

## GENERAL DISCUSSION

**Dr. P. Richmond** (*Unilever, Port Sunlight*) said: I would question the use of eqn (1.1) to obtain molecular polarizabilities. On a macroscopic scale it is true that

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$$

where  $\mathbf{D}$  is the electric displacement,  $\mathbf{E}$  the electric field and  $\mathbf{P}$  the polarization and, if one introduces the permittivity  $\epsilon$  and polarizability  $\chi$  in the usual way, one has

$$\epsilon\mathbf{E} = (1 + 4\pi\chi)\mathbf{E}.$$

However, it is not true in general for condensed media that the *molecular* polarizability  $\alpha$  is given by the relation  $\chi = v\alpha$ , i.e.,  $\epsilon = 1 + 4\pi v\alpha$  where  $v$  is the number density. This latter relation only holds in dilute (gaseous) systems, i.e.,  $4\pi v\alpha \ll 1$ . More generally one might use the Clausius-Mossotti equation:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi v\alpha}{3}$$

which yields for  $4\pi v\alpha = 15/8$  for  $\epsilon \approx 6$ . Even this may not be valid for  $\epsilon$  as high as 6 and one could then use the Kirkwood equations:

$$\frac{(\epsilon - 1)}{(2\epsilon + 1)9\epsilon} = 4\pi v\alpha$$

which yields  $4\pi v\alpha = 5/702$ !

Of course one can always *define* "quasi-molecular" polarizability  $\alpha'$  such that  $\chi = v\alpha'$  but  $\alpha'$  (which is not the same as  $\alpha$ ) must then be accepted as an adjustable parameter.

In any case rather than try and relate  $\alpha$  to an uncertain macroscopic parameter  $\epsilon$ , it would probably be more profitable to understand physically how an anomalously large value of  $\alpha$  could arise.

**Dr. S. Levine** (*Manchester*) (*partly communicated*): It would appear from Richmond's remarks that in our paper eqn (1.1) yields values of the molecular polarizability  $\alpha$  which are too large. However, the dielectric properties of the Stern inner region (our monolayer region) can be quite different from those of the bulk medium having the same composition. In a series of papers <sup>1, 2</sup> and also in a review article <sup>3</sup> Macdonald and Barlow have formulated a quasi-microscopic theory of the dielectric properties of the inner region at the metal/electrolyte solution interface. We make use of their work here in obtaining a general relation between the dielectric constant  $\epsilon_\infty$  and the volume density of molecules  $v$ , for the inner region, of which (1.1) is a special case. We introduce an effective field  $\mathcal{E}_{\text{eff}}$  which acts on a molecule in the inner region, normal to the interface and write this as

$$\mathcal{E}_{\text{eff}} = \mathcal{D} + 4\pi S(\mathcal{P}_1 + \mathcal{P}_2). \quad (1)$$

Here  $\mathcal{D}$  is the normal component of the electric field due to the true charge (the dielectric displacement which equals  $4\pi\sigma_0$ ) and the second term on the right-hand side

<sup>1</sup> J. R. Macdonald and C. A. Barlow, *J. Chem. Phys.*, 1962, **36**, 3062; 1963, **39**, 412; 1966, **44**, 202.

<sup>2</sup> J. R. Macdonald and C. A. Barlow, *Electrochemistry* (Proc. 1st Australian Conf., 1963), ed. J. A. Friend and F. Gutman (Pergamon, London, 1964), p. 199.

<sup>3</sup> C. A. Barlow and J. R. Macdonald, *Adv. Electrochem. Electrochem. Eng.*, 1967, **6**, 1.

of (1) is that part of  $\mathcal{E}_{\text{eff}}$  which is produced by the distribution of dipoles surrounding the given molecule.  $\mathcal{P}_1$  and  $\mathcal{P}_2$  are the polarisations normal to the interface contributed by the induced and permanent dipole moments of the molecules in the inner region, respectively.  $S$  is a constant which depends on the imaging, the local microscopic structure of the inner region and the type of molecular polarisation. The induced polarisation  $\mathcal{P}_1$  is related to  $\mathcal{E}_{\text{eff}}$  and to  $\mathcal{E}$ , the normal component of the ordinary electric field, by

$$\mathcal{P}_1 = v\alpha\mathcal{E}_{\text{eff}} = k_1\mathcal{E}, \quad (2)$$

where  $k_1$  is the susceptibility associated with all dipole effects other than those due to permanent dipoles. We define  $\varepsilon_\infty$  by the relation

$$\varepsilon_\infty = 1 + 4\pi k_1. \quad (3)$$

If  $\langle\mu\rangle$  is the average value of the permanent dipole moment normal to the interface, then

$$\mathcal{P}_2 = v\langle\mu\rangle. \quad (4)$$

Finally

$$\mathcal{D} = \mathcal{E} + 4\pi(\mathcal{P}_1 + \mathcal{P}_2). \quad (5)$$

From the above relations we can derive an expression for  $\alpha$  namely

$$\frac{1}{\alpha} = \frac{4\pi v}{(\varepsilon_\infty - 1)} \left[ 1 + (\varepsilon_\infty - 1)(S + 1) + 4\pi(S + 1)v \frac{\langle\mu\rangle}{\mathcal{E}} \right]. \quad (6)$$

An upper estimate of  $\alpha$  is obtained by neglecting the last term in the square brackets.

