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THE GOUY–CHAPMAN THEORY IN COMBINATION WITH A MODIFIED LANGMUIR ISOTHERM AS A THEORETICAL MODEL FOR ION-PAIR CHROMATOGRAPHY

JAN STÅHLBERG*
Astra Pharmaceutical Production AB, Quality Control, S-151 85 Södertälje (Sweden)

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SUMMARY

A theory for ion-pair chromatography is developed, based on a Langmuir-like adsorption isotherm and the Gouy–Chapman theory for an electrically charged surface. It is found that the predictions made by the theory agree qualitively and semi-quantitatively with experimental results. A useful consequence of the theory is that when the charges of ions Y and R are of equal magnitude but of opposite signs

$$k'_Yk'_R = K_1$$

and when the charges are of equal magnitude and sign

$$k'_Y/k'_R = K_2$$

where the constants are independent of the concentration of amphiphilic modifier in the mobile phase.

INTRODUCTION

Liquid chromatographic analysis of organic ions is often carried out with a mobile phase modified with amphiphilic molecules. This analytical technique is usually called ion-pair chromatography. There are a number of different theories concerning the physico-chemical interpretation of the experimental findings. The theoretical and experimental findings have been summarized in ref. 1.

Most of the published theories define a scheme for the various equilibria that may exist in the system. Relationships between the capacity factor, k', and the corresponding equilibrium constants are then derived. However, it is generally found that when long-range forces between the molecules are of importance the equilibrium constants vary with the composition of the system. A well known example is the Debye–Hückel corrections made for ionic systems.

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* Affiliated to the Institute of Physical Chemistry, University of Uppsala, Uppsala, Sweden.

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This work presents a theory where the contributions from the chemical and electrostatic energies are separated. In ion-pair chromatography the electrostatic energy is related to the electrostatic potential of the surface, which in turn depends on the charge density on the surface, *i.e.*, the concentration of adsorbed amphiphilic ions. The importance of this electrostatic potential for the retention of solute molecules has also been proposed by Cantwell[2]. He writes that "there appears to have been little recognition of the role played by the surface potential created by the sorption of P^+ in enhancing the surface sorption of S^-". An interesting work by Deelder and Van den Berg[3] shows that the Stern–Gouy–Chapman theory well describes the adsorption of sodium 1-dodecanesulphonate on octadecyl modified silica.

This paper derives equations for the adsorption isotherm of the amphiphilic ion used as modifier in the mobile phase. The adsorption isotherm is then used to derive equations for the capacity factor for solute ions. It is of the Langmuir type and has been applied to calculate adsorption isotherms for amphiphilic ions at the oil–water interface[4]. The Gouy–Chapman theory for a plane surface is used to derive the equations relating the amount of adsorbed amphiphilic ions to the electrostatic potential of the surface.

THEORETICAL

The general assumption is that the adsorption of a charged organic molecule, Q^{z_Q}, on the stationary phase is primarily governed by two factors: the electrostatic repulsion (attraction) from (to) the surface, governed by the electrostatic potential of the surface, ψ_0, and the charge of the molecule, z_Q; and the free energy of adsorption of the molecule, $-\Delta G^\circ_Q$ (kJ/mol), when $\psi_0 = 0$. Assuming that the maximum possible concentration of Q^{z_Q} molecules on the surface is n_0 mol/m^2 and using the isotherm that applied previously for adsorption of surfactants at the oil–water interface[4], one obtains

$$n_Q = \frac{Bc_Q \cdot \exp[(-\Delta G^\circ_Q - z_Q F\psi_0)/RT]}{1 + B(c_Q/n_0) \cdot \exp[(-\Delta G^\circ_Q - z_Q F\psi_0)/RT]} \tag{1}$$

where n_Q is the concentration (mol/m^2) of molecule Q^{z_Q} on the surface, c_Q is the concentration (mol/m^3) of the amphiphilic modifier Q^{z_Q} in the mobile phase, F is the Faraday number and B is a constant representing the thickness of the surface layer.

If Q^{z_Q} is added to the solvent as the salt QX and X^{-z_Q} is not adsorbed, the concentration of Q^{z_Q} on the surface determines the electrostatic potential of the surface. To calculate the adsorption isotherm for Q^{z_Q} the relationship between n_Q and ψ_0 has to be determined. This is obtained from the Poisson–Boltzmann equation for a planar surface and the well known Gouy–Chapman theory[5]. Since it is essential for a proper understanding of the final results, a derivation of the equations will be given here. Readers not interested in the derivation may proceed to eqn. 11 which is the isotherm obtained.

