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Surface Electrical Characteristics of Disperse Systems Containing Polymers

A.A.Baran and B.E.Platonov

Studies of the effect of the adsorption of non-ionogenic polymers from aqueous solution on the surface charge density, electrokinetic potential, and surface conductance of dispersed particles are summarised, and theoretical ideas on the mechanism of the effect are examined. Methods for calculating the parameters of adsorbed layers of polymers from surface electrical measurements are described and analysed. A list of 84 references is included.

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I. INTRODUCTION

The interest in disperse systems containing polymers, displayed during recent years by research workers in various countries, is due to the important part played by such systems in various branches of modern industry. Water-soluble polymers are finding ever wider application as effective flocculants and stabilisers, binders and plasticisers, structure-regulating agents. Yet the mechanism of the influence of macromolecular compounds on various properties of disperse systems has been by no means fully studied, while theoretical principles for the selection and application of polymers for the above purposes are at an early stage of development.

It is generally known that the fundamental process largely determining the behaviour of disperse systems containing additions of polymers is adsorption interaction of macromolecules with the particle surface of the dispersed phase. Therefore investigation of the adsorption and the structure of adsorbed layers of polymers will help to reveal the mechanisms of the influence of macromolecular substances on various properties of dispersions, in particular the stability of their state of aggregation.

At least three main parameters—(*a*) the total adsorption, (*b*) the number or proportion of chain units in contact with the adsorbent surface, and (*c*) the density distribution of units normal to the surface or, as a first approximation, the thickness of the adsorbed layer—must be known for a description of the structure of an adsorbed layer of a macromolecular compound[1]. Usually no difficulty arises in determining the first of these parameters, but special methods are required to find the other two.

Macromolecules adsorbed on a heteropolar surface may influence substantially the structure of the electrical double layer; and potentials and charges on the latter in turn affect the conformational state of the macromolecules. Lyklema[2] has postulated that modification of the dense region of the double layer is due to the adsorption only of monomer units in direct contact with the surface, whereas changes in the diffuse region are caused by segments of adsorbed macromolecules extending into the solution as loops and spikes. Fig.1 gives a schematic picture of the adsorption of polymer macromolecules on a heteropolar interface[2]. It undoubtedly represents only a first, extremely crude approximation, but nevertheless enables the position to be understood. Lyklema's division of "spheres of influence" is also arbitrary, since changes in structure of the two regions of the double layer are interrelated.

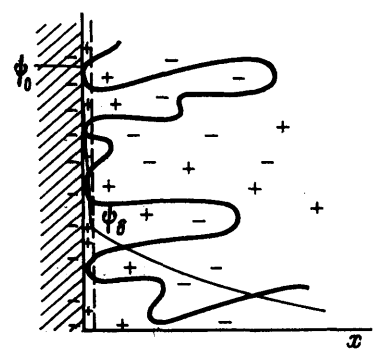


Figure 1. Diagrammatic representation of macromolecule adsorbed on a heteropolar interface, together with the variation in the ψ_0 and ψ_δ potentials with distance x from surface[2,12].

The fact that the adsorption of polymers affects the structure of the electrical double layer makes it theoretically possible to study the structure of adsorbed polymer layers by a combined investigation of the surface electrical characteristics of dispersed particles. Such investigations have been made by electrochemists at a mercury electrode, and a bibliography on this topic can be found in Ref.2,

but for disperse systems this method is novel and promising. Formation of an adsorbed layer of a macromolecular compound leads to a change in several surface electrical characteristics—surface potential and differential capacitance of the double layer, potential of the Stern layer, and the dielectric constant of the surface layer of solution—but the influence of the adsorption of polymers is usually studied on those parameters of the double layer that are susceptible to experimental determination, i.e. the surface charge density σ, the electrokinetic potential (ζ-potential), and recently the conductivity of dispersions. The present Review summarises results largely of studies on systems containing non-ionogenic water-soluble polymers. The general laws of the adsorption of polymers and the structure of the electrical double layer have been discussed in greater detail in monographs[3-5] and in textbooks of colloid chemistry.

II. EFFECT OF ADSORPTION OF POLYMERS ON SURFACE CHARGE DENSITY

The surface charge density of dispersed particles is often determined by potentiometric titration or radiometry (by means of radioactive tracers), which have been described in detail[6-9]. In the case of polymer-containing disperse systems determinations have several peculiarities, which must be taken into account in the interpretation of the effect on surface charge density of the adsorption of macromolecular compounds[1,2].

If polymer macromolecules are adsorbed on particles of a suspension or a sol, there are grounds for supposing that the surface of the dispersed phase accessible to adsorption of macromolecules will differ from the surface available for the adsorption of potential-determining ions. Quantitative aspects of this effect depend on the nature of the dispersed phase and the added polymer, and perhaps on the sequence in which the components are mixed, the concentration of the dispersed particles, and their size. However, in most cases it must be expected that a smaller surface will be accessible to macromolecules than to ions, because the internal surface of narrow pores cannot be reached by macromolecules, and also because of aggregation of particles. The latter factor is responsible for the well known decrease in adsorption of polymers with increase in concentration of the dispersed phase[10,11]. Investigations of the adsorption of polyvinyl alcohol, potential-determining ions, and dyes on particle surfaces in suspensions and sols of silver iodide have shown[1,2,12] that, under otherwise similar conditions, particles of a suspension adsorb a smaller quantity of polymer than do those of a sol, and that in suspensions 35% of the surface is unavailable for polymer adsorption.

It follows from the above that, for dispersions containing added polymers, the observed surface charge density is a composite, "mixed" quantity, somewhere between the value in the absence of an adsorbed layer and the value for portions of the surface modified by adsorption of the polymer. On the assumption that covered and uncovered parts of the surface are independent, we can write[2]

$$\sigma_{av} = f\sigma(\theta) + (1-f)\sigma_0, \qquad (1)$$

where f is the portion of the surface of charge density $\sigma(\theta)$ modified by adsorption, $1-f$ is the portion of unmodified charge density σ_0 and θ is the coverage of the surface by monomer units of adsorbed macromolecules. If f and σ_0 are known, relation (1) can be used to determine $\sigma(\theta)$. Lack of information on the accessibility of the surface to macromolecules may be a source of error in calculations of the parameters of adsorbed layers. Up to the present an aqueous dispersion of silver iodide containing polyvinyl chloride is the only system for which such information has been obtained from systematic investigations[1,2,12].

Another peculiarity is that the observed value σ_{av} is an average parameter, since the adsorption properties are different at different sites on the surface, which leads to inhomogeneity of the adsorbed layer. Combined surface electrical measurements do not yet allow more detailed information to be obtained, but this defect is inherent in most other methods of studying the adsorption of polymers.

The third feature is that the adsorption of compounds of high molecular weight, in contrast to that of the lower surface-active compounds, is in many cases irreversible. Yet the thermodynamics of surface phenomena, which is usually employed for the quantitative interpretation of surface electrical measurements, is applicable only to equilibrium reversible processes. Since the adsorption of polymers at the interface between a solid and a liquid solution depends both on the concentration of the polymer and on the parameters of the electrical double layer, two types of reversibility must be distinguished here—with respect to the concentrations of adsorbate and of potential-determining ions (e.g. pAg for silver iodide and pH for oxides).

The adsorption of macromolecular compounds from solution on colloidal particles is usually irreversible with respect to the adsorbate concentration[2], but it may be reversible (to a considerable degree, if not completely) with respect to the concentration of potential-determining ions, and then the dependence of the parameters of the adsorbed layer on the latter concentration can be subjected to thermodynamic analysis[2]. The degree of reversibility can be inferred from special adsorption experiments and also from certain indirect criteria, e.g. the appearance of hysteresis between σ—pAg or σ—pH curves obtained in the presence of the polymer with increasing and with decreasing concentration of potential-determining ions, and from the presence of a common point of intersection of these curves for different polymer concentrations, which will be discussed below. The actual degree of reversibility depends also on the time factor—on the rate of variation of pAg or pH during the experiment.

Before analysing the experimental results, we shall briefly examine theoretical views on the mechanism by which the adsorption of non-ionogenic water-soluble polymers affects the surface charge density of dispersed particles. This effect is usually due to the combined action of several factors (below).

(*a*) *Variation of χ-potential*[13]. The interphase potential difference $\Delta\phi$ established on contact between particles of a dispersed phase and a liquid solution comprises in general[13] two components: the ionic $\Delta\phi_i$ is due to the presence of an ionic double layer at the interface; and the dipolar χ is caused by the orientation of solvent (water) molecular dipoles in the vicinity of the interface. If adsorption of a polymer is accompanied by orientation of dipolar units of the macromolecules near the adsorbent surface, such orientation will lead to an additional interphase potential difference $\Delta\phi_a$, depending in magnitude and sign on the number and polarity of the monomer units, on the character and the degree of their orientation, and also on the degree of displacement of water molecules from the layer adjacent to the surface. Since for a reversible interface the interphase potential difference is determined unambiguously by the activity of potential-determining ions in the solution[14],

the appearance of $\Delta\phi_a$ will be accompanied by a change in the ionic component $\Delta\phi_i$ and hence† by a change in surface charge density, which may either increase or decrease depending on the relation between the signs of $\Delta\phi_i$ and $\Delta\phi_a$. The change in χ due to $\Delta\phi_a$ has been termed the "adsorption potential difference" and has been successfully invoked to explain several colloid-chemical phenomena[1,2,7,15–20] (see below).

(*b*) *Competition with potential-determining ions.* In each of the above cases the surface charge density varies owing to adsorption (desorption) of some of the potential-determining ions. The displacement of their adsorption equilibrium should be especially marked if they and the adsorbate are adsorbed on the same adsorption centres. The effect is not identical with the "adsorption potential difference", since it is purely statistical and is due to the fact that some of the surface centres suitable for adsorption of the ions are occupied by the adsorbate. Thus, if adsorption of the polymer is due to formation of hydrogen bonds with surface acid-base centres (e.g. hydroxy-groups), the adsorbate may compete with other hydrogen or hydroxide ions depending on the zero-charge point of the oxide and the pH of the solution. At sufficiently low pH, at which a considerable proportion of surface hydroxyls are attached to protons, formation of an adsorption bond is difficult and would be accompanied by displacement of some of the hydrogen ions from the surface. With rise in pH the number of free surface hydroxyls will increase, and competition with hydrogen ions weaken; in this pH range the formation of adsorption bonds with polymer macromolecules is facilitated. Finally, at still higher pH decrease in the total number of undissociated surface hydroxyls will lead to competition with hydroxide ions and will hinder adsorption of the polymer; as a result of competition with potential-determining ions the surface charge density diminishes.

