

CCA-595

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Conference Abstract

Physical Adsorption — a Tool in the Study of the Frontiers of Matter

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Physical adsorption has most often been treated as involving a two-dimensional or thin film state of the adsorbate. That is, while the adsorbent is conventionally regarded as providing an adsorption potential, it usually is otherwise viewed as an essentially inert substrate. By contrast, the general theme of this lecture will be that physical adsorption provides a great deal of information about the nature of the solid surface and, in many cases, important information about the adsorbent-adsorbate as a mutually interacting one.

First, adsorption in the submonolayer to monolayer region is widely used to obtain the surface area of the solid, through the Brunauer-Emmett and Teller equation. At larger coverages, the *universal isotherm* or *t-curve* concept can be used to the same end. Submonolayer adsorption further allows the determination of a site energy distribution; in the case of very heterogeneous surfaces, this distribution is virtually independent of any assumption as to the equation of state of the adsorbed film. Extension of such studies should further allow finding at least a qualitative surface distribution function for the heterogeneities, that is, the probability that sites of particular adsorption energies will be adjacent.

Second, in the case of molecular solids, such as ice, ammonia powder, benzene powder, etc., low temperature adsorption studies provide a maximum value for dispersion interactions. It turns out that such interactions rarely exceed by very much that between adsorbate molecules. Thus the energy of nitrogen adsorption on solids such as the above is only slightly above that of condensation of nitrogen itself. It appears, in fact, that dispersion interaction energies are significantly less than has previously been thought to be the case, and that the semi-empirical estimates that have been made in the case of adsorption on refractory solids such as the various carbon blacks have unwittingly ignored significant surface dipole fields. Further, just as in chemisorption, the surface may be restructured by the adsorption process, so may the same effect occur in physical adsorption. In chemisorption, the adsorption bond can be strong enough to be comparable to the lattice bonds of even quite refractory solid. In physical adsorption, the adsorption bond is much weaker, but with molecular solids or in general with solids near their melting point, the adsorption energy may again be sufficient to occasion surface restructuring. Clear evidence for this is found in the case of *n*-hexane adsorption on ice, in which the character of the adsorption changes markedly around -35°C . In fact, such adsorption studies provide a means of confirming that some form of pre-melting or anomalous surface film formation occurs with ice near its melting point.

Third, adsorption at pressures near the saturation pressure, P_0 , of the adsorbate provides important information about contact angle and wetting processes. In the case of a liquid which forms an equilibrium, non-zero contact angle with the solid, an adsorbed film of finite thickness evidently co-exists with bulk liquid, that is, is in equilibrium with pressure P_0 . The situation clearly implies structural perturbation in the adsorbed film; in the case of systems showing a finite contact angle, the adsorbed film in equilibrium with P_0 cannot have the structure of normal bulk liquid no matter how thick that film may be. It is possible, by means of a simple model, actually to calculate contact angles or spreading coefficients solely from the physical adsorption isotherm of the liquid involved. The model also provides some

insight as to the fundamental characteristics required either for good spreading or, conversely, for the contact angle to be very large.

In summary, a complete physical adsorption isotherm can provide information about the surface area of a solid, and about both the site energy distribution function and the surface site distribution function. It can indicate whether or not significant restructuring of the adsorbent occurs upon adsorption, and whether the adsorbed film, as it thickens, is significantly different from bulk liquid in its structure. The complete adsorption isotherm contains the information needed to obtain contact angles or spreading coefficients.

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Conference Abstract

Thermodynamic Properties of Polyelectrolyte Solutions

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The solutions of polyelectrolytes display large deviations from the ideal behaviour even at very low concentrations. This nonideality is a consequence of the strong electrostatic interaction between highly charged polyion and its counterions.

For the quantitative treatment of a polyelectrolyte solution we need an expression for the electrostatic free energy from which all thermodynamic properties can be derived. Two groups of models are reviewed and discussed: (a) polyion is a penetrable or impenetrable sphere immersed in a salt solution or pure solvent (sphere models); (b) polyion is a stretched rod or a coiled chain immersed in a salt solution or pure solvent (chain models). With only a few exceptions, all of the treatments proposed hitherto employ the Poisson-Boltzmann equation in an attempt to calculate the electrostatic potential in the vicinity of the polyion. From the potential the electrostatic free energy is obtained by a charging process.

The calculations based on the rodlike model are compared with the experimental results for the following thermodynamic properties: osmotic coefficient, activity coefficient of the counterions, mean activity coefficient of the polyelectrolyte, and heat of dilution. The agreement between theory and experiment is reasonable in a wide concentration range. The only adjustable parameter is the linear charge density on the polyion. The same model is also applied for the numerical calculation of the simultaneous distribution of mono- and divalent counterions around a polyion. It is found that the degree of ion binding of the less bound monovalent ions increases and that of the more bound divalent ions decreases with increasing equivalent fraction of the corresponding ionic species. These results are applied for the calculation of the osmotic coefficient and of the ratio of activity coefficients of counterions. A good agreement of these calculations with experimental results is discussed in the light of the rodlike model.