To maintain electroneutrality in the system, the charge of the surface is the same as the charge in the solution but of opposite sign. When performing chromatography with amphiphilic ions as modifiers, the solvent usually contains inorganic ions too and this has to be considered in order to obtain the general solution of the equations. It is assumed that these ions contribute to the double layer but are not adsorbed on the surface. To be able to obtain an explicit solution we must restrict ourselves to the case where all ions in the system have charges of equal magnitude, *i.e.*, $+z$ and $-z$. The condition of electroneutrality is

$$n_Q z_Q F = -|z_Q|F\int_0^\infty\left[\left(\sum_{i,+} c_{0,i}\right)\cdot\exp\left(-\frac{|z_i|F\psi(x)}{RT}\right)-\left(\sum_{j,-} c_{0,j}\right)\cdot\exp\left(\frac{|z_i|F\psi(x)}{RT}\right)\right]\mathrm{d}x \tag{2}$$

where x is the distance from the surface, $\psi(x)$ is the electrostatic potential at x, $|z_i| = |z_Q|$, $c_{0,i}$ represents the concentration of the positively charged ion i at infinite distance from the surface and $c_{0,j}$ is concentration of the corresponding negatively charged ion j; to simplify the equations the concentration unit is mol/m^3. The summation symbols indicate that a number of different positively and negatively charged ions may be present. It is important to point out that the concentration of Q^{z_Q} is included in the summation. Furthermore, there is electroneutrality at infinite distance from the surface, *i.e.*

$$\sum_{i,+} c_{0,i} = \sum_{j,-} c_{0,j} = \sum_{i} c_{0,i} \tag{3}$$

since all the charges are of the same magnitude. By using the definition of sinh(x) we can now rewrite eqn. 2 as:

$$n_Q z_Q F = 2|z_Q|F\left(\sum_i c_{0,i}\right)\cdot\int_0^\infty \sinh\frac{|z_Q|F\psi(x)}{RT}\mathrm{d}x \tag{4}$$

According to the Poisson equation the following relationship holds

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{-\rho(x)}{\varepsilon_0 D} \tag{5}$$

where $\rho(x)$ is the charge density (C/m^3) in the mobile phase at a distance x from the surface, ε_0 is the permittivity in a vacuum and D is the dielectric constant of the mobile phase. The charge density at x can also be written as follows:

$$\begin{aligned}\rho(x) &= |z_Q|F\left[\left(\sum_{i,+} c_{0,i}\right)\exp\left(-\frac{|z_i|F\psi(x)}{RT}\right)-\left(\sum_{j,-} c_{0,j}\right)\exp\left(\frac{|z_i|F\psi(x)}{RT}\right)\right]\\ &= -2|z_Q|F\left(\sum_i c_{0,i}\right)\sinh\frac{|z_Q|F\psi(x)}{RT}\end{aligned} \tag{6}$$

Combining eqns. 4–6 one obtains

$$n_Q z_Q F = \varepsilon_0 D \int_0^\infty \frac{d^2\psi}{dx^2} dx = -\varepsilon_0 D \left(\frac{d\psi}{dx}\right)_{x=0} \tag{7}$$

since $d\psi/dx \to 0$ as $x \to \infty$. Integration of eqn. 5, after inserting the expression for $\rho(x)$ in eqn. 6, gives:

$$\frac{d\psi}{dx} = \left[\frac{8\left(\sum_i c_{0,i}\right)RT}{\varepsilon_0 D}\right]^{1/2} \sinh \frac{|z_i|F\psi(x)}{2\,RT} \tag{8}$$

At the surface $\psi = \psi_0$ and combining eqns. 7 and 8 gives:

$$n_Q z_Q F = \left(8\varepsilon_0 DRT \sum_i c_{0,i}\right)^{1/2} \sinh \frac{|z_i|F\psi_0}{2\,RT} \tag{9}$$

This is the equation obtained from the Gouy–Chapman theory.

Inverting this equation and using the relationship $\sinh^{-1} x = \ln[x + (x^2 + 1)^{1/2}]$, see, *e.g.*, ref. 6, one obtains:

$$\psi_0 = \frac{2\,RT}{|z_i|F} \ln\left\{\frac{n_Q z_Q F}{\left(8\varepsilon_0 DRT \sum_i c_{0,i}\right)^{1/2}} + \left[\frac{(n_Q z_Q F)^2}{8\varepsilon_0 DRT \sum_i c_{0,i}} + 1\right]^{1/2}\right\} \tag{10}$$

When eqn. 10 is substituted into eqn. 1 and considering that it is an odd function, eqn. 11 is obtained:

$$n_Q = \frac{Bc_Q \cdot \exp\left(-\frac{\Delta G^\circ_Q}{RT}\right)}{\left\{\frac{n_Q|z_Q|F}{\left(8\varepsilon_0 DRT \sum_i c_{0,i}\right)^{1/2}} + \left[\frac{(n_Q|z_Q|F)^2}{8\varepsilon_0 DRT \sum_i c_{0,i}} + 1\right]^{1/2}\right\}^2 + Bc_Q/n_0 \cdot \exp\left(-\frac{\Delta G^\circ_Q}{RT}\right)} \tag{11}$$

Solving this equation for n_Q for different values of c_Q gives the adsorption isotherm for Q^{z_Q}.

