THEORY OF THE ELECTRIC DOUBLE LAYER OF STABILIZED EMULSIONS

BY

E. J. W. VERWEY

(Communicated at the meeting of February 25, 1950)

Introduction.

The electrical double layer at the interface of two inmiscible liquids is of the double diffuse type. It is a well known fact that this double layer is generally insufficient to stabilize an emulsion, i.e. to prevent coalescence of the droplets of one phase dispersed in the other. Special measures have to be taken to obtain such a stability; one of them is the addition of a suitable capillary active electrolyte, i.e. an electrolyte for which one ionic species accumulates at the interface. The system of charges as it is formed at the interface when the electrical double layer is modified by the presence of such an "emulsifier" has never been investigated in detail. This problem is of importance for a better understanding of the colloid chemical properties of an emulsion stabilized in this way. In the present paper we will therefore study the distribution of the charges and the electrical potential for such a system.

1. Theoretical.

The original double layer, present at the interface of two liquids in the absence of capillary active ions, is caused by the circumstance that the positive and negative ions present in the system will generally tend towards a mutually unequal distribution between both phases. In a previous paper ¹) we have derived equations for the distribution of the charges and the electrical potential function of such a double diffuse double layer, on the basis of a GOUY-CHAPMAN type theory. The total electrical potential drop is divided into two parts, one on either side of the interface. It is found that most of the electrical potential drop occurs in the phase with the lowest value of the product $n\varepsilon$, i.e. generally in the phase with the lowest dielectric constant (ε) which nearly always will be the phase with the lowest ionic concentration (n) as well. For sake of convenience this phase will be indicated as the "oil" phase; the other one as the "water" phase.

The equations were derived for a flat double layer. Hence they lose their quantitative validity, for instance, when the dimensions of one phase

¹⁾ VERWEY, E. J. W. and K. F. NIESSEN, Phil. Mag., 28, 435, (1939).

(e.g. oil droplets in an oil-in-water emulsion) are of the order of magnitude of DEBYE's characteristic length $1/\varkappa$ in this phase $\left(\varkappa^2 = \frac{8\pi n \nu^2 e^2}{\epsilon kT}\right)$ or smaller $(\nu = \text{valency of the ions of the electrolyte, supposed to be of the sym$ $metrical type; <math>n = \text{concentration of positive or negative ions per cm}^3$; e, k and T have their usual meaning). For a droplet size of 10^{-3} cm $(10\,\mu)$ this will be the case when the ionic concentration becomes less than 10^{-10} eq./1. In that case the diffuse charge in the oil droplets and accordingly the whole double layer cannot develop completely owing to a lack of space ²).

In the following considerations it is assumed that either the dimensions of the oil droplets or the ionic concentrations in the "oil" are sufficiently large that this complication does not occur.

In the present paper we want to consider the electrical double layer for a two-liquid system, to which an amount of capillary active electrolyte has been added with the result that either the positive or negative ions of this electrolyte have been accumulated in the interface. For the system of charges, as present at the interface, we shall use a model similar to that used in the previous paper. The charge layer due to the adsorbed ions will be treated as a surface charge, coinciding with the mathematical plane of the interface separating the continuous phases 1 and 2. For the charge layers in these phases we use again Goux's theory of the diffuse layer. Hence the dimensions of the ions, including those of the capillary active ions, are neglected. As the theory is only applied to systems containing very small amounts of electrolytes the approximations involved in this model seem to be fairly justified.

The number of capillary active ions which can be adsorbed at the interface is obviously more or less limited, either for sterical reasons, or because the electrical potential at the interface reaches such high values that a further adsorption is inhibited. In this paper we will not be dealing with this distribution equilibrium of the capillary active ions themselves. Considering only the electrical problem, we shall treat the surface charge as a given quantity, effected, as a first approximation, by the complete adsorption of such ions added to the system. This assumption of a complete adsorption seems to be a reasonable one for those cases where one phase has a large dielectric constant or a strongly polar character (e.g. water) and the second phase has a low dielectric constant or a non-polar character (e.g. a hydrocarbon). The capillary active ions are generally ions containing a relatively large non-polar group (e.g. a hydrocarbon chain) and a polar, ionogenic end where the ionic charge is located. The polar end restricts the solubility in the oil phase, the non-polar part favours a rather low solubility in the aqueous phase. At the interface, however, where the ion can be oriented in such a way that the polar end

²) VERWEY, E. J. W. and J. TH. G. OVERBEEK, Theory of the Stability of Lyophobic Colloids, Amsterdam, 133 (1948).

is embedded into the water phase and the non-polar part has the oil phase as its immediate surroundings, a maximal amount of interaction is possible, and accordingly the surface active ion has there a much lower energy than in the bulk of either of the two phases. Hence the capillary active ion will accumulate almost completely in the interface.

