Influence of the Hydrocarbon Chain Length of Alkylammonium Chlorides on their Adsorption by Flotation Carriers[†]

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ABSTRACT: Alkylammonium chlorides whose adsorption/micelle energetic ratio (AMER) is close to unity are those adsorbed most effectively on the surface of a solid carrier (adsorbent). A change in the solution pH leads to a change in the hydrocarbon chain length of the alkylammonium chlorides with AMER values close to unity and hence to a positive change on the length of the hydrocarbon chain adsorbed on the carrier surface.

INTRODUCTION

Analysis of experimental investigations devoted to the study of regularities in surfactant adsorption by solid carriers (adsorbents) shows that, in some cases, an increase in the hydrocarbon radical length of the surfactant initially leads to an increase in their adsorption behaviour followed by a subsequent decrease (Pushkaryov and Trophimov 1975; Alexandrovich *et al.* 1983). The reasons for such an influence of the hydrocarbon chain length of surfactants on their adsorption behaviour are not yet clear (Parfitt and Rochester 1986).

We believe that the concept of the adsorption/micelle energetic ratio (AMER) of the surfactant (Skrylev *et al.* 1985) may be helpful in explaining this observation. This ratio corresponds to that between the free energy of adsorption (ΔG^0_{ads}) of the surfactant on the surface of the solid carrier to the free energy of micelle formation (ΔG^0_{mic}) of the surfactant in the solution phase:

$$AMER = \Delta G^0_{ads}/\Delta G^0_{mic} \qquad (1)$$

A comparison of ΔG^0_{ads} and ΔG^0_{mic} is possible since these values are both determined in the same standard states. Thus, the standard states for the calculation of ΔG^0_{ads} are the infinitesimal adsorption layer at infinitesimal equilibrium solution concentration while those for the calculation of ΔG^0_{mic} correspond to infinite dilution of the surfactant in the aqueous solution (Emerson and Holtzer 1965). If the hydrocarbon chain length of the surfactant is small, its AMER is greater than unity since $\Delta G^0_{ads} > \Delta G^0_{mic}$ and, vice versa, AMER is less than unity when $\Delta G^0_{ads} < \Delta G^0_{mic}$. If the surfactants belong to the same homologous series, the values of ΔG^0_{ads} and G^0_{mic} are connected to the length of the hydrocarbon chain via a linear dependence, viz.

$$\Delta G^0_{ads} = an + b \qquad (2)$$

$$\Delta G^0_{mic} = cn + d \qquad (3)$$

where a and b are changes in the free energy of the system as a result of the adsorption of methylene (a) and ionogenic (b) surfactant groups on the surface of the solid body and c and d are changes in the free energy of the system as a result of the transition of methylene (c) and ionogenic (d) surfactant groups to a micellar composition. In both equations, n is the number of methylene groups in the hydrocarbon chain of the surfactant. In this case,

$$AMER = (an + b)/(cn + d) \qquad (4)$$

which corresponds to a linear function of fractional order which may be described by a hyperbola shifted by an amount d/c along the x-axis and by a/c along the y-axis.

Surfactants must exhibit a high adsorption activity towards the carrier surface and, at the same time, their AMER value (which decreases with increasing length of the hydrocarbon chain of the surfactant) must not be less than unity because in that case the process involving adsorption of the surfactant on the solid surface will be less advantageous thermodynamically than micelle formation.

Thus, surfactants with AMER equal to unity and with

$$n = (d - b)(a - c) \qquad (5)$$

must have a maximum adsorption capacity. This has been confirmed by the experimental results described below.

EXPERIMENTAL

The surfactants employed in these studies were alkylammonium chlorides containing from 12 to 18 carbon atoms in their hydrocarbon chains. They were all purified by recrystallization from ethanol and dried by heating at temperatures slightly above ambient value. All the purified surfactants were stored in vacuo. Their purity was confirmed by the absence of minima in their corresponding surface tension curves.

