inorganic electrolytes, and air must be a small positive quantity of the order of 0·1–0·2 V. Inasmuch as the arguments in favour of this concept based on the comparison of the changes of χ under the influence of the adsorption of surface-active substances with similar effects at the solution/mercury interface where recently set forward,[17] there is no need to repeat them here.*

The supposition about the smallness of χ_{H_2O} is in agreement with the approximate

* Of some importance in estimating the value of χ_{H_2O} is the directly measurable quantity $V = \chi_{H_2O} + \phi_0 - \phi_e$, where ϕ_0 is the potential difference (Galvani potential) at the mercury/solution interface in the absence of ionic double layers, and ϕ_e denotes the potential difference at the mercury/vacuum interface. V was given[18] the value $-0{\cdot}33$ V; recent measurements of the Volta potential mercury/solution by Randles[19] and the determination of the zero-charge point of mercury by Grahame[20] give the value $-0{\cdot}26$ V. The value ϕ_0 can be broken up into two items. The first of these ϕ_e', like ϕ_e, depends on the distribution of the electron cloud in the surface layer of the metal; the second item $-\chi^{Hg}_{H_2O}$ depends on the orientation of the dipoles of water: $\phi_0 = \phi_e' - \chi^{Hg}_{H_2O}$. Thus

$$\chi_{H_2O} = \chi^{Hg}_{H_2O} + \phi_e - \phi_e' - 0{\cdot}26. \qquad (1)$$

Hence, neglecting the value $\phi_e - \phi_e'$ and assuming $\chi_{H_2O} = 0{\cdot}1$ V, we get for $\chi^{Hg}_{H_2O}$, i.e. the difference of potential caused by the orientation of the dipoles of water at the solution/mercury interface, a positive value of the order 0·36 V, which is close to the estimate of this value obtained from electrocapillary data[17], 0·2–0·3 V.

equality of maximum shifts of χ towards positive or negative values, which are observed in the presence of surface-active substances.

Another view is held, however, by Kamieński, according to whom the orientation of water dipoles gives rise to a potential difference in the order of 1 V or more. The shifts of χ towards negative values, generally observed in the presence of organic substances with O—C and N—C bonds, are explained by Kamieński not by the orientation of polar bonds, but by the decrease of the initial value of χ_{H_2O}. The supposition about the role played by the orientation of dipole bonds of the solute is considered valid by him only in the case of substances shifting χ_{H_2O} towards more positive values.* The latter effect, however, is considered in a certain sense as being an exception.[3] Unlike the former it is observed, according to Kamieński, only at very high concentrations of the solute, or when dense monolayers are formed.[1] It is to be emphasized, however, that there are no reasons for a different interpretation of the effects of both signs. In fact, by introducing suitable polar groups, it is possible to build up, on the basis of any carbon skeleton, organic molecules causing a shift of χ_{H_2O} in either direction. There is also no doubt that by choosing the proper length of the hydrocarbon chain, it is possible to find, for instance among perfluorocarbonic acids, soluble surface-active substances which will cause the shift of χ_{H_2O} in the positive direction at very small concentrations.

Kamieński's assumptions raise particular objections when the relationship between the value χ_{H_2O} and the hydration energies of ions are considered. As Frumkin[22] and Lange and Mischenko[23] have pointed out, the "real" energies of hydration, representing the changes of energy taking place when the ions pass from the gaseous phase to water through the solution/gas interface, can be calculated from the Volta potentials between mercury and solution and other experimental data. Using this method Klein and Lange[24] for the first time determined the experimental values of the real free energies of hydration. Between the real free energy of hydration of an ion A_r and the "chemical" free energy of hydration A_{ch} which depends on the interaction of the ion with the surrounding molecules of water in the bulk of the solution, there evidently exists the relationship

$$A_{ch} = A_r + nF\chi_{H_2O}, \tag{2}$$

which permits the calculation of A_{ch} from A_r and χ_{H_2O} (n is the number of the positive ionic charges). It is assumed that the A values in (2) are positive, i.e. that they represent the decrease of the free energy of the system during the process of hydration.

By substituting in (2) the experimental values of A_r determined by Randles[19] and the value $\chi_{H_2O} = 1$ V suggested by Kamieński, we find the following values of A_{ch}:

TABLE 1

Na^+	K^+	Cs^+	F^-	Cl^-	I^-	
121	104	91	76	48	34	kcal/mole

* Kamieński ascribed[3] to χ_{H_2O} a negative value in the order of 1 V, and not a positive one, assuming that the common surface-active substances shift this quantity in the direction of more positive values, which called forth some objections on the part of the present author.[21] Presumably, these assumptions were connected with some error in the interpretation of the direct results of measurements, as Kamieński did not resort to them later.

The values of A_{ch} cannot be determined directly from experimental data, and in their computation a model of the hydration shell of the ions must be used. This results in considerable discrepancies between the values of A_{ch} calculated by different authors.[15,16] (2) cannot therefore be used for an exact computation of the value of χ_{H_2O}. However, in spite of the absence of really reliable values of A_{ch}, there can be certainly no doubt as to the impossibility of a model of the hydration shell which would give for K^+ a value of A_{ch} more than twice as large as that for Cl^-, and for Cs^+ a value of A_{ch} almost three times as large as that for I^-, which proves the erroneousness of the value of χ_{H_2O} suggested by Kamieński.

In conclusion, I should like to note that the present criticisms in no way apply to a number of other points considered in Kamieński's papers, in particular to his interesting conclusions about the dependence between the surface potentials and the pH of the solution.

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