DETERMINATION OF DOUBLE LAYER PARAMETERS FROM ELECTROCAPILLARY CURVES OF PARTIALLY IMMERSED ELECTRODES

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The relationship between liquid meniscus height at a partially immersed electrode and potential is discussed on the basis of the modern theory of wetting and the electrocapillary phenomena. The results obtained on an amalgamated gold electrode in potassium iodide solutions show a general agreement with the theory. A quantitative treatment is described which allows the determination of charge graphically from the experimental data. A comparison is made between the charge potential relationship obtained from the experimental data and that obtained from electrocapillary measurements on liquid mercury. It is believed that the influence of the electric field on water orientation as well as on the dispersion interaction at the electrode/solution interface are the main factors for the observed differences between the two charge potential relationships.

In recent publications[1-2] we briefly outlined the theory and experimental technique of a new method for determining the potential of zero charge on metal plates. The method involved the study of the dependence of liquid meniscus height at a partially immersed metal plate on the potential.

Studies on the effect of potential on the wetting of metal surfaces were previously carried out by Frumkin and coworkers[3,4] who measured the contact angle of a gas bubble on an immersed electrode surface. The idea was first tried by Möller[5] and has its origin in the Young equation:

$$\cos \Theta = \frac{\gamma_{S/G} - \gamma_{S/L}}{\gamma_{L/G}}, \qquad (1)$$

where Θ is the contact angle, $\gamma_{S/G}$, $\gamma_{S/L}$ and $\gamma_{L/G}$ are interfacial tensions for the solid/gas, solid/liquid and liquid/gas interfaces. The work based on the bubble method is handicapped by the experimental difficulties and ambiguity in measuring the contact angle. According to Frumkin and coworkers[3] the variation in $\gamma_{S/L}$ is masked by a similar variation in $\gamma_{S/G}$ due to an adsorbed layer of electrolyte between the metal surface and the bubble. Most of these difficulties are eliminated if the meniscus height instead of the contact angle is measured as a function of the potential.

Figure 1 is a schematic representation of the experimentally measured parameter. The meniscus rise h is the difference between the flat level of the solution at the top of the cell and the meniscus

edge at the vertically placed electrode. One notices that the three interfaces are well defined. It is important to mention however that under the experimental conditions the metal surface being a high energy one is covered by a strongly adsorbed film of water. The formation of the latter is accompanied by a gain in energy. This will only results in reducing the nterfacial tension of the metal/gas interface by an amount known as the spreading pressure of water. It is believed however that this water film will function as an insulator and therefore the value of $\gamma_{S/G}$ will not vary when the potential across the metal/solution interface is varied.
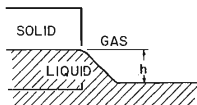

Fig. 1

Liquid Meniscus Rise at a Long Vertical Electrode

The dependence of the meniscus rise h on the contact angle Θ is described by the equation

$$\sin \Theta = 1 - (\varrho g h^2/2\gamma_{L/G}),\qquad(2)$$

where ϱ is the liquid density, g the gravitational constant and $\gamma_{L/G}$ the liquid surface tension. The derivation of equation (2) has only been given in the German literature. For a complete review on this matter the reader is referred to a thesis by Neumann[6]. The equation is obtained by solving the Gauss Laplace differential equation for the two dimensional case of a liquid meniscus surface in the neighborhood of a long immersed plate. The solution is simplified by considering only the central part of the meniscus which is free from the edge effects. Figure 2 shows a plot of meniscus rise h vs contact angle Θ according to equation (2). The slope of the almost linear relationship is about 0·004 cm/degree. Considering the accuracy of measuring contact angles to be between $1-2°$ and that of meniscus rise to be $\pm$ 0·001 cm it can be seen that h is at least 4 times more sensitive function than Θ. It is our opinion therefore that the use of meniscus height measurements can lead to a better understanding of the wetting potential relationship.

It is the purpose of this paper to discuss the theoretical basis of the potential-wetting relationship using data obtained by the meniscus height method. The analysis of the data will be made on the light of the modern theory of wetting and will be confined to the case of a mercury-plated gold plate. The extension of the analysis to other metals will be reported in future publications.