To estimate  $S$  we assume that the value  $\varepsilon_\infty = 6$  chosen in our paper refers to very high electric fields ( $\mathcal{E} \gtrsim 10^8 \text{ V cm}^{-1}$ ), where the omission of the last term in (6) does not cause a serious over-estimate of  $\alpha$ . In classical electrostatic theory of condensed dielectric media under the influence of an electric field  $\mathcal{E}$ , a typical molecule is imagined to be situated in a cavity having one of three particular simple shapes, needle-like, spherical and disc-like. The effective electric fields acting on the molecule situated at the centre of a cavity are respectively

$$\mathcal{E}_{\text{eff}} = \mathcal{E}, \quad \mathcal{E}_{\text{eff}} = \mathcal{E} + \frac{4\pi}{3}\mathcal{P}_1, \quad \mathcal{E}_{\text{eff}} = \mathcal{E} + 4\pi\mathcal{P}_1, \quad (7)$$

where we are neglecting  $\mathcal{P}_2$ . Here all quantities define magnitudes of vectors, provided the axis of the needle is parallel, and the faces of the disc normal, to the electric field. On combining (7) with (1)–(6) we find that  $S = 1$ ,  $-\frac{2}{3}$  and 0 respectively for the three cavity shapes and therefore

$$\alpha = \frac{\varepsilon_\infty - 1}{4\pi v}, \quad \alpha = \frac{3}{4\pi v} \frac{(\varepsilon_\infty - 1)}{(\varepsilon_\infty + 2)}, \quad \alpha = \frac{1}{4\pi v} \frac{(\varepsilon_\infty - 1)}{\varepsilon_\infty} \quad (8)$$

respectively. The first relation in (8) is eqn (1.1) and the second one Clausius–Mosotti. None of the relations in (8) is really satisfactory, bearing in mind the neglect of  $\mathcal{P}_2$  and, as suggested by Richmond,  $\alpha$  should best be regarded as an adjustable parameter. For  $\varepsilon_\infty = 6$ , the three formulae in (7) give  $\alpha$  in the ratio 1:3/8:1/6.

The following considerations give support to choosing the needle-shaped cavity for the monolayer model in our paper. This illustrates the point made above about the difference between the Stern region and the bulk medium, since the spherical cavity seems more appropriate with the latter. In (2.1), the quantities  $\mathcal{E}_0 + \mathcal{E}_w$  and  $\mathcal{E}_0 + \mathcal{E}_a$  are the total effective fields acting on the water and alcohol molecules respec-

tively, where  $\mathcal{E}_w$  and  $\mathcal{E}_a$  are the contributions from the dipole terms. Consider the possible relations

$$\mathcal{E} = -\frac{\Delta V}{d} \approx \theta_w \mathcal{E}_w + \theta_a \mathcal{E}_a = h \mathcal{E}_w, \quad (9)$$

where  $\Delta V$  is the potential drop across the monolayer region as defined in (3.14). If the second relation in (9) is a good approximation, then this is a strong indication that for a molecule in the Stern region, the effective field due to dipoles  $\mathcal{E}_{\text{eff}} \approx \mathcal{E}$ , implying that a needle-shaped cavity is the appropriate one. It is sufficient to test (9) at the two extremes of pure water and pure alcohol. At the pure water end,  $\theta_w = 1$ ,  $\theta_a = 0$ ,  $r_a = 0$ ,  $k = 1$ ,  $q_2 = q_4 = \alpha_w$  and (3.14) simplifies to

$$\Delta V = -\frac{8\pi}{d^2\sqrt{3}} \frac{(r_w p_w - \alpha_w \mathcal{E}_0)}{(1 + \alpha_w c_e/d^3)}, \quad (10)$$

introducing  $N_s = 2/(d^2\sqrt{3})$  for a hexagonal lattice. On examining the corresponding limiting form of (2.18) for  $\mathcal{E}_w$  we find that

$$-\frac{\Delta V}{\mathcal{E}_w d} = \frac{8\pi}{\sqrt{3}c_e} \approx 0.967, \quad (11)$$

since  $c$  is replaced by  $c_e = 15$  in (2.18) to account for non-nearest neighbour interactions between dipoles. At the pure alcohol end,  $\theta_a = 1$ ,  $\theta_w = 0$ ,  $r_w = 0$ ,  $h = 2/3$ ,  $q_2 = \frac{1}{4}q\alpha_a$ ,  $q_4 = \frac{1}{2}q^2\alpha_a$  and (3.14) becomes

$$\Delta V = -\frac{8\pi}{d^2\sqrt{3}} \frac{(r_a p_a - \alpha_a E_0)}{\left(1 + \frac{3}{16} \frac{\alpha_a c_e q^2}{d^3}\right)}. \quad (12)$$

Using (2.11) and (2.18), we now have

$$-\frac{\Delta V}{\mathcal{E}_a d} = \frac{64\pi}{3\sqrt{3}c_e q^2} \approx 0.928, \quad (13)$$

if  $q = 2(1 - 1/c)$  with  $c = 6$ . A value  $c = 15$  in the definition of  $q$  yields for the above ratio the value 0.740, which is consistent with our finding that  $c = 6$  is the better choice. The electric fields  $\mathcal{E}_w$  and  $\mathcal{E}_a$  vary along a line in the inner region normal to the interface, having maxima on the common plane of centres of the water and alcohol dipoles. This implies that the estimates in (11) and (13) are too low.