In those cases where the second phase has still a rather high dielectric constant or a more or less polar character (e.g. in the system water/nitrobenzene) the assumption of complete adsorption of the surface active ion may be less justified. Hence in such a case the theory given in the present paper can only be applied if sufficient information is available about the distribution equilibrium of the capillary active electrolyte and about the electrolytic dissociation of this electrolyte in both phases.

The value of the double layer potential of the original double layer depends on the nature of the electrolytes present in the system. Also the inactive ion of the capillary active electrolyte will take part in the distribution equilibrium and accordingly may alter this value of the double layer potential. However, the conditions at the interface are changed so radically by the presence of the capillary active ions that a possible change of the total double layer potential by the addition of the capillary active electrolyte becomes of minor importance in the final picture. Hence, for the sake of simplicity, we shall neglect this influence of the second ion, and assume that the capillary active electrolyte does not change appreciably the double layer potential of the original double layer.

Following the notation in our previous paper, also summarized in Fig. 1, the double layer potential considered above will be given by

$$\Delta = \frac{e(\varphi_1 - r_2)}{kT}$$

and the partial potential drops in the phases 1 and 2 by

$$-z_1 = -\frac{v_1 e \psi_1(0)}{kT}$$
 and $z_2 = \frac{v_2 e \psi_2(0)}{kT}$

so that

$$\triangle = -z_1 + z_2$$

If the surface charge is denoted by σ , the condition of electrical neutrality yields the basic equation:

$$-\varepsilon_1\int_{-\infty}^0\frac{\mathrm{d}^2\psi_1}{\mathrm{d}\,x^2}\,\mathrm{d}\,x+4\,\pi\,\sigma-\varepsilon_2\int_0^\infty\frac{\mathrm{d}^2\psi_2}{\mathrm{d}\,x^2}\,\mathrm{d}\,x=0.$$

Integration leads to

$$-\varepsilon_1 \varkappa_1 \frac{kT}{e} \left(\mathrm{e}^{z_1/2} - \mathrm{e}^{-z_1/2} \right) + 4\pi\sigma - \varepsilon_2 \varkappa_2 \frac{kT}{e} \left(\mathrm{e}^{z_2/2} - \mathrm{e}^{-z_1/2} \right) = 0$$

$$\mathbf{e}^{\mathbf{z}_1} - \frac{\mathbf{e}}{\mathbf{k}T} \cdot \frac{4 \pi \sigma}{\mathbf{\varepsilon}_1 \mathbf{x}_1 + \mathbf{\varepsilon}_2 \mathbf{x}_2 \cdot \mathbf{e}^{\Delta/2}} \cdot \mathbf{e}^{\mathbf{z}_1/2} - \frac{\mathbf{\varepsilon}_1 \mathbf{x}_1 + \mathbf{\varepsilon}_2 \mathbf{x}_2 \mathbf{e}^{-\Delta/2}}{\mathbf{\varepsilon}_1 \mathbf{x}_1 + \mathbf{\varepsilon}_2 \mathbf{x}_2 \mathbf{e}^{\Delta/2}} = 0$$

or

with the solution

(1)
$$e^{z_1/2} = \frac{e}{kT} \cdot \frac{2\pi\sigma}{\varepsilon_1 \varkappa_1 + \varepsilon_2 \varkappa_2 e^{\Delta/2}} \pm \left[\left(\frac{e}{kT} \cdot \frac{2\pi\sigma}{\varepsilon_1 \varkappa_1 + \varepsilon_2 \varkappa_2 \cdot e^{\Delta/2}} \right)^2 + \frac{\varepsilon_1 \varkappa_1 + \varepsilon_2 \varkappa_2 e^{-\Delta/2}}{\varepsilon_1 \varkappa_1 + \varepsilon_2 \varkappa_2 e^{\Delta/2}} \right]^{1/2}$$