The theory used to calculate the adsorption isotherm for Q^{z_Q} may also be used to calculate the retention of a solute molecule, Y^{z_Y}, as a function of the concentration of Q^{z_Q} on the surface and, thus indirectly, as a function of the concentration of Q^{z_Q} in the mobile phase. The starting equation is again eqn. 1, with all the subscripts Q changed to Y. The next step is to evaluate the relationship between ψ_0 and the concentrations of adsorbed ions on the surface, n_Q and n_Y. This can be done by using eqn. 10 by adding the concentrations of the absorbed species, with proper consideration of their charges, and we obtain the following equation:

$$\psi_0 = \frac{2\,RT}{|z_i|F} \ln\left\{ \frac{F(n_Q z_Q + n_Y z_Y)}{\left(8\varepsilon_0 DRT \sum\limits_i c_{0,i}\right)^{1/2}} + \left(\frac{[F(n_Q z_Q + n_Y z_Y)]^2}{8\varepsilon_0 DRT \sum\limits_i c_{0,i}} + 1 \right)^{1/2} \right\} \qquad (12)$$

This equation has then to be introduced in the equations for the isotherms of n_Q and n_Y, respectively. It is readily seen that it is not possible to obtain an equation where n_Y is solely dependent on n_Q. Thus, it can be concluded that the general case has to be treated by an iteration procedure.

It is the influence on ψ_0 of the adsorbed Y^{z_Y} ions that makes the evaluation difficult. In the limit where this influence is negligible, *i.e.*, when $n_Q z_Q \gg n_Y z_Y$, the equation for the adsorption isotherm of Y simplifies to:

$$n_Y = Bc_Y \cdot \exp[(-\Delta G^\circ_Y - z_Y F\psi_0)/RT] \qquad (13)$$

Since ψ_0 is assumed to be determined by n_Q, eqn. 10 applies giving

$$n_Y = Bc_Y \cdot \exp\left(-\frac{\Delta G^\circ_Y}{RT}\right) \cdot$$

$$\left\{ \frac{n_Q|z_Q|F}{\left(8\varepsilon_0 DRT \sum\limits_i c_{0,i}\right)^{1/2}} + \left[\frac{(n_Q|z_Q|F)^2}{8\varepsilon_0 DRT \sum\limits_i c_{0,i}} + 1 \right]^{1/2} \right\}^{-2Z_Y/Z_Q} \qquad (14)$$

since $|z_Q| = |z_i|$. From the definition of the capacity factor we obtain

$$k'_Y = A' \cdot \exp\left(-\frac{\Delta G^\circ_Y}{RT}\right) \cdot$$

$$\left\{ \frac{n_Q|z_Q|F}{\left(8\varepsilon_0 DRT \sum\limits_i c_{0,i}\right)^{1/2}} + \left[\frac{(n_Q|z_Q|F)^2}{8\varepsilon_0 DRT \sum\limits_i c_{0,i}} + 1 \right]^{1/2} \right\}^{-2Z_Y/Z_Q} \qquad (15)$$

where $A' = BA_s/V_m$ and A_s/V_m is the phase ratio. We have thus obtained an equation for the capacity factor of a solute molecule as a function of the concentration of amphiphilic modifier on the surface, which through eqn. 11 is related to the concentration of amphiphilic modifier in the mobile phase.

RESULTS AND DISCUSSION

The adsorption isotherm

From eqn. 11 it is possible to calculate the adsorption isotherm for the amphiphilic modifier Q^{z_Q}. The relationship between n_Q and c_Q is slightly complex, so when c_Q is known the equation has to be evaluated by suitable numerical methods. Eqn. 11 is derived from eqn. 1 from which it is seen that the amount of Q^{z_Q} adsorbed depends on the following parameters: the concentration of Q^{z_Q} in the mobile phase, c_Q; the free energy of adsorption for Q^{z_Q}, $-\Delta G^\circ_Q$; the electrostatic potential of the surface, ψ_0; the thickness of the surface layer, B; the maximum possible concentration of Q^{z_Q} on the surface, n_0, and the charge of Q^{z_Q}, z_Q. However, according to eqn. 10, the electrostatic potential of the surface, ψ_0, also depends on a number of parameters: the surface concentration of Q^{z_Q}, n_Q; the charge of Q^{z_Q}; the dielectric constant of the mobile phase, D, and the concentration of ions in the mobile phase, $\sum_i c_{0,i}$.

A number of parameters must thus be considered. A few numerical examples are given to demonstrate how some of these parameters influence the adsorption isotherm. These examples are compared with adsorption isotherms from the literature.