Originally we expected that larger values of the polarisabilities  $\alpha_w$  and  $\alpha_a$  would reduce the potential drop  $\Delta V$  due to dipole effects. However, it is clear from fig. 4 in our paper that  $\Delta V$  remains high when  $\alpha_w$  and  $\alpha_a$  are derived from (1.1). Some calculations of  $\Delta V$  have been carried out with values of  $\alpha_w$  and  $\alpha_a$  reduced by the fraction  $\frac{2}{3}$ , according to the Clausius-Mosotti relation, but  $\Delta V$  is found to change only slightly. This behaviour can be understood by examining the approximate form in (9) for  $\Delta V$ . The two terms in the numerator of the expression (2.18) for  $\mathcal{E}_w$  have the same sign over the greater part of the ranges in  $\sigma_0$  and  $\theta_a$ . For example, if  $\sigma_0 > 0$ ,  $\mathcal{E}_0 > 0$ ,  $r_w < 0$  and  $m_p < 0$  except for small  $\sigma_0$  and near the pure alcohol end. The depolarising term  $A$  in the denominator of (2.18) increases with  $\alpha_w$  and  $\alpha_a$ , thereby reducing  $\Delta V$  but this is compensated by a corresponding increase in the term  $-q_2 \mathcal{E}_0$  in the numerator. The quantities  $m_p$  and  $q_2 \mathcal{E}_0$  represent permanent and induced dipole moments, which point in opposite directions, but their difference occurs in the expression (2.18) for  $\mathcal{E}_w$ . It appears that to reduce the magnitude of  $\Delta V$  we must assume one or more of: (i) dipoles of the molecules in the monolayer region pointing

at some angle to the normal, (ii) a smaller surface density of dipoles, (iii) formation of clusters having a smaller resultant dipole moment, as mentioned by Parsons. Conway and Dhar [ref. (5) of our paper] suggest that  $\Delta V$  should be reduced by the factor  $\epsilon_\infty$ . However, once the depolarising effect has been treated in the manner described in our paper such a step means making the same correction twice. The source of a large  $\Delta V$  is an inadequate molecular model for the water + methanol mixture, a point on which we agree with Parsons.

**Prof. J. Lyklema (Wageningen)** said: It is generally observed that the adsorption of dipolar organic molecules at charged surfaces passes through a maximum as a function of  $\sigma_0$ . The surface charge  $\sigma_{0m}$  where this maximum is located is usually virtually independent of the bulk activity of the organic substance, i.e.,

$$\left(\frac{\partial\theta_a}{\partial\sigma_0}\right)_{\sigma_0<\sigma_{0m}} > 0, \quad \left(\frac{\partial\theta_a}{\partial\sigma_0}\right)_{\sigma_0=\sigma_{0m}} = 0, \quad \left(\frac{\partial\theta_a}{\partial\sigma_0}\right)_{\sigma_0>\sigma_{0m}} < 0$$

It appears that fig. 2 of the paper by Levine *et al.* does not represent this trend.

**Dr. R. Parsons (Bristol)** said: This paper represents a useful extension to the previous work of Levine *et al.*, but I feel that it is applied to the wrong system. There is a good deal of evidence<sup>1</sup> especially with mercury electrodes that the main effect of the addition of aliphatic alcohols on the capacity of a mercury electrode in an aqueous electrolyte can be ascribed to an increase in thickness of the inner layer. The model proposed in this paper would be more appropriate to systems containing a bifunctional organic molecule like glycol,<sup>2</sup> butane-1,4-diol<sup>3</sup> or even glycine<sup>4</sup> where it appears that the molecule is oriented with its long axis parallel to the interface. In this case a model of constant thickness but with the organic molecule occupying more sites on the electrode surface than the water would be a good approximation. It is the change in thickness which causes the strong charge dependence of the adsorption. Hence the constant inner layer thickness in the present model leads to the very small dependence on charge pointed out by Lyklema.

Secondly, I believe that the model in this paper does not start with the best assumptions concerning the water molecules in the interface, in that it is assumed that the molecules are essentially independent except for the dipole-dipole interaction. Such a model does not seem to be able to account for the difference of capacity between H<sub>2</sub>O and D<sub>2</sub>O solutions<sup>5</sup> or for the observation that the Langmuir isotherm fits the adsorption of organic molecules with an area several times that of water.<sup>6, 7</sup> The simplest model which shows a possibility of accounting for these observations is one in which water forms small clusters<sup>8</sup> of about three molecules probably limited by hydrogen bonds. A recent development of this simple model<sup>9</sup> has shown that it is possible to account in a reasonably quantitative way for the general shape of the capacity curve of mercury in aqueous solutions and especially the way this varies with temperature.<sup>10</sup> Although this model is certainly oversimplified it seems to

<sup>1</sup> R. Payne, *Adv. Electrochem. Electrochem. Eng.*, 1970, **7**, 1.

<sup>2</sup> S. Trasatti, *J. Electroanal. Chem.*, 1970, **28**, 257.

<sup>3</sup> E. Dutkiewicz, J. D. Garnish and R. Parsons, *J. Electroanal. Chem.*, 1968, **16**, 505.

<sup>4</sup> L. Baugh and R. Parsons, *J. Electroanal. Chem.*, 1973, **41**, 311.

<sup>5</sup> R. Parsons, R. M. Reeves and P. N. Taylor, *J. Electroanal. Chem.*, 1974, **50**, 149.

<sup>6</sup> R. Parsons, *J. Electroanal. Chem.*, 1964, **8**, 93.

<sup>7</sup> B. B. Damaskin, *Elektrokhimiya*, 1965, **1**, 63.

<sup>8</sup> B. B. Damaskin and A. N. Frumkin, *Electrochim. Acta*, 1974, **19**, 173.

<sup>9</sup> R. Parsons, *J. Electroanal. Chem.*, 1975, **59**, 229.

<sup>10</sup> D. C. Grahame, *J. Amer. Chem. Soc.*, 1957, **79**, 2093.

contain the essential features of a first approximation which are required to account for a fairly wide range of experimental observations.