As $e^{z_1/2}$ cannot be negative we need only consider the positive root and can omit the negative sign in eq. (1). For $\sigma = 0$ this equation reduces to

(2)
$$e^{z_1^0} = \frac{\varepsilon_1 \varkappa_1 + \varepsilon_2 \varkappa_2 e^{-\Delta/2}}{\varepsilon_1 \varkappa_1 + \varepsilon_2 \varkappa_2 e^{\Delta/2}},$$

which was already derived in reference 1.



Fig. 1. Electrical potential function associated with the electrolytical double layer at the interface of two liquids for:

Partial potential drops as calculated for this case with the aid of eq. (2):

$$\begin{array}{ll} -\psi_1 \left(0 \right) = & 7.8 \text{ mV or } -z_1 = 0.31; \\ \psi_2 \left(0 \right) = 107.2 \text{ mV or } & z_2 = 4.29 \end{array}$$

Equation (1) can be modified by introducing as a variable the quantity $z_1 - z_1^0$, i.e. the electrical potential at the interface relative to that for $\sigma = 0$. It can be brought into the form

(1a)
$$e^{\frac{z_1-z_1^0}{2}} = A + \sqrt{1+A^2}$$

380

where

$$A = \frac{e}{kT} \frac{2 \pi \sigma}{\{(\varepsilon_1 \varkappa_1 + \varepsilon_2 \varkappa_2 e^{\Delta/2}) (\varepsilon_1 \varkappa_1 + \varepsilon_2 \varkappa_2 e^{-\Delta/2})\}^{1/2}}$$

This equation expresses directly that $z_1 - z_1^0$ is positive for positive values of σ and negative for negative σ . It shows, too, that the absolute value of $z_1 - z_1^0$ is independent of the sign of the surface charge, as

$$\mathrm{e}^{\frac{z_1-z_1^0}{2}} = \{A + \sqrt{1+A^2}\}^{-1} = -A + \sqrt{1+A^2}$$

2. Discussion.

Eq. (1) or (1a) give us immediately the partition of the electrical potential between both phases as a function of the surface charge.

The problem is symmetrical in phases 1 and 2 and in positive and negative values of the potential and we will select arbitrarily the case

$$\varepsilon_1 \varkappa_1 > \varepsilon_2 \varkappa_2$$
 and $\triangle = \text{positive}$.

By considering then the two possibilities

$$\sigma = \text{positive}$$
 and $\sigma = \text{negative}$

we will have covered all eight possible permutations, comprising two groups of four mutually equivalent cases.

(a) $\varepsilon_1 \varkappa_1 > \varepsilon_2 \varkappa_2$, $\triangle = \text{positive}, \sigma = \text{positive}.$

This case is representative for the more general case that the surface charge at the interface has the same sign as the charge in the aqueous phase. We will investigate how the electrical potential function at the interface of the two liquids is changed by a gradually increasing surface charge.

We start from a situation as depicted in Fig. 1, showing the electrical potential as a function of the distance perpendicular to the interface for $\sigma = 0$. The aqueous phase (= phase 1) carries a positive space charge, the oil phase a negative one. The interface has a weak negative potential with reference to a point far in the aqueous solution ($z_1 =$ negative), a comparatively large positive potential with respect to the bulk of the oil phase ($z_2 =$ positive); the potential drop extends farther into the oil phase than into the water phase ($\varkappa_1 > \varkappa_2$). It has been assumed that also $\varepsilon_1 > \varepsilon_2$ and $\varepsilon_1 \varkappa_1 \gg \varepsilon_2 \varkappa_2$.