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Conference Abstract

The Nature of the Adsorption of Polymers from Solution and its Role in Colloidal Phenomena

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A series of publications in recent years has shown that the most prevalent form of adsorption of long chain polymers from solutions is that of coils which adsorb with a limited number of segments while retaining random conformation of the free segment in the adjacent liquid. A number of theories have been developed to explain this behavior which appears to be a consequence of obtaining the minimum of potential energy for interface, polymer and solvents, while retaining a maximum entropy for the latter two components.

The consequences of adsorption by way of loose coils are manifold and make themselves felt in widely different areas. The passage of liquid through narrow capillaries *e.g.* is inhibited because the capillary lumen is reduced by adsorbed layers which can reach thicknesses of up to 1000 Angstroms. Reduced flow rate is then likely to be a factor in the sludging of blood when denatured proteins adsorb on capillary walls or red cells. In dispersions, polymers which are present as protective colloids act by providing an elastic compressible cushion which resists deformation when particles collide. If the protective, adsorbed, polymer is a poly-electrolyte or polyampholyte, the thickness of the adsorbed layer changes drastically with pH and may do so also through binding of ions.

The attachment of polymer segments to surfaces liberates solvent or solute molecules that were themselves attached to interface or polymer. Thus, the entropy of the system may increase during adsorption and the amounts adsorbed may increase with temperature. Desolvation of the polymer with heat may, on the other hand, lead to aggregation and flocculation reactions.

The adsorbed layer of polymer acts also like a heavily swollen membrane that surrounds particle (surfaces) and may retard diffusion to and from the interface, or favor passage of certain solutes in one direction. Vice versa, particles embedded in the polymeric membrane may change the structure of the attached polymer to a depth of several hundred or several thousand Angstroms. At a sufficient density of dispersed particles the mechanical and permeability properties of the membrane may become profoundly altered.

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Conference Abstract

Calculation of Hamaker Constants from Surface Free Energy Measurements

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The development of equations for relating pair potential summations to the work of adhesion at interfaces allows us to calculate directly the Hamaker constants from any experimental data providing information on the work of adhesion, such as surface tension, interfacial tension, contact angles, free energy of adsorption, free energy of immersion, etc. Once we know the Hamaker constants for the various condensed phases we can calculate the appropriate Hamaker constant for any combination of these condensed phases, including three phase systems involving repulsion as well as attraction.

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Conference Abstract

Alteration of Double Layer Properties by Non-Electrolyte Adsorption

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The interface between mercury and an electrolytic solution containing variable concentrations of adsorbable non-electrolyte is well suited for testing of models purporting to account for double layer electrical properties, since it is highly polarizable and interfacial tension, charge density, and differential capacity are all subject to direct measurement. These measurements can be cross checked through the relations $Q = -(\partial\gamma/\partial V)_a$, $C = -(\partial^2\gamma/\partial V^2)_a$ and a theory of any one of the quantities γ , Q , or C implies a theory of the other two.

Following Stern, the double layer can be regarded as consisting of a molecular condenser, capacity C_m , and a diffuse double layer of capacity C_d connected in series, so that $C^{-1} = C_m^{-1} + C_d^{-1}$. C_d can be rather well understood through the Gouy theory, and can be made sufficiently large by making the base electrolyte concentration sufficiently high that $C = C_m$ except for at most a minor correction readily made. Since the molecular condenser composition is chiefly affected by adsorption of non-electrolytes at low concentration the study of C_m is of particular importance in this problem, and it is attractive to choose experimental conditions so that measured quantities can be directly related to properties of the molecular condenser as affected by non-electrolyte adsorption.

Intuition can be misleading in the interpretation of molecular condenser properties, because its composition is field-dependent. Thus

$$C = -(\partial Q/\partial V)_a = (\partial Q/\partial V)_\Gamma - (\partial Q/\partial \Gamma)_V (\partial \Gamma/\partial V)_a.$$

The term $-(\partial Q/\partial V)_\Gamma$ is a constant composition capacity, and that replacement water molecules by organic molecules in the molecular condenser lowers C_m is in accord with intuition. The term $(\partial \Gamma/\partial V)_a$ reflects the field desorption of the organic molecules, and is responsible for the desorption peak in the capacity-polarization curves. The desorption peaks are frequency-dependent, and information regarding the desorption rate process can be inferred from this fact as first shown by Frumkin and Melik-Gaikazyan.

In many systems $(Q_w - Q)/\Gamma = f(V)$, independent of Γ . In this case surface excesses and spreading pressures are of the forms $\Gamma(a, V) = F(ae^{-S\phi/RT})$, $\pi(a, V) = G(ae^{-S\psi/RT})$ with ϕ and ψ functions of V only. This can also be used to reduce spreading pressure-concentration curves obtained at different polarizations to a single curve; Damaskin's treatment is of this sort. The extent to which such superimposability implies $(Q_w - Q)/\Gamma = f(V)$ and further implication of this result for field independence of adsorbate orientations are discussed.

