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Relaxation of the surface properties of aqueous solutions of surfactants and the mechanism of adsorption

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Abstract. The results of experimental studies of the dynamic surface tension and of the nonequilibrium surface electric potential of aqueous solutions of surfactants at various concentrations and temperatures are reviewed. Special aspects of the changes in these quantities as a function of the surface area are analysed. An equation of the thermodynamics of irreversible processes which relates the nonequilibrium properties of the surface to the adsorption and a correlation expression which relates the changes in surface tension to those in the surface potential are discussed. Methods of determining the adsorption mechanism are described. The bibliography includes 65 references.

I. Introduction

Many processes associated with the adsorption of surface-active substances (SAS), including separation, foaming, dispersion, wetting, etc., take place under conditions in which the surface layer and the bulk of the solution are not mutually in equilibrium. Therefore information on the nonequilibrium properties of the surface and on the kinetics of adsorption is needed in order to understand the mechanism of action of the SAS in natural and in technological processes.

Many studies of the kinetics of formation of adsorption layers have been published: this work is aimed mainly at the diffusion of the SAS from the bulk solution in the presence of complicating surface processes such as the electric interaction of the ions, the reorientation of the SAS molecules or ions, adsorption processes in the surface layer, etc. These results have already been extensively reviewed,[1-5] but more recent work aimed specifically at the measurement of the surface tension and the surface electric potential is not included. It should be stressed that the complexity of the nonequilibrium processes taking place on the surface make it impossible to allow for all the factors which affect the measurements. The lack of precision of the hydrodynamic models used to describe the kinetics of the adsorption adds to the unreliability of the results. Lastly, the difficulty met in the purification of the materials and the great sensitivity of the kinetics to a number of trace impurities should not be forgotten.

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All these factors point to an urgent need for improving the existing methods of studying the surface properties of solutions and for discovering entirely new methods. The aim of the present review was to examine the results of the experimental and the theoretical studies of the relaxation of the two most important surface properties of solutions of SAS: their surface tension and their surface potential, and to analyse the methods of determining the adsorption mechanism of the SAS.

II. Experimental study of dynamic surface tension

The first experimental study of the dynamic surface tension of soap solutions was reported by Dupré.[6] In a study of the stability of soap films Rayleigh[7] measured the dynamic surface tension in a jet of soap solution, and showed that in a surface 'aged' for less than 0.01 s the surface tension has a value equal to that of pure water. Different methods of measuring the dynamic surface tension were developed in later work. The oscillating jet, the funnel, the falling meniscus, and other methods were used[4,8-12] to study the fast relaxation of the surface ($10^{-1}-10^{-2}$ s). Slower relaxations (seconds, minutes, hours) were studied successfully by using the maximum bubble pressure, the capillary wave, and some other methods.[4,11-13] The oscillating jet and the maximum bubble pressure method were used most widely.

The relaxation of the surface tension can usually be studied over a reasonably wide range of time by monitoring the maximum pressure in a gas bubble. However, it has been reported[2,12] that in the range of $10^{-3}-10^{-2}$ s the results become less reliable and need additional corrections. The oscillating jet method also requires corrections, both traditional (though often ignored) and recently identified. Let us examine this problem in greater detail.

1. Corrections in the oscillating jet method

The oscillating jet method[14] is one of the most fully developed and accurate dynamic methods. It was proposed by Rayleigh in 1879 as a method of measuring the surface tension of an 'almost ideally pure and continuously regenerated surface'.[7] The changes in shape of a jet emerging under pressure from a noncircular orifice had previously been studied by Bidon and by Magnus and Buff. When the jet emerges from a circular orifice its cross-section remains circular but decreases in area. The cross-section of a jet emerging from an elliptical orifice oscillates about the equilibrium circle because the capillary forces are tending to produce a cylindrical jet. Rayleigh showed how the surface tension is related to the wavelength λ of the oscillations and to other parameters of the jet.

Substantial developments in the theory of the oscillating jet method were introduced by Niels Bohr,[14,15] who allowed for the effects of the viscosity, of the finite amplitude of the jet oscillations, of the density of the surrounding medium, and of the hydrodynamic profile of the velocity within the jet. Eqn (1) shows the modern form of the Bohr formula for the surface tension γ:

$$\gamma = \frac{4G^2(\rho+\rho_1)[1+(37/24)b^2/a^2]}{6a\lambda^2+10\pi^2a^3}K, \qquad (1)$$

where G is the volume flow of liquid, ρ is the density of the liquid, ρ_1 is the density of air, a is the mean radius of the jet, b is the amplitude of the jet oscillations, λ is the wavelength of the oscillations, and K is a coefficient which allows for the effect of the velocity profile in the jet.

The theory of the oscillating jet method requires as precise a description as possible of the form of the flow in the jet issuing from an elliptical orifice, i.e. we must define the velocity profile in the cross-section in order to calculate the correction K. The velocity is substantially greater at the axis of the jet than at its surface, especially near the origin of the jet. Rideal and Sutherland[16,17] pointed out that near the orifice the velocity of an element of the jet is 10% lower than the average velocity calculated from the flow of liquid. As a result of the viscosity of the liquid the scatter of the velocities gradually decreases along the jet.

While attempting to explain the effect of the flow hydrodynamics of the jet on the measured parameters, various workers[8-20] studied the dependence of the wavelength of the oscillations on the wave number, on the average velocity of the jet, and on the dimensions of the elliptical orifice. Semiempirical corrections have been introduced[21-25] to allow for the effect of the velocity profile on the dynamic surface tension. Thus, Hansen et al.[24] used the factor $V_s^{0.64}$ to correct for the wavelength of the fourth and subsequent waves, where $V_s = v_s/v_0$ is the ratio of the velocities of an element of the jet near the surface to the average velocity of the jet. A corresponding general expression for the first three wavelengths could not be obtained. However, Bohr[15] formulated the problem of the oscillations of a jet with a nonuniform velocity profile and proposed the following expression for the correction coefficient:

$$K \equiv \left[4\int_0^1 V(y,Z)y^3\,dy\right]^2, \qquad (2)$$

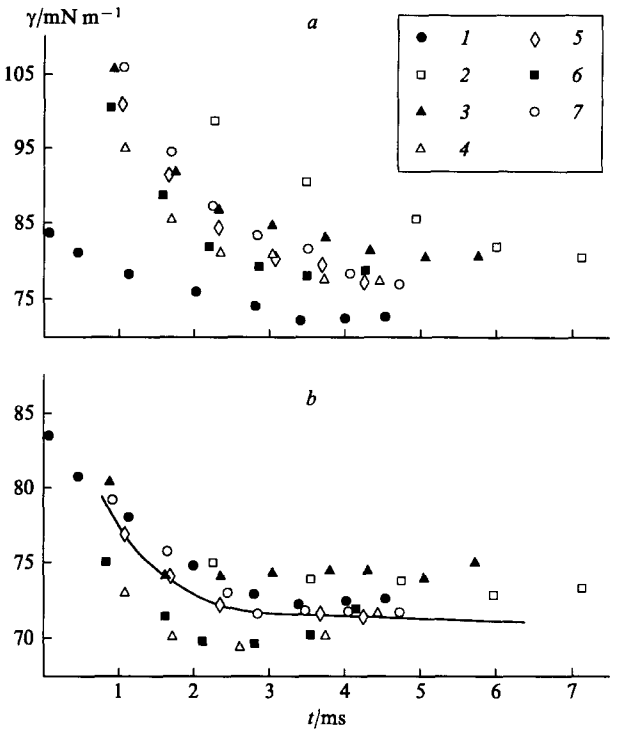
where

$$V(y,Z) = \frac{v_s}{v_0}, \quad y = \frac{r}{a}, \quad Z = \frac{\mu z}{\rho v_0 a^2}.$$

Here v_s is the axial velocity of the element of jet; $v_0 = G/\pi a^2$ is the average velocity of the jet; r is the radial coordinate; z is the axial coordinate (measured from the orifice where the jet is generated).

The present writers have calculated[26] the coefficient K. The theoretical velocity profile $V(y, Z)$ can be described by a Bessel function.[14] In calculations by formula (1) we used the initial velocity profile $V(y, 0)$ obtained experimentally[24] for a tube with a circular cross-section. Data on the velocity profile in a jet of liquid issuing from a capillary orifice have recently been published. A comparison of calculations of the K coefficient from the Bohr velocity profile[14] and from an experimental profile obtained by laser anemometry[27] gave adequately consistent results, tabulated in Ref. 26. The greater the distance z from the orifice, the closer to unity are the K values.

Special experiments[28] in which the dynamic surface tension was measured by using elliptical capillaries having different lengths and radii and different jet velocities showed that introducing the correction coefficient greatly lowers the scatter of the experimental data obtained in experiments carried out under different hydrodynamic conditions. Good agreement with the dynamic surface tension values determined by another method



Point	Length of capillary/cm	Radius of capillary/cm		v_0/cm s^{-1}
		r_{min}	r_{max}	
2	0.702	0.0211	0.0342	242.05
3	0.489	0.0297	0.0322	462.69
4	0.415	0.0160	0.0280	441.36
5	0.415	0.0160	0.0280	400.14
6	0.415	0.0160	0.0280	412
7	0.415	0.0160	0.0280	371

Figure 1. Dependence of the surface tension of water on time at 25 °C (*a*) without and (*b*) with allowance for the velocity profile in the jet. (*1*) from Ref. 29; (*2–7*) from Ref. 28.