**Dr. S. Levine (Manchester)** said: Provided the monolayer density and composition of molecules does not alter, varying the thickness  $d$  of the inner region will not produce significant changes with the present model because the dipole centres of the two molecular species are situated on the same plane. The thickness  $d$  enters into the theory through multiple electrostatic imaging of the dipoles in the two boundaries of the inner region and the effect of this imaging is to increase the co-ordination number  $c_e$  from about 11 to 15. An increase in  $d$  would diminish  $c_e$  slightly and also reduce the van der Waals term  $E_w''$  (eqn (3.4)). To produce a more pronounced effect by varying  $d$ , one probably needs to assume different planes for the centres of the two polar molecules. The inner region thickness  $d$  can then be regarded as a weighted mean of the thickness assigned to the two molecular species, resulting in a linear relation between  $d$  and fraction of area coverage  $\theta_a$ .

We were aware of the difficulties in choosing the mixture water+methanol to illustrate our general model, particularly in view of the hydrogen-bonding properties of water. Our approach seems highly suitable for treating the mixture model of single water molecules and clusters of such molecules for the inner region at the mercury/water interface, as proposed by Damaskin and Frumkin and improved by Parsons. An attractive feature of this mixture model is that it will reduce considerably the potential drop  $\Delta V$ . However, there are a number of features which are omitted in this cluster theory, such as lateral interactions between dipoles and a proper account of molecular polarisability. An important objective in our theory is to avoid introducing a dielectric constant  $\epsilon_\infty$  to describe a medium with fixed dipoles but rather to regard the inner region as a vacuum occupied by molecules. Such an approach is more informative because it forces one to seek a model in which proper cognizance is taken of molecular structure. Assigning a dielectric constant  $\epsilon_\infty$  to the inner region may reduce the potential drop  $\Delta V$  to a realistic value, but what is required is a molecular theory which replaces the use of the parameter  $\epsilon_\infty$ .

According to our fig. 2, a plot of fraction of alcohol coverage  $\theta_a$  against surface charge density  $\sigma_0$  at fixed bulk composition  $x_a$  shows only a slight increase in  $\theta_a$  in the direction of more positive  $\sigma_0$ . However, this small dependence of  $\theta_a$  on charge  $\sigma_0$  need not be due to the condition of constant thickness of the inner region. For example, corresponding plots of  $\theta_a$  against  $\sigma_0$  for values of  $\alpha_w$  and  $\alpha_a$  which are smaller by the fraction  $\frac{2}{3}$  show a much stronger dependence of  $\theta_a$  against  $\sigma_0$ . The relation between  $\theta_a$  and  $\sigma_0$  is a monotonic increase, i.e., no maximum in  $\theta_a$  has been observed. We are unable to predict at present the modifications in our theory which would produce such a maximum.

**Prof. G. M. Bell (Chelsea)** said: With dipolar forces, interactions at greater than first-neighbour distance are important and Levine *et al.* take account of them, as well as of image effects, by changing the effective coordination number from 6 to 15 at a late stage of the treatment. However further-neighbour interactions could have been introduced from the start. A zeroth-order or randomized statistical method like that used here is, in fact, a better approximation when further-neighbour pairs have to be considered than for the case of first-neighbour interactions alone. Although the unequal sizes of the two components makes the theory more complicated a reasonable assumption would be the chance of a given component occupying an  $n$ th neighbour site, when  $n > 1$ , is proportional to the corresponding "area fraction".

In this way an effective coordination number could be obtained in a fashion consistent with the beginning of the argument.

**Drs. B. Vincent (Bristol) and J. F. Padday (Kodak) (communicated):** The theoretical composite isotherms presented in fig. 3 of Levine *et al.* do not appear to be compatible with isotherms found experimentally, e.g., for the polystyrene/solution<sup>1</sup> or air/solution<sup>2</sup> interfaces. Both these systems show a preferential adsorption of n-alcohol molecules at low alcohol mole fractions, followed by a large preferential adsorption of water at high alcohol mole fractions. Perhaps the authors would care to comment on this.

**Dr. S. Levine (Manchester)** said: The composite isotherms for the adsorption of alcohol from water+ethanol and water+propanol mixtures on to a polystyrene latex surface, shown by Ottewill and Vincent in their fig. 1 shows a characteristic maximum with increase of alcohol fraction of water at the high alcohol mole fractions. Clearly, our particular model of the inner region and the values chosen for the relevant parameters do not apply to ethanol and higher alcohols. It is possible for example, that in our exchange condition (3.5) an alcohol molecule may be replacing water molecules which are situated in more than one layer or which form a cluster. Our theory requires further development in a number of directions among which are (a) proper account of hydrogen bonding, (b) allowance for more than two dipole orientations, (c) quadrupole and higher multipole interaction effects, (d) correction to the random distribution approximation and (e) extension of the theory to two or more layers. Nevertheless, we suggest that the general approach adopted in our paper does attempt to deal with the intricate inter-molecular structure in the inner region.

**Prof. J. Lyklema (Wageningen)** said: Considering the complexity of the adsorption of hydrolyzable cations at charged oxide surfaces, there seems something to be said in favour of the existence at the interface of flat hydroxocomplexes. The metal ion would then be in direct contact with an oxygen or hydroxyl group of the solid but the lateral electrostatic repulsion between the multivalent ions in the Stern layer would be considerably screened by the hydroxyl groups laterally surrounding the cations. Is such a picture incorporated in the model of James *et al.* or, for that matter, is it compatible with it?

