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All-Union Correspondence Course,
Polytechnic Institute,
Moscow

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BRIEF COMMUNICATIONS

THEORY OF THE ELECTRICAL DOUBLE LAYER IN CONCENTRATED SOLUTIONS. II. METAL-SOLUTION INTERFACE

V.S. Krylov and V.G. Levich

In the preceding paper¹ the general theory of the electrical double layer in fairly concentrated solutions was developed on the basis of the statistical method proposed by Kirkwood and coworkers^{2,3}, and the problem of the distribution of potential in a discrete double layer at a dielectric-solution interface was solved. In the present paper the solution of the analogous problem for a metal-solution interface is given.

Using the previous notation¹, we shall characterise the region I, which in this case is the metal, by the mean surface charge density q at the boundary $x = -\beta$. We shall denote by ψ_0 the potential of the metal relative to bulk of the solution. The distribution of potential $\psi(\vec{r})$ should then be described by the equation

$$\Delta \psi(\vec{r}) = -\frac{4\pi e z_0}{D_1} \delta(x) \sum_{mn} \delta(y - y_{mn}) \delta(z - z_{mn}); \Delta \psi_3(\vec{r}) = -\left(\frac{4\pi}{D_3}\right) \rho(\vec{r}) \quad (1)$$

with the boundary conditions

$$\begin{aligned} \psi_3(-\beta, y, z) &= \psi_0; \frac{\partial \psi_3}{\partial x}(x = -\beta) = -\frac{4\pi q}{D_1}; \psi_3(\gamma, y, z) = \psi_3(\gamma, y, z); \\ D_1 \frac{\partial \psi_3}{\partial x}(\gamma, x, z) &= D_3 \frac{\partial \psi_3}{\partial x}(\gamma, y, z); \psi_3(\infty, y, z) = 0. \end{aligned} \quad (2)$$

It has been shown¹ that when the effect of the short-range interaction between the ions of the solution and the external field in a symmetrical binary electrolyte is neglected,

then in terms of the parameters $\epsilon_2 = e^2 c^{1/3} / D_3 kT$ and $\epsilon_3 = |e \bar{\psi}_3(\gamma)| / kT$ the bulk charge density $\rho(\vec{r})$ is to a first approximation given by

$$\rho(\vec{r}) = -\frac{D_3 \kappa^3}{4\pi} H(\vec{r}),$$

where $H(\vec{r})$ is a function satisfying the linear integrodifferential equation

$$\Delta (H(\vec{r}) + \frac{\kappa^2}{4\pi} \int_{x > \gamma} G(|\vec{r} - \vec{r}'|) H(\vec{r}') d\vec{r}') = 0, \quad (3)$$

where

$$G(|\vec{r} - \vec{r}'|) = \frac{\exp(-\Phi^{(s)}(|\vec{r} - \vec{r}'|) / kT)}{|\vec{r} - \vec{r}'|}$$

$[\Phi^{(s)}(|\vec{r} - \vec{r}'|)]$ is the potential energy of the short-range interaction between two ions].

Since in the given case the external field, which determines the symmetry of the problem, is set up by the charged metallic plane $x = -\beta$ and the adsorbed ions whose centres lie in the plane $x = 0$, the function $H(\vec{r})$ may be represented as a sum of two terms each of which corresponds to one of the components of the external field. Accordingly the charge density $\rho(\vec{r})$ can also be written in the form

$$\rho(\vec{r}) = \sum_{mn} \rho_1^{(mn)}(\vec{r}) + \rho_2(x),$$

where

$$\begin{aligned} \rho_1^{(mn)}(\vec{r}) &= \vec{r} = -\frac{D_3 \kappa^3}{4\pi} H_1^{(mn)}(\vec{r}), \\ \rho_2(x) &= -\frac{D_3 \kappa^3}{4\pi} H_2(x), \end{aligned}$$

each of the functions $H_1^{(mn)}(\vec{r})$ and $H_2(x)$ satisfying condition (3).