(the falling meniscus method) is obtained (Fig. 1).[29] Applying the K coefficient to measurements[30] of the dynamic surface tension of carbon tetrachloride showed that in a simple liquid the dynamic and the static surface tension are identical, whereas in water and in aqueous solutions the two surface tensions are markedly different.

An additional correction is needed if the dynamic surface tension is determined by the oscillating jet method with an SAS solution rather than with a pure liquid.

The adsorption of the SAS at the liquid–gas interface can induce a marked elasticity of the surface, which influences the nature of the flow and of the oscillations of the jet of liquid in a way for which no allowance is made in the Bohr formula (1). In this case the difference between the true surface tension γ' and the value calculated by Eqn (1) is given by the formula[31]

$$\frac{\gamma'-\gamma}{\gamma'} = -\frac{2E(\pi g a v_0\mu/\lambda - E)}{g[E^2+(\pi g a v_0\mu/\lambda - E)^2]}, \qquad (3)$$

where $E = -(\Gamma\,d\gamma/d\Gamma)$ is the surface elastic modulus, Γ is the adsorption, $g \equiv (\pi a^2\mu_0\rho/\lambda\mu)^{1/2}$, and μ is the viscosity.

As E is increased (and therefore as Γ is increased and γ is decreased) the correction changes from zero to $-1/g$, after which it again approaches zero and changes sign at $E = gka v_0\mu/2$, then continues to increase, reaching $1/g$ as $E\to\infty$. According to our calculations[31] adding a correction to the experimental data for an aqueous solution of heptanol gives a satisfactory agreement between measurements of the surface tension by the oscillating

jet method and the adsorption potential jump method (in which the hydrodynamics of the liquid jet can be legitimately ignored).

Each measured value of the dynamic surface tension should be related to the age of the surface to which the measurement applies, whose accurate determination presents a separate problem.

The age of an element of fresh surface formed when the jet emerges from its orifice is defined by the expression

$$t = \frac{z}{v_s(z)}, \tag{4}$$

where z is the distance to the orifice and $v_s(z)$ is the velocity of the element of surface of the jet.

The quantity $v_s(z)$ can be determined, allowing for the velocity profile in the jet, by using Hansen's tabulations.[24,32] The error in the determination of the surface tension by formula (1) and of the age of the surface by formula (4) varies with the distance from the orifice. Near the orifice we usually find $\gamma \simeq \pm 2.5\%$, $t \simeq \pm 1\%$, and far from the orifice $\gamma \simeq \pm 1.5\%$ and $t \simeq \pm 0.1\%$.[26]

Let us examine some special features of the relaxation of the surface tension. The magnitude and the form of the change in the dynamic surface tension depend on the age of the surface, the composition of the solution, and the temperature. In different time intervals their rates of change can increase or decrease. The latter behaviour indicates the presence of an adsorption barrier.

On a young surface we also observe phenomena such as temperature and concentration inversion. The relaxation of the surface properties is also strongly influenced by the presence of inorganic salts in the SAS solutions.

2. Temperature inversion of the dynamic surface tension

For short growth times (1–3 ms) of water[29,33] and of binary solution surfaces[34,35] the surface tension increases with temperature (Figs 2–4), whereas on older surfaces it decreases with temperature, i.e. we see an inversion of the temperature dependence of the surface tension. However, in ternary water–SAS–salt systems the inversion is not always observed (see Figs 5 and 6). By comparing this behaviour with equilibrium data we conclude that an inversion of the temperature dependence of the surface tension is seen only rarely and only in solutions, where it can be attributed to differences in the temperature dependence of the adsorption (which affects the surface tension) and of the surface tension. On the other hand in pure liquids thermodynamic considerations allow only one type of dependence: a decrease in surface tension with increase of temperature. This is evident from the expression

$$\frac{d\gamma}{dT} = \tau\rho_s(s_\alpha - s_s), \tag{5}$$

where γ is the thickness, ρ_s is the molar density, s_α is the molar entropy of the bulk phase, and s_s is the molar entropy of the surface layer.[37] Under equilibrium conditions the entropy in the surface is higher than in the bulk, and therefore $d\gamma/dT < 0$.

It can be assumed that in surfaces departing only slightly from equilibrium, as in our measurements, the thermodynamic relationship (5) is valid (even if only qualitatively). In this case a positive value of $d\gamma/dT$ shows that the molar entropy of the layer is lower than the corresponding value for the bulk phase. However, we know[38] that under nonequilibrium conditions the dependence of γ on T is not the only reason for the difference between s_s and s_α.

A temperature inversion is observed in young surfaces, on which the adsorption is still far from equilibrium, and the dynamic surface tension of the solution of SAS is close to the dynamic surface tension of water and largely determined by the character of the relaxation of the surface structure of the water.

Special experiments with a jet of water showed[39] that heating the jet to 40–50 °C restores the equilibrium value in 3 ms. In water a temperature of 40 °C is known as the Mendeleev temperature, at which the network structure of the water is loosened, the activation energy of the electrical conductivity decreases, and the extent of dissociation increases. These processes also strongly increase the rate at which the equilibrium structure of the water surface is established upon increasing the temperature. For $T_1 > T_2$ we have

$$\left|\frac{d\gamma}{dt}\right|_{T_1} > \left|\frac{d\gamma}{dt}\right|_{T_2}.$$

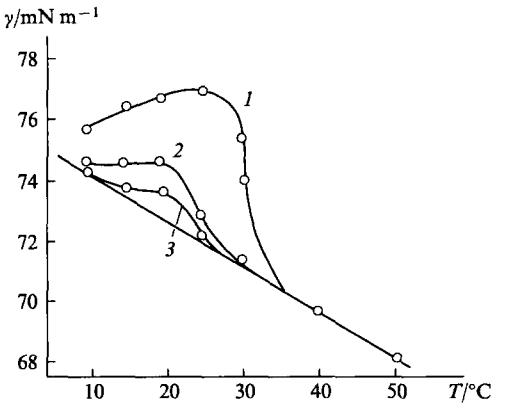


Figure 2. Temperature dependence of the dynamic surface tension of water. t/ms: (*1*) 1.4; (*2*) 2.2; (*3*) 3.0; the straight line corresponds to the equilibrium tension.

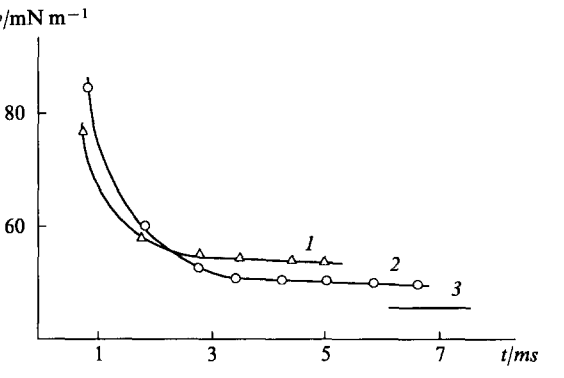


Figure 3. Dynamic surface tension in the water–sodium monobutylnaphthalenesulfonate system. c/mol dm^{-3} = 2.8 × 10^{-4}; T/°C: (*1*) 15; (*2*) 25; (*3*) $\gamma = \gamma_\infty$.

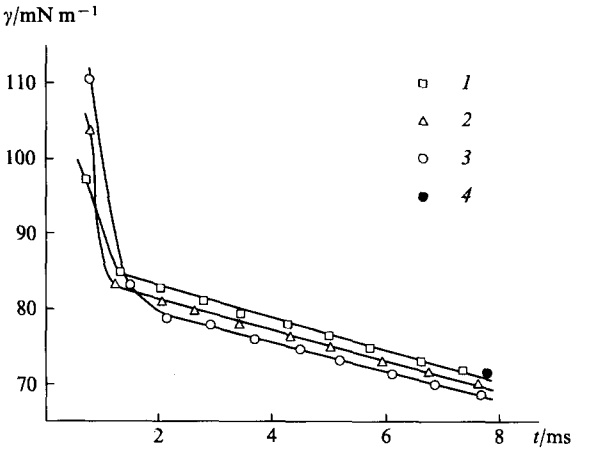


Figure 4. Dynamic surface tension in the water–cetyltrimethylammonium bromide (CTAB) system.[35] $c/10^{-4}$ mol dm^{-3} = 5.6; T/°C: (*1*) 15, (*2*) 20, (*3*) 25, (*4*) from Ref. 36.

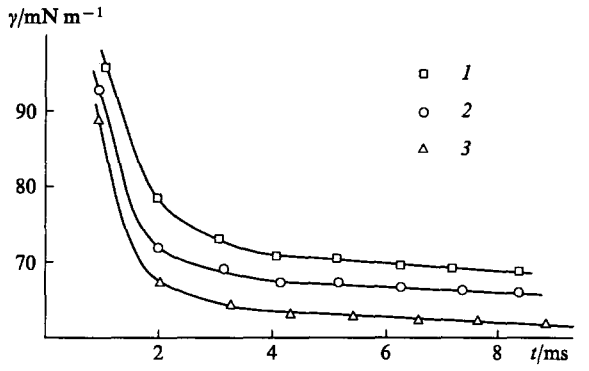


Figure 5. Dynamic surface tension in the water–potassium chloride–CTAB system.[35] $c_{KCl}/10^{-4}$ mol dm^{-3} = 5.6, c_{CTAB}/mol dm^{-3} = 0.56; T/ C°: (*1*) 15, (*2*) 20, (*3*) 25.