GLOSSARY

- γ = boundary tension, electrode-electrolyte interface
- V = electrode polarization referred to electrocapillary maximum potential in base electrolyte
- Q = surface charge density, electrode side of double layer
- C = differential capacity per unit area of interface

- Q_w = Q for base electrolyte solution
 C_w = C for base electrolyte solution
 c = non-electrolyte concentration, moles/liter
 a = non-electrolyte activity
 S = non-electrolyte molar area, cm^2/mole
 R = gas constant
 Γ = non-electrolyte surface excess, moles/ cm^2
 Θ = $S\Gamma$
 $\pi(a, V)$ = spreading pressure due to non-electrolyte at activity a and polarization $v, i. e.$
 $\pi(a, V) = \gamma(o, V) - \gamma(a, V)$
 $\psi(a, V) = \frac{1}{S} \int_0^v (Q_w - Q)/\Gamma dV, a \text{ fixed}$
 $\varphi(a, V) = \frac{1}{S} \int_0^v (\partial Q/\partial \Gamma)_V dV, a \text{ fixed}$

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Conference Abstract

Theory of Double Layer Interaction between Colloidal Particles in Aqueous Medium

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The methods of statistical mechanics are used to determine the Helmholtz free energy associated with the electric double layers of charged colloidal particles in aqueous medium. The Poisson-Boltzmann equation for the potential distribution in the diffuse layer is first assumed. It is shown that a number of equivalent expressions can be obtained for the double layer free energy, and the physical meaning of these expressions are explained. The double layer force acting on a colloidal particle due to neighbouring particles is derived from the free energy. These general results are applied to give the double layer interaction energy of two parallel plate-like particles and of two identical spherical particles. A comparison is made between the two conditions of constant surface potential and constant surface charge. The contribution to the interaction energy from the Stern layer of adsorbed ions is considered. The interpretations to be given to the Schulze-Hardy rule and the lyotropic series are mentioned.

The nature of the corrections to the Poisson-Boltzmann equation is examined. In particular ion-size effects, dielectric saturation, self-atmosphere and image effects and the so-called cavity potentials are considered. The corresponding additional terms in the Helmholtz double layer free energy and their effect on the interaction of colloidal particles are given. The analogy between the discreteness-of-charge effect for adsorbed ions and the cavity effect is stressed. The limitations of the method of local thermodynamic balance to obtain a modified Poisson-Boltzmann equation are indicated and results derived from thermodynamic balance and from statistical mechanics are compared.

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Conference Abstract

The Discreteness-of-Charge Effect in Ionic Double-Layer Theory

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The discreteness-of-charge or discrete-ion effect provides an explanation of a number of properties of charged interfaces in aqueous electrolyte-systems, which are at variance with the classical Gouy-Chapman-Stern theory of the electric double layer. This effect usually applies to adsorbed ions in the Stern layer, but it can also refer to ions in the diffuse layer. It arises from the fact that the discrete charge of an ion causes a local distortion in the average spatial charge distribution in its vicinity. In strong electrolyte theory, this is known as the self-atmosphere effect, but in the very complex inhomogeneous environment at a charged interface, so-called cavity and image effects also contribute to this local distortion.

The best evidence for this effect comes from a study of the mercury/aqueous electrolyte interface. Three experimental results for this system in conflict with classical theory are (i) the so-called Esin-Markov effect which is concerned with the rate of change of interfacial potential with electrolyte activity at the electrocapillary maximum (ii) a strong dependence of the apparent Stern adsorption energy of counter-ions on the charge density of primary surface ions and (iii) a maximum in the magnitude of the potential at the outer Helmholtz plane with change in interfacial potential at fixed ionic strength. Corresponding maxima in the electrophoretic mobility of silver bromide and emulsion particles have been observed. Also maxima in the surface potential across a fully ionised anionic monolayer when the area per film molecule is varied at constant ionic strength in the substrate.

Certain experimental results in stability of hydrophobic colloids are inconsistent with the Derjaguin-Landau-Verwey-Overbeek theory. In the presence of divalent and trivalent counter-ions, the electrolyte concentration required for flocculation of silver iodide sols is found to decrease with increase in surface potential of the colloidal particles. The so-called phenomenon of mutual antagonism in coagulation by mixtures of electrolytes cannot be explained by the D.L.V.O. theory. The experimental dependence of the stability retardation factor in slow coagulation on the surface potential of silver iodide particles is in the opposite direction to that predicted by the D.L.V.O. theory.

All the above discrepancies between experiment and classical double layer and stability theory can be resolved by invoking the discreteness-of-charge effect. An additional term in the energy of an adsorbed counter-ion in the inner Stern region is introduced to account for the discrete character of the ionic charge.