**Drs. R. O. James, P. Stiglich and T. W. Healy (Melbourne)** said: The suggestion by Lyklema has motivated other workers who have sought to ascertain, by various spectroscopic methods<sup>3-6</sup> the existence of direct co-ordination of surface hydroxyl groups with the multivalent ion; no evidence of such direct co-ordination into the inner sphere of the cation has been obtained. Our own evidence is circumstantial in that plateau adsorption corresponds to a monolayer of primary solvated-hydroxylated cations. In addition, our calculations<sup>7</sup> show that extremely large desolvation energies would be required (i.e., work must be done to desolvate upon adsorption) if

<sup>1</sup> R. H. Ottewill and B. Vincent, *J.C.S. Faraday I*, 1972, **68**, 1533.

<sup>2</sup> J. F. Padday, unpublished data.

<sup>3</sup> D. Cornet and R. L. Burwell Jr., *J. Amer. Chem. Soc.*, 1968, **90**, 2589.

<sup>4</sup> K. M. Sancier and J. S. Mills, *J. Phys. Chem.*, 1963, **67**, 1438.

<sup>5</sup> T. Nortia and S. Laitinen, *Suomen Kem.*, 1968, **41**, 136.

<sup>6</sup> B. J. Hathaway and C. E. Lewis, *J. Chem. Soc. A*, 1968, 1176.

<sup>7</sup> R. O. James and T. W. Healy, *J. Colloid Interface Sci.*, 1972, **40**, 65.



the surface groups were to co-ordinate with the inner sphere of the adsorbing cation. We note Lyklema's suggestion as it may be helpful as we seek an understanding of the significance of the large  $\Delta G_{\text{chem}}$  term required to match theory to experiment in the  $\text{Cd}^{\text{II}} - \text{FeOOH}$  system in particular.

The large  $\Delta G_{\text{chem}}$  term required for  $\text{Cd}^{\text{II}}$  and other cation adsorption on oxide surfaces with a net positive charge may reflect a re-orientation energy on the part of the water molecules at the surface; no such drastic re-orientation is necessary for hydrated cation or hydroxo complex adsorption on oxide surfaces with a net negative surface charge.

**Prof. A. M. Posner** (*Western Australia*) said: It seems to me that all three models proposed by the authors are indistinguishable since the various metal ion species are in equilibrium with one another through hydrolytic reactions.

The actual proton release would be determined by the relative selectivities of the surface for the various hydrolysed species. Thus if they are all equally selected there could be no pH change, if the hydrolysed species is preferred the solution will go acid, while it will go alkaline if the lesser hydrolysed species is preferred. Since the selectivities could change with the change in charge on the surface resulting from adsorption and also from ionic strength and pH changes, so could the ratio of metal ion adsorption to proton release. Because all proposed mechanisms are equivalent, proton release data cannot help to distinguish them. It only indicates whether hydrolytic processes promoted by the presence of the surface are involved without distinguishing whether they actually take place on the surface or in the bulk.

**Drs. R. O. James, P. Stiglich and T. W. Healy** (*Melbourne*) said: We have to agree with Posner that the mathematical descriptions of the models of metal ion uptake by colloidal oxides appears so similar that it is difficult to distinguish these conceptually different models. Yet, as pointed out in our paper, there is a difference between the simple ion exchange model (1) and the adsorption and surface hydrolysis (2) or the adsorption of hydrolysed species (3) in the stoichiometry of the reactions.

For example, for (1) we write the distribution coefficient, (3):

$$D^1 = \Sigma K_n^s \overline{\text{SH}}^n / [\text{H}^+]^n,$$

whereas for model (II), eqn (12):

$$D^1 = \bar{S} \Sigma * \beta_n^s / [\text{H}^+]^n = * \beta_0^s \bar{S} \Sigma (\pi^* K_n^s) / [\text{H}^+]^n.$$

From  $D^1$  against  $[\text{H}^+]^{-1}$  and other expressions we can estimate the products  $K_n \overline{\text{SH}}^n$  and  $S^* \beta_n^s$ . For  $n = 1$ , these expressions are indistinguishable; however, if  $n \geq 2$  model (I) predicts a quadratic or higher dependence of  $K_n \overline{\text{SH}}^n$  on the surface area of the colloid whereas model (2) and model (3) are linear functions of the surface area.

To use this method requires data of very high accuracy and reproducibility as well as uniformity of surface sites. We are continuing investigations in this area. It is doubtful if we can learn a great deal more from thermodynamic adsorption measurements and more information on the kinetics of adsorption and desorption is obviously required.

**Dr. M. A. Malati** (*Medway and Maidstone College*) (*communicated*): On the adsorption of cations from aqueous solution by oxide particles, a change in the pH of the suspension is observed. During the attainment of equilibrium, this change in pH would alter the surface charge of the particles and hence affect their adsorption

capacity. The results of James *et al.* might have been affected by this factor. To minimise such effects, we have transformed the surface of the particles, e.g.,  $\beta$ - $\text{MnO}_2$  to the  $\text{Na}^+$  form prior to adsorption.<sup>1</sup> Solutions used for studying the adsorption of cations were  $10^{-2} \text{ mol dm}^{-3}$  in  $\text{Na}^+$  ion.<sup>2</sup>