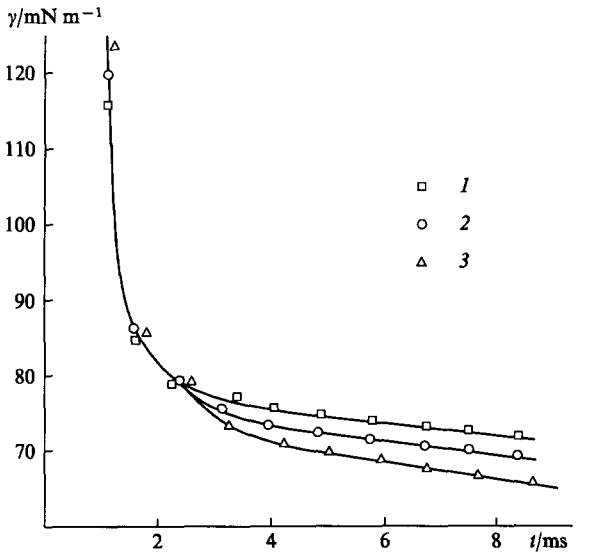


Figure 6. Dynamic surface tension in the water–potassium iodide–CTAB system.[35] c_{KI}/mol dm^{-3} = 0.56, $c_{CTAB}/10^{-4}$ mol dm^{-3} = 1.4. T/°C: (*1*) 15, (*2*) 20, (*3*) 25.

3. Conversion inversion of the dynamic surface tension

Fig. 7 shows the time dependence of the dynamic surface tension for water and aqueous solutions of cetyltrimethylammonium bromide (CTAB) at 25 °C. For t < 1.5 ms the rate of decrease of the surface tension is high and almost independent of the concentration of SAS. For $t \simeq 2$ ms the process becomes slower and the curves for different concentrations diverge (but intersect again at longer times). As a result the dynamic surface tension of SAS solutions at times between 1.5 and 6 ms is higher than that of water, and the effect is magnified as the concentration is increased. Under equilibrium conditions the surface tension of the solution of SAS decreases as the concentration is increased.

Thus under dynamic conditions we observe an inversion of the concentration dependence of the surface tension. A similar anomalous effect, in which the surface tension of the SAS exceeded that of the pure solvent during the initial period of adsorption, was observed by Thomas and Hall,[36] who attributed it to orientation effects involving the SAS molecules. As suggested, at high surface concentrations the SAS molecules 'inhibit' the orientation of their neighbours, and the higher the concentration, the slower is the molecular reorientation on the surface, with a corresponding decrease in the surface

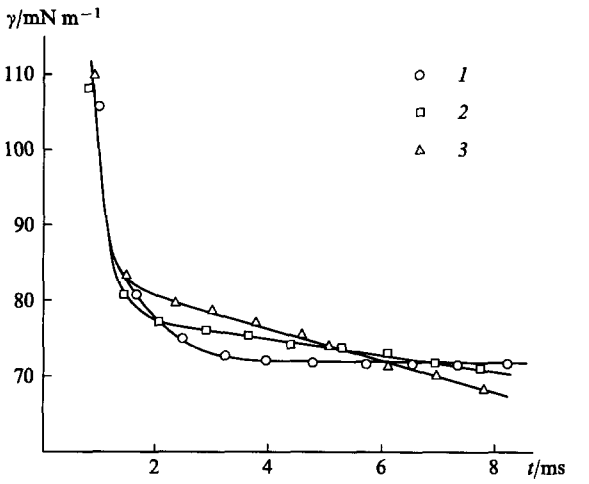


Figure 7. Dynamic surface tension in the water–CTBA system at 25 °C.[35] $c/10^{-4}$ mol dm^{-3}: (1) 0, (*2*) 2.8, (*3*) 5.6.

tension. Therefore as long as the structure of the surface layer differs substantially from the equilibrium structure the surface tension for high concentrations in solution remains higher than at low concentrations.

4. Effect of salts on the change in the surface tension of SAS solutions

In water–SAS–salt systems the ageing of a freshly created surface is accompanied by adsorption of the SAS, desorption of the salt, and relaxation of the properties of the solvent (water). The combined effects of these changes complicate the relaxation of the surface properties of the solutions.

Experiments[22,35] with water–salt solutions of SAS have shown that the addition of a salt accelerates the decrease in surface tension (Fig. 8).

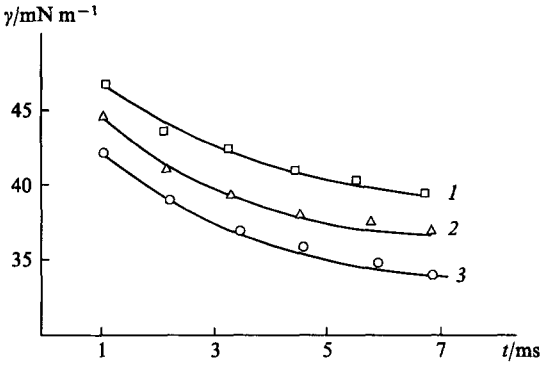


Figure 8. Effect of a salt on the dynamic surface tension of an aqueous solution of sodium dodecyl sulfate (c/mol dm^{-3} = 0.03) at 52 °C.[22] (*1*) no electrolyte; (*2*) c_{NaCl}/mol dm^{-3} = 0.03; (*3*) c_{MgCl_2}/mol dm^{-3} = 0.03.

The faster adsorption of the SAS produced by the desorption of the salt is explained by the salting-out effect of the salt itself, which increases with its concentration. This phenomenon is most clearly seen when the composition of the salt includes a structure-forming ion. It is evident from the results[35] reproduced in Fig. 9 that the addition of KI (a salt containing the strongly structure-forming iodide ion) accelerates the decrease in surface tension of a CTAB solution more markedly than the addition of KCl.

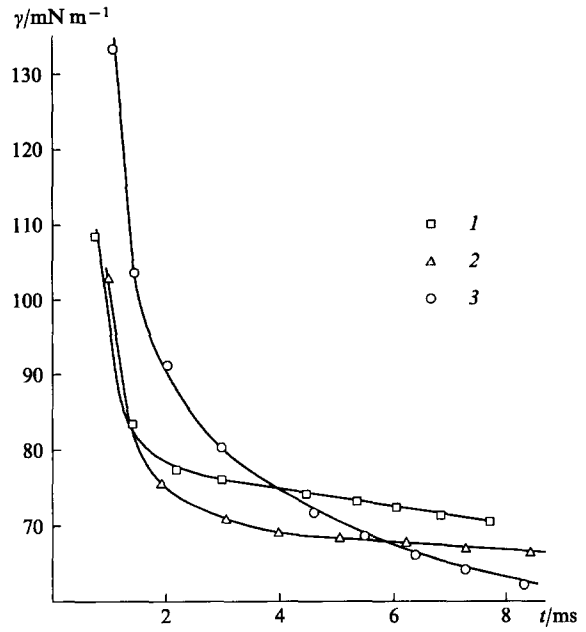


Figure 9. Effect of KCl and KI on the dynamic surface tension of an aqueous solution of CTAB at 25 °C.[35] (*1*) H_2O–CTAB; (*2*) H_2O–KCl–CTAB; (*3*) H_2O–KI–CTAB; $c_{CTAB}/10^{-4}$ mol dm^{-3} = 2.8, c_{KCl}/mol dm^{-3} = 0.56, c_{KI}/mol dm^{-3} = 0.56.

III. Experimental study of the nonequilibrium surface electric potential

The measurement of the electric potential of the surface is an independent method of studying the nonequilibrium properties of solution surfaces. The theory of the oscillating jet method is based on observing the flow and the vibrations of the jet emerging from an elliptical orifice, and relies on a number of assumptions. Unlike the surface tension, the surface potential is determined directly during the experiment (as opposed to being calculated from hydrodynamic equations). This offers some definite advantages in studies of the adsorption kinetics of SAS. The surface potential χ is the difference between the electric potentials at the boundary of two phases. In particular, at the solution–air interface χ is equal to the change in the electric potential between the air and the solution (treated as positive if the potential is increased, and negative if it is decreased on passing from the air to the solution). Being a Galvani potential the surface potential is not directly measurable. We can only determine changes in surface potential $\Delta\chi$ (for example, the time-changes caused by the ageing of a fresh surface or by changing the concentration of the solution). The change in surface potential seen on going from a standard to an experimental solution (containing additions of an adsorbable substance) is called the adsorption electric potential φ.

The methods most commonly used to measure $\Delta\chi$ or φ include the vertical jet method (Thomson–Kenrick), the radioactive probe method (Frumkin–Guyot), and the vibrating condenser method (Thomson–Zisman). The relaxation of a fresh surface is most conveniently studied by using a jet of liquid. In this case the age of the surface is easily calculable (as in the oscillating jet method), and the time-changes of the surface potential or of the adsorption potential can be determined without difficulty.

The adsorption potential of SAS is usually measured in solutions containing electrolytes as additives. Our measurements[40] on a liquid jet were aimed at monitoring the changes of the surface potential in aqueous solutions without added electrolytes. Furthermore the measurement method automatically excluded changes in the potentials of the measuring electrodes in air and in the solution during the experiment.[40] This was achieved by making measurements for a reference point at a fixed distance (in our experiments,[40] ~0.6 cm) from the orifice of the capillary which produced the jet. At this distance the surface potential has reached its equilibrium value and does not show any further changes along the jet. Thus we obtain from the experiment

$$\Delta\chi_t = \chi_t - \chi_0 , \qquad (6)$$

where χ_t is the surface potential for an element of surface of age t, [see formula (4)], and χ_0 is the surface potential at the reference point.