(*c*) *Competition with gegenions in the Stern layer.* If the energies of adsorption of units of a polymer chain and of gegenions in the Stern layer are comparable, adsorption of the polymer may involve displacement of gegenions from this layer into the diffuse region of the double layer. This is equivalent to an increase in thickness of the double layer and, provided that the interphase potential difference is constant, should lead to a decrease in surface charge density, i.e. to desorption of some of the potential-determining ions. This mechanism was suggested[21] to explain the decrease in surface charge density on silver iodide as a result of the adsorption of lower aliphatic alcohols, and then was transferred to the adsorption of polymers[1,16]. The influence of competition in the Stern layer on surface charge density may be expected to depend on the density of charges in this layer and hence on the ionic strength of the solution. Yet good agreement has been observed[1] between results obtained in solutions of high and low ionic strength. On the other hand, the adsorption of heptan-1-ol on silver iodide is accompanied by desorption of potential-determining (and silver and iodide) ions only in the presence of a supporting electrolyte[22]. This suggests that the observed effect is a consequence of competition in the Stern layer, not of competition between alcohol molecules and potential-determining ions, as has been assumed[22]. Furthermore, it is difficult to imagine competition between neutral molecules and these ions, especially for adsorption centres on the surface of an ionic crystal.

(*d*) *Variation in distribution of gegenions in diffuse region of double layer.* Although several investigators of polymer-containing disperse systems have suggested that adsorption of the polymer does not affect the distribution of gegenions in the diffuse region of the double layer[6,17,20,23–25], it can reasonably be assumed that this does not apply at sufficiently high surface coverage. For the adsorption of flexible macromolecules on a surface of constant charge density Brooks[26] suggested a model in which the distribution of gegenions was affected by the excluded volume (this model will be examined in greater detail in Section III,1). Provided that the interphase potential difference is constant, the excluded-volume effect should be accompanied by a decrease in surface charge density.

(*e*) *Variation in dielectric constant of surface layer of liquid.* If the dielectric constants of the adsorbate and of water are different, that of the layer adjacent to the surface will change as it becomes enriched with adsorbed macromolecules, with consequent changes in capacitance of the double layer and, the interphase potential difference remaining constant, in surface charge density (for the diffuse ionic double layer $\sigma \propto \varepsilon^{\frac{1}{2}}$).

The relative contribution by each of the above factors to the total change in surface charge density depends on the nature of adsorbate and adsorbent, on the surface coverage and structure of the adsorbed layer, and also on the concentration of potential-determining ions, the composition, and the ionic strength of the solution. At the zero-charge point, of course, where the ionic double layer is absent, factors (*b*)–(*d*) are inoperative, for they are associated with the effect of the polymer on the structure of this layer. With increase in the ionic strength of the solution factor (*c*) should become stronger, and (*d*) weaker. In addition to the above factors we must consider the possibility that the activity coefficients of the ions may vary in polymer solutions, and also that the adsorption of macroions of pseudopolyelectrolytes, whose formation has been suggested by several workers[27,28] for non-ionogenic polymers in concentrated solutions of salts.

The displacement of the adsorption equilibrium of potential-determining ions on the adsorption of a polymer will lead to a more or less considerable change in their activity in solution, so that a cautious approach must be made to the principle of constancy of the interphase potential difference. Furthermore, the above theoretical analysis suggests that the adsorption of polymers and that of simple surface-active compounds have largely similar effects on the surface charge density.

Most of the experimental work on the effect of the adsorption of polymers on surface charge density has been done on classical hydrophobic dispersions of silver iodide or of metal sulphides, as well as on dispersions of oxides.

Silver iodide

The interface between silver iodide and an aqueous solution is one of the most thoroughly studied by colloid-chemical methods, so that it is not surprising that the effect of the

†It is assumed that, with the exception of the cases specially mentioned, the potential difference between the surface and a point inside a solid phase is constant. Variations in $\Delta\phi_i$ may then be identified with those in the surface potential ψ_0.

adsorption of non-ionogenic water-soluble polymers on the surface charge density of colloidal particles was first investigated precisely on aqueous dispersions of silver iodide. Lyklema and his coworkers[1,2,6,12,29] have used potentiometric titration to study the effect of the adsorption from aqueous solution of several specimens of polyvinyl alcohol, differing in molecular mass and in acetate-group content, on the surface charge density of silver iodide particles. The typical σ–pAg relations illustrated in Fig. 2 show that (i) the adsorption of polyvinyl alcohol diminishes the slope of the curves, (ii) the zero-charge point is displaced to more positive values, and (iii) all the curves pass through a common point of intersection. The effect produced depends on the characteristics of the specimen of polyvinyl alcohol used: it is stronger for a polymer containing 12% of acetate groups than for one containing 2%.

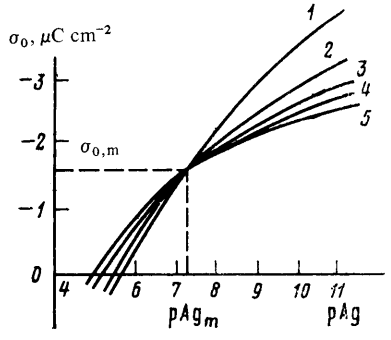


Figure 2. Surface charge density of silver iodide particles in presence of adsorbed pva of mol.wt.106500 in 0.1 M KNO_3 for various quantities of polymer adsorbed[2,12] (mg m^{-2}): *1*) 0; *2*) 0.05; *3*) 0.18; *4*) 0.38; *5*) 0.4.

The decrease in slope of the σ–pAg curves is equivalent to a decrease in the differential capacitance of the double layer, and should be attributed[1] to two main factors—displacement of the originally specifically adsorbed gegenions by monomer units of the polymer, and decrease in the dielectric constant of the layer adjacent to the surface by replacement of water molecules by units of the polymer chain, i.e. the above factors (*c*) and (*e*).

The shift in the zero-charge point may be due to change in the specific adsorption of ions, the activity coefficient of potential-determining ions, or the electrokinetic potential when water dipoles in the surface layer are replaced by the dipoles of polymer units. The last factor probably predominates, since the change in the activity coefficient appears[1] to be negligible, while the specific adsorption of nitrate ions is insignificant at the zero-charge point. The observed shift was explained[1,2,12] in terms of ideas developed earlier[7,15,30] in relation to the adsorption of simple compounds on silver and mercury iodides. The important conclusion was reached that electrochemically the adsorption of polyvinyl alcohol has much in common with that of simple compounds, and that a layer of the polymer adsorbed on the surface of silver iodide can be regarded as comprising 50% of butanol and 50% of ethylene glycol molecules. Such an approach enabled the proportion of occupied sites in the first dense layer of adsorbate to be calculated (see below for greater detail).

A common point of intersection has been observed also in the adsorption of substances of low molecular weight on silver and mercury iodides[7,30]. Examination of the Gibbs adsorption equation shows that the point of intersection then corresponded to the surface charge density at which maximum surface excess of adsorbate relative to water occurred[2,7]. The existence of a common point of intersection of σ–pAg curves in the adsorption of a polymer suggests that the adsorption of monomer units directly in contact with the surface is reversible with respect to pAg, at least if changes in pAg are not too large. At σ_m the maximum number of units are in contact with the surface, and the θ–σ relation, in effect the θ–pAg relation, can be subjected to thermodynamic analysis, even if the total polymer adsorption is irreversible with respect to concentration[2]. The position of σ_m depends on the nature of adsorbate and absorbent and on the composition of the solution[1,2,12]; it is characteristic of the system, independently of the total polymer adsorption. For silver iodide $\sigma_m = -1.6$ and -2.2 μC cm^{-2} in aqueous solutions of polyvinyl alcohols pva-2 and pva-12 with potassium nitrate as inert electrolyte (here and subsequently the numerals denote the contents (%) of unsaponified acetate groups in the polymer)[1,12]. The value obtained for the "50% butanol + 50% ethylene glycol" model was $\sigma_m = -1.7$ μC cm^{-2}, in good agreement with the experimental value for pva-2.[1] The differences observed in the electrochemical behaviour of pva-2 and pva-12 were not explained[1].

The effect of the adsorption of polyvinyl alcohol and another non-ionogenic polymer—polyethylene oxide (peo)—from aqueous solution on the surface charge density of silver iodide has been investigated by a radioactive tracer method[17–19,24,31]. The silver iodide surface was labelled with radioactive iodine-131 by isotopic exchange, and the variation in the adsorption of potential-determining iodide ions was assessed from the radioactivity of the liquid after 24-h contact of the radioactive precipitate with solutions of the polymers varying in molecular mass. The results indicate that under the experimental conditions adsorption of the polymers on a negatively charged precipitate of silver iodide is not accompanied (as in the case of non-ionogenic surface-active agents[32]) by desorption of potential-determining iodide ions.

Ideas on the "adsorption potential difference" were successively applied to explain the influence of the adsorption of polyethylene oxide on the surface charge density and the electrokinetic potential of colloidal precipitates[16–20,33]. It was concluded that, during adsorption on silver iodide particles, $\Delta\phi_a$ and $\Delta\phi_i$ are opposite in sign at negative surface charge densities, and of the same sign at positive values of the latter. Hence dipolar units of adsorbed macromolecules in contact with the surface are oriented with the negative pole (i.e. the oxygen atom) towards the liquid phase, independently of the sign of the surface charge, in agreement with other results[34]. The positive shift in the surface potential of a mercury electrode in solutions of polyethylene oxide has also been explained[35] by the adsorption of oriented dipoles. However, without additional information on the degree of displacement of water from the layer adjacent to the surface and on the polarity of the adsorbate, or on the character of the bond between polymer and surface, the sign of $\Delta\phi_a$ cannot be regarded as evidence of a particular orientation of the adsorbed units.

Antimony sulphide

Results have been published also on the influence of polyvinyl alcohol and polyethylene oxide on the surface charge density of antimony sesquisulphide[17-19,23,24]. Variation in the latter was assessed from that of the total absorption of calcium gegenions from solutions of the chloride or nitrate labelled with calcium-45, at electrolyte concentrations ensuring that the adsorption isotherms of the gegenions reached saturation.

The results of radiometric and adsorption measurements in Table 1 indicate a significant difference between antimony sulphide and silver iodide particles in their surface interaction with polyethylene oxide. With increase in adsorption of the polymer the surface charge density of the sulphide falls to a certain level, after which it remains unchanged. It is significant that this decrease, for a given quantity adsorbed, is independent of the molecular mass of the polymer.

Table 1. Adsorption of peo and Ca^{2+} from aqueous solution on Sb_2S_3 particles[19].

[peo], g litre^{-1}	$M_{peo} = 6000$		$M_{peo} = 1\,300\,000$	
	[peo], mg g^{-1}	[Ca^{2+}], μg-equiv. g^{-1}	[peo], mg g^{-1}	[Ca^{2+}], μg-equiv. g^{-1}
0	0	42.0	0	42.0
0.1	5	38.9	5	38.5
0.3	15	35.8	15	36.4
1.0	—	35.2	38	36.4
2.5	37	35.2	55	36.4

The decrease in the surface charge density of the sulphide accompanying adsorption of polyethylene oxide was regarded[17-19] as indicating that $\Delta\phi_a$ and $\Delta\phi_i$ had the same sign. Since the sulphide surface is negatively charged in water, $\Delta\phi_a$ must have a minus sign. This suggests that the orientation of monomer units is opposite to that on silver iodide, and has the oxygen atom towards the surface[19]. Such orientation may result from hydrogen bonding between oxyethylene oxygen and hydrogen of acidic groups on the sulphide surface, as infrared spectroscopy has established[36] for the aqueous silica-polyethylene oxide system. The decrease in negative values of $\Delta\phi_i$ (and ψ_0) due to such orientation should be accompanied by a decrease in the surface charge density of the antimony sulphide particles, as has been observed. Hence the statement[32] that the orientation of dipolar molecules adsorbed from aqueous solution is independent of the nature of the surface is hardly applicable to the specific interaction of adsorbate molecules with the surface of dispersed particles.