Now eq. (1) shows that, with increasing positive values of σ , the quantity $e^{z_1/2}$, starting with a value between 0 and 1, increases continually. Hence the value of $-z_1$ decreases and z_2 increases. Initially the space charge in the water phase and the surface charge are positive; together they are balanced by a negative charge in the oil phase. For a certain value of σ the quantity $e^{z_1/2}$ reaches 1, or $z_1 = 0$. In this point the potential drop and the charge in the aqueous phase are both zero, and we have only a positive surface charge balanced by a negative space charge in

the oil phase. For still larger values of σ we enter finally the region $e^{z_1/2} > 1$, or z_1 positive. The space charge and the potential drop in phase 1 are now inversed in sign, and the electrical potential function reaches a peak value at the interface. Hence we have now obtained a true *triple layer*: a positive surface charge surrounded at two sides by negative space charges. In an oil-in-water emulsion of corresponding properties the positive capillary active ions will convert the charge of the oil droplets (including the adsorbed layer) from a negative into a positive one. Also the ζ -potential of the oil droplets, the sign of which is determined by the sign of the potential gradient in the aqueous phase, will be converted from a negative into a positive value at this "inversion point" ³).

Fig. 2 shows a number of electrical potential curves for different magnitudes of the surface charge.

Qualitatively, these results are not surprising. It is of interest, however, to investigate what factors determine the amount of adsorbed ions in the inversion point, the form of the electrical potential curve, etc.

The inversion point is reached for $e^{z_1/2} = 1$.

Substituting this into (1), or more simply into the quadratic equation of which (1) is the solution, we find the following relation for σ ($z_1 = 0$) or σ_0 :

(3)
$$4 \pi \sigma_0 \cdot \frac{e}{kT} = \varepsilon_2 \varkappa_2 (e^{\Delta/2} - e^{-\Delta/2}).$$

This result may be illustrated by a numerical example. We will assume that the electrolyte is one-one valent (v = 1), that the oil phase contains only 10^{-10} eq./1 of dissociated electrolyte and that the dielectric constant of this phase is of the order of one tenth that of water, hence $\varepsilon_2 \varkappa_2 = 10^4$ cm⁻¹. Supposing now that $\varphi_1 - \varphi_2 = 460$ mV (or $e^{\Delta/2} = 10^4$) we find a value of σ_0 corresponding to 1.7×10^{12} elementary charges per cm². For $\varphi_1 - \varphi_2 = 230$ mV (or $e^{\Delta/2} = 10^2$) we find accordingly a value of only 1.7×10^{10} charges/cm². Especially the latter value corresponds to a relatively thin packing density of the capillary active ions in the interface, considering that the maximal amount to be adsorbed for this type of ions is of the order of 10^{14} ions/cm².

Such low values for $\varepsilon_2 \varkappa_2 e^{\Delta/2}$, and therefore for σ_0 , will only be found when the "oil" phase is completely non-polar and accordingly its ionic concentration in equilibrium with an "aqueous" phase containing small amounts of electrolyte is extremely low. In many cases, however, the chemical difference between the two immiscible liquids may be less, or the system may contain some electrolyte, so that $\varepsilon_2 \varkappa_2$ is not so small. It may also be, in some cases, that the double layer potential is rather

³) Hence we use the concept "inversion" here in the limited sense of inversion of potential or charge. This inversion should not be confused with the inversion of an emulsion, being the transformation of for instance an oil-in-water system into a water-in-oil emulsion.



Fig. 2. Same as fig. 1, for the case that the interface carries a surface charge σ of the magnitude as indicated with each curve (σ in elementary charges per cm²; electrical potential in units kT/e = 25 millivolts).

high (or that the valency of the electrolyte is high). The double layer potential is greatly determined by differences between the solvation energies of positive and negative ions in both phases⁴) and may easily reach values of several hundreds of millivolts. For such cases we must expect that much larger quantities of capillary active ions are necessary to neutralize the original double layer and reach the inversion point. It may even be that they would exceed saturation quantities and cannot be realized at all. Actually different two-liquid systems show marked differences in their liability to be converted into the form of an emulsion with the aid of an emulsifier and also in the stability of the emulsions thus obtained. Our equations enable, however, to distinguish between the different factors determining these phenomena. We also see the

importance of conductivity measurements and of experimental determination of double layer potentials for different sets of liquids as preliminaries to the study of emulsification by capillary active ions.