The adsorption potential φ_t for a surface of age t is determined from the difference $\Delta\chi_t$ between the experimental and the standard solution. Let us examine the results obtained in studies of the adsorption potential of various substances.

1. Alcohols

Several studies of aqueous solutions of normal primary alcohols (from propanol to decanol) have been reported.[41–46] The time interval needed to establish the equilibrium value of the potential is determined by the concentration of the solution and by the length of the hydrocarbon chain of the alcohol. As the molecular mass of the alcohol is increased, the concentration range in which a change in potential takes place at times between 2 and 20 ms is shifted towards lower values. An increase in the age of the surface makes the potential more positive (Fig. 10). The potential is relatively insensitive to changes in temperature: $d\varphi/dT \approx -0.0002$ V K^{-1}. A similar dependence was obtained[46] for the equilibrium potential.

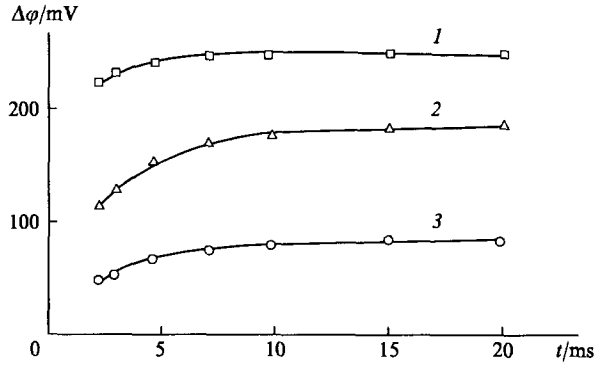


Figure 10. Adsorption potential step of solutions of hexanol in HCl (0.01 mol dm^{-3}) at 20 °C.[45] c/mmol dm^{-3}: (*1*) 10, (*2*) 4, (*3*) 2.

2. Aliphatic acids

Normal aliphatic acids are anion-active SAS. These electrolytes are weaker than the corresponding saturated alcohols: their surface activity is suppressed by the presence of the more polar carboxyl group.

Aqueous solutions of pentanoic, heptanoic, and octanoic acids have been studied in our laboratory.[47] In the lower homologues adsorption equilibrium is reached in less than 10^{-3} s, and the time dependence of the adsorption has not yet been established for these materials. On the other hand acids with a longer hydrocarbon chain (beginning with nonanoic acid) are very sparingly soluble in water, and meaningful measurements are not possible at the very low concentrations which are experimentally accessible. It is found that the adsorption of pentanoic acid is completed in 2×10^{-3} s, and that the equilibrium adsorption potential is ~100 mV at a concentration of 7.5×10^{-3} mol dm^{-3} and ~140 mV at 1.25×10^{-2} mol dm^{-3}. Within the error limits of ±5 mV the φ values are consistent with the equilibrium values given by Frumkin.[48]

Results for hexanoic, heptanoic, and octanoic acid are shown in Figs 11–13. The potential changes towards more positive values during the measurements. The largest change in the potential is observed for octanoic acid: in the other two acids the initial region (up to 7 ms) shows an initially fast change in potential followed by a slower change.

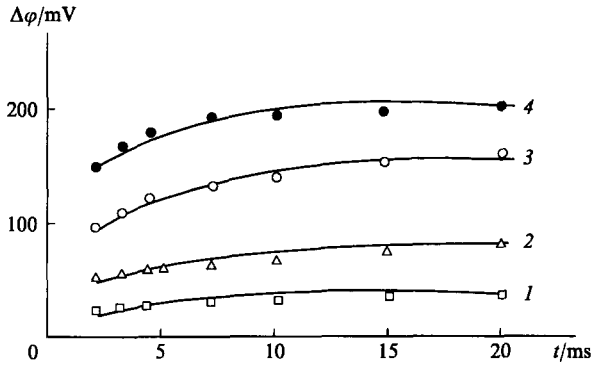


Figure 11. Electric adsorption potential of solutions of hexanoic acid.[47] $c/10^{-3}$ mol dm^{-3}: (*1*) 1, (*2*) 2, (*3*) 4, (*4*) 6.

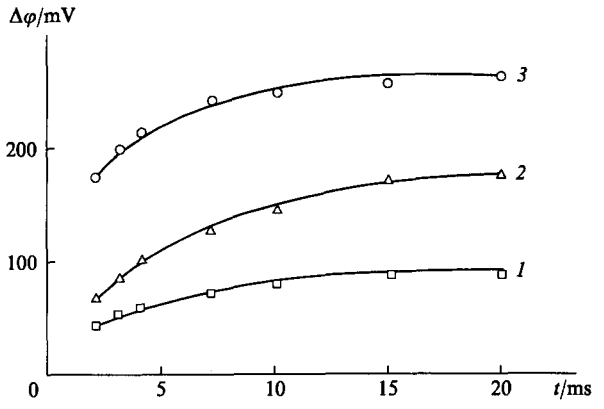


Figure 12. Electric adsorption potential of solutions of heptanoic acid.[47] $c/10^{-3}$ mol dm^{-3}: (*1*) 1, (*2*) 2, (*3*) 4.

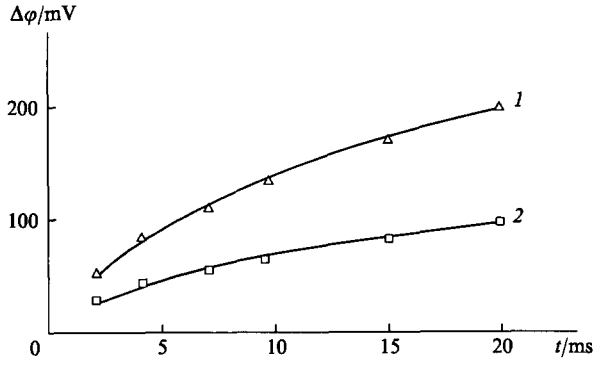


Figure 13. Electric adsorption potential of solutions of octanoic acid.[47] $c/10^{-3}$ mol dm^{-3}: (*1*) 0.75, (*2*) 1.5.

3. Cation-active SAS

Published measurements[41,49] show that in the case of cation-active SAS the potential usually changes (over times between 1 and 2 ms) towards more negative values, corresponding to the location of the cations closer to the air interface than the anions (Figs 14–17). For a given concentration the rate of the process decreases as the lifetime of the surface increases, and for a given lifetime it increases with the concentration. The absolute value of $\Delta\chi$ increases with the age of the surface, and with increasing concentration, indicating an increase in the adsorption of the SAS. At very low concentrations of the SAS, corresponding to low adsorptions, we observe a time dependence of the surface potential similar to that seen in water: $\Delta\chi$ moves towards more positive values (Fig. 17).

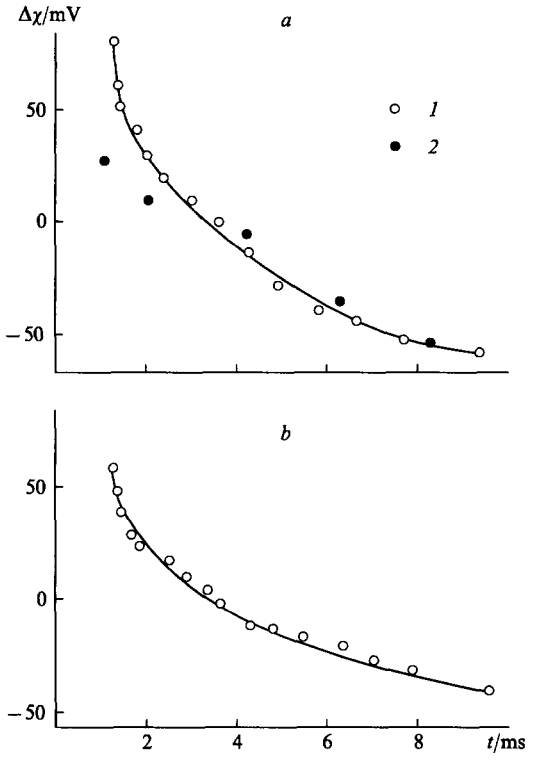


Figure 14. Time changes of the surface electric potential in the water–CTAB system. (*a*) c/mol^{-4} mol dm^{-3} = 5.6; (*1*) from Ref. 49, (*2*) from Ref. 41; (*b*) $c/10^{-4}$ mol dm^{-3} = 2.8.

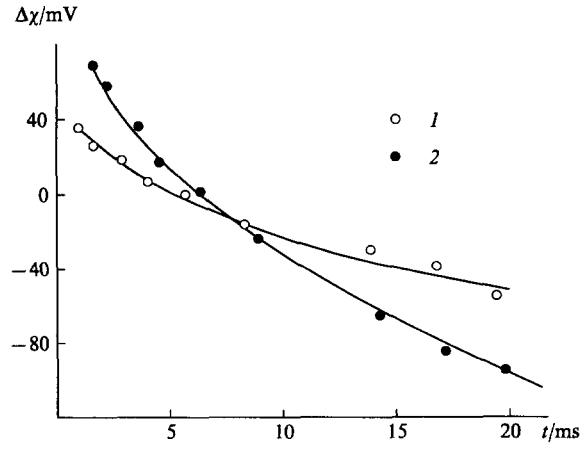


Figure 15. Time changes of the surface electric potential in the water–cetyltrimethylammonium chloride (CTAC) system. $c/10^{-4}$ mol dm^{-3}: (*1*) 2.8, (*2*) 5.6.

