Invariance of Double Layer Capacitance to Polarized Potential in Halide Solutions

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Abstract This paper aims at evaluating the dependence of double-layer capacitance at a platinum wire electrode both on concentrations of four kinds of halide ions and the dc potential in the double-layer region (from 0.0 to 0.4 V vs. Ag/AgCl) from a viewpoint of frequency-dispersion of the capacitance. Attention was paid to shape of the double layer capacitance vs. dc-potential curves. The equivalent circuit used for analysing the double-layer impedance was a parallel combination of a double layer capacitance and an apparent resistance. The latter is caused by the time-derivative of the capacitance, which belongs to an in-phase component. It was inversely proportional to the frequency and the electrode area, but unaffected by the potential and the variation of concentrations of halide ions. On the other hand, the parallel capacitance decreased linearly with logarithm of the frequency, and was proportional to the electrode area. It showed almost a value common to concentrations from 1 mM to 2 M ($= \text{mol} \cdot \text{dm}^{-3}$) and four halide ions. Variations of the capacitance with the dc-potential in 0.1 M KF, KCl and KBr solutions are ca. 10 %. Therefore, the capacitance has negligible influence on the localization of ions by the Gouy-Chapman theory.

Keywords Impedance Measurement, Capacitance and Resistance of Electrical Double Layer, Gouy-Chapman Theory, Halide

1. Introduction

An important property of electric double layers is the dependence of the double layer capacitance, C_d , on dc-potential, E , at an electrode. The dependence can provide excess charge on the electrode by integration of C_d with respect to E . The potential dependence has been classified roughly into three types [1, 2]; a U-shape as predicted from the Gouy-Chapman (GC) theory [3, 4], a bell-shape as predicted from the Modified Poisson-Boltzmann equation [5-7], and a camel-shape as predicted from the Gouy-Chapman-Stern model. In addition, some authors reported variations small enough for the classification [8-15].

It is interesting to search conditions exhibiting these shapes.

We surveyed here thirty four documents, and classified shapes of C_d vs. E curves into a valley [3, 8, 12, 13, 16-21], one peak [1, 2, 22-27], two peaks [1, 2, 17, 26, 28-32], a plane [8-15, 33-36] and exceptions [9, 17, 25, 34, 37, 38]. The classification is based on whether a curve varies by over 30 % of the relative variation, $\Delta C/C_{av}$, where C_{av} is the arithmetic mean of the variations of C_d with E . The number of the classified publications is shown in Fig. 1A for every available electrode. The classified distributions depend on electrode materials; the valley being predominant at mercury [8, 16-19, 21], the one peak being predominant at platinum [23, 25, 39], a plane being at carbon [9, 10, 12, 14, 34]. The plane seems to be observed when non-ionic substances are adsorbed on electrodes [16, 17], especially for carbon. The percentage of the classified shapes without distinction of electrodes is shown on the right ordinate in Fig. 1B. Although the valley-shape has been widely acknowledged as a proof of the GC theory, it accounts for only a quarter of the number of the reports. The percentage for reports by computer simulation [1, 2, 27, 35] is also in Fig. 1B. The simulated results, including only few reports on the plane-shape, are not in accord with the experimental results, probably because most researchers on the simulation have paid attention to ionic interactions which depend strongly on potential.

Although the shape is a noticeable feature, the classification depends on values of $\Delta C/C_{av}$. We classified experimental C_d with E curves by values of $\Delta C/C_{av}$, which is shown in Fig. 2. Seventy percent of the curves belong to the group with $\Delta C/C_{av} < 0.9$ in Fig. 2A. Figure 2B shows assignment of $\Delta C/C_{av}$ to electrode materials. Curves with $\Delta C/C_{av} > 0.61$ are nearly assigned to Hg [8, 16-19, 21] and Ag [22, 28, 30]. Platinum [8, 25, 38], gold [13, 20, 29, 31] and carbon [8-10, 12, 14, 34] show small variations of $\Delta C/C_{av}$. In contrast, the theoretical prediction is opposite to the above. The mean field approximation has presented 11 curves [1, 2] for $\Delta C/C_{av} > 0.91$, and 2 curves [2, 27] for $0.61 < \Delta C/C_{av} < 0.90$. The ion-cell model [35] on the assumption of non-overlap of ions has predicted a plane-shape curve with $\Delta C/C_{av} < 0.3$ at high salt concentrations.