In contrast to polyethylene oxide, pva-2 and pva-12 added to an electrolyte solution up to a polymer concentration of 0.75 g litre^{-1} hardly affect the absorption of calcium genenions[23]: i.e. the surface charge density of antimony sulphide remains unchanged in the presence of adsorbed polyvinyl alcohol. This makes it highly probable that the number of monomer units of adsorbed macromolecules in contact with the sulphide surface is small: i.e. certain qualitative deductions can be made concerning the structure of an adsorbed polymer layer.

Oxides

Though polymer-containing dispersions of inorganic oxides have the greatest practical value among all the systems examined, their study began only during recent years and has been predominantly incidental. The hydrophilic character of oxide surfaces, the presence on them of functional hydroxy-groups, and characteristic structural features of the electrical double layer (the existence of a porous gel-like layer, permeable to potential-determining ions and gegenions, on the surface of certain oxides[37-40]) distinguish oxide dispersions as a special independent group of systems, whose study is of both theoretical and practical interest.

All results published at the present time have been obtained by potentiometric titration of polyvinyl alcohol–oxide systems. Adsorption of the polymer affects neither the position of the zero-charge point nor the surface charge density of haematite[2], gibbsite[41], and amorphous silica (Aerosil)[42]. The explanation for iron(III) and aluminium oxide was[2] that their surface charge was not concentrated at the surface but spread inside the superficial (gel-like) layer of solid, and this region of the electrical double layer was "invisible" to the polymer. In the Reviewers' opinion the reason may be "spreading" of the Stern layer owing to diffusion of gegenions inside the gel, which under the conditions of a potentiometric titration (solution of high ionic strength) should diminish the influence on surface charge density of competition in this layer. Furthermore, the effects of polymer adsorption on surface charge density outlined above may in considerable measure all be levelled off by the redistribution of charges and potentials in the gel-like layer, so that the change in surface charge density represents only an insignificant part, difficult to detect experimentally, of the total change in space charge.

Potentiometric titration of suspensions of Aerosil in the presence of polyvinyl alcohol has been undertaken at both high and low ionic strengths[42,43]. Since a gel-like layer is not present at the surface of Aerosil particles[44], the insensitivity of surface charge density to polymer adsorption is obviously due in this case to the insignificant number of contacts between adsorbed macromolecules and adsorbent surface.

Although potentiometric titration has not given positive results in relation to the adsorption of polyvinyl alcohol on iron(III) and aluminium oxides, the view[2] that this method is inapplicable to polymer-containing oxide dispersions can be accepted only for oxides whose surface is coated with a gel-like layer. But even in this case we cannot speak in advance of the inapplicability of potentiometric titration, since, with adsorbed macromolecules having a sufficiently strong influence on the structure of the electrical double layer, a change in surface charge density might nevertheless be detected. Finally, the surface charge density of zinc oxide is affected significantly by the adsorption of polyvinyl alcohol[45], with displacement of the zero-charge point of the oxide to higher pH. This should be regarded as indirect evidence of absence of a gel-like layer from the surface of zinc oxide, but the results[45] indicate a considerable number of polymer chain units in contact with the surface.

Thus even with dispersions of oxides study of the influence of the adsorption of polymers on surface charge density can give valuable information. Nevertheless, the above survey shows that the range of systems studied by this method is narrow, and further research on these lines is extremely desirable.

III. ADSORPTION OF POLYMERS AND ELECTROKINETIC POTENTIAL OF DISPERSED PARTICLES

The adsorption of polymers may lead to changes not only in surface charge density but also in magnitude and sometimes even sign of the electrokinetic potential. Results obtained in the study of these properties of disperse systems supplement each other.

The combined action of three factors—change in potential of the outer Helmholtz plane ψ_δ, displacement of the plane (more precisely region) of slippage within the liquid phase as a consequence of the formation of a sufficiently thick adsorbed layer on the adsorbent surface, and change in the distribution of gegenions in the diffuse region of the electrical double layer—is able to explain the influence of adsorption of a non-ionogenic polymer on the electrokinetic potential. The first of these obviously predominates at low surface coverage, and the second when adsorption is sufficiently great; the only attempt to use the third factor to explain experimental results is the Brooks model discussed below.

Changes in ψ_δ are in most cases due to corresponding changes in $\Delta\phi_i$, ψ_0, and σ (see footnote in Section II), so that a theoretical interpretation of the influence of polymer adsorption on electrokinetic potential involves discussion of its above effects on surface charge density. This potential may either increase, decrease, or change sign as a consequence of changes in ψ_δ. Displacement of the slippage plane into the solution is accompanied solely by a decrease in the electrokinetic potential and depends on the thickness of the adsorbed layer and the degree of immobilisation of liquid in it. The relative contributions by each of these factors to the resultant change in potential depends on the same characteristics of the system as does the change in surface charge density (Section II), in particular on the quantity of polymer adsorbed, and the structure and thickness of the adsorbed layer. With the exception of quantity adsorbed, direct experimental determination of these characteristics is not possible. Since they are related to such parameters of the system as the concentrations of polymer and potential-determining ions, and the composition and ionic strength of the solution, the immediate task of experimental study of the electrokinetic behaviour of polymer-containing disperse systems is to establish the dependence of the electrokinetic potential on these parameters.

1. Dependence on Polymer Concentration

Electrokinetic results are most often presented as ζ–c curves, where c is the equilibrium or initial polymer concentration. Fig. 3 shows the dependence of the electrokinetic potential of the particles in silver iodide and antimony sulphide sols on the concentrations of added polyvinyl alcohol and polyethylene oxide solutions[24]. Increase in the polymer content of the system is accompanied by a continuous

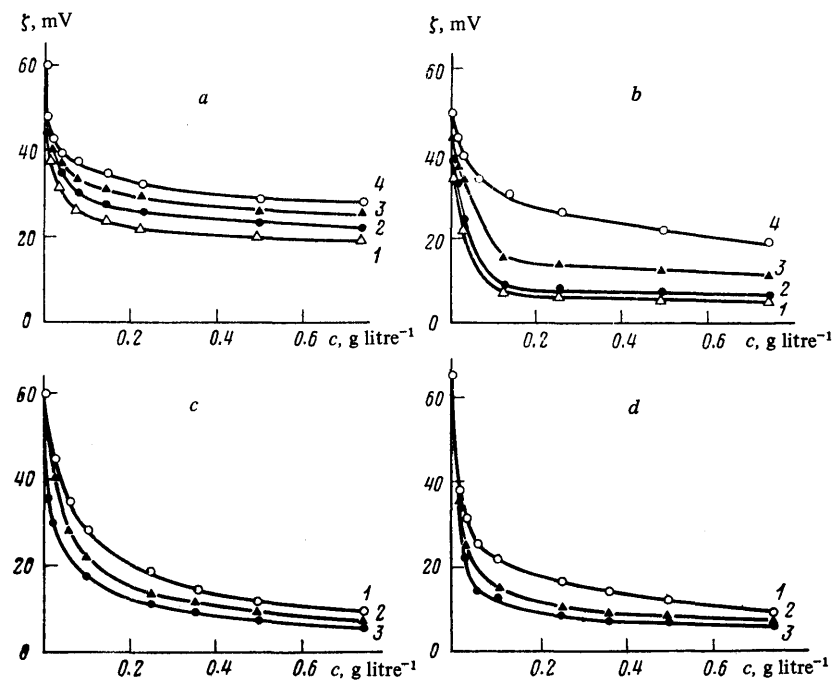


Figure 3. Effects on the electrokinetic potential of sol particles of (*a*) AgI and (*b*) Sb_2S_3 of the addition[24] of polyvinyl alcohols varying in molecular mass (10^{-4} *M*): *1*) pva-12 (2.2); *2*) pva-2 (4.1); *3*) pva-12 (5.9); *4*) pva-18 (6.5); and for (*c*) AgI and (*d*) Sb_2S_3 of the addition of polyethylene oxides (10^{-6} *M*): *1'*) 0.23; *2'*) 1.3; *3'*) 2.6.

decrease in the potential. The main fall usually occurs with small additions of polymer, after which the curves become more gently sloping, with a tendency to emerge on a plateau. Similar curves have been observed in the adsorption of these polymers on silica[16,42], negatively charged precipitates of silver iodide and antimony(III) sulphide[20,24,33], and aluminium oxide[41].

Such variation in the electrokinetic potential indicates the dominant effect of displacement of the slippage plane, some decrease in ψ_δ, or parallel action of the two factors. Since the adsorption of polyethylene oxide and polyvinyl alcohol on silver iodide and of the latter on antimony(III) sulphide particles is not accompanied by decrease in the negative surface charge density (above), the decrease in the negative electrokinetic potentials is due to the dominant effect of displacement of the slippage plane inside the solution. The fall in potential in the antimony sulphide–polyethylene oxide system is due to the combined action of the two factors, since adsorption of this polymer on the sulphide surface leads to some decrease in surface charge density. Finally, the latter remains unchanged during the adsorption of polyvinyl alcohol on silica[42] and gibbsite[41], so that the fall in potential can be attributed solely to the formation of quite thick adsorbed polymer films on these precipitates.

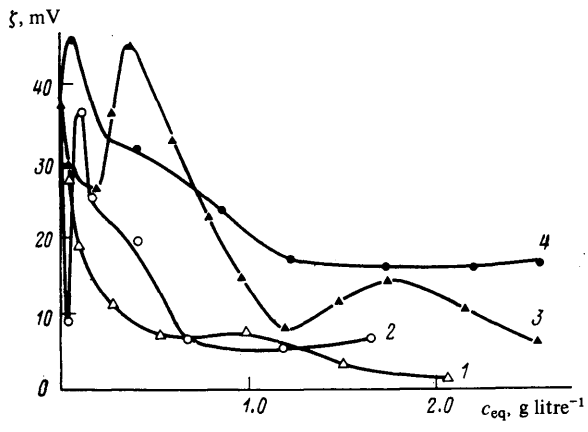


Figure 4. Dependence of electrokinetic potential of zinc oxide particles on equilibrium solution concentration[46] of polyvinyl alcohols (10^{-4} *M*): *1*) pva-12 (5.0); *2*) pva-2 (5.6); *3*) pva-18 (5.9); *4*) pva-18 (9.8).