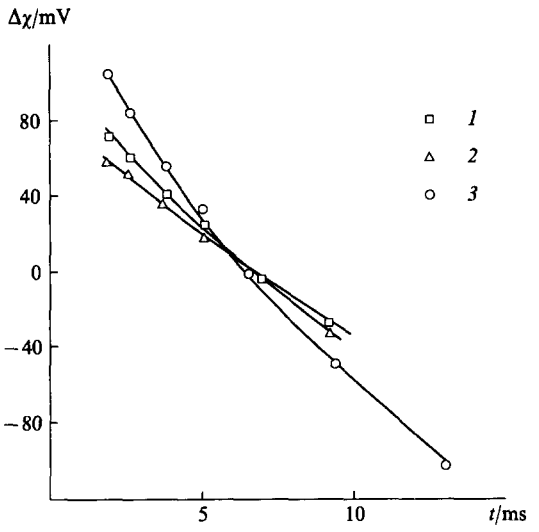


Figure 16. Time changes in the electric potential of hexadecylpyridinium bromide. $c/10^{-4}$ mol dm^{-3}: (*1*) 1, (*2*) 5, (*3*) 10.

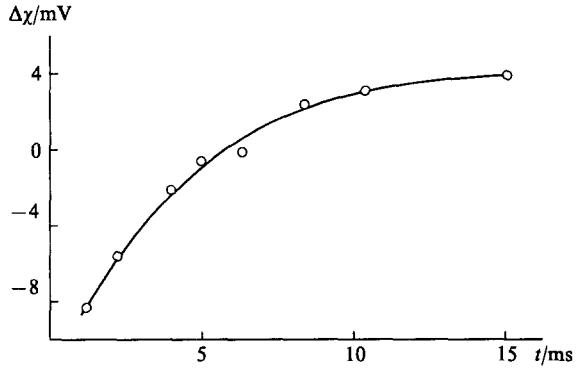


Figure 17. Changes in the surface electric potential of a solution of dodecylammonium chloride. $c/10^{-3}$ mol dm^{-3} = 2.6.

4. Cation-active SAS with added inorganic salts

The time-dependences of the surface potentials for aqueous solutions of cetyltrimethylammonium bromide and chloride with additions of KCl and KI are shown in Figs 18–21. By comparing the $\Delta\chi$ values in solutions of the SAS with and without salt additions we conclude that in young surfaces (up to 6–8 ms) the change in potential is almost independent of the salt concentration. On the other hand, data on the dynamic surface tension indicate a salting-out effect associated with the additions of salt. Evidently, this behaviour is due to the differences in the polarity and in the relative electric potentials of the SAS and inorganic salt double layers, which make the relationship between the adsorption of the SAS and the surface potential less unambiguous than in the binary SAS–water system.

As the age of the surface is increased we observe a shift in the potential towards more positive values (most clearly seen in the solution with KCl additions, but relatively weak in the solution with KI). The effect becomes more marked as the salt concentration is increased, though it is relatively insensitive to the concentration of the SAS. These effects were explained by assuming micelle formation under dynamic conditions:[49] as the flow of adsorbed SAS ions meets the flow of desorbed salt in the near-surface layer the critical concentration may be exceeded, inducing micelle formation. Being surface-inactive the micelles should migrate towards the bulk of the solution, removing some of the SAS from the surface layer and as a result lowering the charge on the surface double layer and producing a positive shift of the potential.

Unfortunately there are no published data on the non-equilibrium surface potential for other SAS.

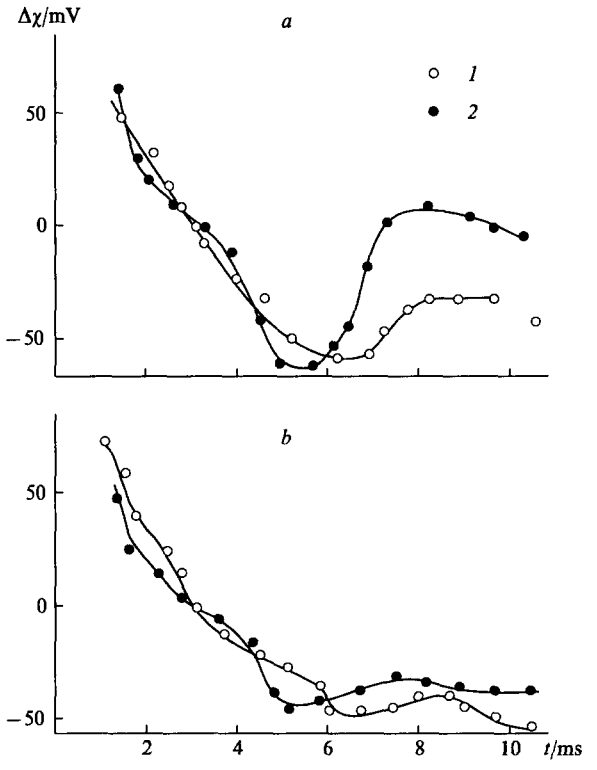


Figure 18. Time changes in the surface electric potential in the water–potassium chloride–CTAB system.[49] $c_{CTAB}/10^{-4}$ mol dm^{-3}: 5.6 (*a*), 2.8 (*b*); c_{KCl}/mol dm^{-3}: 0.12 (*1*), 0.56 (*2*).

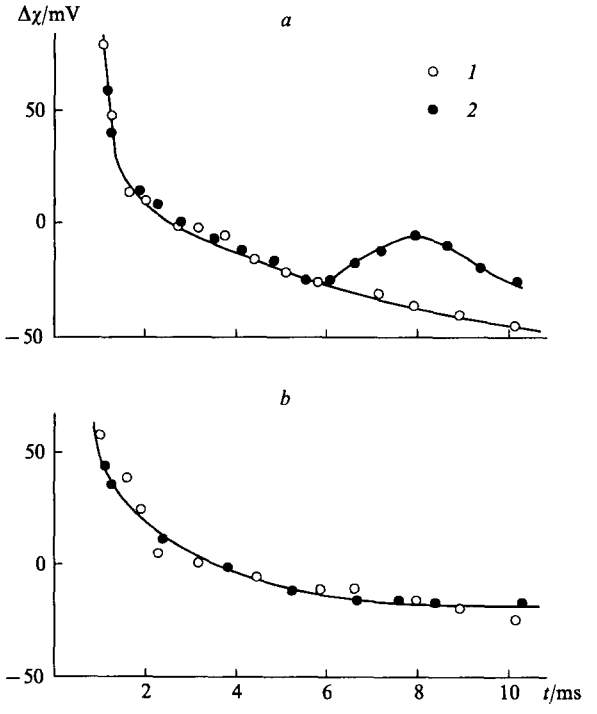


Figure 19. Time changes in the surface electric potential in the water–potassium iodide–CTAB system.[49] $c_{CTAB}/10^{-4}$ dm^{-3}: 2.8 (*a*), 1.4 (*b*); c_{KI}/mol dm^{-3}: 0.12 (*1*), 0.56 (*2*).

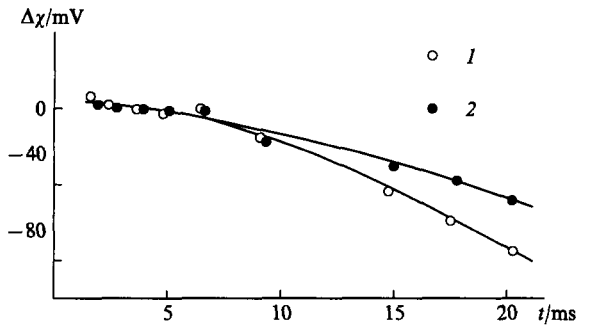


Figure 20. Time changes in the surface electric potential in the water–potassium chloride–CTAC system.[49] c_{KCl}/mol dm^{-3}: 0.12 (*1*), 0.56 (*2*); $c_{CTAC}/10^{-4}$ mol dm^{-3} = 2.8.

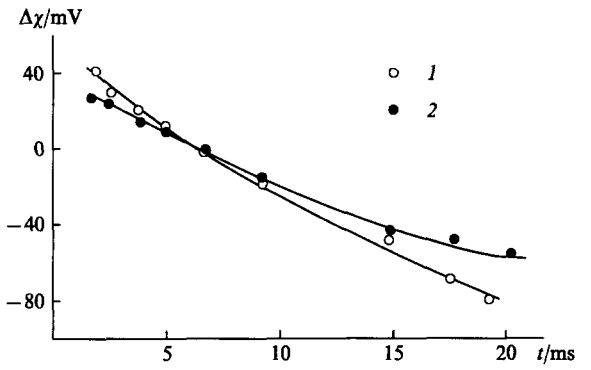


Figure 21. Time changes in the surface electric potential in the water–potassium chloride–CTAC system.[49] c_{KCl}/mol dm^{-3}: 0.12 (*1*), 0.56 (*2*); $c_{CTAC}/10^{-4}$ mol dm^{-3} = 5.6.