Figure 1. Change classification of 34 publications about the double layer capacitance vs. potential curves into five shapes; (A) the number of publications for every available electrode material and (B) ratio of number of publications belonging to a given shape for simulation and experimental work.

Figure 2. The number of experimental capacitance vs. potential curves classified with values of $\Delta C/C_{av}$ (A) without and (B) with assignment to electrode materials.

The GC theory mentions that application of positive voltage to an electrode [33] enhances concentration of anions near the electrode by the electrostatic force to increase the capacitance. The dependence of C_d on E should be related with that on ionic concentrations. The capacitance has been demonstrated to be independent of concentrations of chloride ions [40], and hence may be controlled by solvents rather than ions. It is necessary to examine the C_d vs. E curves in the context of the dependence on the ionic concentration.

An electrode frequently used for measurements of double layer capacitance is a disk, the circumference of which is coated with an insulator. A boundary between the exposed electrode and the insulating wall yields floating capacitance, depending on fabrication of electrodes, periods of use of electrodes, and dc-potential. A technique of suppressing the floating capacitance is to use a wire electrode without insulator. The area of the exposed surface is determined by

the immersion length of the electrode [40]. A wire electrode may be helpful for accurate and reproducible determination of C_d vs. E curves.

This report deals with obtaining the relations of the capacitance to the dc-potential and the concentrations of four halide ions at the platinum wire electrode by ac-impedance. It has been believed that F^- is non-specifically adsorbed on mercury electrodes whereas Cl^- , Br^- , and I^- are specifically adsorbed [17, 18, 41]. This is not consistent with the finding that the capacitance is caused by solvent molecules rather than ions at platinum electrodes [40]. Our concern here is to examine whether this well-known knowledge at mercury is valid at platinum electrodes in the polarized potential domain, taking into account the frequency dispersion of the capacitance. The double layer capacitance used here is the net capacitance without parallel resistance of the double layer.

2. Materials and Methods

2.1. Chemicals

KF, KCl, KBr and KI solutions were prepared by analytical grade chemicals and ion-exchanged distilled water (18 MΩ cm). HF solutions were stored in polyethylene (PE) containers.

2.2. Impedance Measurement at Platinum Wire Electrodes

Working electrodes were platinum wires 0.1 mm in diameter, 10 mm in length immersed into solution. An Ag|AgCl (in saturated KCl) and a platinum coil (0.5 mm in diameter, 120 mm in length) were used for a reference electrode and a counter electrode, respectively. The platinum wire and coil were cleaned according to our early work [40]. A salt bridge including the sample solution was set between the reference electrode and the bulk solution via a glass filter. All electrolytes were deaerated by nitrogen gas for 20 min before electrochemical experiments.

The potentiostat was Compactstat (Ivium, Netherlands), equipped with a lock-in amplifier. Applied alternating voltage was 10 mV in amplitude. The dc-potential domain on which the ac-voltage was superimposed was selected on the basis of 30% enhancement of the cyclic voltammetric current from the linear increment of the voltammogram. It ranged from 0.0 to 0.4 V vs. Ag|AgCl. In-between every impedance measurement, cyclic voltammetry was made in order to confirm agreement between the voltammograms before and after the ac-impedance measurements.

Delay of the potentiostat was checked in our previous work [40]. No abnormality was observed so far as $|Z_2|/|Z_1| > 0.04$, where Z_1 and Z_2 are the real and the imaginary components of the ac impedance, respectively. For frequencies larger than $|Z_2|/|Z_1| < 0.04$, $|Z_2|$ values were overestimated. Most experimental conditions of the double

layer measurements were in the domain of $|Z_2|/Z_1 > 0.04$.

3. Results and Discussion

3.1. Concept of Impedance of Double Layers

When ac voltage, $V = V_0 \exp(i\omega t)$, at the frequency, ω , and the amplitude, V_0 , is applied to an electric double layer, the responding current should be the time-derivative of the double layer charge, q , i.e., $I = dq/dt$. If the double layer capacitance, C , has frequency-dependence, the time-derivative of $q = CV$ is given by

$$I = \frac{d(C(\omega)V(t))}{dt} = C(\omega) \frac{dV(t)}{dt} + V(t) \frac{\partial C(\omega)}{\partial \omega} \frac{d\omega}{dt} \quad (1)$$

Figure 3. Equivalent circuits of the series combination of the double layer impedance and the solution resistance R_s . The double layer impedance is composed of (A) a parallel combination of the capacitance, C_p , and the resistance, R_p . (B) is the conventional equivalent circuit, composed of a series combination of the solution resistance, R_{sd} and the double layer capacitance, C_d . Circuit (C) corresponds to the impedance at identical two electrodes.