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Conference Abstract

Polymer Adsorption at Solid/Liquid Interfaces

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Some of the theoretical treatments of polymer adsorption will be briefly discussed. Specifically, the diffusion equation approach as developed by Simha, Frisch, and Eirich and the direct combinatorial evaluation of the partition-function approach as presented by Silberberg and modified by Hoeve, DiMarzio, and Peyser and by Roe will be described. An attempt will be made, without using all the detailed mathematical treatments, to describe the fundamental reasoning used in the theoretical approach and predictions regarding the shape of the isotherm. The purpose of this initial portion of the talk will be to present the audience with a brief overall view of the current status of polymer adsorption theory.

The remainder of the lecture will be concerned with experimental results of polymer adsorption with emphasis on determination of chain configuration.

The results of the ellipsometric studies of the extension normal to the substrate surface of adsorbed polystyrene will be given. In the case of solid surfaces, the extension is found to increase with time for a given molecular weight and concentration, finally achieving a plateau value. These plateau values were found to increase linearly with $Mw^{1/2}$. All of this was interpreted to indicate a molecular configuration that changed with increasing surface population from a rather flat molecule with many attachments to a molecule with dimensions relatively close to that of a random coil at a boundary.

The work of Eirich and Rowland using viscosity methods will be briefly described, the results compared, and the agreement noted. The work of Thies, Peyser, and Ullman who reported a decrease in p , the fraction of attached segments, with increasing values of adsorbance will also be mentioned. Their results support the concept of a change in the configuration of the molecule during the adsorption period, *i. e.*, with increasing surface population.

The ellipsometric studies on liquid mercury are somewhat different from the results on solid metals. No change in extension was observed during the adsorption period, and more significant no change in extension with molecular weight. This may be attributable to the larger value of the contribution of the London dispersion forces, γ^d , to the surface free energy of the liquid mercury.

The studies of the extension of adsorbed polystyrene on a quartz prism by attenuated total reflection (ATR) techniques in the ultraviolet region will be briefly described. The measured polymer extension agreed rather well with the ellipsometric and viscosity results.

Studies on a polar polymer, a polyester, will also be reported. In contrast to the polystyrene results, the results show an independence of configuration with increase in surface population.

Finally, the results of a study of the rates of adsorption, desorption, and exchange of tagged polystyrene on a chrome metallic surface from cyclohexane will be given. At the concentrations studied, the rates of adsorption were found to be slow and approximately independent of solution concentration. This appears to support the concepts obtained from ellipsometry regarding the rearrangement on the surface during the adsorption period. Rates of exchange (same molecular weight) were found to be approximately equal to rates of desorption, implying a distribution in the value of p for the adsorbed molecule.

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CCA-603

546.212:542.952.6

Conference Abstract

Polywater — Molecular Structure as Determined by Infrared and Raman Spectra

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The infrared and Raman spectra of a form of water prepared in fused quartz capillaries and previously designated as *anomalous* water have been obtained. The infrared spectra appear to be unique with the apparent absence of the O—H stretching bands prominent in normal water spectra, and the appearance of new bands near 1600 and 1400 cm^{-1} . The interpretation is that new and previously unreported strong symmetric O—H—O bonds are formed, isoelectronic with FHF^- . The approximate bond distances are given as 2.3 Å for O...O and 1.15 Å for H—O, compared to a O...O distance near 2.8 Å for normal H_2O . These bands are regarded as responsible for the remarkable properties of the material and have considerable covalent character. They are so strong that they cannot be considered as normal O...H hydrogen bonds. Extensive electron delocalization could occur in structures which involve oxygen atoms in three equivalent bonds, where each O—H unit has a bond order of $2/3$. The bond energy per O—H—O unit is given as approximately 125 to 210 kJoule/mole (30 to 50 kcal/mole), and an energy of 250 to 420 kJoules (60 to 100 kcal) per H_2O structural unit. Several structures are proposed which are consistent with the spectral data and the remarkable properties of the material. It is concluded that the material is a true polymer of water, and, therefore, is named polywater.

CCA-604

541.18:538

Conference Abstract

Application of Magnetic Resonance Techniques to the Study of Solid/Liquid Interfaces

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Magnetic resonance techniques offer powerful tools for investigating the most varied phenomena in physics and chemistry. An account will be given of their application to the field of solid-liquid interfaces. Illustrations will be drawn from the researches carried out at Princeton University. The first part of the lecture will deal with the phenomena of magnetic resonance: electron, protonic and nuclear. The approach will be experimental, stressing the determination of the position, fine structure, hyperfine structure, intensity width of lines, shapes of lines, microwave and radiofrequency saturation effects. A simple interpretation will be given of these observables in terms of atomic and molecular models.

Electron spin resonance of colloidal particles labelled by adsorbed stable free radicals will be used to characterize the surface and the Brownian motion of the particles (spin labelling). Examples will be given of adsorption of molecules on surfaces by electron transfer.