If the above two factors have opposite effects, while the increase in ψ_δ predominates in a certain polymer concentration range, extrema appear on the ζ–*c* curves. Fig. 4 illustrates this relationship for zinc oxide in aqueous solutions of four specimens of polyvinyl alcohol[46] having different contents of acetate groups. The surface charge density of the oxide becomes more positive in solutions of pva-2 ($M = 56000$),[45] which is equivalent to increases in $\Delta\phi_i$ and ψ_δ for a positively charged surface, and should tend to raise a positive electrokinetic potential. Quantitatively this effect and also the thickness of the adsorbed polymer layer depend on the specimen of polyvinyl alcohol used.

When the increase in ψ_δ is sufficiently large, a maximum appears on the ζ–*c* curves in the corresponding concentration range (curves *2*–*4*). Among all the specimens studied[46] pva-12 gives the greatest adsorption, and forms a thick adsorbed layer even at low concentrations, which leads to a sharp drop in potential (curve *1*) and "masks" the effect of the increase in ψ_δ. Analogous ζ–*c* relations are observed on silica[42], although adsorption of polyvinyl alcohol does not affect the surface charge density[42]. Thus the presence of extrema in the curves should not by itself be regarded as evidence of change in σ, $\Delta\phi_i$, or ψ_0.

The form of the curves depends substantially on the magnitude and sign of the surface charge, i.e. on the concentration of potential-determining ions. Fig. 5 shows ζ–*c* curves for a precipitate of silver iodide in polyethylene oxide solutions with different contents of non-inert electrolytes[18,20,31]. At low polymer concentrations some increase is observed in the electrokinetic potential of a negatively charged surface and a sharp drop in potential of a positively charged precipitate (to zero), change in sign of charge, and rise in potential of opposite sign.

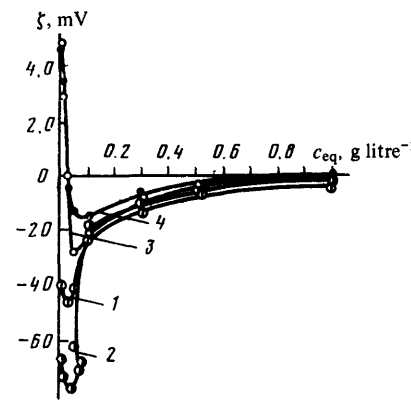


Figure 5. Dependence[17,20] of electrokinetic potential of silver iodide particles on concentration of polyethylene oxide (molecular mass 1.05×10^6) in: *1*) water; *2*) 0.1mM KI; *3*) 0.5mM $AgNO_3$; *4*) 1mM $AgNO_3$.

Change in sign on a positively charged surface of silver iodide in solutions of polyethylene oxide, observed also[34] in the coagulation by electrolytes of silver iodide sols stabilised by this polymer, has been explained[18,20,31] by the establishment of a considerable "adsorption potential difference" when the polymer is adsorbed on silver iodide particles. As noted above, with $\Delta\phi_a$ and $\Delta\phi$ having the same sign, $\Delta\phi_i$ should decrease when $\Delta\phi$ is constant. If the difference $\Delta\phi_a$ is sufficiently large ($\Delta\phi_a > \Delta\phi_i$), its compensation may require change not only in the absolute magnitude but also in the sign of $\Delta\phi_i$, which is evident in electrokinetic measurements as a change in sign of the ζ-potential.

If it is assumed, as for the interface between mercury and aqueous polyethylene oxide[35], that dipolar units of the polymer chain are oriented with their positive poles towards

the hydrophobic surface of silver iodide (independently of the sign of its charge), the sign of $\Delta\phi_a$ will be the same as or opposite to that of $\Delta\phi$ according as the silver iodide particles are positive or negative. This should lead to an increase in negative values of $\Delta\phi_i$, ψ_δ, and hence the electrokinetic potential, as well as a decrease and change in sign of positive $\Delta\phi_i$ and ζ, as is observed experimentally. With increase in concentration of polyethylene oxide the ζ-potential falls, independently of the sign of the particle charge, as a result of formation of a thick adsorbed polymer film and displacement of the slippage plane deep into the solution.

As already noted, we have explained the changes in the electrokinetic potential of hydrophobic silver iodide and antimony sulphide surfaces in aqueous solutions of polyethylene oxide and polyvinyl alcohol mainly[16-18,20,33] in terms of an "adsorption potential difference", since this is the only factor explaining the change in sign of the surface charge accompanying polymer adsorption. Yet changes in ψ_δ and hence the ζ-potential may be due also to competition between dipolar units of adsorbed macromolecules and gegenions in the dense region of the electrical double layer. Since such competition leads to a decrease in surface charge density (above), it may cause decreases in ψ_0, ψ_δ, and ζ. On the other hand, diminution in the charge density of gegenions in the dense region may be accompanied by increases in ψ_δ- and ζ-potentials, even with a general decrease in surface charge density. These ideas have been used to explain the influence of added alcohols on the stability of aqueous dispersions of silver iodide[21], but in published studies of adsorbed layers of macromolecular compounds they receive only casual mention[2].

Although most authors, when analysing electrokinetic measurements regard the interphase potential difference as unchanged for a given activity of potential-determining ions in the solution, attempts have also been made to use a constant-charge model. When studying the electrokinetic potentials of erythrocytes, quartz, and latices in aqueous salt solutions of dextran and polyethylene glycol, Brooks[47,48] observed a rise in this potential with increase in the polymer concentration. He explained and gave a quantitative basis to these results on the hypothesis that the excluded-volume effect arising within the electrical double layer on adsorption of a polymer leads to expansion of the diffuse region of the layer and a rise in the surface potential with the surface charge density unchanged[26]. If the displacement of the slippage plane is not too great, the electrokinetic potential rises also, and this plane may even lie within the adsorbed polymers layer[26]. This model is obviously not generally applicable, since the adsorption of non-ionogenic polymers may be accompanied not only by a rise but also by a sharp drop in the electrokinetic potential, even with little adsorption, when it is difficult to expect significant movement of the slippage plane. Furthermore, other reasons for a rise in electrokinetic potential are possible, although the excluded-volume effect probably also makes a definite contribution. The Brooks theory has been subjected to critical analysis[2].

2. Dependence on Adsorbed Quantity of Polymer

Adsorption and electrokinetic measurements on the same systems will give the dependence of ζ-potential on polymer adsorption, which Fig. 6 illustrates for particles of silver iodide and antimony(III) sulphide sols coated with adsorbed polyvinyl alcohol or polyethylene oxide[24]. In general these

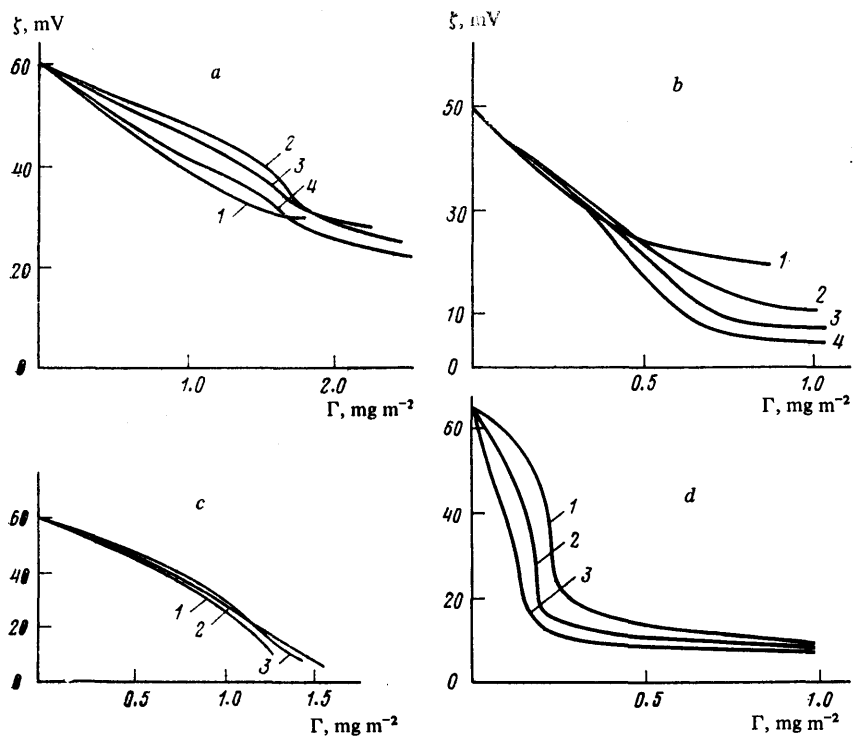


Figure 6. Variation[24] of ζ-potential of sol particles with quantity of adsorbed polymer: *a*) pva on AgI; *b*) pva on Sb_2S_3; *c*) peo on AgI; *d*) peo on Sb_2S_3. Numbering of curves as in Fig. 3.

curves resemble those for the dependence of the potential on the quantity of added polymer (Fig.3), but with the difference that increase in polymer adsorption is accompanied by an initial slow fall in electrokinetic potential followed by a more rapid drop, which is replaced by another gradual decrease, after which in many cases a plateau ensues. Since the fall in ζ-potential on the adsorption of polyvinyl alcohol on silver iodide and antimony sulphide surfaces, and of polyethylene oxide on the former, is due to displacement of the slippage plane from its original position, a ready explanation for the initial slow decrease is that the early portions of the polymer, which form a thin adsorbed layer comparable in thickness with the Stern layer, are unable to produce a significant drop in potential by this mechanism. After the first (dense) layer has been formed, further accumulation of macromolecular compound at the surface of the dispersed phase is due to lengthening of loops and spikes of adsorbed macromolecules, i.e. to thickening of the layer.

If the slippage plane is assumed to have moved to or at least near the boundary of the polymer envelope, the observed sharp drop in electrokinetic potential can reasonably be attributed to formation of the adsorbed layer, a process whose termination is indicated by emergence of the curves on a plateau (Fig.6). The sharper drop in the potential at low surface coverage of the antimony sulphide precipitate with polyethylene oxide[17,18,31] is due to the accompanying decrease in surface charge density. Good correlation has been noted[16] also in the influence of the molecular mass of polyethylene oxide on the electrokinetic potential of quartz immersed in its solutions and on the limiting adsorption of the polymer on Aerosil.

3. Dependence on Concentration of Potential-determining Ions

The influence of the concentration of potential-determining ions on the electrokinetic potential of polymer-containing disperse systems has been studied[1,2,6,12,49], and results obtained for quartz in aqueous solutions of polyethylene oxide are illustrated in Fig.7.[49] This polymer lowers substantially the ζ-potential of quartz in acid and weakly alkaline pH ranges, the decrease at constant pH being little dependent on the polymer concentration, for adsorption saturation of the quartz surface is already reached at low concentrations. With rise in pH above 9.5 the effect of the polymer on the potential diminishes, which is consistent with the decrease in adsorption of the polymer on amorphous silica (Aerosil) with rise in pH.