Model (2) in the paper by James *et al.* does not clarify the hydration state of the ions exchanged and does not indicate their location in the double layer. We have suggested an ion-exchange mechanism involving a hydrated proton or a hydrated  $\text{Na}^+$  ion in the outer Helmholtz (O.H.L) or Stern layer and a hydrated cation in solution,<sup>3</sup> according to:



where  $\text{M}^+ = \text{H}^+$  or  $\text{Na}^+$  and  $\text{M}^{z+} = \text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Rb}^+$  or  $\text{Cs}^+$ . In the adsorption of any of the latter cations by quartz, precipitated silica,  $\beta$ - or  $\delta$ -manganese dioxide, the simple ion-exchange mechanism was found to be in agreement with the following observations: (i) the adsorption affinity sequence, following the Hofmeister series<sup>3-6</sup>; (ii) the results of  $\xi$  potential measurements for the particle/electrolyte system<sup>5</sup>; (iii) the effect of the cations on the co-adsorption of oleate by the solid particles<sup>7</sup>; (iv) the activating effect of the cations on the flotation of the particles by oleate<sup>7</sup>; (v) the sign and magnitude of the initial heat of adsorption.<sup>3, 8</sup>

A clearer understanding of the mechanism of adsorption of cations by oxide particles requires studies of the effect of the surface and of the cations on the cluster-structure of liquid water.<sup>9</sup> In this connection, the concept of the field strength of the solid<sup>10</sup> has been recently discussed.<sup>11, 12</sup> However, it has to be stressed that the calculated "bulk" field strength<sup>10</sup> may not reflect the behaviour at the surface of an oxide,<sup>3, 13</sup> which could be different from the bulk.

**Drs. R. O. James, P. Stiglich and T. W. Healy (Melbourne)** said: In reply to Malati we point out first that our present adsorption results are, as stated, in a background or supporting electrolyte concentration of  $10^{-2} \text{ mol dm}^{-3}$   $\text{KNO}_3$ . Furthermore, we cannot agree that the path of attainment of a particular state of equilibrium can affect the energy of that state. Adsorption of hydrolysable metal ions including Ba has been considered elsewhere in respect to the effect of total electrolyte concentration. Again the surface charge of a particular interface is a result of the particular solution and hence interfacial conditions imposed on it, including the adsorption density of the metal ion species. Thus it is difficult to understand what effects are being minimized by converting  $\beta$ - $\text{MnO}_2$  to the  $\text{Na}^+$  form and working on  $10^{-2} \text{ mol dm}^{-3}$   $\text{Na}^+$  supporting electrolyte. The state of equilibrium attained will be identical provided the supporting electrolyte concentration is maintained at  $10^{-2} \text{ mol dm}^{-3}$ .

<sup>1</sup> M. W. Rophael and M. A. Malati, *Chem. Ind.*, 1972, 768.

<sup>2</sup> A. A. Yousef, M. A. Arafa and M. A. Malati, *J. Appl. Chem. Biotech.*, 1971, **21**, 200.

<sup>3</sup> M. A. Malati, R. J. Mazza, A. J. Sherren and D. R. Tomkins, *Powder Tech.*, 1974, **9**, 107.

<sup>4</sup> M. A. Malati, A. A. Yousef and S. F. Estefan, *Chim. Ind. (Milan)*, 1970, **103**, 1347.

<sup>5</sup> S. F. Estefan and M. A. Malati, in *Recent Advances in Science and Technology of Materials* (Plenum, New York) 1974, **1**, 351.

<sup>6</sup> M. J. Gray and M. A. Malati, to be published.

<sup>7</sup> S. F. Estefan and M. A. Malati, *Trans. Inst. Min. Met.*, 1973, **82**, C237.

<sup>8</sup> M. A. Malati and S. F. Estefan, *Chem. Ind.*, 1975, 704.

<sup>9</sup> M. A. Malati and S. F. Estefan, *Disc. Faraday Soc.*, 1971, **52**, 377.

<sup>10</sup> T. W. Healy, A. P. Herring and D. W. Fuerstenau, *J. Colloid Interface Sci.*, 1966, **21**, 435.

<sup>11</sup> F. Dumont and A. Watillon, *Disc. Faraday Soc.*, 1971, **52**, 352.

<sup>12</sup> W. Stumm, C. P. Huang and S. R. Jenkins, *Croat. Chem. Acta*, 1970, **42**, 223.

<sup>13</sup> M. J. Gray, M. A. Malati and M. W. Rophael, submitted for publication.



Concerning the comments on the ion exchange model we would once again stress that such models allow various quantities to be calculated from experimental data; model 3 is the only predictive model. As pointed out in our reply to Posner, there is a difference between model 1 (simple ion exchange) and model 2 (adsorption and surface hydrolysis). However, it is important to note that our own and other workers data are consistent with all three models. Further equilibrium evidence of the kind noted by Malati does not prove the validity of the simple ion exchange model to the exclusion of other models.

**Prof. A. M. Posner** (*Western Australia*) (*communicated*): In referring to the model proposed by Bowden *et al.*, James *et al.* state that “ $K_{\text{ads}}$  values for only certain individual hydrolysis products were used and these were used as adjustable parameters to obtain curves of best fit”. Bowden *et al.* found it necessary to invoke the adsorption of only certain of the species in equilibrium with one another. The use of other species did not improve the fit to the data. This procedure is little different from the one used where  $\Delta G_{\text{chem}}$  is an adjustable parameter.

**Dr. R. O. James** (*Melbourne*) (*communicated*): In the original model proposed by James and Healy the adsorption of hydrolysable metal ions was calculated using an adsorption isotherm and the free energy of adsorption. The term was estimated from the coulombic, solvation and “chemical” energy changes on adsorption. The solvation term governed the selectivity of ionic adsorption and its relation to hydrolysis since  $\Delta G_{\text{solv}}$  is repulsive for most cation/oxide combinations and  $\Delta G_{\text{solv}}$  is proportional to  $Z^2$ . We assigned the same value  $\Delta G_{\text{chem}}$  to each of the hydrolytic species so as not to give further preferential prejudice to the adsorption of any solute.