Proton resonance of liquids will be used to investigate the behavior of liquids in fine pores and to determine how far into the liquid, the effect of the surface proceeds.

The change in the degree of hydration of the surface aluminum and sodium ions will be determined by the resonance studies of these nuclei.

Electron spin resonance. — The hyperfine structure of free radicals has been shown to be strongly influenced by the ease of mobility of the radical during the time of measurement. Professor Hardin McConnell has proposed to use this to characterize the surface state of large biological molecules.

A report will be given of the work characterizing the behavior of inorganic colloidal particles which have stable free radicals adsorbed on them. In another application, electron transfer between adsorbed molecules and surfaces with electrons and holes will be discussed and the rules of such adsorption phenomena will be indicated.

The proton resonance of water confined in pores of small diameter such as is found in zeolites and porous glass has been investigated. The position and width of the proton resonance line as a function of the pore size and the temperature was determined. It was found that the melting point of ice in the pores is lower, the smaller the pore size and is sharp for silica surface but is gradual for zeolite surfaces. Other examples will be given of the use of proton resonance techniques for the determination of the state of the liquid near the solid-liquid interface.

Nuclear resonance of sodium and aluminum ions on the surfaces of zeolites has been used to interpret the nature of bonding of water and these ions to the surface.

GLOSSARY

Magnetic Resonance — adsorption of radiation of a fixed frequency by a material placed in a magnetic field of appropriate field strength due to transitions between energy levels split by the magnetic field. The energy levels may be those of an unpaired electron or of a nucleus with a spin different from zero.

Free radicals are organic molecules with an unpaired electron.

Spin Label — use of a stable free radical attached to the surface of a macromolecule to determine the mobility of the macromolecule or the nature of conformation in the surface of the macromolecule.

Zeolites are crystalline aluminosilicates whose water of hydration can be removed without destroying the crystal structure of the aluminosilicate, e.g. faujasite $\text{Na}_{56}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136} \cdot n\text{H}_2\text{O}$.

Porous glass is silica glass obtained by annealing a sodium borosilicate glass until the sodium borate crystallizes out and then leaching the sodium borate out with hydrochloric acid. The product has a pore volume of 50% and pores of 40 Å.

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CCA-605

541.11:541.183-145
Conference Abstract**Quasi-Thermodynamic and Statistical Models in Adsorption from Solution**

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In formulating a general theory of adsorption it is first essential to recognize that concepts such as »amount adsorbed«, insofar as they appear to suggest an amount of material in some neighborhood of an interface, are inherently ambiguous and that all measurements of »adsorption« in fact measure surface excesses. In the simplest case of a uniform solid occupying the half-space $x < 0$ and a multi-component fluid occupying the halfspace $x > 0$ with its components negligibly soluble in the solid the surface excess of component i is given by

$$\Gamma_i = \int_0^{\infty} [C_i(x) - C_i^{\infty}] dx$$

Because the interface is not physically a plane the magnitude of Γ_i depends on specification of the plane $x = 0$. It will be shown that various methods of measuring adsorption (*e. g.*, weight changes, concentration changes, β -emissions, ellipsometry as well as boundary tensions) lead directly to surface excesses.

The set of numbers Γ_i giving the surface excesses of various components at an interface can be satisfied by an infinite set of concentration distributions $C_i(x)$. For example $\int_0^{\infty} y dx = 1$ can be satisfied by an uncountably infinite set of choices of $y = f(x)$, including functions of the sort $y = ke^{-kx}$ for all positive values of k . Examples of widely different distributions deduced from the same surface excess — concentration data will be given to illustrate this inherent lack of uniqueness.

In continuum models of adsorption it is assumed that a molecule located at a distance x from the solid has a potential energy $\varepsilon(x)$ referred to its potential energy at great distance from the surface. This function and equation of state information imply the function $C(x)$. This approach dates back to Polanyi. The Steele and Halsey treatment of gas imperfections due to presence of solids reduces to

$$\lim_{C_{\infty} \rightarrow 0} \frac{\Gamma}{C_{\infty}} = \int_0^{\infty} (e^{-\varepsilon/kT} - 1) dx$$

with specification of the form of $\varepsilon(x)$. These concepts are readily extended to continuum models in adsorption from solution.

The Langmuir isotherm results from a lattice model of adsorption. The most straightforward parallel treatment of adsorption from solution is that of Belton and Evans. Modifications to account for monolayer non-ideality and for binary solutions of unequal sizes are given. The Kipling-Tester, Schay-Nagy, Shereshefsky and Lucassen-Reynders models are also discussed as well as problems resulting from the monolayer restriction.