The carriers employed were silicon dioxide, potassium manganese hexacyanoferrate(II) ($K_2Mn[Fe(CN)_6]$) and n-octadecane. The potassium manganese hexacyanoferrate(II) was prepared directly in solution by the interaction of manganese sulphate with potassium hexacyanoferrate(II) while the n-octadecane was used in a finely dispersed state which was achieved through use of a UZDN-2T ultrasound disperser.

Experiments to determine the extent of adsorption of the surfactants on the various carriers were undertaken as follows. A fixed amount of carrier was placed in a 100 ml volume glass flask containing 50 ml of a freshly prepared solution of one of the alkylammonium chlorides whose concentration was less than that of the critical micellar concentration (CMC). The flask was well corked with a ground glass stopper and shaken until adsorption equilibrium had been achieved. The contents of the flask were then centrifuged using a CLS-3 laboratory centrifuge at 3000 rev/min and the separated solution analyzed for its alkylammonium chloride content (Lurie and Rybnikova 1966) as the difference between the concentration in the solution before and after adsorption had occurred. The data thus obtained were then employed for plotting the corresponding adsorption isotherms (Figure 1).

The free energies of adsorption for the various alkylammonium chlorides at the solution/carrier phase boundary were calculated from the equation (Koganovsky and Klimenko 1978):

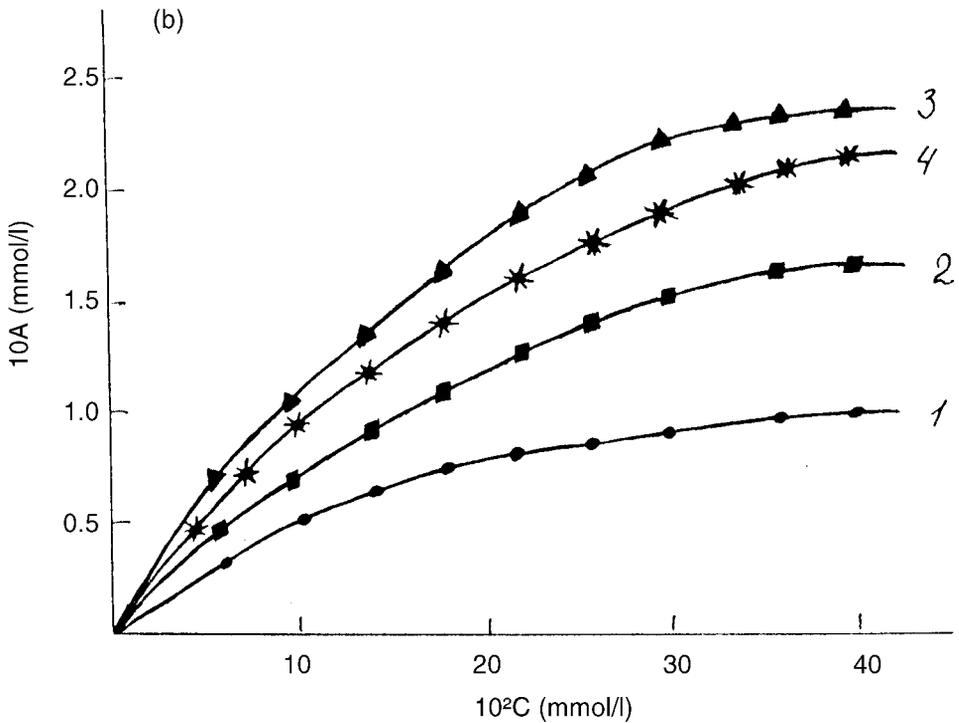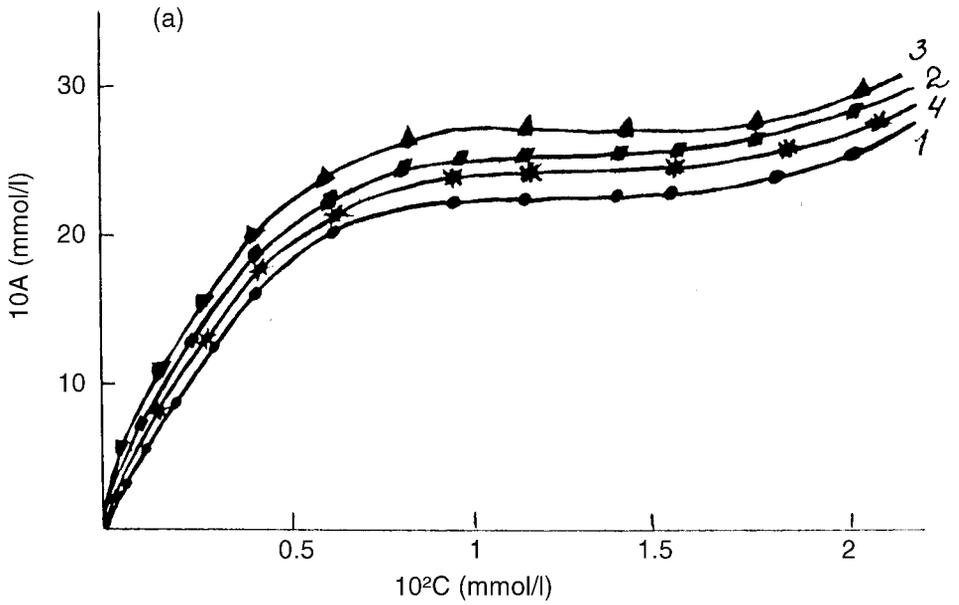$$\Delta G^0_{ads} = -RT \ln K \qquad (6)$$