IV. Thermodynamic relation between surface tension and the surface electric potential under nonequilibrium conditions

1. Adsorption equation for a nonequilibrium surface

The most general and commonly met case of adsorption with polarisation of a fresh solution surface as a result of the orientation of polar molecules and of the formation of a double layer has been studied during the development of the thermodynamics of irreversible processes.[38, 50, 51] Whereas the double layer is formed naturally during the adsorption of the ions, and can be described without introducing additional variables, the orientation of the polar molecules creates a new specific problem which complicates the thermodynamics of the surface phenomena.

As was shown by Sanfeld,[50] six variables are sufficient to describe the orientation of dipoles: for example, the average components of the dipole moment $\langle m_x \rangle$ and of its square $\langle m_x^2 \rangle$, or of the modulus $\langle |m_x| \rangle$ ($x = x, y, z$). In Defay's multilayer model the multicomponent two-phase liquid–gas system with a flat surface layer is divided into elementary layers (within which the electrochemical or chemical potentials are assumed to be constant), and the generalised adsorption equation for the nonequilibrium surface becomes

$$d\gamma = -\bar{s}\,dT - \sum_i \Gamma_i\, d\tilde{\mu}_i^{\alpha} - \sum_{i,k} \frac{N_i^k}{A} d(\tilde{\mu}_i^k - \tilde{\mu}_i^{\alpha}) - \frac{1}{A}\sum_{i,k,x}\left(A_{ix}^k\, d\langle m_{ix}^k \rangle + B_{ix}^k\, d\langle m_{ix}^{k\,2} \rangle\right), \quad (7)$$

where $\bar{s}$ is the entropy excess per unit surface area, T is the temperature, A is the area of the surface, Γ_i and $\tilde{\mu}_i$ are the adsorption and the electrochemical potential of the particles of species i, N_i^k is the number of particles of species i in the sublayer k of the surface layer, $\langle m_{ix} \rangle$ and A_{ix}^k are the average component of the dipole moment of the molecules of species i in the direction ($x = x, y, z$) and the corresponding affinity; $\langle m_{ix}^2 \rangle$ and B_{ix} are the mean-square component of the dipole moment of the molecules of species i and the corresponding affinity. The difference $\tilde{\mu}_i^k - \tilde{\mu}_i^{\alpha}$ plays the role of the adsorption affinity for the k-th elementary layer in the region between the phases. The superscript α refers to the bulk phase α (the liquid solution). In the right-hand side of Eqn (7) the last two sums allow for the presence of nonequilibrium processes. At equilibrium these processes disappear, and Eqn (7) reduces to the Gibbs adsorption equation. This equation can be used as the relaxation equation for the fresh surface, and also as an equation describing the dependence of the surface tension on the parameters of state (and in particular on the concentration of the SAS).

2. Relaxation equation for the fresh surface

Eqn (7) can be simplified when applied to the relaxation of a surface for a given composition and state of the bulk phase α. The first two terms in the right-hand side vanish because the temperature and the chemical potentials of the phase α are fixed. In a single relaxation process $\langle m_{ix}^k \rangle^2$ values can be assumed to be proportional to m_{ix}^k (in practice we have only one component of $\langle m_{ix}^k \rangle$ in the direction of the normal z to the surface, since both $\langle m_{ix}^k \rangle$ and $\langle m_{iy}^k \rangle$ are equal to zero according to the symmetry conditions).[50] Noting also that each orientational affinity is proportional to the rate of change of the corresponding variable the relaxation equation which follows from (7) can be written in the form[52]

$$\frac{d\gamma}{dt} = -\sum_{i,k} N_i^k \frac{d(\tilde{\mu}_i^k - \tilde{\mu}_i^{\alpha})}{dt} - \sum_{i,k} C_i^k \left(\frac{d\langle m_{iz}^k \rangle}{dt}\right)^2, \quad (8)$$

where t is the time and C_i^k are constants.

The right-hand side of the relaxation equation (8) consists of two terms: a diffusion term and an orientation term. The quantity $\langle m_{iz}^k \rangle$ is related to the dipole component χ_d of the surface potential χ by the electrostatic equation

$$\chi_d = 4\pi \sum_{i,k} \langle m_{i,z}^k \rangle \frac{N_i^k}{A}. \quad (9)$$

Since the orientation is established mainly in the surface monolayer we can put $k = 1$. To simplify the problem we shall assume that only one component undergoes orientation, i.e. that $i = 1$. In this way we obtain from Eqn (9)

$$\langle m_z \rangle = \frac{\chi_d A}{4\pi N^{\sigma}}, \quad (10)$$

where N^{σ} is the number of molecules in the monolayer. In this model we obtain the following expression from Eqn (8):

$$A\frac{d\gamma}{dt} = -\sum_{i,k} N_i^k \frac{d(\tilde{\mu}_i^k - \tilde{\mu}_i^{\alpha})}{dt} - C\frac{d\langle m_z \rangle}{dt}. \quad (11)$$

Here C is equal to the C_i^k value for the monolayer model with one component. Obviously, $C > 0$, since the surface tension decreases as more molecules become oriented. It is clear from Eqn (11) that the decrease in surface tension is independent of the signs of $\langle m_z \rangle$ and χ_d.

Eqn (11) can be used to establish the relation between the dynamic surface tension and the nonequilibrium surface potential. We shall examine the two extreme cases in which only the orientation or only the diffusion relaxation mechanism (respectively) is operating.

a. Orientational relaxation mechanism

We shall assume initially that the orientation process is much slower than the diffusion of ions or molecules, so that in practice the process takes place under the condition of diffusion equilibrium ($\mu_i^k = \mu_i^\alpha$). Obviously, the electrochemical potentials in the surface layer is held constant by a change in the number of adsorbed ions and molecules during the orientation process. However, if we are considering a relaxation state close to equilibrium (as is found experimentally) in which the adsorption layer remains relatively dense we can assume that $N^\sigma = \text{const}$, and $d\chi = d\chi_d \approx d(m_z)$. Allowing for (10), Eqn (11) can then be rewritten

$$\frac{d\gamma}{dt} = -\frac{CA}{(4\pi N^\sigma)^2}\left(\frac{d\chi}{dt}\right)^2. \tag{12}$$

Hence we arrive at the expression

$$\frac{d\gamma}{d\chi} = -\frac{CA}{(4\pi N^\sigma)^2}\frac{d\chi}{dt}, \tag{13}$$

which shows that $d\gamma/d\chi \to 0$ for $t \to \infty$, since $d\chi/dt \to 0$.

b. Ion-diffusion relaxation mechanism

We shall now assume that the diffusion and the orientation of polar molecules are very fast processes and that the rate-limiting step of the relaxation is the formation of an ionic double layer.

In this case Eqn (11) gives

$$d\gamma = -\sum_{i,k}\left(\frac{N_i^k}{A}\right)d(\tilde{\mu}_i^k - \tilde{\mu}_i^\alpha), \tag{14}$$

where the summation with respect to i refers to the ions. Using the standard expressions for the electrochemical potentials,

$$\tilde{\mu}_i = \mu_i + q_i\varphi, \tag{15}$$

where μ_i is the chemical potential, q_i is the charge on the ion, and φ is the electric potential at the place where the ion is sited. Inserting (15) into (14) and dividing by $d\chi$ gives

$$\frac{d\gamma}{d\chi} = -\sum_{i,k}\frac{N_i^k}{A}\frac{d(\tilde{\mu}_i^k - \tilde{\mu}_i^\alpha)}{d\chi} - \sum_k q^k\frac{d(\varphi^k - \varphi^2)}{d\chi}, \tag{16}$$

where q^k is the charge on the elementary layer k per unit area,

$$q^k \equiv \sum_i \frac{q_i N_i^k}{A}.$$

The right-hand side of Eqn (16) contains two terms. The first describes the effect of the adsorption of ions (accompanied by the formation of the surface potential χ) on the distribution of chemical potentials in the double layer. The derivative $d\mu_i^k/d\chi$ should be large in the case of massive surface-active ions at the formation stage of the adsorption monolayer. If this stage dominates the formation of the equilibrium diffusion layer of counterions the derivative is small during the final stage of the relaxation. Obviously, the same derivative is small for the counter-ions, which usually have a small mass, if their concentration is small.

The second term of Eqn (16) is purely electrostatic. We note that it differs from zero even in an electrically neutral surface layer, and it lowers the surface tension irrespectively of the sign of the surface potential. For the last elementary layer we can write $d(\varphi^k - \varphi^\alpha)/d\chi = -1$ (By definition of χ); it follows immediately that the right-hand side of Eqn (16) remains finite at $t \to \infty$. This means that, in contrast to the orientational relaxation, a linear term appears in the dependence of $(\gamma - \gamma_\infty)$ upon $(\chi - \chi_\infty)$.

Thus the presence or absence of a linear term in the asymptotic dependence of $(\gamma - \gamma_\infty)$ upon $(\chi - \chi_\infty)$ allows us to identify the relaxation mechanism. If it is found experimentally that the dependence does not contain a term in which $(\chi - \chi_\infty)$ appears in the first power we may conclude that the surface potential is formed by the reorientation of the polar molecules. If a first-power term is detected the surface potential is the result of the formation of an ionic double layer.