GLOSSARY OF SYMBOLS AND TERMS

T = absolute temperature
p = pressure
V = volume

- γ = surface or interfacial tension
 C_i^α = concentration, moles/cm³, of component i in phase α
 $C_i(x)$ = concentration, moles/cm³, at a distance x from a reference plane in the interface
 x_i^α = mole fraction of component i in phase α
 E = internal energy of system, defined by ΔE = heat absorbed by system plus work done on system
 S = entropy of system
 H = enthalpy of system ($E + PV$)
 G = Gibbs free energy of system ($E - TS + PV$)
 μ_i = chemical potential of component i in system
 Γ_i = surface excess of component i at an interface (magnitude varies with defining convention)
 k = Boltzmann's constant
 $C_{i\infty}$ = $\lim_{x \rightarrow \infty} C_i(x)$ = bulk concentration of i

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CCA-606

541.18.041.2

Conference Abstract

Stability of Non-Aqueous Lyophobic Colloids. General Principles

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The theories and experiments concerning the stability of colloids have been mainly restricted to aqueous systems. When the problems of stability in non-aqueous media are considered one may in the first place try to adapt the existing ideas for aqueous systems.

In principle, the equations available for aqueous systems are also applicable to non-aqueous media, but the values for some of the leading constants may be different. This in turn can lead to different regions of applicability of the equations.

In the van der Waals attraction formulae the only quantity that changes is the Hamaker constant.

In the equations for the electrochemistry of the electrical double layer the dielectric permeability, ϵ , plays a key role. In media of low ϵ the double layer is extremely tenuous, with a high potential at low surface charge (low capacitance). Under these conditions the screening of the surface charge by counterions is ineffective and the simple Coulombic equations become good approximations for the potential in the double layer and for the electrostatic repulsion energy. Another advantage is that, due to the slow potential decay in the double layer ψ_0 may safely be identified with ζ .

The influence of polymers on the stability is two-fold. At low concentration they may promote flocculation (sensitization or adsorption flocculation) at high concentration they stabilize (protection). The main factors determining the behaviour of polymers at interfaces are: molecular weight, chemical composition, flexibility, interaction free energy with surface and solvent as well as kinetic factors. Principally, these factors are the same in aqueous as well as non-aqueous media although of course the quantitative aspects are different. There exist a number of theories for protection, but an adequate description for adsorption flocculation and/or sensitization remains to be given.

It may therefore appear, from a theoretical viewpoint, that the stability of colloidal dispersions in media of low ϵ is not very different from that in aqueous systems, and in some instances it may even be easier to treat. However, from the experimental side a number of problems emerge that need careful consideration. Among these the influence of trace amounts of water, adsorbing tenaciously at some interfaces is often a major problem.

GLOSSARY OF SYMBOLS

- a particle radius
- A Hamaker constant (A_{11} between two particles 1 in vacuo; A_{12} between particle 1 and particle 2 in vacuo; $A_{1(2)}$ between two particles 1 in medium 2)
- d distance between colloidal surfaces (flat plate approximation)
- H ($R - 2a$)
- n_i number of ions i per unit volume
- Q total charge on a particle
- r distance to particle center (spherical particles)
- R distance between the centers of two spherical particles
- s R/a
- v Interaction energy (V_A attractive, negative; V_R repulsive, positive)

y dimensionless potential $\frac{ze\psi}{kT}$ ($y_0 = \frac{ze\psi_0}{kT}$ etc.)

z_i valency of ion i , sign included

$\gamma = \frac{\exp(y/2) - 1}{\exp(y/2) + 1} = \tanh(y/4)$

ϵ dielectric permeability

ζ electrokinetic potential

κ reciprocal Debye length = $\left(\frac{4\pi e^2 \sum_i n_i z_i^2}{\epsilon kT} \right)^{1/2}$

ψ potential (ψ_0 surface potential; ψ_δ potential of the diffuse part of the double layer)

σ charge per unit surface area (σ_0 surface charge, σ_m Stern charge, σ_d diffuse charge)

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CCA-607

541.183:541.18.041.2

Conference Abstract

The Influence of Adsorption at the Solid/Liquid Interface on the Stability of Dispersions

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The adsorption of surface active agents at the solid/liquid interface often depends on the nature of the charge of the solid surface and on the type of surface active agent used, for example, whether this is cationic, anionic or non-ionic. The adsorption behaviour encountered with all three types of surface active agents with solids such as silver iodide, graphon and polystyrene will be discussed.

The stability of a hydrophobic colloidal dispersion can be considered to arise as a consequence of the electrical repulsion between the particles. Adsorption of an ionic surface active agent of opposite charge to that of the particle leads to flocculation in the first instance, but with more extensive adsorption the charge is reversed and stabilisation occurs. In addition the presence of an adsorbed layer of surface active agent modifies the attractive forces between the particles and enhances stability. An interpretation of the phenomena observed experimentally by kinetic measurements can be given in terms of the balance between the electrical repulsive and van der Waals attractive energies. Extensive experimental measurements have been made with various systems and the techniques used and the interpretation of the results will be discussed.