Figure 1. Adsorption isotherms of (1) dodecyl-, (2) tetradecyl-, (3) hexadecyl- and (4) octadecyl-ammonium chlorides with (a) potassium manganese hexacyanoferrate(II) and (b) n-octadecane.

where K is the adsorption distribution constant which may be connected to the Langmuir constant β via the expression:

$$K = \gamma\beta S_p/S_a \tag{7}$$

where γ is the number of moles of solvent per kg while S_a and S_p are the areas on the carrier surface occupied by surfactant molecules adsorbed from solution and solvent molecules, respectively.

The values of the constant β were calculated via a graphical solution of the Langmuir equation since the investigations undertaken showed that the adsorption isotherms of the alkylammonium chlorides corresponded to the Langmuir equation over their initial stages (see Figure 1):

$$C/A = 1/(\beta A_\infty) + C/A_\infty \tag{8}$$

where C is the equilibrium concentration of the surfactant in solution, A_∞ is the maximum extent of surfactant adsorption as a monomolecular layer on the carrier surface while A is the extent of surfactant adsorption corresponding to the equilibrium concentration of residual surfactant in the solution.

The values of the free energies of micelle formation by the alkylammonium chlorides were calculated from the equation:

$$\Delta G^0_{mic} = 2RT \ln CMC \tag{9}$$

The CMC values of the various alkylammonium chlorides necessary to effect such a calculation were taken from the literature (Abramson and Gayevoy 1979). If such CMC values were not available, they were determined experimentally using a conductivity method.

RESULTS AND DISCUSSION

The investigations undertaken showed that the maximal adsorption capacity on the solid carrier surface was exhibited by that member of the homologous series of alkylammonium chlorides which had an AMER value equal or close to unity, i.e. hexadecylammonium chloride (see Figure 2). If AMER < 1 (which occurred for higher surfactant homologues), the process of micelle formation involving surfactant molecules in the solution was more advantageous thermodynamically. The extent of ion adsorption decreased as the concentration of micelles increased in the solution, the micelles thus formed being shielded by polar groups. Such micelles were adsorbed to only a very limited extent by carrier surfaces since the surface charge was insufficient to allow the adsorption of large surfactant associates. If AMER > 1 (which occurred for lower surfactant homologues), the surface activity decreased so that adsorption of the alkylammonium chlorides on the solid carrier surface was hindered, the extent of such hindrance increasing the greater the value of AMER.