Figure 4. Nyquist plots for 0.01 M ($M = \text{mol dm}^{-3}$) KF and KBr solutions at the two wire electrodes with 7 mm separation.

The first term on the right hand side is $i\omega CV$, belonging to the out of phase. In contrast the second term includes no imaginary number, and hence belongs to the in phase, i.e. a

resistive component. Since the current in (1) is a sum of the real and the imaginary current, the equivalent circuit can be represented as a parallel combination of C (defined as C_p) and the resistance ($1/(\partial C/\partial t) = R_p$), as is illustrated in Fig. 3A including the solution resistance, R_s . The conventional equivalent circuit is a series combination of the solution resistance, R_{sd} and the double layer capacitance, C_d , as shown in Fig. 3B. The equivalent circuit for the two identical electrodes is given in Fig. 3C. If the capacitance is invariant to ω , as has been assumed conventionally, the current has only out of the phase component. When we applied this concept to the double layer impedance at the platinum electrode in KCl solution, we found a linear variation of C_p with $\log(\omega)$ [40]. Then the parallel resistance, $(dt/d\omega)/(\partial C_p/\partial \omega)$, is proportional to $(dt/d\omega)/\omega$. We have already demonstrated the inverse proportionality of R_p to ω [40]. So far as the double layer impedance is composed of an ideal capacitance, the parallel resistance cannot be taken into account in the analysis. It cannot be incorporated into the analysis including the Nernst-Planck-Poisson equations [42], either.

Figure 5. Variations of the parallel capacitances with logarithmic frequency for (A) KF, (B) KCl, (C) KBr and (D) KI at concentrations of (open circles) 2 M, (triangle) 0.5 M, (full circles) 0.1 M and (squares) 0.01 M. Values of C_p were obtained at two electrodes without any reference electrode. $M = \text{mol} \cdot \text{dm}^{-3}$. The conventional equivalent circuit, as is shown in Fig. 3(B), is a series combination of the double layer capacitance, C_d , and the solution resistance, which includes the parallel resistance in the double layer, according to (1). Relations between the two equivalent circuits are given by

$$R_{sd} = R_s + \frac{R_p}{1 + (\omega C_p R_p)^2} \quad (2)$$

$$C_d = C_p + \frac{1}{\omega^2 C_p R_p^2} \quad (3)$$

The in-phase component, R_{sd} , called "conventional solution resistance" is larger by the double layer resistance, $R_p/[1 + (\omega C_p R_p)^2]$ than the true solution resistance. Since R_p is inversely proportional to ω [40], R_{sd} is approximated as $R_s + k/\omega$ for a constant k . On the other hand, the conventional double layer capacitance contains $1/\omega^2 C_p R_p^2$. Since ωR_p is independent of ω [40], C_d may vary only slightly with ω . If R_p is independent of dc-potential, C_d should have the dc-potential dependence similar to C_p , according to (3).

The real impedance, $Z_1 (= R_{sd})$, and the imaginary one, $Z_2 (= -1/\omega C_d)$, were obtained from the ac-current responding to the dc-superimposed ac-voltage at frequencies, $f (= \omega/2\pi)$, ranging from 1 Hz to 50 kHz. Extracting C_p and R_p from (2) and (3) yields

$$C_p = \frac{-Z_2}{\omega} \frac{1}{(Z_1 - R_s)^2 + Z_2^2} \quad (4)$$

$$R_p = \frac{(Z_1 - R_s)^2 + Z_2^2}{Z_1 - R_s} \quad (5)$$

R_s was evaluated from the relation, $Z_1 = R_s + k/\omega$ for $f \rightarrow \infty$ or $Z_2 \rightarrow 0$ in the Nyquist plot, as shown in Fig. 4. The plots are lines rather than hemi-circles, because the impedance contains no Faradaic process. Values of C_p and R_p were determined from Z_1 , Z_2 and R_s for each f by use of (4) and (5).