EXPERIMENTAL

The measurements were carried out on amalgamated gold plates. Mercury was plated on rectangular gold plates which has an area of 4 × 2 cm and 0·1 cm thickness. The purity of the gold plates were 99·99%. The plating was made from a cyanide solution as described elsewhere[7]. An amalgamated gold wire was used as an anode for the plating process. After removal from the cell the plated electrodes were washed very thoroughly in distilled water and then rubbed gently with filter paper for smoothing the surface. They were again washed in distilled water, acetone

and finally in isopropyl alcohol before they were dried at about 100°C. The dry electrodes were immediately used after being dipped for few seconds in triply distilled mercury.

The apparatus was described in a previous publication[1]. The meniscus height at the vertical and partially immersed electrode was observed by a cathetometer with an accuracy of ± 0.010 cm. The cell was in the form of a round teflon beaker of 7·6 cm i.d. and 3·9 cm height. Teflon was chosen because of its non-wetting properties. The latter property was essential to allow the solution to rise over the edge of the cell and form a flat top. Measurements were taken while the cell was placed inside a closed box of plexy glass. A platinum foil was used as a counter electrode. A saturated calomel electrode was used as a reference electrode. Helium was bubbled through the solution for at least $\frac{1}{2}$ hour before the experiment and was continuously bubbled into the plexy-glass box from a water bubbler during the measurement. Solutions were prepared from reagent grade chemicals and bidistilled water which was prepared by distillation from a potassium permangamate solution.

The potential was controlled potentiostatically using a wenking potentiostat. The reversibility of the meniscus rise made it possible to start the experiment at any potential within the polarizable range from either the extreme anodic or extreme cathodic region. Therefore it was possible to observe by varying the potential both advancing and receding meniscus height.

RESULTS

Fig. 3 shows meniscus height potential relationship for a mercury-plated gold electrode in 1·0M-KI solution. The different points represent the results of three experiments plotted on the same curve. The first experiment was carried out by varying the potential from the extreme cathodic to a potential of -0.735 volts vs N.H.E. In the second, the potential was followed from the extreme anodic to the extreme cathodic, followed by the third in which the potential was followed in the reverse direction up to the extreme anodic potential. The first experiment was done at a lower electrode position than the second and third which were carried out at the same but a higher position. It is noticed that the cathodic meniscus height is free from hysteresis between the advancing and receding meniscus height. The anodic meniscus height is lower in the second experiment than in the third particulary at potentials not too far from the minimum. This is attributed to the presence of a chemisorbed layer of oxygen which is probably reduced in the third experiment and thus resulting in higher anodic meniscus height. This hysteresis, however, is negligible and has a very slight effect on the position of the minimum. It is noticed that h has a negative sign at the bottom section of Fig. 3. This means that the meniscus is depressed and the meniscus edge is located below the solution level in the cell. Such meniscus depression corresponds to contact angles above 90°. The minimum in Fig. 3 is located at a potential of -0.54 ± 0.01 V vs N.H.E. It is important to mention that the meniscus usually reached constant height in a time less than it took to adjust the cathetometer to the new value which was less than one minute.

Fig. 4 shows meniscus height potential plots for a mercury-plated gold electrode in 0·1M-KI solution. It is noticed that the direction in which the potential is varied influences both the meniscus height as well as the position of the minimum. The

most important observation with this solution is the shift in the minimum to more positive potentials of about 0·15 V when the potential is varied from the cathodic to the anodic direction. The cathodic meniscus height is also characterised with more hysteresis than the anodic height. Fig. 4 also shows that the curve obtained by following the potential from the cathodic to the anodic side is asymmetrically shaped. The minimum of the curve obtained by following the potential from the anodic to the cathodic side is located at −0·435 V *vs* N.H.E.

Figure 5 shows the charge *vs* rational potential relationship calculated from the meniscus height potential plot of Fig. 3 by means of equation (5). It is noticed that compared to the plot obtained from electrocapillary data on mercury[8], this charge is less at rational potentials more positive than −0·4 V and higher at more negative potentials.