These results agree with those for the flotation isolation of alkylammonium chlorides using finely dispersed n-octadecane as the carrier (Figure 3). The data depicted in this figure demonstrate that, of the homologous series of alkylammonium chlorides studied, hexadecylammonium chloride was that best isolated by flotation by the carrier employed.

Changing the pH of the solution leads to a change in the value of AMER and hence in the adsorption capacity (Figure 4). Hence, acidifying solutions of the alkylammonium chlorides led to a shift of the corresponding AMER values to higher values, leading to a shift in the maximum adsorption value (A_∞) towards those alkylammonium chlorides with a longer hydrocarbon chain. Thus, at pH 11 for example, AMER = 1 for dodecylammonium chloride, whereas at pH 3 this was so for octadecylammonium chloride. It is not surprising, therefore, that dodecylammonium chloride was best adsorbed at pH 11 while octadecylammonium chloride was the surfactant best adsorbed
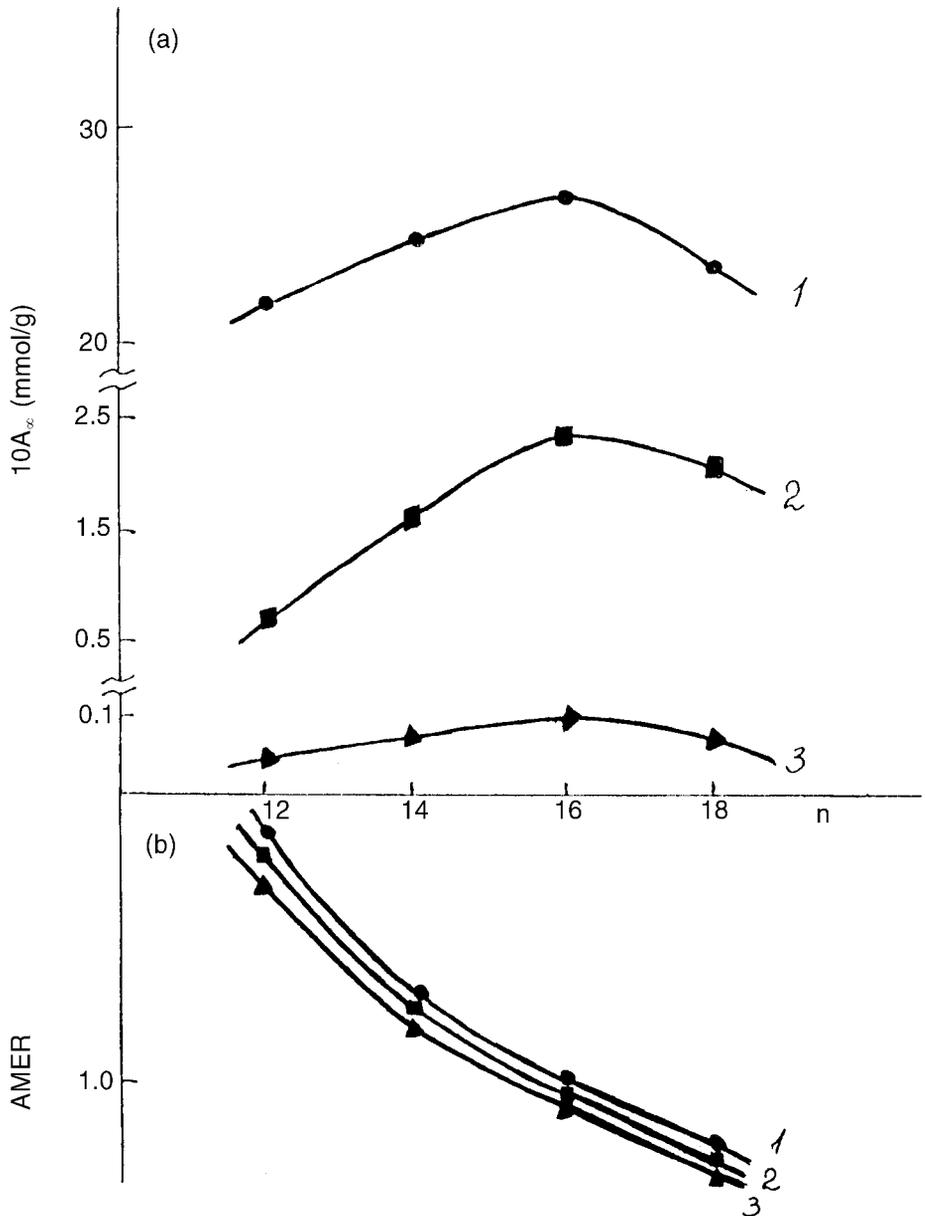
Figure 2. The influence of the number of carbon atoms (n) in the chain of the alkylammonium chloride molecule on (a) the maximal adsorption value (A_∞) on (1) potassium manganese hexacyanoferrate(II), (2) n-octadecane and (3) silicon dioxide, and (b) the adsorption/micelle energetic ratio (AMER).