With non-ionic surface active agents, as adsorption occurs the particle is transformed from the hydrophobic to hydrophilic state. A stable dispersion can then be prepared even in the absence of a charge and the additional effect of solvation has to be taken into account. In these conditions the strength and extent of the interaction of the water with the hydrophilic groupings is important as well as the thickness of the adsorbed layer. In order to explain the results a theory has been developed based on the interaction between the adsorbed layers which includes a term to account for the interaction between the surface active molecule and the solvent.

Some experiments involving the direct measurement of surface forces have been carried out to test the theory.

Specific Adsorption at the Electrode-Solution Interface

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The methods for describing the adsorption of ions and molecules at the electrode-solution interface have been comprehensively discussed recently by Delahay¹ and by Damaskin² and his co-workers. Nevertheless there still remain several points which are incompletely understood or about which there is still some controversy.

Since the work of Stern³ the concentration of ions in the inner part of the electrical double layer has been expressed in terms of an adsorption isotherm. He used the Langmuir⁴ isotherm:

$$\Theta/(1 - \Theta) = \beta a \quad (1)$$

in a slightly modified form⁵. Here the interaction of the adsorbed species with itself is represented by the $(1 - \Theta)^{-1}$ factor in terms of a spatial requirement; while the interaction of the adsorbed species with the electrode surface is represented by the adsorption coefficient β . The latter can be expressed as a standard free energy of adsorption:

$$\Delta G^\ominus = -RT \ln \beta \quad (2)$$

Stern did not discuss explicitly the way in which the standard free energy of adsorption depends on the observable electrical properties of the electrode. He expressed this dependence in terms of the potential ϕ_1 at the site of the adsorbed particle. Subsequent work⁶⁻¹³ has shown how difficult this quantity is to define. It was proposed¹⁴ some years ago that the electrode-particle interaction would remain constant if the charge on the electrode were kept constant and most published work on specific ionic adsorption has followed this proposal. It was further proposed¹⁵ that the activity a in equation 1 is the salt activity and not the activity of the adsorbing ion. More recent experiments¹⁶ have led to results which are not in accord with this identification. However, these results and some others on weakly adsorbed ions^{17,18} which cannot be explained by current theories, lead to the suggestion that reduced imaging in the diffuse layer is playing an important role in dilute solutions.

There is less agreement about the method of describing the adsorption of unchanged species. Frumkin and Damaskin^{2,19} strongly favour holding the electrode potential constant rather than the charge. Since it is very difficult to devise a convincing test of the two assumptions when the isotherm is not congruent, *i.e.* when the function f in the isotherm

$$f(\Theta) = \beta a \quad (3)$$

is dependent on potential or charge, the present situation is inconclusive. Tests²⁰ of the individual assumptions in the theory have shown that experimental results on small organic molecules will fit either a constant charge or a constant potential model if the isotherm is congruent. Substances obeying non-congruent isotherms seem to show similar deviations from the predictions of both models. On the other hand the experimental capacity curves can be very well^{2,19} fitted using constant-potential noncongruent isotherms, though this may be a consequence of a number of adjustable parameters.

In most of this work the properties of the solvent enter into the isotherm by way of allowance for space-filling and indirectly through the capacity of the

base solution. A molecular model which takes into account the orientation of solvent molecules has been proposed^{21,22}. In fact this effect is considered to be the principal cause of the behaviour of adsorbed molecules. Satisfactory agreement with experiment is again claimed but some details can be criticized^{17,20}.

A system in which the use of constant charge isotherms appears to be essential is that in which the solvent is varied from one pure solvent through the complete range of mixtures to the other pure solvent. A recent analysis²³ of three such systems suggests that they can be described over most of the composition range by the Flory-Huggins-Zhukovitskii isotherm of the form

$$\Theta \exp(A \Theta)/r (1 - \Theta)^r = \beta a \quad (4)$$

if r is calculated from the projected areas of the solvent molecules assuming that water exists on the surface as monomers.

SYMBOLS

- A Measure of net particle-particle interaction
- a Activity of species in solution
- β Adsorption coefficient
- ΔG^\ominus Standard free energy of adsorption
- R Gas constant
- r Ratio of projected area of adsorbing species to that of the solvent molecule it replaces
- T Absolute temperature
- Θ Fractional coverage by adsorbed species

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CCA-609

541.138

Conference Abstract

Electrode Behaviour of Coordination Compounds

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General theories of redox reactions predict, at least as regards the rate, close correlations between electrode and homogenous redox reactions. The same general relation can be expected also for the mechanism of the process, nature of intermediates and products, if reactions having the same mode of interaction are compared. It should thus be possible to draw general chemical conclusions from the electrode behaviour of compounds.

However, before this can be made, specific effect of the electrode process are to be eliminated. Among the effect to be taken into account are: adsorption of the depolarizer, intermediates and products; double layer effect and specific interactions with the electrode and in the double layer.