We shall seek a solution of the system of equations (1) in the form

$$\psi_3(\vec{r}) = \sum_{mn} \psi_3^{(mn)}(\vec{r}) + M(x + \beta) + \psi_0, \quad (4)$$

$$\psi_3(\vec{r}) = \sum_{mn} \psi_3^{(mn)}(\vec{r}) + \psi_3^*(x), \quad (5)$$

where the functions $\psi_3^{(mn)}(\vec{r})$ and $\psi_3^*(x)$ satisfy the system of equations

$$\Delta \psi_3^{(mn)}(\vec{r}) = -\frac{4\pi e z_0}{D_1} \delta(x) \delta(y - y_{mn}) \delta(z - z_{mn}); \Delta \psi_3^*(x) = -\frac{4\pi}{D_3} \rho_1^{(mn)}(\vec{r}), \quad (6)$$

with the boundary conditions

$$\begin{aligned} \psi_3^{(mn)}(-\beta, y, z) &= 0; \psi_3^{(mn)}(\gamma, y, z) = \psi_3^{(mn)}(\gamma, y, z); \\ D_1 \frac{\partial \psi_3^{(mn)}}{\partial x}(\gamma, y, z) &= D_3 \frac{\partial \psi_3^*}{\partial x}(\gamma, y, z); \psi_3^*(\infty, y, z) = 0, \end{aligned} \quad (7)$$

and the function ψ_3^* satisfies the equation

$$\frac{d^2 \psi_3^*(x)}{dx^2} = -\frac{4\pi}{D_3} \rho_2(x) \quad (8)$$

and the boundary condition $\psi_3^*(\infty) = 0$. The second constant, which determines the solution of Eqn. (8), and also the constants M and ψ_0 may be found from the conditions

$$M = -\frac{4\pi q}{D_1} - \frac{\partial \psi_3^*}{\partial x}(x = -\beta); M\delta + \psi_0 = \psi_3^*(\gamma); D_1 M = D_3 \frac{d\psi_3^*}{dx}(\gamma), \quad (9)$$

where

$$\frac{\partial \psi_3^*}{\partial x}(x = -\beta) = \lim_{s \rightarrow -\infty} \frac{1}{s} \iint_{-\infty}^{\infty} dy dz \sum_{mn} \frac{\partial \psi_3^{(mn)}}{\partial x}(-\beta, y, z). \quad (10)$$

The solution of (6)–(7), which can be readily obtained in terms of Green functions, has the form

$$\psi_2^{(mn)}(\vec{r}) = \int_0^\infty \{A_2(\lambda) e^{\lambda x} + B_2(\lambda) e^{-\lambda x} + \frac{e z_0}{D_2 \lambda} e^{-\lambda |x|}\} J_0(\lambda R_{mn}) \lambda d\lambda, \quad (11a)$$

$$\psi_3^{(mn)}(\vec{r}) = \int_0^\infty A_3(\lambda) \{a(\lambda) \exp[-\xi_1(\lambda)x] - b(\lambda) \exp[-\xi_2(\lambda)x]\} J_0(\lambda R_{mn}) \lambda d\lambda, \quad (11b)$$

where

$$A_2 = \eta \omega_2 (1 - e^{2\lambda\beta}) (\omega_2 - e^{2\lambda\delta})^{-1}, \quad (12)$$

$$B_2 = \eta (\omega_2 - e^{2\lambda\gamma}) (\omega_2 - e^{2\lambda\delta})^{-1}, \quad (13)$$

$$A_3 = \eta (1 - \omega_2) (e^{2\lambda\beta} - 1) (\omega_2 - e^{2\lambda\delta})^{-1} [ae^{-\gamma(\lambda+\xi_1)} - be^{-\gamma(\lambda+\xi_2)}]^{-1}, \quad (14)$$

$$\omega_2 = \frac{a(D_2 \xi_1 - D_2 \lambda) \exp[\gamma(\lambda - \xi_1)] - b(D_2 \xi_2 - D_2 \lambda) \exp[\gamma(\lambda - \xi_2)]}{a(D_2 \xi_1 + D_2 \lambda) \exp[\gamma(\lambda - \xi_1)] - b(D_2 \xi_2 + D_2 \lambda) \exp[\gamma(\lambda - \xi_2)]}. \quad (15)$$

$$\pi D_2 A_3(\lambda) \{a(\lambda) \exp[-\xi_1(\lambda)x] - b(\lambda) \exp[-\xi_2(\lambda)x]\} = \int_{-\infty}^\infty \frac{P^{(mn)}(k)}{k_x^2 + \lambda^2} e^{-ik_x x} dk_x, \quad (16)$$

$$\delta = \beta + \gamma, \quad \eta = -e z_0 / D_2 \lambda.$$

In order to determine the function $H_2(x)$, we obtain a solution of Eqn. (3) in the form

$$\frac{d^2 H_2(x)}{dx^2} = -\frac{\kappa^2}{2} \int_0^\infty H_2(x') dx' \frac{d^2}{dx^2} \int_{|x-x'|}^\infty F_2^{(0)}(t) dt.$$