3.2. Variation of the Capacitance with Frequency and Concentration

Two platinum wires with common length were used for obtaining dependence of C_p and R_p on kinds of halides and

their concentrations without a reference electrode. Reasons for using the two-electrode system are (i) to keep ionic concentrations in the cell against leakage of ions from the reference electrode, and (ii) to retain the solution resistance in a given arrangement of electrodes geometrically constant in order to discern it from R_p . Then the equivalent circuit is given by Fig. 3C. Figures 5A-5D show the frequency dependence of C_p at several concentrations of KF, KCl, KBr and KI, respectively. All the values of C_p were linear to $\log(f)$, i.e. $C_p = (C_p)_{f=1} - k_1 \log(f)$, regardless of kinds of halides and their concentrations. The ratio, C_d/C_p , ranged from 1.01 to 1.03 in the present frequency domain. Since C_d is numerically similar to C_p , it has frequency dependence similar to in Fig. 5. The frequency dispersion is thought to be relevant to reformation of double-layer by the solvent dipoles at electrodes[43, 44], movements of ions along both lateral and vertical directions and surface roughness[26, 45, 46]. We do not discuss here a reason for the frequency dispersion.

Figure 6. Dependence of C_p at $f = 1$ Hz on concentrations of (open circles) KF, (triangles) KCl, (full circles) KBr and (squares) KI

Values of the slope in Fig. 5 were almost common, $-0.99 \pm 0.04 \mu\text{F}$, to four kinds halides in the domain of the concentration. The intercepts of the linear variations in Fig. 5 decreased slightly with a decrease in the concentrations. We choose the parallel capacitance at $f = 1$ Hz as a representative of the capacitance for the discussion of dependence on concentrations and kinds of ions. Values of $(C_p)_{f=1}$ are plotted against concentrations in Fig. 6. Use of low concentrations increases both Z_1 and R_s in (4), and hence the difference $Z_1 - R_s$ includes large errors. Accurate evaluation of R_s at low concentrations requires high frequency measurements, at which $|Z_2|$ was overestimated by a property of the potentiostat to yield underestimation of R_s . The average value of $(C_p)_{f=1}$ in Fig. 6 is $(1.2 \pm 0.1) \mu\text{F}$ or $(38 \pm 3) \mu\text{F cm}^{-2}$.

Concentration dependence of double layer capacitance has seldom been discussed. The GC theory mentions that the double-layer capacitance has the square-root dependence of ionic concentration [3, 4]. The capacitance at the nitrobenzene|water interface by Wandlowski et al. increased

with the concentrations, showing the dependence of the square-root of the concentrations [47], similar to the GC theory. The ion-cell model has suggested the dependence of $1/3$ powers of the concentration [35]. The almost constant values of $(C_p)_{f=1}$ common to F^- , Cl^- , Br^- and I^- indicate that the value of double-layer capacitance should be controlled by solvent molecules rather than ions. This prediction will be proved in latter discussion. The common values have already been reported [36].

Figure 7. Variations of the parallel resistance with frequency on the logarithmic scale for (circles) 0.5 M KF and (triangles) 0.5 M KCl

Figure 7 shows the variation of the parallel resistance with frequency for KF and KCl. The plots for KBr and KI overlapped with those for KF and KCl. The plots were independent of the concentration range of 0.01 to 2 M for the four halides. Since the slope of the lines is -1, the resistance should be inversely proportional to the frequency. The frequency dependence is caused by $\partial C_p / \partial \omega$ in (1) through the linear variation of C_p with $\log f$. Slopes of the linearity were common to four halides. Therefore, the frequency dependence of R_p should be common to the halides.

3.3. Potential Dependence of Capacitance and Resistance

We used the three-electrode system at the Pt wire working electrode in order to obtain variations of the capacitance with dc-potential. Since we confirmed that C_p and R_p were independent of ionic concentrations, fluctuation of ionic concentration by the reference electrode has a negligible effect on C_p and R_p . The impedance at the Pt wire electrode in KF, KCl, KBr and KI solutions at concentrations from 1 mM to 1 M were obtained at ac voltage superimposed on 0.2 V vs. Ag|AgCl. The impedance analysis was made by use of the model (A) in Fig. 3. We confirmed that all the values of R_p and C_p were very close to the data obtained at the two electrode system (model (C)). In order to vary the electrode area, we changed the immersed length of the Pt wire from 1 to 11 mm by 1 mm per-step. Values of C_p of KCl were proportional to the area of the electrode, as predicted[40]. In contrast, those of R_p were inversely proportional the area, as

shown in Fig. 8.

The inverse proportionality can be explained by inserting $C_p = KA$ into $R_p = (dt/d\omega)/(\partial C_p / \partial \omega)$, i.e., $R_p = (dt/d\omega)/(A \partial K / \partial \omega)$, where K is a function of ω . This expression is composed of variables of interface, A and K , rather than those of bulk solution. Therefore R_p has the property of the interface.