Solutions of less adsorbeds ions than iodide were tried but the results showed that a greater section of the meniscus height potential curve was characterised with negative meniscus height (below the solution level). Because of the uncertainty
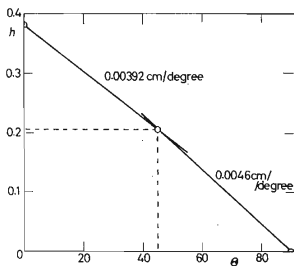

FIG. 2

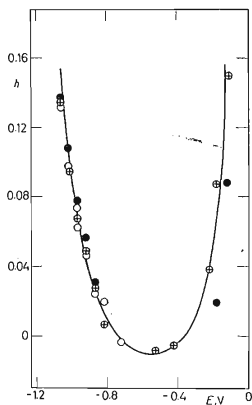Meniscus Rise *h*(cm) as a Function of Contact Angle Θ (degree)

FIG. 3

Liquid Meniscus Rise *h*(cm) as a Function of Potential *E* (V *vs* N.H.E.) for an Amalgamated Gold Electrode in 1M-KI

● Cathodic to minimum, ○ anodic to cathodic, ⊕ cathodic to anodic.

in determining such meniscus potential relationships we shall postpone reporting the data until it will be possible to extend the use of the present method to meniscus variations below the solution level.

DISCUSSION

The wetting of a metal surface by water can be expressed quantitatively by the Young equation. When the contact angle is zero water will spread on the surface and equation (1) gives

$$\gamma_{L/G} = \gamma_{S/G} - \gamma_{S/L} .$$

The spreading coefficient S defines the magnitude of this spreading

$$S = \gamma_{S/G} - \gamma_{S/L} - \gamma_{L/G} .$$

For contacts angles higher than zero, S is negative and water does not spread on the metal surface. According to Harkins[9], $\gamma_{S/G}$ for a metal surface is much higher than either $\gamma_{S/L}$ or $\gamma_{L/G}$ and therefore S is a positive quantity which means the spreading of water on the metal surface. This belief however is no more shared by many investigators. Modern theories on the wetting phenomena have shown that the actual magnitude of interaction between pure water and an oxide free metal surface is not sufficient to cause the spreading of water on the metal surface. Fowkes[10] showed theoretically that the only forces of interaction between a metal such as mercury and water are those of London dispersion type. Neither the metallic bonding nor the hydrogen bonding in water contribute to the forces of interaction. By introducing the principle of addition of intermolecular forces Fowkes[10] predicted the interfacial tension values for the Hg–H$_2$O system according to the equation

$$\gamma_{Hg/H_2O} = \gamma_{Hg/G} + \gamma_{H_2O/G} - 2 \sqrt{(\gamma_{Hg/G}^{d}\gamma_{H_2O/G}^{d})} , \qquad (3)$$

where $\gamma_{Hg/G}$ and $\gamma_{H_2O/G}$ are the surface tensions of mercury and water and $\gamma_{Hg/G}^{d}$ and $\gamma_{H_2O/G}^{d}$ are the dispersion forces contributions to their surface tensions. Equation (3) predicts a value of 424 ± 4.4 dyn/cm for γ_{Hg/H_2O} which is in a good agreement with experimentally measured value of 426 dyn/cm.

The possibility of using the wetting phenomena to obtain electrocapillary curves follows directly from the above discussion and from our knowledge of the Lippman equation. It is of extreme importance that water does not wet mercury, otherwise any electrocapillary studies based on the wetting phenomena would have been meaningless.

When an electric field is applied across the metal–electrolytic solution interface, the interface is charged and the interfacial tension is decreased. The decrease in the interfacial tension is given by the Lippman equation

$$q = - (\partial\gamma/\partial E)_\mu , \qquad (4)$$

where q is the surface charge and E the potential measured against a reference electrode. The decrease in the interfacial tension results according to the Young equation in a decrease in the magnitude of the contact angle and according to equation (2) to an increase in the meniscus height. At the potential of zero charge the contact angle will be maximum and the meniscus height minimum. At the potential of zero charge and in the absence of specific adsorption it is reasonable to assume that the interfacial tension for the Hg–electrolytic solution system corresponds to that of Hg–pure water.