The binary function $F_2^{(0)}(t)$ is physically significant only when $t \geq 0$. However, if we determine it, albeit illegitimately, in the region $t < 0$, we obtain a simpler equation for $H_2(x)$

$$\frac{d^2 H_2(x)}{dx^2} = \frac{\kappa^2}{2} \int_{-\infty}^\infty \frac{dF_2^{(0)}(x-x')}{dx} H_2(x') dx'. \quad (17)$$

If the short-range interaction between the ions is described in terms of a model consisting of rigid spheres with diameter r_0 , the function $F_2^{(0)}(x-x')$ in Eqn. (17) should have the form of two steps:

$$F_2^{(0)}(x-x') = \begin{cases} -1 & (-\infty < x-x' \leq -r_0), \\ 0 & (-r_0 < x-x' < r_0), \\ 1 & (r_0 \leq x-x' < \infty). \end{cases}$$

Eqn. (17) then becomes

$$\frac{d^2 H_2(x)}{dx^2} = \frac{\kappa^2}{2} \int_{-\infty}^\infty \{\delta(x-x'+r_0) + \delta(x-x'-r_0)\} H_2(x') dx',$$

and has the following solution which is accurate enough to satisfy the condition of electroneutrality of the double layer:

$$H_2(x) = C \left\{ \exp\left(-y_1^{(0)} \frac{x}{r_0}\right) - \exp\left[\left(y_2^{(0)} - y_1^{(0)}\right) \left(\frac{x}{r_0} - 1\right) - y_2^{(0)} \frac{x}{r_0}\right] \right\}, \quad (18)$$

where C is an arbitrary constant and $y_1^{(0)}$ and $y_2^{(0)}$ are the roots of the equation $y^2 - (\kappa r_0)^2 \cosh y = 0$ closest to the imaginary axis. On substituting Eqn. (18) in Eqn. (8) and solving the latter, we obtain

$$\psi_3(x) = \frac{C(\kappa r_0)^2}{(y_1^{(0)})^2 (y_2^{(0)})^2} \left\{ (y_2^{(0)})^2 \exp\left(-y_2^{(0)} \frac{x}{r_0}\right) - (y_1^{(0)})^2 \exp\left[\left(y_2^{(0)} - y_1^{(0)}\right) \left(\frac{x}{r_0} - 1\right) - y_2^{(0)} \frac{x}{r_0}\right] \right\}. \quad (19)$$

The condition of electroneutrality of the double layer is defined by

$$\frac{4\pi(q+z)}{D_2 \kappa^2} = \int_{-\infty}^\infty \left\{ \frac{2\pi z}{e z_0} H_1(x, 0) + H_2(x) \right\} dx, \quad (20a)$$

where

$$H_1(x, \lambda) = \frac{1}{(2\pi)^3} \int_{-\infty}^\infty h_1(k_x, \lambda) e^{-ik_x x} dk_x,$$

$h_1(k_x, \lambda)$ being the Fourier component of the function $H_1^{(mn)}(\vec{r})$.

Using Eqns. (18) and (9), we can write condition (20a) as follows:

$$\int_{-\infty}^\infty H_1(x, 0) dx = \frac{2e z_0}{D_2 \kappa^2} \left(1 + \frac{q}{\sigma} + \frac{D_2 M}{4\pi\sigma} \right). \quad (20b)$$

This differs from condition (15) in the previous paper¹ by the multiplier $(1 + q/\sigma + D_2 M/4\pi\sigma)$. The same multiplier also distinguishes the functions $a(\lambda)$ and $b(\lambda)$ from the corresponding formulae in the earlier paper¹. However, it follows from Eqns. (11b), (14), and (15) that a constant common multiplier of $a(\lambda)$ and $b(\lambda)$ does not affect the distribution of potential. This means that the functions $a(\lambda)$, $b(\lambda)$, $\xi_1(\lambda)$, and $\xi_2(\lambda)$ are defined by Eqns. (25)–(27) of Ref. 1.