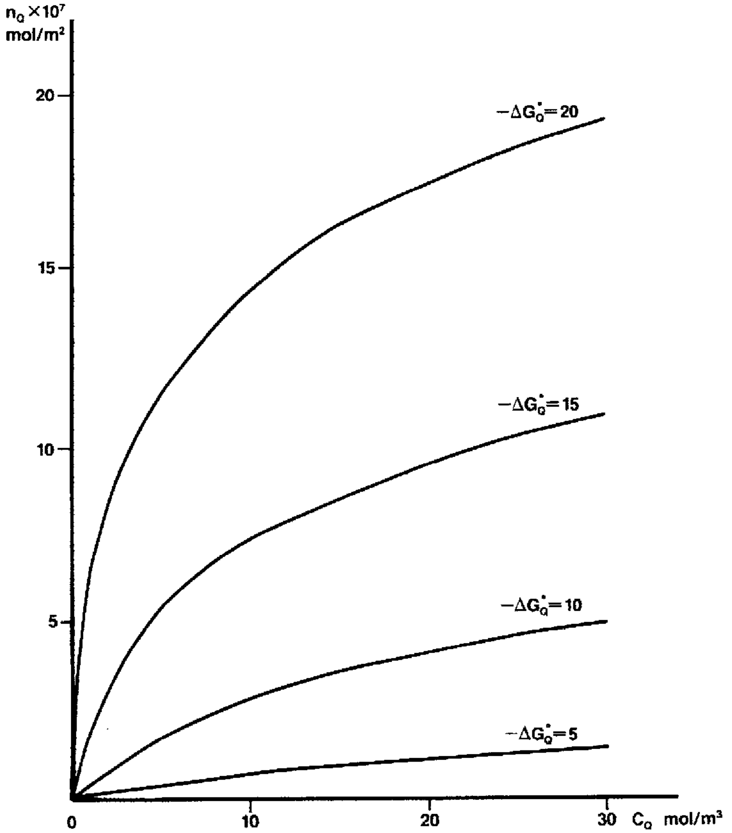

Fig. 1. Calculated adsorption isotherms for Q^{z_Q} from eqn. 11 with $z_Q = \pm 1$, for different values of ΔG°_Q (kJ/mol). $T = 298$K; $D = 80$; $\Sigma c_{0,i} = 500$ mM; $n_0 = 3.321 \cdot 10^{-6}$ mol/m²; $B = 2 \cdot 10^{-9}$ m.

It is important to note that the theory cannot be expected to give a full quantitative description of an adsorption isotherm as determined by liquid chromatographic (LC) methods. Its validity is determined by the limitations of the Gouy–Chapman theory and the use of a Langmuir-like isotherm. Some of these limitations are:

the theory is derived for a planar surface but the particles used in LC are highly porous. The measured adsorption will therefore depend on the distribution of pore radii

the thickness of the surface layer, *B*, and the value of ΔG°_Q are unknown

the theory is a mean-field approximation and as such it does not consider correlation effects between the ions

the ΔG°_Q value may depend on the concentration of Q^{z_Q} at the surface

It is also important to note that if the pH of the system is such that the silanol groups on the surface are ionized, a proper correction must be made for the corresponding electrostatic potential.

Fig. 1 shows calculated adsorption isotherms for various values of $-\Delta G^\circ_Q$ (kJ/mol). It is seen that a plateau is reached and that its value increases when the hydrophobicity of the ion Q increases; this is in accordance with experimental findings, *e.g.*, ref. 7. The logarithmic derivatives of these curves, Fig. 2, can be compared to the adsorption isotherm for various quaternary ammonium ions, Fig. 3, obtained by Bartha and Vigh[7]. The qualitative information in the two figures is the same, *e.g.*, as $-\Delta G^\circ_Q$ increases the slope of the curve decreases. Another way to change the value of $-\Delta G^\circ_Q$ is to change the composition of the mobile phase. In the same paper[7], the adsorption isotherm of tetrabutylammonium bromide from mobile phases containing

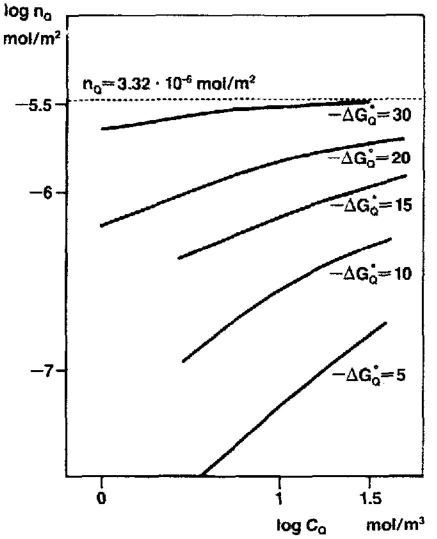

Fig. 2. The adsorption isotherms in Fig. 1 with a log–log scale.

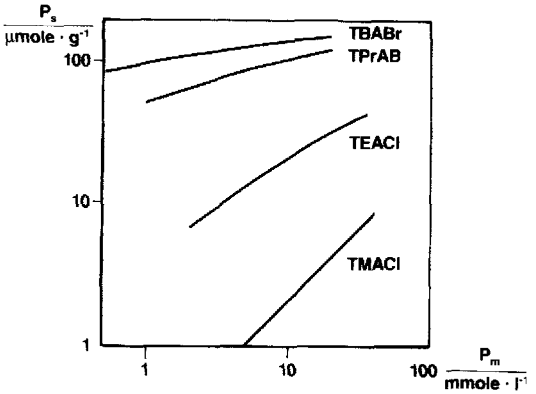

Fig. 3. Adsorption isotherms of tetramethylammonium chloride (TMACl), tetraethylammonium chloride (TEACl), tetrapropylammonium bromide (TPrAB) and tetrabutylammonium bromide (TBABr) on LiChrosorb RP-18 from 25 m*M* orthophosphoric acid–25 m*M* sodium dihydrogenphosphate (pH = 2.1) buffer at constant bromide concentration (200 m*M*) at 25°C (from ref. 7) (P_s = concentration of quaternary ions on the surface; P_m = concentration of quaternary ions in the mobile phase).