As an example of this correspondance it is noted that the interfacial tension for Hg–KOH solution at the potential of zero charge was reported to be 424 dyn/cm[8]. This most probably means that with such solutions, at the potential of zero charge the only interaction is due to dispersion forces between the water molecules and the metal surface.
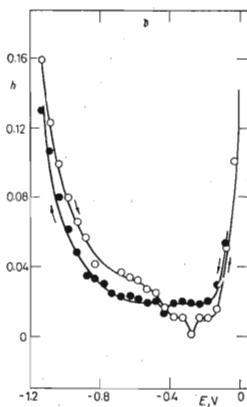

FIG. 4

Liquid Meniscus Rise h(cm) as a Function of Potential E (V vs N.H.E) for an Amalgamated Gold Electrode in 0·2M-KI

○ Cathodic to anodic, ● anodic to cathodic.
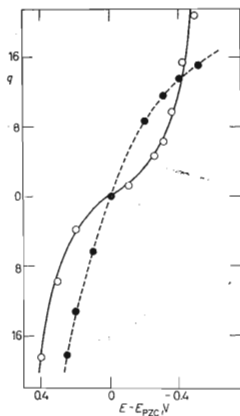
FIG. 5

Charge q (μC/cm^2) as a function of the Rational Potential (V) on an Amalgamated Gold Electrode in 1·0M-KI

○ Calculated for meniscus rise data with 1M-KI, ● from electrocapillary rate on liquid Hg in 1M-NaI.

The results shown in Figs 3—4 agree with the general theory outlined above. This conclusion is based on a) the type of variation of meniscus rise with the potential b) the agreement between the meniscus height minima and potential of zero charge for mercury in the same solution. The meniscus minima are slightly more positive than the potential of zero charge. The difference however is not more than 0·020 V and can be attributed to a difference in work functions. It is expected that the presence of gold in the mercury film will increases its work function, c) the reversibility of the meniscus rise potential relationships. The hysteresis observed in the cathodic meniscus height of 0·1M-KI solution will be discussed later on.

For a more accurate analysis of the results a quantitative treatment is required. One possible approach is to derive an electrocapillary equation relating $(\partial h/\partial E)_\mu$ the slope of the meniscus height potential relationship with q, the charge density. Such an equation can be used for graphical determination of the charge and possibly other double layer parameters. The use of meniscus height in graphical determinations is preferable to the contact angle due to the more sensitive dependence of the former parameter on the potential.

Equations (1), (2) and (4) can be solved simultaneously to give the following expression for the charge density.

$$q = 265\,(1 + 8\cdot5\,h^2)\,(\partial h/\partial E)_\mu\,. \qquad (5)$$

The complete derivation of equation (5) is to be found in the appendix. Fig. 5 shows that q calculated from the experimental data using equation (5) is lower than q obtained from electrocapillary data on liquid mercury at rational potentials more positive than $-0\cdot4$ V. At more negative rational potentials than $-0\cdot4$ V the former quantity is higher than the latter.

The apparently higher charge densities obtained from the meniscus height data at cathodic rational potentials more negative than $-0\cdot4$ V are most probably due to a stronger adhesion of water molecules to the negatively charged electrode surface. The adhesion is a result of the dipole–dipole interaction between the water molecules and the metal surface. This type of interaction is not accounted for by the Young equation which is derived for non charged interfaces. If this explanation is valid, these dipole–dipole forces must start at more positive rational potentials than $-0\cdot4$ V but because of another opposing effect their influence is not observed at such potentials. The presence of this strongly adsorbed water layer may also explain the shift to more positive potential of the meniscus height minimum in 0·1M-KI solution, when the potential is followed from the cathodic to the anodic direction. It is interesting to note that the same conclusion concerning the influence of water adsorption in shifting the potential of zero charge to more positive potentials was also reported by other authors on the basis of double layer studies. Muller[11] discussed the latter subject in detail. It is reasonable then to assume that the minimum of Fig. 4 (empty

circles) corresponds to the minimum of adhesion of water and this of Fig. 4 (full points) corresponds to the potential of zero charge of the mercury-plated gold electrode. The occurrence of the former minimum may be related to the much discussed capacity hump which according to Parsons[12] could be related to some pecularity of water structure.