As Posner points out, they were able to use their model by assigning a  $\Delta G_{\text{chem}}$  or  $K_{\text{ads}}$  to only *one* of the hydrolytic species. This approach then means that there is an arbitrary assignment of adsorption energies of individual species, e.g., some finite value for  $\Delta G_{\text{ads}}$  (or  $K_{\text{ads}}$ ) or  $\Delta G_{\text{ads}}$  is zero. Hence as a predictive model there is some difficulty in selection of values. In our model we can usually obtain isotherms in the correct order of magnitude by guessing  $\Delta G_{\text{chem}} \approx -20$ – $-30$  kJ mol<sup>-1</sup>. We intend to attempt to improve on the models by using improved charge and potential models similar to those used by Bowden *et al.*

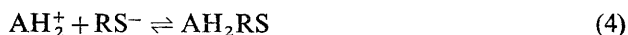
**Dr. B. Vincent** (*Bristol*) said: It is perhaps somewhat surprising that for alumina particles, with increasing concentration of an ionic surfactant of opposite charge, there appears to be the onset of lateral hydrophobic association between the adsorbed organic ions *before* the isoelectric point is reached. With hydrophobic particles, such as silver iodide and polystyrene latex, the reverse is certainly the case. One might suppose that on a hydrophilic surface the strongest interaction would be the Coulombic attraction between the positive surface sites and the organic anions, rather than hydrophobic associations at the surface, particularly as any lateral associations of hydrocarbon chains will be opposed by the Coulombic repulsion between the negative polar head groups of the surfactant ions.

**Drs. T. W. Healy** (*Melbourne*) and **D. E. Yates** (*Bristol*) said: The use of eqn (3) by Fuerstenau and Wakamatsu (F and W) for an oxide colloid like Al<sub>2</sub>O<sub>3</sub> has been shown by Levine and Smith<sup>1</sup> (L and S) to be unjustified. However, if we employ

<sup>1</sup> S. Levine and A. L. Smith, *Disc. Faraday Soc.*, 1971, **52**, 290.

the model of L and S it would appear that since  $\Delta pK$  for  $Al_2O_3$  is small in comparison to that of  $SiO_2$  for example, the use of eqn (3) by F and W is not greatly in error. The L and S analysis also suggests that surfactants would show different adsorption patterns on  $SiO_2$  and  $Al_2O_3$  and indeed such differences have been observed.<sup>1,2</sup>

A much more serious error is, however, inherent in the use of the classical Nernst equation [eqn (3) of F and W] if we use the site binding model of Yates, Levine and Healy<sup>3</sup> (Y, L and H) to analyse surfactant adsorption. In brief, we can represent proton, in different ion ( $Na^+$  and  $Cl^-$ ) and surfactant ion ( $RS^-$ ) equilibria as<sup>3</sup>



and to account for the observed (fig. 4 of F and W) reversal of electrokinetic potential,



The reactions given by eqn (6) will represent the hemimicelle situation and will become dominant for adsorption densities above region 1 of the isotherms; eqn (1)–(5) will describe region 1. We may now derive alternate, more general forms of eqn (3), (5) and (5a) of F and W. One example will suffice to emphasize the restrictive nature of the classical model. Thus the general form of eqn (3) (F and W), the classical Nernst equation is

$$\psi_0/kT = -2.303\Delta pH - \frac{1}{2} \ln(\theta'_+/\theta'_-) \quad (7)$$

where for surfactant adsorption the last term becomes a function of pH and the adsorption densities of chloride, sodium and surfactant ions. An interesting conclusion from such an analysis is that in region 1 there are very large changes in adsorption density of chloride with pH at constant adsorption density of surfactant ions. It also follows that increase in  $\psi_0$  with decrease in pH is strongly regulated and retarded at concentration-pH conditions above the hemimicelle condition.

**Dr. R. Parsons (Bristol)** said: I think that the analysis given by Fuerstenau and Wakamatsu is unnecessarily oversimplified. Eqn (5) was suggested by Grahame nearly 30 years ago and even then was recognised as a simplification of very limited validity. In effect this equation first assumes Henry's law modified by the electrostatic effect expressed as  $\psi_\delta$ . Secondly it uses the Stern approximation of identifying the potentials in the inner and outer Helmholtz plane. As Grahame showed, and many others have shown since, this latter assumption is far from valid. One result of this can be seen clearly if  $\Delta G_{ads}$  is put equal to zero (as in this paper at the lower concentrations), then there is no operational distinction between inner and outer Helmholtz planes; ions at a potential of  $\psi_\delta$  are in effect counted twice. Better models of the double layer are now available and are not too difficult to use in reasonable approximation.

I am surprised that a significant contribution to the adsorption of the long chain ion arises from the diffuse layer since the concentration of these ions is usually much

<sup>1</sup> P. L. de Bruyn, *Trans. A.I.M.E.*, 1955, **202**, 291.

<sup>2</sup> P. Somasundaran and D. W. Fuerstenau, *J. phys. Chem.*, 1966, **70**, 90.

<sup>3</sup> D. E. Yates, S. Levine and T. W. Healy, *J.C.S. Faraday I*, 1974, **70**, 1807.

less than that of the sodium chloride ( $2 \text{ m mol dm}^{-3}$ ). The ratio of sulphonate ions to chloride ions in the diffuse layer is the same as that in the bulk if simple Gouy-Chapman theory is used. Is there any significant *specific* adsorption of chloride in this system?