For relatively large values of σ , i.e. for the case that the triple layer is well developed, we can easily derive approximate equations for the charge distribution and the electrical potential at the interface. As soon as the first term under the square root becomes much larger than the second one equation (1) approaches

(4)
$$e^{z_1/2} = \frac{e}{kT} \cdot \frac{4 \pi \sigma}{\varepsilon_1 \varkappa_1 + \varepsilon_2 \varkappa_2 e^{\Delta/2}}.$$

Under these conditions z_1 reaches appreciable values so that also $e^{-z_2/2}$ can be neglected against $e^{z_1/2}$, and a fortiori $e^{-z_2/2}$ against $e^{z_2/2}$. The ratio of the space charges in both phases

$$R = Q_1/Q_2,$$

which according to the derivation in section 1, equals

$$R = \frac{\varepsilon_1 \,\varkappa_1 \,(\mathrm{e}^{z_1/2} - \mathrm{e}^{-z_1/2})}{\varepsilon_2 \,\varkappa_2 \,(\mathrm{e}^{z_2/2} - \mathrm{e}^{-z_1/2})} \,,$$

approaches then the simple equation

(5)
$$R = \frac{\varepsilon_1 \varkappa_1}{\varepsilon_2 \varkappa_2 e^{\Delta/2}}.$$

Both equations (4) and (5) show that the relative importance of the values $\varepsilon_1 \varkappa_1$ and $\varepsilon_2 \varkappa_2 \cdot e^{\Delta/2}$ greatly determines the properties of the triple layer. In the extreme case that

$$\varepsilon_1 \varkappa_1 \gg \varepsilon_2 \varkappa_2 \cdot \mathrm{e}^{\Delta/2}$$

we will find that the space charge balancing the surface charge due to the adsorbed layer is predominantly found in the aqueous phase. Simultaneously eq. (4) approaches the equation for the electrical potential

⁴) VERWEY, E. J. W., Rec. trav. chim., **61**, 127 (1942). Rec. trav. chim., **61**, 564 (1942). drop in a double layer of the GOUX-type (surface charge balanced at one side by a diffuse space charge), which, for large values of z, reads

$$\mathrm{e}^{z/2} = rac{e}{kT} \cdot rac{4 \,\pi \,\sigma}{\epsilon \,\varkappa} \,.$$

How for $\varepsilon_1 \varkappa_1 > \varepsilon_2 \varkappa_2 e^{\Delta/2}$ the electrical potential function at the aqueous side of the triple layer approaches that of a simple Gouv layer may again be illustrated by a numerical example (1 — 1 valent electrolyte), assuming that $\varepsilon_1 \varkappa_1 = 10^7$ cm⁻¹ (roughly corresponding to distilled water), $\varepsilon_2 \varkappa_2 = 10^4$ cm⁻¹, and $\sigma = 10^{14}$ adsorbed ions per cm²:

$$\begin{aligned} \varphi_1 - \varphi_2 &= 230 \text{ mV}, \ \varepsilon_2 \varkappa_2 \cdot \mathrm{e}^{\Delta/2} = 10^6 \text{ cm}^{-1}, \ z_1 &= 13.0 \text{ or } \psi_1(0) = 325 \text{ mV} \\ \varphi_1 - \varphi_2 &= 460 \text{ mV}, \ \varepsilon_2 \varkappa_2 \cdot \mathrm{e}^{\Delta/2} = 10^8 \text{ cm}^{-1}, \ z_1 &= 8.4 \text{ or } \psi_1(0) = 210 \text{ mV} \end{aligned}$$

Hence we see that in the second case the peak potential is appreciably lowered by the presence of the positive space charge in the "oil" phase. In the first case the potential is almost equal to that for a GOUY layer with a charge of 10^{14} charges/cm², viz. 330 mV.

(b) $\varepsilon_1 \varkappa_1 > \varepsilon_2 \varkappa_2$, $\triangle = \text{positive}$, $\sigma = \text{negative}$.