Figure 8. Dependence of R_p of 1.0 M KCl on the area of the electrode at f = (open circles) 320, (triangles) 541, (squares) 1082 and (full circles) 2475 Hz.

Figure 9. Dependence of the double layer capacitance on dc-potential in 0.1 M solutions of (squares) KF, (circles) KCl and (triangles) KBr, where the capacitance values are extrapolated to 1 Hz.

Figure 9 shows the plots of $(C_p)_{f=1}$ in 0.1 M KF, KCl and KBr solutions against the dc potential, E , exhibiting independence of the potential. The negligible variance of C_d vs. E curve was also found in halide ionic solutions[15].

The plots belong actually to the planar shape with $\Delta C_p / C_{p,av} \approx 0.1$. The planar shape implies negligible contribution of the electrostatic interaction between ions and the dc-electric field to the capacitance[9, 36], being not satisfied with the GC theory. Consequently, the capacitance is caused mainly by solvent molecules rather than ions. This inference agrees with the invariance of the capacitance to the ionic concentrations (in Fig. 6). The plots in Fig. 9 demonstrate no difference in the capacitance among KF, KCl

and KBr. It has been widely believed that fluoride is a non-specific adsorbed species whereas chloride and bromide are adsorbed specifically on electrodes. This statement may be valid for mercury electrodes [17, 18, 41], whereas it is invalid for platinum ones. Since iodide solution showed a narrow polarized domain (0.15 V), it is insignificant to discuss the shape of C_p vs. E curves.

Figure 10. Variations of the double layer capacitance in KCl solution at (open circles) 1 M, (filled circles) 0.1 M, (triangles) 0.01 M and (squares) 0.001 M with the dc-potential, where the capacitance values are extrapolated to 1 Hz.

Figure 11. Comparison of the potential-dependence of $(C_p)_{f=1}$ and cyclic voltammetry in 0.1 M KCl solution.

Figure 10 shows dependence of $(C_p)_{f=1}$ for KCl on the dc-potential for several concentrations. No dependence was found even at the lowest concentration (1 mM). Therefore, the electrostatic interaction of ions with the electric field plays a minor role in forming the double layer capacitor. The independence was also observed for KF and KBr at the concentrations of the above domain.

Dependence of C_p on concentrations is barely noticeable in Fig. 10 as well as Fig. 5 and 6. We evaluated the solution resistance by means of extrapolating Z_1 to infinite frequency conveniently in order to avoid deterioration of electrode surfaces by a long term measurements. Values of R_s by this

technique were unfortunately smaller than those evaluated from [40] variations of Z_1 with the distance between the two wire electrodes by 30-50 % when halide concentrations were less than 0.1 M. The underestimation of R_s provides smaller values of C_p through (4) than those determined by the latter method. Consequently the values of C_p in Fig. 5, 6, and 10 at low concentrations are smaller than those at high concentrations. The underestimation of R_s by the extrapolation may be due to delay of the potentiostat. Accurate determination of the concentration dependence would require meticulous calibration of a potentiostat, especially at low concentration and high frequency.

Figure 11 shows the variation of double layer capacitance in the wide potential domain, showing a valley shape. The cliff-like variation occurred at the potential which gives rise to faradic reactions, as is compared with the cyclic voltammogram. The increase in the capacitance by faradic currents has been found at Ir(100) in 0.1 M HCl [15], and at Pt(111) electrode in 0.1 M HClO₄ [23]. Capacitances with a valley shape reported so far may include faradaic impedance. Participation in the faradaic currents has been applied to electroactive film-coated electrodes in order to enhance capacitance largely [48, 49].

4. Conclusion

The double layer impedance is expressed by a parallel combination of the capacitance and the resistance. The latter is not a real resistance, but appears noticeably at low frequency. It is necessarily associated with the measurements of ac impedance through (1). Since it results from the frequency-dependence of the capacitance, it is a property of the double layer. Values of R_p are common to four halides and concentrations, and are independent of dc-potential in the polarized domain.

C_p varies linearly with $\log(f)$ in solutions of four halides at concentrations more than 1 mM. This linear variation causes R_p through $1/(\partial C_p / \partial \omega)$. C_p is independent both of dc-potential in the polarized domain and ionic concentration of halides so that the shape of capacitance vs. potential curves is a plane. The capacitance is caused by water molecules rather than ions. A valley shape is possibly ascribed to participation in faradaic currents, i.e., a decrease in the component of the out of phase of faradaic impedance.

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