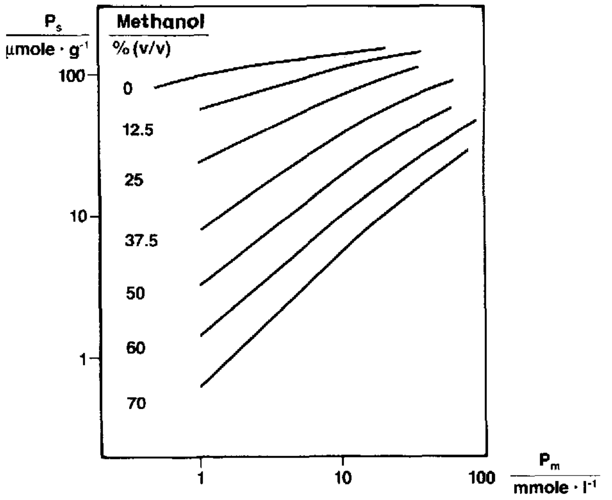

Fig. 4. Adsorption isotherms of tetrabutylammonium bromide on LiChrosorb RP-18 from 0, 12.5, 25, 37.5, 50, 60 and 70% (v/v) methanol–aqueous phosphate buffer eluents (25 m*M* orthophosphoric acid–25 m*M* sodium dihydrogenphosphate; pH = 2.1–3.4; [Br⁻] = 200 m*M*; 25°C) (from ref. 7).

different concentrations of methanol was reported, Fig. 4. An increase in the concentration of methanol will give a lower $-\Delta G^\circ_Q$, so the results can also be qualitatively compared to Fig. 2.

The adsorption isotherms of the different quaternary ammonium ions are not suitable for a quantitative comparison with the theory because the unknown parameters ΔG°_Q and n_0 are difficult to predict. However, these parameters are semi-quantitatively predictable for linear amphiphilic molecules by comparison of data from

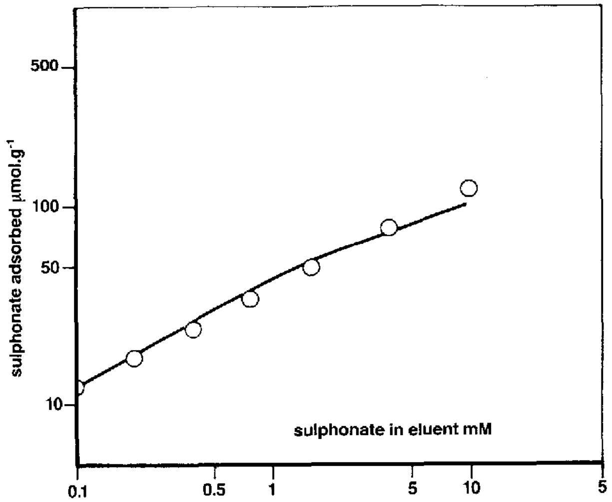

Fig. 5. Comparison between the calculated (full line) and experimental (O) adsorption isotherms for sodium 1-octanesulphonate on octadecylsilica at 40°C. Eluent: phosphate buffer (50 m*M* Na⁺; pH = 3.00). Experimental points from ref. 3.

a water–oil interface[4]. Deelder and Van den Berg[3] measured the adsorption isotherms of octanesulphonate and dodecanesulphonate in the RP-18–water system. A semi-quantitative comparison of the theoretical adsorption isotherm with the reported adsorption isotherm is made in the following way:

the value of n_0 is set to $3.32 \cdot 10^{-6}$ mol/m^2 (50 Å^2 per molecule), approximately the same as that found for linear molecules at the oil–water interface (45–55 Å^2 per molecule)[9];

the thickness of the surface layer is set to 20 Å;

the reported value for n_Q at the lowest concentration, c_Q, is used to calculate ψ_0 according to eqn. 10;

the value of ΔG°_Q is then calculated from eqn. 1;

the value obtained for ΔG°_Q is then used in eqn. 11 to calculate the complete adsorption isotherm.

Calculation of $-\Delta G^\circ_Q$ according to this procedure gives ≈16 kJ/mol for octanesulphonate and ≈37 kJ/mol for dodecanesulphonate. From measurements at the oil–water interface, these values are expected to be 20–25 and 30–38 kJ/mol, respectively[4]. So the calculated value for $-\Delta G^\circ_Q$ is lower than expected for octanesulphonate but is in the expected range for dodecanesulphonate.

In Figs. 5 and 6 the theoretical adsorption isotherms for octanesulphonate and dodecanesulphonate are compared with the results of Deelder and Van den Berg[3]. Despite the previously mentioned limitations of the theory, the quantitative agreement between the theoretical and experimental data is good.

Eqn. 11 shows that the concentration of Q^{z_Q} on the surface, n_Q, increases with the concentration of non-adsorbed ions in the mobile phase, $\Sigma c_{0,i}$, when the concentration of Q^{z_Q} in the mobile phase is kept constant. This is in agreement with the experimental findings, *e.g.*, ref. 1.

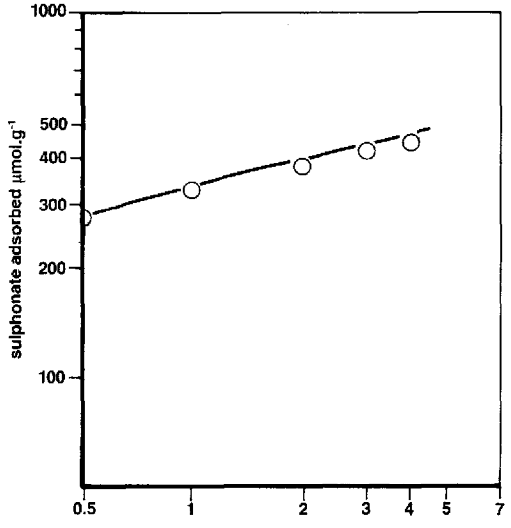

Fig. 6. Comparison between the calculated (full line) and experimental (○) adsorption isotherms for sodium 1-dodecanesulphonate on octadecyl silica from phosphate buffer at 40°C (10 m*M* Na$^+$; pH = 3.00). Experimental points from ref. 3.