If water is oriented preferentially with the positive end of its dipoles towards the metal surface, a variation in the electric field at positive potentials to the potential of zero charge must result in the reorientation of water molecules. The latter process could explain at least partly the apparently lower values of q calculated from meniscus height data at potentials positive to the potential of zero charge. It is certain however that there are other factors, besides the reorientation of water molecules, which account for decreasing the meniscus height and result in the apparent lower values of charge. One important factor could be that the amalgamated gold electrode has a smaller dispersion energy than liquid mercury. The dispersion energy of mercury was reported[10] to be 200 ± 1 dyn/cm. Other noble solid metals such as gold and silver are known to have much lower dispersion energies. The dispersion energy of gold was reported[13] to be 65.5 dyn/cm. It is unlikely that these dispersion forces will remain constant with the variation in potential. More likely they will interact with other coulombic and noncoulombic forces at the charged interface. A combination of the last two factors could result in that the dispersion energy of interaction at the amalgamated gold/water interface decreases to more lower values as a function of the potential compared to the mercury electrode. This decrease is more than offset, however, at high cathodic potentials by the orientation of water molecules towards the metal surface.

Other factors which might reduce the amount of charge and therefore the meniscus height cannot be overruled. Of particular importance is the effect of impurity which should be more significant with a large plate than in the case of a narrow capillary. The same effect of impurity however cannot explain the increase in meniscus rise at high cathodic potentials. The variation in the frictional properties of the interface with the potential can result in a variation of meniscus height. It has been shown by Bockris and coworkers[14] that the frictional coefficient is a maximum at the potential of zer charge. This can hardly explain the variation of meniscus height with potential reported in this paper, unless it can be shown that the rate of decrease of frictional coefficient with the potential is greater in the cathodic than it is in the anodic side.

The decrease in meniscus height can also be attributed to a decrease with potential in the value of $\gamma_{S/G}$. It has been mentioned earlier, that the metal surface is covered with an water film. The diffusion of ions from the bulk solution into this film can results in a dependence of $\gamma_{S/G}$ on the potential. Such a diffusion process must be time dependent and could result in a meniscus rise variation with time. Since the latter variation has not been observed, the effect of such a factor is ruled out.

APPENDIX

The following is a derivation of equation (5). We have the Young equation (1). Doubts on the validity of this equation has been eliminated by Johnson[15] who gave a thermodynamic proof of the equation based on surface tensions. We also have equations (2) and (4). Using the mathematical identity $\cos^2 \Theta + \sin^2 \Theta = 1$ equation (2) can be written in the form

$$\cos \Theta = h \, (2K - K^2 h^2)^{1/2} \, , \tag{2a}$$

where $K = \varrho g / 2\gamma_{L/G}$ and is a constant for a certain solution.

Assuming the electrode to be ideally polarizable and $(\partial \gamma_{S/G} / \partial E) = 0$ we can obtain by combining equations (1) (2a) and (4) and differentiating with respect to the potential the following:

$$q = - \frac{\gamma_{L/G}(2K - 2K^2 h^2)}{(2K - K^2 h^2)^{1/2}} \left(\frac{\partial h}{\partial E} \right)_\mu \, .$$

The last equation can be further simplified by using the expansion series

$$(1 - \tfrac{1}{2}Kh^2) = 1 - (Kh^2/4) - (K^2 h^4/32) - \ldots$$

but all terms after the second on the right side are negligible and accordingly we obtain

$$q = - \gamma_{L/G}(2K)^{1/2} \, (1 + 1{\cdot}25Kh^2) \, (\partial h/\partial E)_\mu \, ,$$

where $\gamma_{L/G}(2K)^{1/2}$ is a constant for each solution.

Expressing values of $\gamma_{L/G}$ and K the last equation leads for dilute aqueous solutions to equation (5).

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