By definition [Eqn. (10)] we have

$$\frac{\partial \psi_2}{\partial x}(x = -\beta) = \frac{2\pi z}{e z_0} \lim_{\lambda \rightarrow 0} \left\{ A_2 \lambda e^{-\lambda\beta} + B_2 \lambda e^{\lambda\beta} + \frac{e z_0}{D_2} e^{-\lambda\beta} \right\} = \frac{4\pi z}{D_2} \frac{2\gamma - (\partial \omega_2 / \partial \lambda)_{\lambda=0}}{D_2 \delta - (\partial \omega_2 / \partial \lambda)_{\lambda=0}}.$$

Using Eqn. (15), we can find a solution of the system of equations (9):

$$M = -\frac{4\pi q}{D_1} - \frac{4\pi z}{D_2} \times \frac{D_2 y_1^{(0)} y_2^{(0)} [y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}] + D_2 r_0 [(y_2^{(0)})^2 \exp y_2^{(0)} - (y_1^{(0)})^2 \exp y_1^{(0)}]}{D_2 y_1^{(0)} y_2^{(0)} [y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}] + D_2 r_0 [(y_2^{(0)})^2 \exp y_2^{(0)} - (y_1^{(0)})^2 \exp y_1^{(0)}]}. \quad (21)$$

$$\psi_0 = \frac{4\pi q}{D_2} \times \frac{D_2 \delta y_1^{(0)} y_2^{(0)} [y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}] + D_2 r_0 [(y_2^{(0)})^2 \exp y_2^{(0)} - (y_1^{(0)})^2 \exp y_1^{(0)}]}{D_2 y_1^{(0)} y_2^{(0)} [y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}] + D_2 r_0 [(y_2^{(0)})^2 \exp y_2^{(0)} - (y_1^{(0)})^2 \exp y_1^{(0)}]} + \frac{4\pi z D_2 y_1^{(0)} y_2^{(0)} [y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}] + D_2 r_0 [(y_2^{(0)})^2 \exp y_2^{(0)} - (y_1^{(0)})^2 \exp y_1^{(0)}]}{D_2 y_1^{(0)} y_2^{(0)} [y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}] + D_2 r_0 [(y_2^{(0)})^2 \exp y_2^{(0)} - (y_1^{(0)})^2 \exp y_1^{(0)}]}. \quad (22)$$

$$C = \frac{4\pi y_1^{(0)} y_2^{(0)} \exp \left[y_2^{(0)} + \frac{\gamma}{r_0} y_1^{(0)} \right]}{D_2 \kappa^2 r_0 [y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}]} \left\{ q + z \times \frac{D_2 y_1^{(0)} y_2^{(0)} [y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}] + D_2 r_0 [(y_2^{(0)})^2 \exp y_2^{(0)} - (y_1^{(0)})^2 \exp y_1^{(0)}]}{D_2 y_1^{(0)} y_2^{(0)} [y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}] + D_2 r_0 [(y_2^{(0)})^2 \exp y_2^{(0)} - (y_1^{(0)})^2 \exp y_1^{(0)}]} \right\}. \quad (23)$$

The potential in region III, averaged over the coordinates y and z , can be found by means of Eqn. (14) of Ref. 1:

$$\psi_3(x) = \frac{4\pi r_0 (q+z)}{D_2 y_1^{(0)} y_2^{(0)}} \frac{(y_2^{(0)})^2 \exp \left[y_2^{(0)} + \frac{\gamma-x}{r_0} y_1^{(0)} \right] - (y_1^{(0)})^2 \exp \left[y_1^{(0)} + \frac{\gamma-x}{r_0} y_2^{(0)} \right]}{y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}}. \quad (24)$$

The potential jump in the inner region of the double layer is

$$\psi_0 - \bar{\psi}_3(\gamma) = \frac{4\pi q(\beta + \gamma)}{D_1} + \frac{4\pi z\gamma}{D_2}. \quad (25)$$

It is striking that the average potential $\bar{\psi}_3(x)$ and the potential jump in the inner region of the double layer at the electrocapillary maximum ($q = 0$) are the same as those at a dielectric-solution interface.