Is it possible to distinguish a normal, attractive interaction between adsorbed ions, perhaps involving two-dimensional condensation, from the formation of hemimicelles or is the latter just a description of the former?

**Dr. L. Ter-Minassian-Saraga** (*U.E.R. Biomedial*) said: The data for sulphonate adsorption densities and concentrations in solution for conditions where the zeta potential is reversed and where hemicelles begin to form may be interpreted as follows.

A *surface* c.m.c. may be defined in an analogous way to the surface pH, dependent on the electric potential at the particle surface. We assume that the hemicelle concentration  $c_{\text{HM}}$  corresponds to this c.m.c. and equate the electrochemical potentials of the three forms of the sulphonate ion  $\text{X}^-$ .

$$\tilde{\mu}_{\text{X}} = \mu_{\text{X}}^{\circ} + kT \ln c_{\text{HM}} = \mu_{\text{X}}^{\circ} + kT \ln \overline{\text{c.m.c.}} - e\psi_{-}$$

where symbols with a bar designate adsorbed species.

We deduce  $\psi_{-}$  using the surface charge density  $\sigma_0$  of table 1 of the paper by F and W and the Gouy-Chapman equation for an ionic strength  $10^{-3} \text{ mol dm}^{-3}$ .

If the value of the c.m.c. is assumed to be independent of  $\psi_{-}$ , the plot of  $\log c_{\text{HM}}$  against  $\psi_{-}$ , by extrapolating to  $\psi_{-} = 0$ , gives:

$$\ln c_{\text{HM}(\psi_{-}=0)} = \ln \overline{\text{c.m.c.}} + (\mu_{\text{X}}^{\circ} - \mu_{\text{X}}^{\circ}/kT).$$

This value may be compared to the bulk c.m.c.  $= 1.15 \times 10^{-2} \text{ mol dm}^{-3}$ ,<sup>1</sup> for which  $\mu_{\text{X}}^{\circ} = \mu_{\text{X}}^{\circ}$ . The plot in fig. 1 provides a value of  $c_{\text{HM}(\psi_{-}=0)} = 2 \times 10^{-2} \text{ mol dm}^{-3}$ .

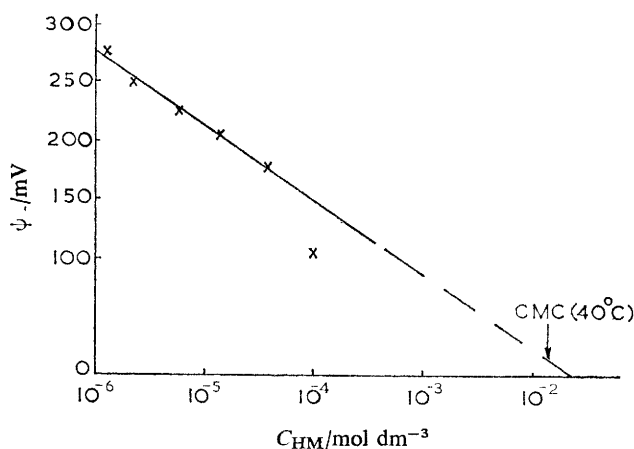


FIG. 1

**Dr. Th. F. Tadros** (*ICI, Jealott's Hill*) said: I find it difficult to visualise how hemimicelles can form on the surface of alumina since from adsorption isotherms (fig. 1 and 2), in the region of hemimicelle formation, the area/surfactant ion say at pH 3.2 is of the order of  $3 \text{ nm}^2$  or higher. This means that the surfactant ions are separated on the surface, and it seems difficult to see how they aggregate. Would

<sup>1</sup> I. J. Lin and S. Somasundaran, *J. Colloid Sci.*, 1971, **37**, 731.

bilayer formation, with first surfactant layer with the head groups pointing towards the surface and the other with the head groups pointing towards the solution, be an easier picture to draw. Have any contact angle measurements been made? Does the surface become more hydrophobic as the surfactant concentration increases and does it revert back to a more hydrophilic surface with further adsorption? Measurements by Elton<sup>1</sup> on silica using a cationic surfactant cetyltrimethylammonium bromide (CTABr) showed that the contact angle of water on a fused silica plate increases with increase in surfactant concentration until a maximum at  $1 \times 10^{-5}$  mol dm<sup>-3</sup> CTABr was reached and then decreased again, at higher concentrations. During adsorption of the first layer, the surface of silica became more hydrophobic and the contact angle increased. When the second layer began to build up, the surface regained its hydrophilic character and the contact angle decreased.

**Prof. A. M. Posner** (*Western Australia*) (*partly communicated*): Kavanagh in our laboratory has recently completed a study on the adsorption of various phenoxyacetic acid herbicides on goethite ( $\alpha\text{-FeO} \cdot \text{OH}$ ). He too found little or no adsorption until the surface acquires a net positive charge, i.e. the pH is below the p.z.c. He also ascribes this to hemimicelle formation due to hydrophobic bonding with the absence of specific adsorption forces between the surface and adsorbing ion. A further phenomenon associated with the adsorption is flotation occurring well below monolayer coverage. Presumably the hemimicelles are sufficiently large to give regions of the surface with sufficient hydrophobicity for the bubbles to attach themselves. When adsorption exceeds a further level, still below monolayer coverage, the surface becomes hydrophilic presumably with the formation of a second layer of adsorbed molecules on the hemimicelles with their hydrophilic groups sticking out into solution.

<sup>1</sup> G. A. Elton, *Proc. 2nd Int. Congr. Surface Activity*, 1957, 3, 161.