If the surface charge has a sign opposite to that of the charge of the aqueous phase, the phenomena are more or less the inversal of those in case (a). With increasing negative σ the potential at the interface with respect to the bulk of the aqueous solution will be lowered and the potential drop in this phase increases therefore continually. It is now the oil phase in which the charge will be inversed in sign. Quantitatively, however, the changes induced by this surface charge will be different, corresponding to the fact that we start from an unequal distribution of the potential drop. Actually, the surface charge for which z_2 goes through zero (σ_{00}) is given by the equation (equivalent to eq. (3)):

$$4\pi\sigma_{00}\cdotrac{e}{kT}=arepsilon_1\,arkappa_1\,(\mathrm{e}^{-\Delta/2}-\mathrm{e}^{\Delta/2})$$

and, because $\varepsilon_1 \varkappa_1 > \varepsilon_2 \varkappa_2$, $|\sigma_{00}|$ will always be larger than $|\sigma_0|$.

For still larger values of $-\sigma_{00}$ the potential z_2 becomes negative and we have again a triple layer in which now a negative surface charge is balanced by positive space charges at either side of the interface.

Assuming again 1 - 1 valent electrolyte, and $\triangle = 9.2$, we find following values for σ_{00} for different values of $\varepsilon_1 \varkappa_1$:

$$\begin{split} \varepsilon_1 \varkappa_1 &= 10^7 \text{ cm}^{-1} \text{ (distilled water):} - 4\pi \sigma_{00} \cdot \frac{e}{kT} = 10^9 \text{ or } \sigma_{00} = 1.7 \times 10^{13} \\ & \text{ionic charges/cm}^2 \end{split}$$

$$\epsilon_1 \varkappa_1 = 10^8 \, {\rm cm}^{-1} \, (\infty \, 10^{-3} \, {\rm n. \ electrolyte}): \sigma_{00} = 1.7 \times 10^{14} \, {\rm ionic \ charges/cm^2}.$$

The latter value is already about the maximal amount of capillary active ions which can be adsorbed per cm². Hence saturation may easily be attained in this case before this second inversion point is reached, especially if, for instance, $\varphi_1 - \varphi_2$ is still larger than 230 mV.

Both cases (a) and (b) are summarized in the set of curves of Fig. 2, representing the electrical potential function in the neighbourhood of the interface for different values of σ . In this graph, holding again for 1-1 valent electrolyte, the physical constants have been chosen such that

$$arepsilon_1arkappa_2 > arepsilon_2arkappa_2\cdot \mathrm{e}^{ riangle/2}$$

In order to enable a better illustration of the properties of these curves both the chemical differences between the two media and the value of the double layer potential were assumed to be rather small $(\varepsilon_1 \varkappa_1 = 27 \cdot \varepsilon_2 \varkappa_2;$ $e^{\Delta/2} = 10$). Also the ratio R does not differ very much from 1 (for large values of $|\sigma|$, see eq. (5), R = 2.7). Accordingly for large values of the surface charge the space charges at both sides of the interface are roughly of the same order of magnitude (27/37 part of the total charge in the aqueous phase, 10/37 in the oil phase).

Some data for z_1 and z_2 , corresponding to the case of Fig. 2 are given in Table I. The values of z_1 and z_2 are symmetrical with respect to the values z_1^0 and z_2^0 , for equal absolute values of the surface charge, as expressed by eq. (1a).

σ/e	<i>z</i> 1	2 ₂	σ/e	<i>z</i> 1	z ₂
0	- 0.31	4.29	0	— 0.31	4.29
1010	- 0.24	4.36	- 1010	- 0.38	4.22
$0.42 imes 10^{11}$	0	4.6	$-0.42 imes 10^{11}$	- 0.62	3.98
1011	0.43	5.03	-10^{11}	- 1.05	3.55
1012	3.77	8.37	-10^{12}	- 4.36	0.24
	-		$-1.11 imes 10^{12}$	- 4.6	0
1013	8.34	12.94	- 1013	- 8.96	-4.36
1014	12.95	17.55	1014	-13.57	- 8.97

TABLE I

In conclusion, the author wishes to thank Prof. H. EILERS and Dr M. VAN DER WAARDEN of the Koninklijke / Shell Laboratory, Amsterdam, for a number of valuable remarks.

Summary.

The electrical potential function and the distribution of the charges at the interface of two inmiscible liquids have been calculated, with the aid of a GOUY-CHAPMAN type of theory, for the case that in addition to the original double layer a surface charge is present at the interface.

> Natuurkundig Laboratorium N.V. Philips' Gloeilampenfabrieken, Eindhoven.