In the limiting case $\kappa r_0 \ll 1$ we have $y_1^{(0)} = \kappa r_0$ and $y_2^{(0)} = \ln[2/(\kappa r_0)^2]$, and Eqn. (24) becomes

$$\bar{\psi}_3^{(0)}(x) = \frac{4\pi(q+z)}{D_2 \kappa} e^{-\kappa(x-\gamma)};$$

i.e. in region III the average potential varies in accordance with the Gouy-Stern law. This result, which we also obtained in the case of a dielectric-solution interface, reveals the region of applicability in the theory of the diffuse double layer of the linearised Poisson-Boltzmann equation.

SUMMARY

1. The new statistical method¹⁻³ which makes it possible to determine important properties of the discrete electrical double layer at relatively high electrolyte concentrations (up to 0.1–0.5 M) is applicable in investigations of a metal–solution interface.
2. The results obtained show that, as the electrolyte concentration increases, the potential in the diffuse part of the double layer decreases with distance (towards the bulk of the solution) much more rapidly than would follow from the Gouy–Stern theory.

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INTERACTION OF METHYLENE BLUE WITH AMINES

V.V. Yushina and L.A. Nikolaev

A number of compounds containing the amino-group are capable of decolourising Methylene Blue in solutions¹. In our investigation of the catalytic action of this dye in oxidation reactions, we observed that the formation of the leuco-form in some cases occurred at an appreciable rate even in the dark. The action of light as a rule led to a sharp increase in the rate of decolourisation.

This paper describes the action on Methylene Blue of monoethanolamine, diethanolamine, triethanolamine, diethylenetriamine, triethylenetetramine, and polyethylenepolyamine, and its mechanism is discussed.

EXPERIMENTAL

In all cases the change in the optical density of the solution was measured with a spectrophotometer using an automatic recorder of type SF-2M. The amines, purified by vacuum distillation†, were present in solution in a considerable excess in relation to the dye. The concentration of Methylene Blue was usually 8 mg ml⁻¹. The cuvette (volume 2–4 ml) was protected from the access of air by a special lid and in a few experiments a layer of liquid paraffin was placed on the surface of the solution. The illumination was carried out in an air thermostat using a 1000 W lamp at a distance of 30 cm from the illuminated object (cuvette). The absorption maximum of the dye in aqueous

solution is at 668 mμ, and is displaced to 500, 548, 530, and 410 mμ in the presence of monoethanolamine, diethanolamine, diethylenetriamine, and triethylenetetramine respectively.

When dissolved in the amines the dye is converted into semiquinone forms and is rapidly decolourised when the temperature is raised. This process is at least partly reversible, the solution acquiring on cooling the brownish red colour characteristic of the semiquinone. The effect is particularly distinct with polyethylenepolyamine. At room temperature in the dark only diethanolamine is active. Diethylenetriamine and triethylenetetramine are least active.

Table 1 shows the effect of the amines in the dark and during illumination. The duration of illumination was 20 min. The plus sign indicates decolourisation during this period and the minus sign the absence of any effect.

In aqueous solutions the amines are much more active. Almost all of them decolourise the dye both in the dark and on illumination. Polyethylenepolyamine in aqueous solution has little activity in the dark. The curve in Fig. 1 shows the variation of the optical density of the dye solution in diethanolamine (without water) in the dark. The colour is restored when the decolourised solution is shaken with air. Fig. 2 illustrates the fall of the optical density of the dye solution in the dark in the aqueous solution of triethylenetetramine which in the pure state does not decolourise Methylene Blue. The optical density falls rapidly in the initial period and then much more slowly.

Only after illumination of appropriate duration and in the presence of an appropriate concentration of amine in solution is there a sharp weakening of the colour. This

TABLE 1.

Amine in which the dye was dissolved	Effect of the amine	
	In the dark	In the light
Diethanolamine	+	+
Triethanolamine	—	+
Diethylenetriamine	—	—
Triethylenetetramine	—	—
Polyethylenepolyamine	—	+

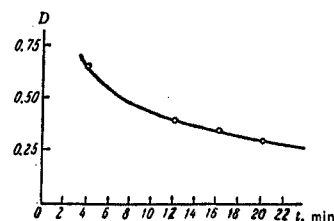


Fig. 1. Variation of the optical density of Methylene Blue solution in pure diethanolamine in the dark. Optical density measured at 668 mμ.

† The polyethylenepolyamine was obtained from the Plastics Institute and was not further purified.