These effects can be demonstrated on the electrode behaviour of $\text{Co}(\text{CN})_5\text{X}^{a-}$ complexes, on the oxidation of $\text{Co}(\text{CN})_5^{3-}$ as well as on other systems.

Supposing the specific effects of the electrode reaction were eliminated a correlation between homogeneous and heterogeneous redox processes is found.

CCA-610

541.18.02-145

Conference Abstract

Aggregation, a Step towards Precipitation in Long-Chain Amine Systems?

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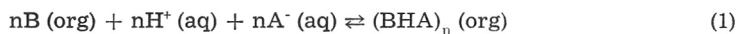
Long-chain amines are finding increasing use in hydrometallurgy^{1a}, the atomic energy field²⁻⁴ as well as in other technical applications⁵. Fundamental studies of such systems are of interest not only for the purpose of optimizing technical processes but also from the possibility of gaining insight into a rather important and exciting area.

Experimental methods. — Several experimental techniques have been used in the study of amine extraction. For metal extraction mainly radiometric and spectroscopic methods have been used⁶. For the study of acid extraction potentiometric methods have been used extensively^{6,7}. Besides various physicochemical methods have been used in order to obtain information about aggregation in these systems, such as freezing point measurements, osmometry, ultracentrifugation etc.

Most of the discussion will be confined to the potentiometric and osmometric methods. Moreover, most of the examples will be for the extraction of acid, the mechanism of acid extraction has to be understood before one can successfully attack the metal extraction.

Results. — In practice both primary, secondary and tertiary amines have been considered. In technical applications the most commonly used acids are H_2SO_4 ^{2,3} and HNO_3 ⁴, while in basic research also the hydrohalic acids have been studied^{1b,c,8,9}. Weak acids such as HF ^{10,11} and monocarbonic acids^{1d} have also been studied. It is found that while weak acids form mononuclear complexes with long-chain amines, polynuclear complexes are formed with strong acids.

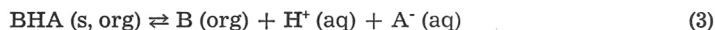
In the acidity range where amine base is transformed to acid the predominating species all have the 1:1 composition. For that reason the extraction of acid (HA) by amine (B) can in this range be described by



With knowledge of (1) it is possible to evaluate the equilibrium constant of the reaction:



Reaction (2) has also been studied directly by osmometry and cryoscopy. From emf-measurements it is also possible to evaluate the equilibrium constant of the reaction:



where $\text{BHA}(\text{s, org})$ represents a solid precipitate or formation of complexes so large that they can be treated formally as a separate phase. Some typical examples will be given in the lecture.

The excess acid range. — While weak acids readily form complexes beyond the 1:1 composition, one has to go to rather high acidities in order to extract more than one acid molecule per amine for the strong acids. This is the range where metal extraction is performed. While studies at low acidities suggest aggregation the data in this range for both metal and excess acid are best described by neglecting aggregation. This virtual contradiction is a very important problem in the field at present. Some illustrative examples will be given.

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CCA-611

541.18.041

Conference Abstract

Studies on Model Colloidal Systems

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Although several theories have been proposed to explain the multiplicity of phenomena which are observed in colloidal systems, direct tests of the theories have proved difficult. Part of the difficulty has been associated with the irregular shape of the particles often used and the polydisperse nature of many of the systems studied.

Polymer latices, however, can be prepared as highly monodisperse dispersions of spherical particles. In the past few years at Bristol work has been carried out on methods for preparing such dispersions. In addition the surface properties of the particles have been characterised by several techniques, for example, electrophoresis and infra-red spectroscopy.

The dispersions have then been used in investigations designed to test current theories of colloid stability. The experiments carried out include:

- 1) an examination of the electrophoretic properties of particles of different sizes;
- 2) the flocculation of particles having an ionogenic surface with various types of electrolyte: these experiments were carried out kinetically in order to evaluate the energy barrier to flocculation;
- 3) direct measurements of the force of repulsion against distance for spherical particles: these results were obtained from pressure measurements under equilibrium conditions.

The transition of a dispersion from the lyophobic to the lyophilic state has also been examined. The transition was achieved by adsorbing non-ionic surface active agents on to the particles. In order to explain the results obtained a theory has been developed in terms of interaction between adsorbed layers of non-ionic molecules, which includes a term to allow for the interaction between the adsorbed layer and the solvent.

CROATICA CHEMICA ACTA izlazi godišnje u četiri broja. Pretplata godišnje 100 N Din (ili 9 \$), a za članove 10 N Din (ili 2 \$). Za izdavača odgovara odgovorni urednik. Glavni i odgovorni urednik Prof. Dr Božo Težak, Zagreb, II. Cvjetno naselje 24. Uprava Zagreb, Marulićev trg 19/II. (Pošt. pret. 131). Žiro račun Hrvatsko kemijsko društvo, Zagreb, broj 301-8-2068.

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