Such diminished effect suggests competition between hydroxide ions and polyethylene oxide for acidic adsorption centres on the surface, as well as certain conclusions on the nature of the bond between polymer and adsorbent surface. These deductions are supported by infrared spectral results[36], indicating hydrogen bonding between oxygen atoms in the polymer chain and undissociated silanol groups of the silica surface. As a consequence of this competition the pH values of maximum electrokinetic potential shift to a more alkaline range. It is significant that this maximum is about the same for all the curves and is independent of the presence of polyethylene oxide. This was regarded[49] as unambiguous evidence that at pH ≥ 11 the number of vacant undissociated adsorption centres is too small to ensure adsorption of the polymer.

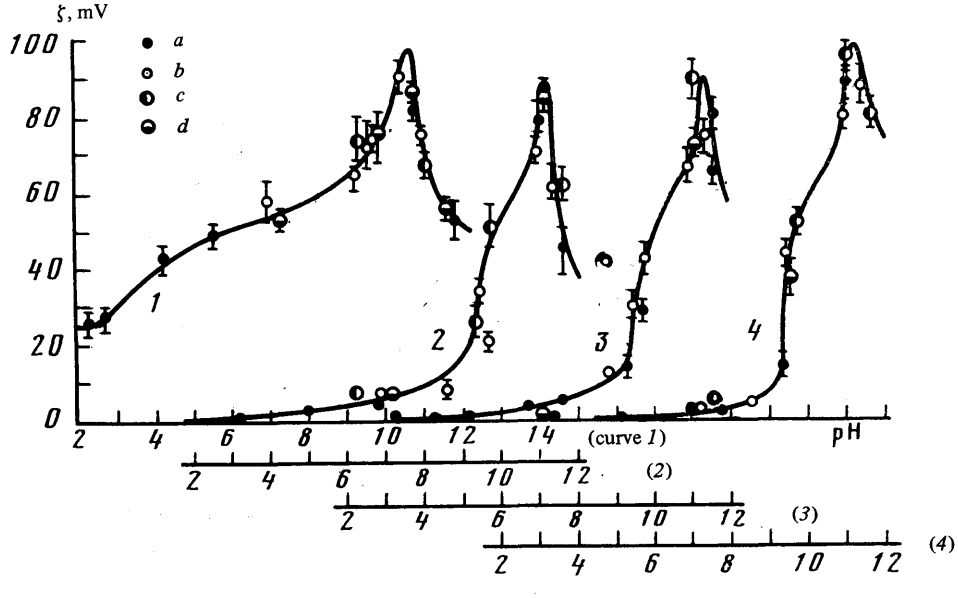


Figure 7. Dependence[49] of ζ-potential of quartz on pH for different concentrations of polyethylene oxide (g litre^{-1}); *1*) 0; *2*) 0.1; *3*) 0.3; *4*) 0.5 in: *a*) HCl; *b*) LiOH; *c*) NaOH; *d*) KOH.

The electrophoretic particle mobility of silver iodide sols in the presence of polyvinyl alcohol has been measured[1,2,6,12] as a function of pAg (Fig.8). Adsorption of the polymer is accompanied by a shift in the isoelectric point to more positive values, decrease in mobility in the region of a plateau, and diminished slope of the curves at this point. The shift in the point has been attributed[1,2,12] to displacement of dipolar water molecules from the surface layer by units of adsorbed macromolecules. The most marked shift in isoelectric point occurs with the initial portions of adsorbed polymer, which complete mainly a compact layer in contact with the particle surface. Subsequent portions are adsorbed predominantly by the lengthening of loops and spikes of adsorbed macromolecules, and the shift gradually reaches saturation. The lowering of the electrokinetic potential in the region of the "plateau" (Fig.8) and the decrease in slope of the curves at the isoelectric point are explained by movement of the slippage plane deep inside the solution on adsorption of the polymer. The shift in the isoelectric point and the diminution in slope have been used[1,2,12] to calculate certain parameters of adsorbed layers of polyvinyl alcohol on the surface of silver iodide particles (Section IV).

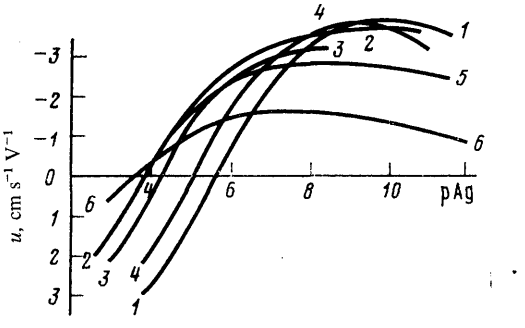


Figure 8. Dependence of electrophoretic mobility of particles of AgI sol in lmM KNO_3 on pAg in presence of different quantities (mg m^{-2}) of adsorbed pva-2 ($M = 106500$): *1*) 0; *2*) 0.12; *3*) 0.37; *4*) 0.50; *5*) 0.75; *6*) 1.00.

4. Dependence on Ionic Strength of Solution

Published information on the influence of ionic strength on the electrokinetic potential of particles in polymer-containing dispersions is extremely limited. Research[43,46,50] has actually been devoted to the effect of added inert electrolytes on the ζ–c relation. The changes observed with increase in ionic strength are explained by the effect of the added electrolyte on the thermodynamic character of the solvent, the quantity of polymer adsorbed, and the structure of adsorbed and electrical double layers. The adsorbed polymer sheath is regarded[51] as becoming increasingly permeable hydrodynamically with increase in the ionic strength of sufficiently concentrated electrolyte solutions, with a consequent displacement of the slippage plane into the adsorbed layer, approaching ever closer to the solid surface.

IV. EFFECT OF ADSORPTION OF POLYMERS ON CONDUCTIVITY OF DISPERSIONS

The electrokinetic charge σ_s usually constitutes only a small fraction of the charge in the outer part of the double layer of colloidal particles. The surface charge is in general balanced not only by the electrokinetic charge but also by gegenions present in the Stern layer and also—in the presence of a hydrodynamically stationary boundary liquid layer[52–54] or a gel-like layer (as on oxide surfaces[37–40])—by a mobile charge located in them. Fridrikhsberg et al.[55,56] showed that the mobility of ions in the stationary liquid boundary layer is closely similar to mobilities in bulk. Hence measurements of surface conductance or dielectric constant at low frequencies, which are sensitive to the ionic concentration throughout the diffuse region of the double layer, may give information on the potential ψ_δ at the boundary of the Stern layer. A quantitative theory of such an approach taking into account polarisation of the double layer has been developed by Dukhin et al.[3,4].

Calculation from measured specific surface conductances κ^σ of ψ_δ-potentials in the presence of adsorbed macromolecules is of interest from several points of view. Firstly such results supplement information, obtained from electrokinetic measurements, on the influence of the adsorption on the structure of the electrical double layer of particles. Secondly they help to reveal the mechanism of the stabilising effect of macromolecular compounds on colloidal solutions, whose stability may be determined under certain conditions, even in the presence of an adsorbed polymer layer, by the repulsion of electrical double layers[57,58]. Thirdly the possibilities of investigating the three-dimensional structure of adsorbed layers of non-ionic macromolecules are considerably increased if study of the electrokinetic potential is paralleled by that of the effect of polymer adsorption on specific surface conductance.

Whereas dozens of studies have been published on the surface conductance of dispersed particles (and have been reviewed[3]), the problem of the effect of adsorbed macromolecules on specific surface conductance has merely been posed. One of the Reviewers[59] has examined the influence of the adsorption of polyethylene oxide and polyvinyl alcohol on the conductivity of suspensions of spherical particles of antimony sulphide and polystyrene latex, as well as rod-shaped particles of the mineral palygorskite. The relative conductivity $\bar{K}/K$ of the suspensions ($\bar{K}$ being the conductivity of the suspension and K that of the dispersion medium) varied linearly with volume fraction p of the solid phase in all cases, the slopes of the straight lines diminishing as the electrolyte concentration in the system increased (Fig.9). This is explained by gradual diminution in the contribution to conductivity of surface conductance owing to the increase in conductivity of the dispersion medium and compression of the electrical double layer. With polarisation of the double layer taken into account the dependence of $\bar{K}/K$ on p for spherical and needle-shaped particles is described[3] by the equations

$$\frac{\bar{K}}{K} = 1 + 3p\left[-\frac{1}{2} + \frac{3}{2}\frac{\mathrm{Rel}}{(1+2\mathrm{Rel})}\right], \qquad (2)$$

$$\frac{\bar{K}}{K} = 1 + p\left[-\frac{5}{3} + \frac{2}{3}\mathrm{Rel}\left(1 + \frac{2}{1+2\mathrm{Rel}}\right)\right], \qquad (3)$$

where

$$\mathrm{Rel} = \varkappa^\sigma / Ka, \qquad (4)$$

is a dimensionless parameter[3,60] representing the contribution

by such polarisation to surface electrical phenomena and a is the particle radius. With high electrolyte concentrations, ensuring a negligible contribution by specific surface conductance, the theoretical limiting negative slopes of the dependence of $\overline{K}/K$ on p are realised experimentally, respectively $-\frac{3}{2}$ and $-\frac{5}{3}$ for spherical and needle-shaped particles—formulae (2) and (3).

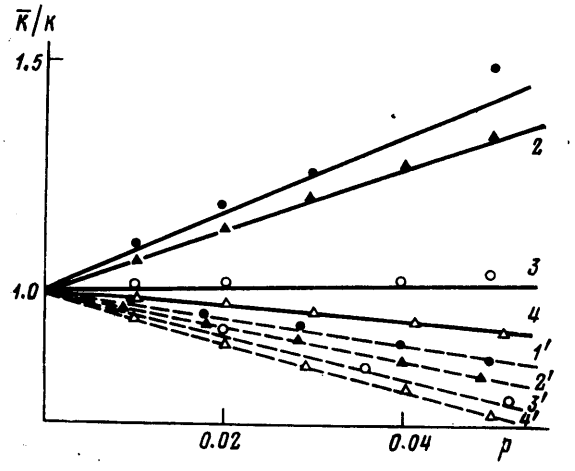


Figure 9. Dependence[59] of relative conductivity of palygorskite suspensions on proportion by volume of solid phase in sodium nitrate solutions of different concentrations (nM): *1*) 0.02; *2*) 0.1; *3*) 0.5; *4*) 5. The primes denote the presence of adsorbed pva-2 of molecular mass 48000.

Adsorption on charged particles of non-ionic polymers leads in all cases (with the electrolyte concentration unchanged) to a diminution in the slope of the relative-conductivity lines, i.e. to a decrease in the conductivity of the dispersion, the effect being larger the greater the quantity of macromolecular compound adsorbed per unit surface (Fig.9). Polymer adsorption may even change the sign of the slope. For example, addition of polyvinyl alcohol (1 mg m^{-2}) to a suspension of antimony(III) sulphide or palygorskite containing 0.01–0.1 M sodium nitrate changes the slope of the dependence of $\overline{K}/K$ on p from positive to negative (Fig.9). Furthermore, adsorption of non-ionogenic polymers gives negative slopes of the straight lines greater in absolute magnitude than would correspond to the limiting theoretical value.