The capacity factors of solute molecules

The reservations made concerning the validity of the equation for the adsorption isotherm also apply to the equation for the capacity factor. Another important restriction of eqn. 15 is that it is valid only when adsorption of the solute molecule does not change the electrostatic potential of the surface. If this condition is not fulfilled in the chromatographic system, the adsorption isotherm for the solute will depend on its concentration in the mobile phase.

Eqn. 15 gives the relationship between the capacity factor for a solute molecule and the concentrations of the amphiphilic molecules on the surface. It is seen that, with all factors kept constant, the capacity factor depends only on the surface concentrations of the amphiphilic molecules. It is shown in ref. 10 that this is the case for various alkanesulphonates.

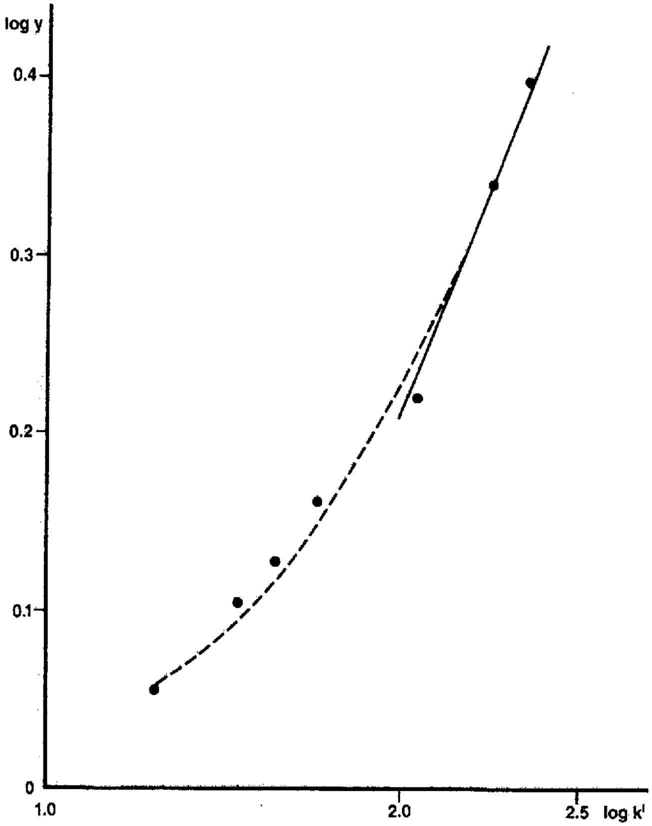

Fig. 7. Comparison between the limiting law, eqn. 16, and experimental results from ref. 11 where:

$$y = \frac{n_Q|z_Q|F}{(8\varepsilon_0 DRT\Sigma c_{0,i})^{1/2}} + \left[\frac{(n_Q|z_Q|F)^2}{8\varepsilon_0 DRT\Sigma c_{0,i}} + 1\right]^{1/2}$$

For experimental conditions, see Table I.

For comparison of eqn. 15 with experimental data we rewrite it as follows

$$\log\left\{\frac{n_Q|z_Q|F}{(8\varepsilon_0 DRT\Sigma c_{0,i})^{1/2}} + \left[\frac{(n_Q|z_Q|F)^2}{8\varepsilon_0 DRT\Sigma c_{0,i}} + 1\right]^{1/2}\right\} = -\frac{z_Q}{2z_Y}\log k' + \alpha \qquad (16)$$

where α is unknown and is assumed to be a constant and independent of n_Q. Since, eqn. 16 only holds in the limit $(n_Y z_Y/n_Q z_Q) \to 0$, an experimental plot according to this equation will give a slope $(-z_Q/2z_Y)$ in the high concentration limit. Fig. 7 shows experimental adsorption data obtained by Tilly-Melin[11] which are expressed in accordance with eqn. 16 where Q = tetrabutylammonium ion and Y = naphthalenesulphonate ion. The numerical value for D in this mixture of solvents is estimated to be 78 from $(X_1D_1 + X_2D_2)$ where X_i is the mole fraction of solvent component i and D_i is the dielectric constant of the pure solvent i. The full line represents the theoretical line with slope = $\frac{1}{2}$ and it is seen that the slope of the experimental curve tends to this value in the high concentration limit of Q. The values for c_Q and c_Y for the experimental point with the lowest concentration of amphiphilic modifier are $5.6 \cdot 10^{-5}$ and $\approx 1 \cdot 10^{-5}$ M respectively. So eqn. 16 cannot be expected to hold for the lower concentrations.

From eqn. 11 it is possible to calculate n_Q for a given c_Q, and the obtained value may be inserted in eqn. 15 giving k'_Y as a function of c_Q.