3. Concentration dependence of the surface tension

When considering the concentration dependence of the surface tension (at constant temperature) we must allow for the second term in the right-hand side of the adsorption equation (7) as well as for the effects discussed above. Using once again the expression (15) we can write

$$\sum_i \Gamma_i\, d\tilde{\mu}_i^\alpha = \sum_i \Gamma_i\, d\mu_i^\alpha + \sum_i \Gamma_i q_i\, d\varphi^\alpha$$
$$= \sum_i \Gamma_i\, d\mu_i^\alpha + q\, d\chi,$$
$$q \equiv \sum_i \Gamma_i q_i, \tag{17}$$

where q is the overall charge on the surface. The electroneutrality condition ($q = 0$) is usually assumed for systems in equilibrium (which may, however, be charged), but in dynamic processes electroneutrality is not, of course, a necessary condition.

It has been reported [52-55] that the formation of a fresh surface may involve local breakdown of the electroneutrality of the electric double layer. According to Lopatenko and Kontush [54] the charging of a liquid surface takes place in a particular time interval during the formation of the surface because of the presence of a nonequilibrium electric potential which varies along the surface. The formation conditions of the fresh surface have a strong influence on the resulting surface charge. Thus, in the formation of an air bubble in an aqueous solution of NaCl the surface charge [52] is 4×10^{-5} to 4×10^{-7} C cm^{-2}, whereas in the formation of a drop of the same solution in air the charge [54] is $\sim 1.5 \times 10^{-12}$ C cm^{-2}. The formation of surface charge is most likely at low concentrations of electrolyte, when the electric double layer is relatively stretched and easily deformed. The Jones–Ray effect (the appearance of a minimum on the surface tension isotherm at low concentrations of electrolyte, of the order of 10^{-3} mol dm^{-3}) has been attributed [56] to the formation of surface charge.

The charging of droplets of electrolyte solutions has been observed not only with inorganic electrolytes but also with solutions of SAS. As an example we show in Fig. 22 the dependence of the charge on drops of an aqueous solution of cetylpyridinium chloride on the concentration of the solution.[57]

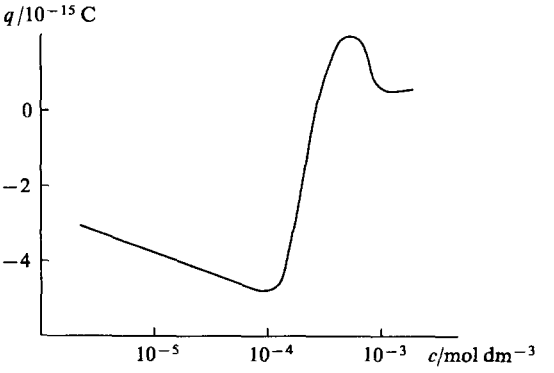


Figure 22. Dependence of the charge of drops on the concentration of a solution of cetylpyridinium chloride.[57]

We shall now rewrite Eqn (7) for the case of constant temperature in the system and on the assumption that the orientation and diffusion processes are significantly faster than the re-establishment of the electroneutrality of the surface:

$$d\gamma = -\sum_i \Gamma_i \, d\mu_i^{\alpha} - q \, d\chi . \tag{18}$$

In particular, for a dilute solution of a 1-1 electrolyte Eqn (8) simplifies to

$$d\gamma = \frac{-2RT\Gamma}{c} dc - q \, d\chi , \tag{19}$$

where c is the conconcentration of electrolyte in the bulk phase. This equation can be used, for example, to determine the dependence of the surface tension on the concentration.[56] In the case of an SAS on a fairly well aged surface, when the adsorption is substantial, the first term in the right-hand side of Eqn (19) can play the dominant role. The second term can make a significant contribution when the surface is still relatively fresh.

V. Methods of studying the adsorption mechanism

We know that the kinetics of the adsorption of SAS can be diffusion-controlled (in which case the relaxation time is determined by the diffusion of the SAS to the surface), adsorption-controlled (with an energy barrier on the surface), or under mixed control (when both the diffusion and the rate of establishing equilibrium in the surface and the subsurface layers must be allowed for). Even for one given substance different types of kinetics may be observed, depending on the concentration and temperature of the solution and on the duration of the process:[4, 58, 59] this must be allowed for when experimental data are analysed. Let us now examine the methods of studying the mechanism of adsorption of the SAS.

1. Calculations from experimental data by the diffusion theory

The relaxation of the surface properties of aqueous solutions of SAS characterises their adsorption kinetics. The time dependence of the adsorption can be obtained from experimental values of the surface tension $\gamma(t)$, of the surface electric potential $\Delta\chi(t)$, or of the adsorption potential $\varphi(t)$ by using the equilibrium isotherms of the surface tension $\gamma(c)$, of the adsorption potential $\varphi(c)$, and of the adsorption $\Gamma(c)$. Identical dependences of the dynamic surface tension or of the adsorption potential on the adsorption for equilibrium and for nonequilibrium conditions are assumed. In other words it is assumed that the molecules become oriented relatively rapidly and that the process is controlled exclusively by the rate of arrival of the adsorbate at the surface.

In the case of purely diffusion-controlled kinetics the dependence of the adsorption Γ on the time t can be calculated using the Ward–Tordai equation[60]

$$\Gamma(t) = 2c_0\left(\frac{Dt}{\pi}\right)^{1/2} - \left(\frac{D}{\pi}\right)^{1/2} \int_0^t \frac{\bar{c}(t')}{(t-t')^{1/2}} dt' , \tag{20}$$

where c_0 is the bulk concentration of the SAS, D is the diffusion coefficient, and $\bar{c}(t)$ is the concentration of SAS in the part of the bulk solution directly adjacent to the surface layer (known as the subsurface concentration). Because of the difficulty of determining this quantity experimentally the parameter c is often obtained by using one of the conventional adsorption isotherms. Thus, by adopting the linear adsorption isotherm

$$\Gamma = \varepsilon c , \tag{21}$$

Sutherland[61] converted Eqn (21) into:

$$\Gamma(t) = \varepsilon c_0\left[1 - \exp\left(\frac{Dt}{\varepsilon^2}\right) \operatorname{erfc}\left(\frac{\sqrt{Dt}}{\varepsilon}\right)\right]. \tag{22}$$

The adsorption kinetics are often studied in a jet of liquid. A study[61] of the effect of the velocity profile in the jet on the adsorption gave the following expression for $\Gamma(t)$:

$$\Gamma(t) = 2c_0\left(\frac{Dt}{\pi}\right)^{1/2} - \left(\frac{D}{\pi}\right)^{1/2} \int_0^t \frac{c(t')}{(t-t')^{1/2}} dt'$$

$$+ \frac{1}{(2\pi D)^{1/2}} \int_0^t \int_0^{t'} \int_0^{\infty} \frac{y'}{(t'-t'')^{3/2}} \exp\left[-\frac{(y')^2}{4D(t'-t'')}\right]$$

$$\times v_r(y', t') \, F(y', t'') \, dy' dt' dt'' \tag{23}$$

Here $v(r)$ is the radial component of the velocity, and $y' = a - r$ (where a is the radius of the jet and r is the radial coordinate); also,

$$F(y', t'') = \left(\frac{\partial c}{\partial y'}\right)_{t''} .$$

The first two terms of Eqn (23) are identical to the right-hand side of the Ward–Tordai equation, and therefore they allow for the transport of matter by molecular diffusion. The third term is a small correction for the effect of a nonuniform velocity profile.

Experimental dependences of the adsorption on time can be compared with dependences calculated by the diffusion theory [Eqns. (20)–(22)]. Good agreement between experimental and calculated values of $\Gamma(t)$ denotes diffusion-controlled adsorption kinetics. This is found, for example, for aqueous solutions of alcohols with moderately long hydrocarbon chains.[44] Data for an aqueous solution of heptanol are shown in Fig. 23 as an example. The curve was calculated by the Ward–Tordai equation. The points give the $\Gamma(t)$ values obtained from measurements of the adsorption potential.[45] The agreement between the experimental results and those calculated by the theory of diffusion is satisfactory.

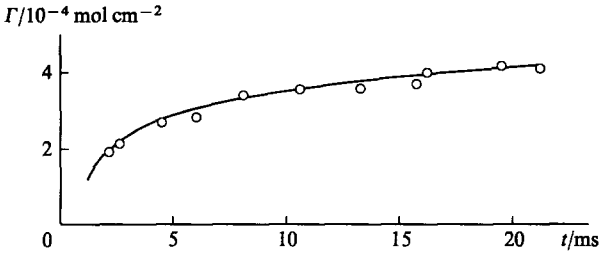


Figure 23. Time dependence of the adsorption of heptanol.[45] $c/10^{-3}$ mol dm^{-3} = 2.5.

In some cases the association of the dissolved substance is one of the main factors responsible for slow adsorption, as was shown by measurements of the adsorption potential of solutions of aliphatic acids.[47] The most significant difference between acids and alcohols is the presence of the polar carboxylic acid group –C(O)OH, which balances the hydroxyl and the hydrophobic parts of the acid molecule. For this reason the normal aliphatic acids can form associations, unlike the corresponding alcohols. The carboxylic acid group also enables the aliphatic acids to form relatively strong hydrogen bonds (as compared with the alcohols). Experimental results (Figs 24 and 25) show that the rate of adsorption is suppressed (as compared with the diffusion-controlled kinetics by increasing the concentration of the solution and by shortening the hydrocarbon chain. The adsorption barrier is lowered by the transition from C_6 to C_7, but it is raised by an increase in concentration. These results justify the conclusion that the adsorption is hindered by the formation of associations of the aliphatic acids.