Adsorption measurements[23,61] have shown that under the above experimental conditions all the macromolecular compound introduced into the system is entirely absorbed by the dispersed phase. Therefore surface effects—decrease in cross-section for passage of current in surface layer (which leads to a decrease in κ^σ) and increase in effective particle thickness owing to formation of a thick adsorbed layer—are solely responsible for the observed decrease in $\overline{K}/K$. Both effects cause the parameter Rel to decrease, which theoretically—formulae (2)–(4)—should produce the observed smaller slope of the straight lines. It must be borne in mind that the movement of ions in the adsorbed layer may be hindered not only by monomer units of the macromolecule but also by the few layers of water firmly bound to hydrophilic groups of the polymer, which have lost their solvent power. This view is supported in particular by an investigation by nuclear magnetic resonance of the hydration of polyethylene oxide and polyvinyl alcohol[62,63].

Application of Eqns.(2)–(4) to the results permitted calculation of the specific surface conductance κ^σ and ionic mobility u# within the double layer, as well as their variation in the presence of adsorbed polymer. The calculated values given as example in Table 2 show that increase in polymer adsorption is accompanied by a gradual decrease in κ^σ and u in the double layer, in full agreement with the above qualitative considerations.

Table 2. Effect of adsorption of non-ionic polymers on κ^σ and u of dispersions of palygorskite in 0.1mM $NaNO_3$.[59]

Polymer	10^{-4} M	Γ, mg m^{-2}	$10^9\kappa^\sigma$, ohm^{-1}	u, cm^2 ohm^{-1} g-equiv.$^{-1}$
		—	3.0	5.5
pva-2	4.8	0.3	2.8	5.1
peo	130	0.6	2.2	4.0
pva-23	6.4	0.9	0.9	1.7

The influence of the adsorption of macromolecules on the surface conductance of dispersions has recently been examined theoretically by Dukhin[64] on the view that the structure of the adsorption sheath, like that of a gel[65], can be described by a model of randomly oriented cylinders forming an obstacle to the passage of current. The decrease in the conductivity of a gel K_g relative to that of the electrolyte K is represented[64] by a linear dependence on the volume fraction P_p of the gel (in the present case adsorbed segments of the macromolecule):

$$K_g = K(1 - BP_p). \tag{5}$$

For strongly charged particles ($\tilde{\psi}_\delta = \psi_\delta / kT > 3$–4), provided that change in dielectric constant has little effect on the structure of the double layer, the adsorption P_p of segments diminishes the surface conductance by the factor

$$\beta = \kappa^\sigma(P_p)/\kappa^\sigma(0). \tag{6}$$

The term BP_p can be evaluated from the simplified relation[64]

$$\beta = (1 - BP_p)(1 + 3m)^{-1}, \tag{7}$$

which is valid at high electrolyte concentrations, i.e. when $\kappa h \gg 1$. Here m is a dimensionless parameter representing the contribution to κ^σ by the transport of charges by electro-osmotic flow of the liquid, which can be calculated theoretically, h is the thickness of the adsorbed polymer layer, and κ is the reciprocal of the Debye radius. Thus, by measuring the specific surface conductance in the presence and in the absence of an adsorbed polymer sheath $\kappa^\sigma(p)$ and $\kappa^\sigma(0)$, we can calculate BP_p and then[64] make a choice in favour of a particular dependence of density of adsorbed segments on distance from surface.

More detailed information on the calculation of u will be found in Ref.3.

V. DETERMINATION OF PARAMETERS OF ADSORBED LAYERS OF POLYMERS FROM SURFACE ELECTRICAL MEASUREMENTS

Information on the most important parameters of adsorbed polymer layers—the proportion ν of monomer units in direct contact with the surface, the surface coverage θ by adsorbed units, and the effective thickness h of the adsorbed layer—can be obtained from measurements of surface charge, electrokinetic potential, and surface conductance of particles in the presence of adsorbed macromolecular compounds. Comparison of these parameters with the dimensions of macromolecular coils in solution and with adsorption measurements also leads to definite conclusions on the degree of deformation of macromolecules when adsorbed and on the density distribution of segments along the normal to the surface $\rho(x)$.

Determination of the above characteristics is based on an assumed analogy in structure between the electrical double layer and a surface polymer sheath[1,2,12]. Like the former, which is arbitrarily divided into a dense region (or Stern layer), in which specific interaction takes place between ions and surface, and a diffuse region (Gouy layer) with an exponential fall in concentration of gegenions with distance from the surface, an adsorbed polymer film can be divided into a first (dense) layer of monomer units in direct contact with the surface and a loose layer of spikes and loops directed towards the solution, in which the density of segments gradually diminishes with distance[1]. Many factors—quantity of polymer adsorbed, energy of adsorption of a monomer unit, nature of solvent, flexibility of polymer chain, etc.—determine the nature of the function $\rho(x)$.[5,66-69] The Stern layer and a dense layer of adsorbed units are similar in thickness (~0.4–0.5 nm). Therefore investigation of the former (which is possible in concentrated electrolyte solutions, in which the electrical double layer is strongly compressed) may give information on the parameters of the first layer of units of adsorbed macromolecules, directly attached to the surface. Measurement of the characteristics of the diffuse ionic layer (in dilute electrolyte solutions) gives indications of spikes and loops located beyond the dense layer, the thickness of the adsorbed film, etc.

Determination of Surface Coverage θ

The surface coverage with adsorbed monomer units can be calculated[1,2,6,12,29] from data on the displacement of the zero-charge or isoelectric point as a consequence of adsorption. The basis of the first method, originally developed for the adsorption of organic molecules on a mercury electrode, is that, in the absence of specific adsorption of ions, the shift in the zero-charge point is proportional to the number of adsorbed molecules per unit area[7]:

$$\Delta_{zcp} = \text{const} \cdot n_a. \tag{8}$$

The shift is attributed in this case to displacement of water dipoles from the surface layer by adsorbed molecules of a surface-active substance. Transfer of these ideas to the adsorption of macromolecular compounds encounters several difficulties, which have been analysed in detail by Lyklema et al.[1,2,12] for the example of silver iodide and polyvinyl alcohol solution. The first difficulty is that the thermodynamics of surface phenomena, used to analyse the electrical double layer in the presence of organic compounds, is applicable only to reversible adsorption processes. Although the adsorption of polymers is irreversible with respect to change in their concentration in solution, it may be reversible with respect to change in concentration of potential-determining ions. Furthermore, the requirement of reversibility concerns only a small proportion of the total quantity of monomer per units adsorbed (those in direct contact with the surface), which is apparent on the measurement of surface charge. The second difficulty is the difference in surface area accessible to macromolecules and to potential-determining ions. Therefore an "average" charge σ_{av} (Eqn.1) is normally used in the calculation of surface coverage.

According to Frumkin[70] the charge $\sigma(\theta)$ on a surface partly covered with surface-active molecules can be written as a linear combination of the charge σ_0 on an uncovered surface and the charge $\sigma(\theta=1)$ on the surface completely (100%) covered with adsorbate:

$$\sigma(\theta) = (1-\theta)\sigma_0 + \theta\sigma(\theta=1). \tag{9}$$

This relation has been used[1,2,12] to calculate the surface coverage of silver iodide with adsorbed polyvinyl alcohol $[CH_2.CH(OH)]_n$ on the basis that the adsorption of monomer units directly attached to the surface is a reversible function of pAg. Here the Stern layer can be regarded as comprising $\frac{1}{2}\theta$ $CH_2 + \frac{1}{2}\theta$ $CH(OH) + 1 - \theta$ vacancies. The symbols $\sigma(\theta)$ and σ_0 denote the measured surface charge densities in the presence and in the absence of adsorbed polyvinyl alcohol, while $\sigma(\theta=1)$ is found indirectly by regarding the Stern layer at maximum surface coverage as a hypothetical layer 50% covered with CH_3 (as in the case of butanol) and 50% with CH(OH) groups (as for ethylene glycol). Thus at a given ψ_0-potential

$$\sigma_{pva} = (1-\theta)\sigma_0 + \frac{1}{2}\theta[\sigma(\theta=1)_{BuOH} + \sigma(\theta=1)_{egl}], \tag{10}$$

or for the shift in the zero-charge point

$$\Delta_{zcp,\,pva} = \frac{1}{2}\theta[\Delta_{zcp.}(\theta=1)_{BuOH} + \Delta_{zcp.}(\theta=1)_{egl}]. \tag{11}$$

The surface coverage in the first (dense) layer of units is clearly $\theta = n_a(\theta)/n_a(\theta=1)$, or from Eqn.(8) [29]

$$\theta = \frac{\Delta_{zcp.}(\theta)_{pva}}{\Delta_{zcp.}(\theta=1)_{pva}} = \frac{2\Delta_{zcp.}(\theta)_{pva}}{\Delta_{zcp}(\theta=1)_{BuOH} + \Delta_{zcp.}(\theta=1)_{egl}}, \tag{12}$$

where n_a is the number of adsorbed units per unit surface area. The calculation was based[1,2,6,12] on published values of the shift in the zero-charge point of silver iodide on the adsorption of butanol and ethylene glycol[7,30] and measured values of $\Delta_{zcp}(\theta)_{pva}$. The maximum surface coverage was found to be $\theta = 0.85$: i.e. even with complete surface coverage of silver iodide with polyvinyl alcohol 15% of the Stern layer is "vacant" for the polymer.

Surface coverage can be calculated also[1,2,12] from electrophoretic data—from the change in the isoelectric point of particles in the presence of adsorbed polymer—which has the advantage that the isoelectric point can be measured more accurately than the zero-charge point. Moreover, the former measurements can be made on particles of a sol, whose surface, in contrast to the suspensions on which surface charge density is measured, are completely accessible to adsorbed macromolecules.

The fact that the initial portions of polyvinyl alcohol adsorbed on silver iodide produce the largest shifts in the isoelectric point, after which the latter reach saturation, has enabled[1,2] surface coverage to be calculated from the relation

$$\theta = \frac{\Delta_{iep.}(\theta)}{\Delta_{iep}(\theta=1)}\theta_{max}. \tag{13}$$

where $\theta_{max} = 0.85$. Fig.10 shows that, with increase in adsorption, surface coverage of silver iodide by monomer units increases rapidly to ~0.7 mg m^{-2}, which indicates that the greater part of the polymer has been adsorbed as a flat layer having many contacts with the surface. Further adsorption is accompanied by a slow increase in coverage, the excess of polymer accumulating as spikes and loops.

Determination of surface coverage by the two methods gives closely similar results. It is significant that the coverage is determined mainly by the quantity of polyvinyl alcohol adsorbed, and is little dependent on the molecular mass or the content of acetate groups.