Fig. 8 presents calculated curves for the case when the charge of the solute

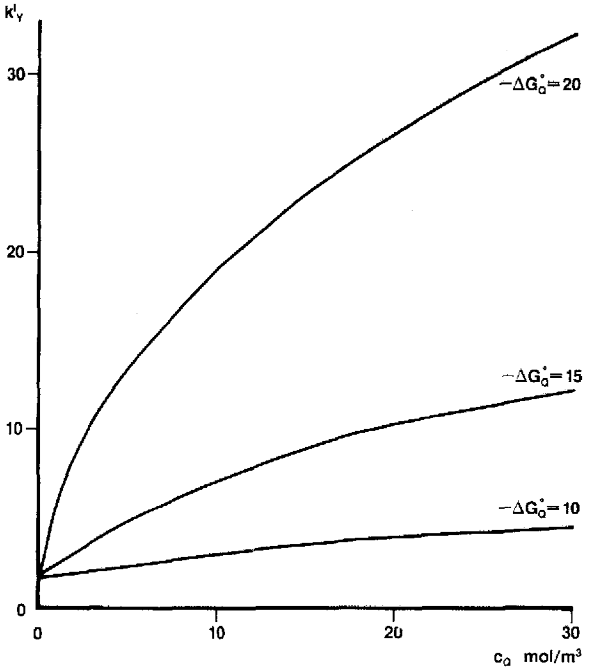

Fig. 8. Capacity factors calculated from eqns. 15 and 11 as a function of c_Q for different values of ΔG°_Q (kJ/mol). $z_Q = -z_Y = \pm 1$; $-\Delta G^\circ_Y = 5$ kJ/mol; $\Sigma c_{0,i} = 500$ mM; $D = 80$; $T = 298$ K; $n_0 = 3.321 \cdot 10^{-6}$ mol/m²; $A' = 0.2$.

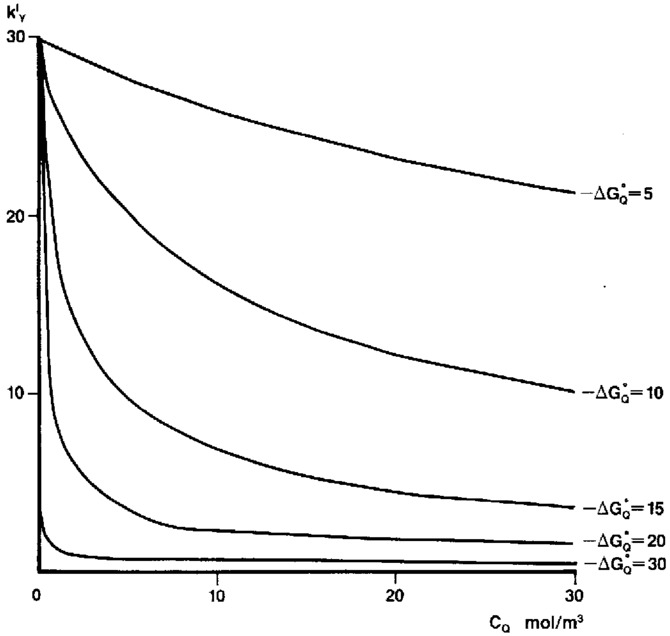

Fig. 9. Capacity factors calculated from eqns. 15 and 11 as a function of c_Q for different values of ΔG°_Q (kJ/mol). $z_Q = z_Y = \pm 1$; $-\Delta G^\circ_Y = 12.4$ kJ/mol; $\Sigma c_{0,i} = 500$ m*M*; $D = 80$; $T = 298$ K; $n_0 = 3.321 \cdot 10^{-6}$ mol/m²; $A' = 0.2$.

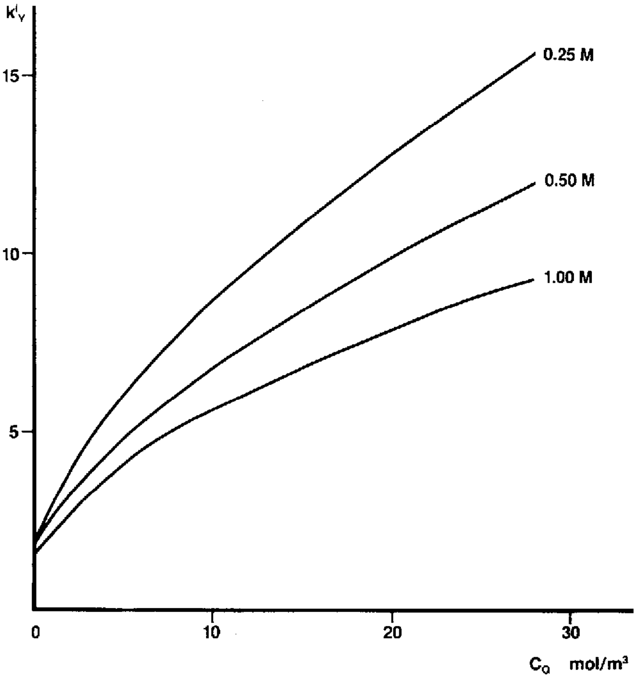

Fig. 10. Capacity factors calculated from eqns. 15 and 11 as a function of c_Q for different values of $\Sigma c_{0,i}$. $-\Delta G^\circ_Q = 15$ kJ/mol; $-\Delta G^\circ_Y = 5$ kJ/mol; $z_Q = -z_Y = \pm 1$; $D = 80$; $n_0 = 3.321 \cdot 10^{-6}$ mol/m²; $T = 298$ K; $A' = 0.2$.