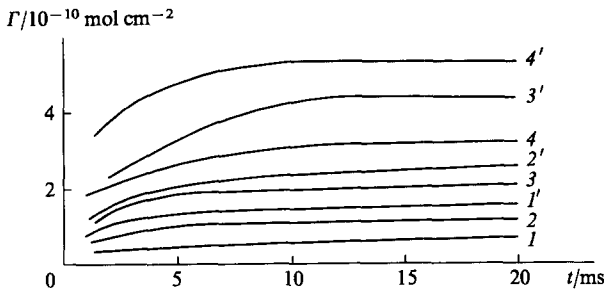


Figure 24. Time dependence of the adsorption of hexanoic acid.[47] $c/10^{-3}$ mol dm^{-3}: (*1,1'*) 1, (*2,2'*) 2, (*3,3'*) 4, (*4,4'*) 6; (*1–4*) calculated from experimental adsorption potential data, (*1'–4'*) calculated by the Ward–Tordai equation.

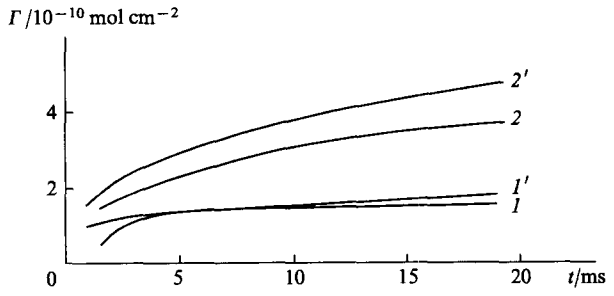


Figure 25. Temperature dependence of the adsorption of heptanoic acid.[47] $c/10^{-3}$ mol dm^{-3}: (*1,1'*) 1; (*2,2'*) 2; (*1*) and (*2*) calculated from experimental adsorption potential data, (*1'*) and (*2'*) calculated by the Ward–Tordai equation.

In the case of a purely diffusional adsorption mechanism we can replace the calculation of $\Gamma(t)$ by a calculation of the surface tension followed by a comparison with the experimental value. The surface tension is determined from the surface pressure $\pi(t)$:

$$\gamma(t) = \gamma_{H_2O}(t) - \pi(t) = \gamma_{H_2O}(t) - RT\Gamma(t), \qquad (24)$$

where $\gamma_{H_2O}(t)$ is the experimental value of the dynamic surface tension of water, and $\Gamma(t)$ is defined for a purely diffusional mechanism [for example, by formula (22)]. This approach does not require the traditional stipulation of local equilibrium between the surface and the subsurface layers, which is legitimate only for a purely diffusional adsorption mechanism.

Fig. 26 shows the experimental time dependence of the surface tension of a solution of CTAB and the same dependence calculated by formula (24). For surfaces aged up to 1.5 ms the two dependences are indistinguishable, but the curves show a significant deviation for $t > 1.5$ ms, probably associated with the appearance of an adsorption barrier. In this case the barrier is probably of the electrostatic type, since it has been shown [35] that in the adsorption of CTAB the absolute value of the surface electric potential increases, with a corresponding increase in the mutual repulsion of the adsorbed active cations and of those approaching the surface. The concept of an activation barrier was first proposed by Doss.[62]

An alternative method of revealing the presence of an adsorption barrier was discussed by Owens.[22] The rate of diffusion is markedly temperature-dependent. It follows that a lack of a temperature dependence of the rate of decrease of the surface tension (i.e. the rate of increase of adsorption) indicates the appearance of an adsorption barrier. Let us consider the above example of a solution of CTAB (see Fig. 26), in which an adsorption barrier appears to be formed for $t > 1.5$ ms (see also Fig. 4).

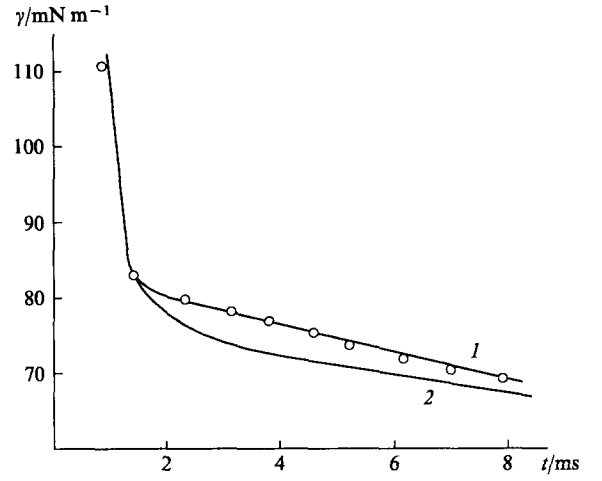


Figure 26. Experimental (*1*) and calculated time dependences (*2*) of the surface tension in the water–CTAB system at 25 °C with $c/10^{-4}$ mol dm^{-3} = 5.6 (see Rakhimov et al.[35]).

At $t > 1.5$ ms the rate of decrease of the dynamic surface tension becomes independent of temperature: this is interpreted by Owens as evidence for the formation of an adsorption barrier.

Thus we conclude from the behaviour of the CTAB solution that the different methods of identifying the mechanism of adsorption by studying the relaxation of the surface properties of the solution give adequately consistent results.

2. Analysis of the experimental dependence of the surface tension on the surface potential

Under equilibrium conditions the contribution to the surface tension from the orientation of the dipoles is proportional to the square of the discontinuity in the electric potential created at the surface.[63,64] As was said above, when the ionic double layer is formed under nonequilibrium conditions we find a term proportional to the first power of $\Delta\chi$.

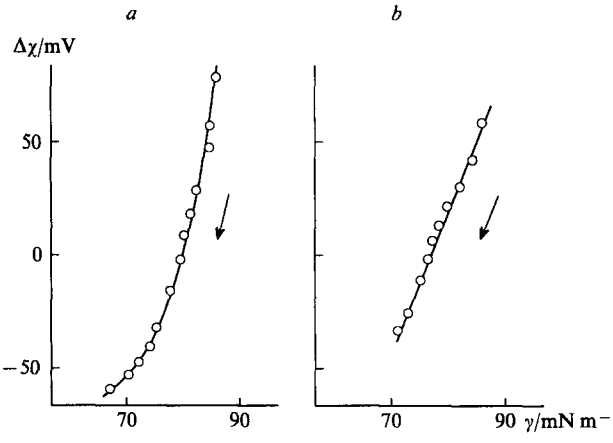


Figure 27. Dependence of $\Delta\chi$ on γ in the water–CTAB system with $c/10^{-4}$ mol dm^{-3} = 5.6 (*a*) and 2.8 (*b*).

Fig. 27 shows the $\gamma(t)-\Delta\chi(t)$ dependence for solutions of CTAB of two concentrations. At the lower concentration the $\gamma-\Delta\chi$ correlation is linear, but at the higher concentration we find a deviation from linearity. This means that in the former case the adsorption mechanism is diffusion-controlled, whereas in the latter case an adsorption barrier may be present.

3. Analysis of the experimental dependence of the adsorption on the surface potential

It has been shown[65] that under equilibrium conditions the adsorption potential increases linearly with the adsorption. This is explained by assuming that the molecular orientation is retained when the adsorption is increased. For a purely diffusional mechanism the calculation of adsorption by the Ward–Tordai equation assumes the presence of local equilibrium between the surface and the subsurface. It may be thought that for a diffusion-limited adsorption mechanism the parameter $\Delta\chi$ should be linearly dependent on Γ ($\Delta\chi$ and Γ are compared at the same instant). Therefore if Γ is calculated by the Ward–Tordai equation and φ(or $\Delta\chi$) is taken from experimental results a linear dependence of $\Delta\chi$ on Γ suggests a diffusion-controlled mechanism whereas deviations from linearity suggest the presence of a barrier.

The correctness of these views is confirmed by experiments with aqueous solutions of CTAB.[35] In the time region for which other methods had detected an adsorption barrier the dependence of $\Delta\chi$ on Γ was nonlinear. A similar analysis for aqueous solutions of hexadecylpyridinium bromide and dodecylammonium and cetyltrimethylammonium chlorides showed that in every case (except the cetyltrimethylammonium chloride of concentration 5.6×10^{-4} mol dm^{-3}) a linear relation between $\Delta\chi$ and Γ was obtained, indicating diffusion-controlled adsorption. In the exceptional case an adsorption barrier appears to be rate-limiting at short times (Fig. 28).

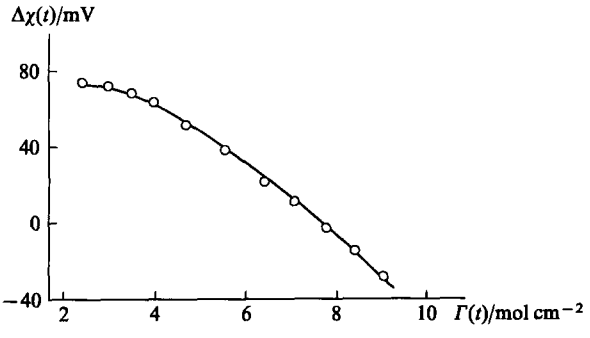


Figure 28. Dependence of $\Delta\chi$ on Γ calculated from experimental data for a solution of CTAC with $c/10^{-4}$ mol dm^{-3} = 5.8.

* * *

Thus the study of the properties of freshly created surfaces such as dynamic surface tension and surface electric potential allows us to compare different views on the structure of SAS solution surfaces.

The thermodynamic description of the relaxation of the surface layer offers practiclally useful conclusions on the mechanism of adsorption.

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