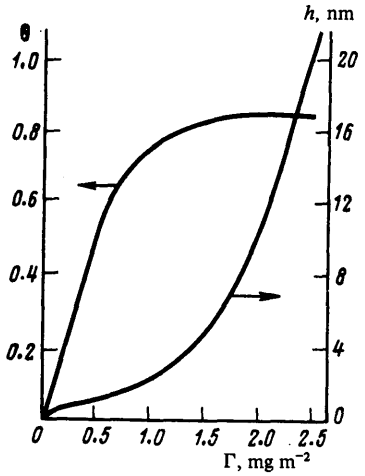


Figure 10. Effects[2,112] of quantity of polyvinyl alcohol adsorbed on surface coverage θ of silver iodide particles and on thickness *h* of adsorbed layer.

Determination of Proportion of Monomer Units in Direct Contact with Surface ν

From data on surface coverage for various quantities of polymer adsorbed Γ (in mg m^{-2}) we can calculate also an important parameter of the adsorbed layer—the proportion of monomer units in a macromolecule that are in direct contact with the surface[12]:

$$\nu = [M_{mu}/N_A a_0]\theta/\Gamma, \qquad (14)$$

where N_A is Avogadro's number, M_{mu} the molecular mass of a monomer unit, and a_0 (nm^2) the area occupied by one unit. This area can be calculated from the density of the dry polymer and its molecular mass as the projected area of the effective hydrodynamic sphere. Monomer units of water-soluble polymers can be assumed[23,29,61] to be adsorbed with the whole firmly bound hydration sphere, which e.g. for polyvinyl alcohol and polyethylene oxide comprises two water molecules per monomer unit[62,63]. Therefore the calculation of a_0 must take account also of coordinated water. This gives values of 0.30 and 0.28 nm^2 respectively for $[CH_2.CH_2.O].2H_2O$ and $[CH_2.CH(OH)].2H_2O$. Fig.11 illustrates the ν(Γ) dependence calculated from Eqn.(14) for the adsorption of polyvinyl alcohol on silver iodide. Even at low surface coverage with the polymer ν ≠ 0.4–0.5, while the proportion of units attached to the surface diminishes with increase in polymer adsorption, in good agreement with other measurements[5,71,72].

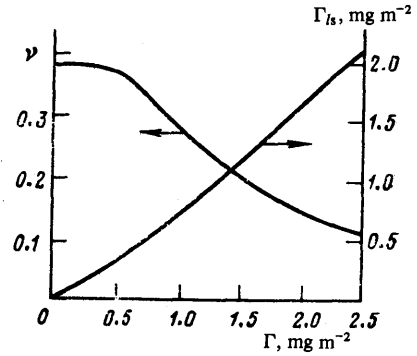


Figure 11. Dependence[12] of proportion ν of monomer units directly in contact with surface and of quantity Γ_{ls} of polymer present as spikes and loops on quantity of polyvinyl alcohol adsorbed on silver iodide particles.

The Reviewers evaluated ν from data on the number of contacts of an adsorbed macromolecular chain with the surface calculated from values of $\Delta\sigma_i$ for the surface of antimony sulphide particles during the adsorption of polyethylene oxide[19]. The total potential difference between the phases consists of ionic and dipolar components[13] (Section I), and the proposed method is based on the view that, in solutions of moderate ionic strength, the major part of the potential difference occurs in the dense region of the double layer, whose thickness is comparable with the length of a monomer unit in polyethylene oxide(0.4–0.5 nm). With an insignificant change in capacitance of the double layer in the presence of the polymer the condition of constant surface potential can then be replaced by constancy of the surface charge: $\sigma = \sigma_i + \sigma_d = \text{const}$, where σ_i is the ionic component of the surface charge, and σ_d the total charge of the ends of adsorbed dipoles oriented along the normal to the surface. By equating the observed value of $\Delta\sigma_i$ to σ_d we can calculate the number *n* of ends of dipoles oriented in the adsorbed polymer layer from the relation $\Delta\sigma_i = \sigma_d = Dn/l$, where *D* (in D) is the dipolar moment of a monomer unit and *l* the length of a dipole.

The results[19] indicate that (i) for a given quantity of polyethylene oxide adsorbed the number of contacts between polymer and surface is independent of molecular mass, (ii) with increase in surface coverage the proportion per adsorbed molecule of units in contact with the surface diminishes, and (iii) even with small amounts adsorbed the proportion of units directly attached to the surface does not exceed one-third of the total number of adsorbed units, in good agreement with published values for other polymer–solid systems[5,71–74].

Calculation of Quantity of Polymer in Loops and Spikes Γ_{ls}

From data on the area a_0 occupied by a monomer unit and the surface coverage θ it is easy to calculate the quantity of polymer Γ_1 in direct contact with the surface, i.e. in the first (dense) part of the adsorbed film. Subtraction from the total quantity adsorbed Γ will then give the quantity of polymer Γ_{ls} present on the surface as loops and spikes. Fig.11 illustrates the variation in Γ_{ls} with increase in the adsorption of polyvinyl alcohol on silver iodide particles[12].

Determination of Thickness of Adsorbed Film *h*

The adsorption of macromolecular compounds usually lowers the electrokinetic potential of particles (above). If the surface charge of the latter is not significantly changed[19, 23,50], it can reasonably be assumed that the observed decrease in potential is due primarily to displacement of the slippage plane into the liquid phase as a result of surface formation of adsorbed films of increasing thickness. In such case, even if adsorption leads to a change in surface charge density, it is usually observed at low surface coverage, and can be allowed for in the calculation of electrokinetic potential.

Film thickness can be calculated from $\zeta-\Gamma$ relations plotted from a comparison of adsorption and electrokinetic measurements on the same system. The method involves calculating the shift in the slippage plane, which is identified with the effective thickness of the polymer sheath relative to the boundary of the Stern layer. It is assumed that the adsorbed polymer does not affect the distribution of potential in the double layer and that the polymer sheath is hydrodynamically impermeable. From the equilibrium distribution of potential in the vicinity of the particles we can then calculate for each measured ζ-potential the coordinates of the slippage plane, by means of the well known theoretical formula of the diffuse double layer[13]

$$\tanh\left(\frac{ze\zeta}{4kT}\right) = \tanh\left(\frac{ze\psi_\delta}{4kT}\right)e^{-\kappa x},\quad h = x + \delta, \qquad (15)$$

in which κ^{-1} is the Debye shielding radius, z the valency of the gegenions, e the elementary charge, δ the thickness of the Stern layer, and x the distance from the slippage plane to the boundary of this layer, the ψ_δ-potential usually being equated to the ζ-potential in the absence of polymer. This method has been used to calculate film thickness h for the adsorption of polyethylene oxide and polyvinyl alcohol on particles of silver iodide and antimony sulphide[23,24,50,61,75] as well as on latices[76].

The results show that the adsorbed layers increase in thickness to several tens of nanometres with increase in polymer adsorption (Fig.12). It is significant that at a given adsorption the thickness varies little with molecular mass, and for polyvinyl alcohol with the content of acetate groups[23,24,50,61]. This implies that the mean length of adsorbed loops and spikes is also little affected by molecular mass. The values found for the film thickness agree to within 20–50% with those obtained by other methods—for polyvinyl alcohol on silver iodide viscosimetrically[6,29], for polyethylene oxide on the same surface by electron microscopy[77], and for polyvinyl alcohol on latex particles by measurement of precipitate volume, ultracentrifugation, and diffusion[76].

The present method has been criticised[2] on the grounds firstly that difficulties are involved in calculating electrokinetic potentials from electrophoretic mobility data owing to polarisation of the double layer, and secondly that the true potential at the boundary of the Stern layer is usually unknown and its replacement by ζ_0 is an approximation. It must be borne in mind also[50,51,76] that formula (15) gives the potential distribution in a planar double layer, and its

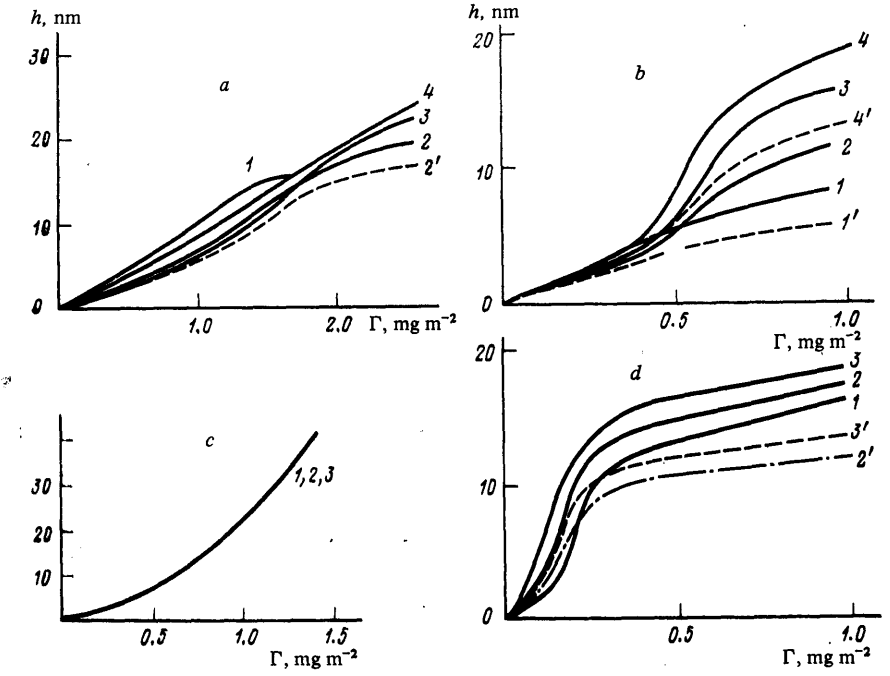


Figure 12. Variation, calculated from electrophoretic measurements[24], of thickness of polymer sheath on sol particles with quantity of polymer adsorbed. Lettering of diagrams and numbering of curves as in Figs.3 and 6 [sic].

application is valid only provided that $\kappa a \gg 1$. Furthermore, the condition of hydrodynamic impermeability of the adsorbed polymer layer may break down in solutions of high electrolyte concentrations[51].