molecule is of the opposite sign, and Fig. 9 the same sign, as the amphiphilic modifier, for different values of the free energy of adsorption of the amphiphilic modifier. The curves are similar to those usually obtained in chromatographic experiments. It is also seen that the capacity factor changes sensibly with the value for $-\Delta G^\circ_Q$, see *e.g.*, refs. 10 and 12. In Fig. 10 is shown an example calculated from eqns. 11 and 15 of how the ionic strength influences the capacity factor. It is found that, when the ionic strength increases, the capacity factor decreases when the charge of the solute ion is opposite to that of the amphiphilic modifier, but when the charge of the solute ion is the same as that of the amphiphilic modifier k' increases. Both of these trends are in accord with the experimental findings[8].

From eqns. 10 and 13 it can be concluded that for two solute molecules, Y and R, the following relationships hold

$$k'_Y k'_R = A'^2 \cdot \exp(-\Delta G^\circ_R - \Delta G^\circ_Y) \approx \text{constant} \tag{17}$$

where the charges of R and Y are of equal magnitude and of opposite sign and

$$\frac{k'_Y}{k'_R} = \exp(+\Delta G^\circ_R - \Delta G^\circ_Y) \approx \text{constant} \tag{18}$$

where the charges of R and Y are of equal magnitude and sign. These relationships are easily obtained by considering the fact that the electrostatic potential, ψ_0, is independent of the solute molecule. The experimental data[11,13] presented in Tables I and II are in accordance with the obtained equations. It must be pointed out that eqn. 15 holds only in the limit $(n_Y z_Y / n_Q z_Q) \to 0$. Since c_Y is $\approx 1 \cdot 10^{-5}$ M this condition is not fulfilled which may explain the small trend observed. These data give strong support to one of the hypotheses made in this work, *i.e.*, when varying c_Q it is the electrostatic potential of the surface that determines the changes in the capacity factor for organic ions.

A phenomenon that is not included in the present theory is the effect of sec-

TABLE I

THE DEPENDENCE OF k'_Y, k'_R AND $k'_Y k'_R$ ON c_Q

Y = Naphthalenesulphonate; R = ω-diethylamino-2,6-dimethylacetanilide; QX = tetrabutylammonium phosphate. Data are from ref. 11. Experimental conditions: mobile phase, acetonitrile–water (10:90); phosphate buffer pH = 3.0; $\sum_i c_{0,i} = 0.1$ M; column, μBondapak C$_{18}$, surface area = 150 m^2/g (according to the manufacturer), dimensions 200 × 3 mm; 296 K.

10^4 c_Q (M)	k'_Y	k'_R	$k'_Y k'_R$
0.563	20.3	5.28	107
1.90	34.7	3.17	110
2.85	43.3	2.76	120
4.76	57.4	2.24	129
19.0	111	1.21	134
47.5	178	0.782	139

TABLE II

THE DEPENDENCE OF k'_Y, k'_R AND k'_Y/k'_R ON c_Q

Y = D-propoxyphene; R = Transergan®; QX = tetrabutylammonium phosphate. Mobile phase: acetonitrile–water (25:75), pH = 3.0; $\Sigma c_{0,i}$ = 0.1 *M*. The data are from ref. 13.

$10^3\ c_Q$ (M)	k'_Y	k'_R	k'_Y/k'_R
1.50	7.19	5.81	1.24
2.99	5.54	4.50	1.23
4.99	4.53	3.71	1.22
6.99	3.94	3.28	1.20

ondary ions[14]. Since similar effects are well known in colloid chemistry as the Hofmeister or lyotropic series this deviation from the theory is expected.

CONCLUSIONS

It can be concluded that the theory described is in good agreement with the general observations made in chromatographic practice. Since the theory is developed from the Gouy–Chapman theory and from the Langmuir isotherm it is also well founded in physical chemistry.

An observation that has been the subject of many discussions is that k' reaches a plateau and may even decrease when the concentration of the amphiphilic modifier in the mobile phase increases, *e.g.*, refs. 1,10. In some cases the decrease is explained by the fact that the concentration of amphiphilic modifier is above the critical micelle concentration[1]. The possibility of solute-induced micelle formation at concentrations below the critical micelle concentration of the amphiphilic modifier must also be considered. However, these effects may not explain all the cases where a decrease is found and an additional explanation is required. That a plateau is reached is explained by the present theory, since it is based on the Langmuir isotherm. It is shown in ref. 10 that the decrease in k' is mainly due to an increase in the ionic strength of the mobile phase. Thus, the decrease in k' may be explained on the basis of eqn. 15 by a combination of three effects: the concentration of Q^{z_Q} on the surface, n_Q, approaches the maximum possible, n_0; the increase in QX in the mobile phase decreases k' because $\Sigma c_{0,i}$ increases and it is usually found that for uncharged molecules k' decreases with increasing concentration of Q^{z_Q} on the surface[10]. This indicates that the adsorption energy for these solute molecules decreases. A corresponding decrease in ΔG°_Y is expected.

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