One of us[51] used the adsorption of polyethylene oxide on fine particles ($a \approx 11$ nm) of antimony sulphide as example to make a detailed analysis of the influence of various complicating factors—polarisation of the double layer, curvature of the surface, presence of electrolytes—on the calculation of film thickness from electrophoretic data. With κ, a, and Rel having the respective values 1, 3, and 2 (the parameter $\mathrm{Rel} = e^{\frac{1}{2}\psi\delta - 1}/\kappa a$ represents the contribution by polarisation of the double layer to surface electrical phenomena; this polarisation can be neglected when $\mathrm{Rel} \ll 1$ [60,78]), i.e. when polarisation of the double layer must be taken into account, film thicknesses found from electrokinetic potentials calculated with and without allowance for such polarisation ζ_W§ and ζ_S differ by at most 10%. Such a small difference in thickness with a substantial difference in electrokinetic potentials ($\zeta_W \cong 2\zeta_S$) is due firstly to the occurrence of the distance of the slippage plane from the surface in the exponent in Eqn.(15), so that the thickness is insensitive to the ζ-potential, and secondly to the dependence of h not on absolute values of ζ but on the ratio of their hyperbolic tangents. A more substantial error in the thickness is due to disregard of surface curvature: values of h calculated from formulae for a spherical double layer are usually smaller than those calculated for a planar surface[50]. From results obtained[79] with the condition $\kappa h < 1$ a first correction for surface curvature will yield for spherical particles the formula[51]

$$\kappa h = \left[\left\{\tanh\left(\frac{ze\zeta_0}{4kT}\right)\Big/\tanh\left(\frac{ze\zeta}{4kT}\right)\right\} - 1\right]\left[1 - \left\{1/\kappa a \cosh^2\left(\frac{ze\zeta_0}{4kT}\right)\frac{\mathrm{th}\,(ze\zeta_0/4kT)}{\mathrm{th}\,(ze\zeta/4kT)}\right\}\right]. \quad (16)$$

This shows that the error when h is determined without any correction for curvature increases as ζ and κa decrease: whereas with $\kappa a = 5$ and $\zeta_0 = 100$ mV the error is only 2–3%, when $\kappa a \approx 1$ the formula from which (16) was obtained itself gives an error already exceeding 10%.[79] In general, when both surface curvature and concentration polarisation of the double layer are taken into account, the use of formula (15) with ζ-potentials determined by Smolukhovskii's method with $\kappa a \leq 1$ may produce significant distortion of the results. Thus comparison of h calculated by means of Eqn.(15) with thicknesses determined from results[81] for ζ_0 values of 50, 100, and 150 mV gives differences of 49%, 73%, and 65% respectively[51].

It was shown[51] also that the increase in effective particle radius due to polymer adsorption must also be taken into account in the calculation of thickness, i.e. that it is more correct to use $\kappa(a+h)$ instead of κa, but then the parameter h itself must be determined. This requires a set of equations to be solved, one of which defines the dependence of the equilibrium potential on the distance from the particle surface with a known potential ζ_0, while the second is obtained from the dependence of the observed electrophoretic mobility on the ζ-potential and the corresponding quantity $\kappa(a+h)$. Analytical solution of such a problem is quite laborious, even when a computer is used, so that one of us has suggested a graphical method (see Ref.51 for details). Thicknesses obtained in this way will be the most accurate, since polarisation of the double layer, curvature of the surface, and variation in effective particle radius during coating with thickening adsorbed polymer films have all been taken into account.

§The ζ_W potential is calculated in this case from Wiersema's tables[80].

It was shown also[51] that thicknesses of polyethylene oxide on antimony sulphide particles calculated from electrokinetic potentials in relatively concentrated (>0.01 M) electrolyte solutions are improbably small (≤3 nm). This may be due to enhancement of permeability of the adsorption sheath with increase in ionic strength of the solution. In such case the slippage boundary, from which the layer thickness h is assessed, will pass into this layer and move nearer the surface of the dispersed phase. Under these conditions the determination of thickness from electrophoretic data on the basis of the above simple ideas is incorrect. New possibilities for calculating h in the case of permeable adsorbed layers are revealed by a theory developed recently[64].

In view of the above limitations and difficulties involved in calculating thickness from the fall in the electrokinetic potential, Lyklema[2] suggested calculating h on silver iodide particles from the slope of the experimental variation in ζ as a function of pAg at or near the isoelectric point. The basis of the proposed method was the decrease in slope with increase in h. For a planar double layer in a uni-univalent electrolyte the equation

$$\left(\frac{d\zeta}{dpAg}\right)_{\sigma\to 0} = 58.16\,\frac{\mathrm{sech}^2(e\psi_\delta/4kT)}{\mathrm{sech}^2\,(e\zeta/4kT)}\,\frac{C}{C_d}\exp(-\kappa h), \quad (17)$$

was derived, and use of the Debye–Hückel approximation gave

$$\left(\frac{d\zeta}{dpAg}\right)_{\sigma\to 0} = 58.16\,\frac{C\exp(-\kappa h)}{C_d(a+h)} \quad (18)$$

for a spherical double layer[2,12]. In these equations C is the total capacitance of the double layer, which can be found from potentiometric data, while the capacitance C_d of the diffuse ionic layer can be obtained from the theoretical relation $C^{-1} = C_m^{-1} + C_d^{-1}$ provided that the surface potential and the electrolyte concentration are low (C_m is the capacitance of the molecular capacitor, which is usually 20 $\mu F/cm^{-2}$). The value of ψ_δ in Eqn.(17) is calculated from data on surface charge density determined by titration. Thus the only unknown in Eqns.(17) and (18) is h. The variation in the thickness of the polymer sheath calculated in this way for the adsorption of polyvinyl alcohol or particles of silver iodide is shown in Fig.10. The results are somewhat smaller than viscosimetric values for the same system and thicknesses of this polymer on latex particles measured by hydrodynamic methods[6,26,76]. Nevertheless, the course of the $h-\Gamma$ dependence and the absolute thicknesses are closely similar to those found from the fall in the electrokinetic potential (above).

Our discovery of a decrease in the relative conductivity of dispersions having a polymer sheath for values below those predicted theoretically suggests a new method for estimating film thickness. Its basis is that appearance of a "hypertheoretical" slope in the plots of $\bar{K}/K$ against p during adsorption is associated with an increase in relative particle volume due to formation of an adsorbed polymer layer within which water is immobilised. The difference Δp corresponding to points of intersection of a straight line parallel to the abscissae axis with the $\bar{K}K^{-1}-p$ straight lines for suspensions with and without added macromolecular compounds gives the increase in relative volume due to polymer adsorption. From this difference and the corresponding volumes it is easy to calculate h. For the adsorption of polyvinyl alcohol on palygorskite particles, for example, the resulting thickness (~15 nm) is extremely plausible.

Knowing the film thickness for various adsorbed quantities and parameters of macromolecular coils in solution found by viscosimetric or optical (light-scattering) methods, we can define a probable model for the adsorption of non-ionic polymers on colloidal particles. The Reviewers' calculations for the adsorption of polyvinyl alcohol and polyethylene oxide on silver iodide and antimony sulphide particles[50,82] enabled them to eliminate for these systems a model of monomer units arranged flat on the surface in the form of similar (equal-sized) loops with a regular alternation of units attached to the surface along the macromolecular chain, and also as undeformed random coils. Calculated values of h were appreciably less than double the radius of inertia of a polymer coil in solution $2\langle s^2\rangle^{\frac{1}{2}}$ (thus for polyethylene oxide of molecular mass 2.3×10^5 on antimony sulphide with $\Gamma = 1.0$ mg m^{-2} we have $h = 20$ nm, whereas $2\langle s^2\rangle^{\frac{1}{2}} \approx 50$ nm [82]), the difference between $2\langle s^2\rangle^{\frac{1}{2}}$ and h increasing rapidly with increase in molecular mass[50,83]. These facts indicate appreciable deformation of the macromolecular coils of these polymers when adsorbed on the above inorganic surfaces.

The experimental results can be explained satisfactorily by the Bulas–Hoeve–Hesselink model of an adsorbed film[60–69,83], according to which the polymer sheath on the surface consists of a denser first layer and a layer of dissimilar loops and spikes pointing towards the liquid, with an exponential size distribution. At the boundary of the first layer the density of segments changes abruptly, while beyond this layer the variation $\rho(x)$ along the normal to the surface is described for homopolymers by the exponential relation[68]

$$\rho(x) = 12\frac{x}{il_{st}^3}\exp\left(-6x^2/il_{st}^3\right), \qquad (19)$$

in which l_{st} is the length of a statistical chain unit (segment) and i the number of segments in a loop. It can be shown for such a model that the mean number of segments in a loop $\bar{i}$ and the length l_{st} are interrelated[6,29]:

$$\bar{i} = 2b\sqrt{6}/l_{st}\,p_H, \qquad (20)$$

where b is a numerical constant approximating to 0.7 [6,29] and the parameter p_H is a function of the proportion ν of units attached to the surface (it is calculated as the ratio of the number n_1 of units in the first layer to their total number n per unit surface; n_1 has been calculated from the area occupied by a unit together with the surface coverage θ found by the above method) and the dimensionless constant $K_H < 1$ determined by the flexibility of the polymer chain. This constant is evaluated by calculating from the relation[6,29]

$$h - \delta' = \frac{n-n_1}{K_H\rho_0}\ln\left(\frac{K_H\rho_0}{\rho_{eff}}\right) \qquad (21)$$

(which holds for $\Gamma \geq 0.5$ mg m^{-2}) the theoretical dependence of layer thickness h on quantity of polymer adsorbed that best coincides with the experimental curve. Here δ' is the thickness of units in the first layer, $\rho_0\delta' = n_1$, and the effective density of the adsorbed film ρ_{eff} is calculated from the theory of polymer solutions as the density of a statistical coil of radius equal to the thickness of the polymer sheath. Thus the same variation of density of segments with distance is assumed in the adsorbed film (from the surface) and in the statistical coil (from its centre of gravity): i.e. $\rho_c(i) = \rho_{eff}$ and $\bar{i} = h$. This, of course, is only an approximation, but is fairly accurate, since the thickness found from formula (21) is not very sensitive to the effective density[6,29]. For example, with $K_H = 0.8$ and $10^4\rho_0 = 70$ Å^{-3} the value of h decreases by only 17% for an increase in ρ_{eff} of 50%.[29]

The Reviewers' experimental results[23,25] on the adsorption of polyvinyl alcohol on silver iodide and on antimony sulphide corresponded most closely to the values 0.3 and 0.25 respectively for K_H; for polyethylene oxide on silver iodide K_H varied from 0.07 to 0.1 depending on the molecular mass of the specimen. From values of $\bar{i}$ calculated in this way it is easy to find the number of groups adsorbed by unit surface as $N_1 = n_1/\bar{i}$, where n_1 is the number of units attached as loops to the surface, calculated as the difference between n and n_1.

Table 3. Parameters of macromolecular chains of polyvinyl alcohol and polyethylene oxide in surface layer of silver iodide particles[23,50].

Polymer	10^{-4} M	Γ_1, mg m^{-2}	$\bar{i}$ with Γ (mg m^{-2})			$10^{-16}N_1$, m^{-2}
			0,4	0,7	1,0	
pva-12	2.2	0.17	3.8	6.6	13	11.6
peo-1	23	0.15	21	50	78	6.6
peo-2	130	0.15	23	55	87	5.9
peo-3	260	0.15	32	76	120	4.3

Thus combined adsorption, electrokinetic, and viscosimetric measurements open up a path to determination of the most important parameters of adsorbed polymer films—the number and length of loops N_1 and $\bar{i}$ adsorbed by unit area—which are required for theoretical calculation of the energy of repulsion V_R of colloidal particles covered with a polymer sheath. Table 3 lists several parameters of macromolecular chains of polyethylene oxide and polyvinyl alcohol on the surface of silver iodide and antimony sulphide particles found by the above method. The Reviewers have used them to calculate the polymer component of the energy of repulsion of the particles and for a theoretical interpretation of the stabilisation of the sols by additions of these polymers[57,58,84].

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Institute of Colloid and Water Chemistry,
Ukrainian SSR Academy of Sciences,
Kiev