at pH 3. The main cause for the change in AMER value with pH is the increase in the free energy of adsorption (ΔG^0_{ads}) as a result of a change in the adsorption mechanism brought about by a change in the surface charge of the carrier as determined by the pH of the solution (Koganovsky *et al*. 1979). The value of the free energy for micelle formation (ΔG^0_{mic}) is hardly affected by acidification of alkylammonium chloride solutions (Shinoda *et al*. 1968).
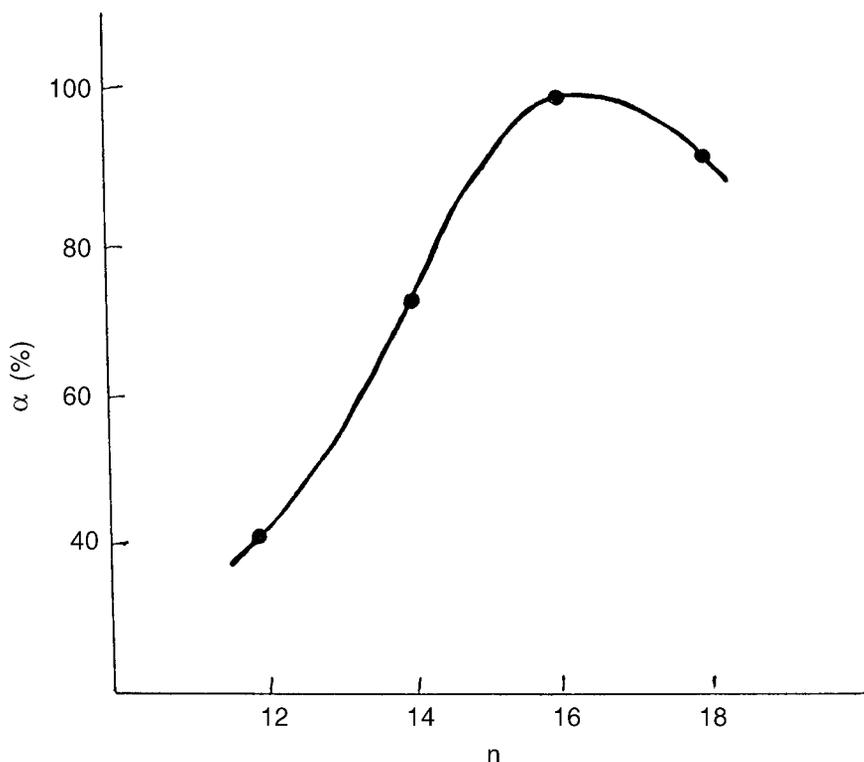
Figure 3. The influence of the number of carbon atoms (n) in the chain of alkylammonium chloride molecules on their degree of flotation isolation (α) by finely dispersed n-octadecane.

CONCLUSIONS

1. The results described clearly demonstrate that a dependence exists between the extent of adsorption of surfactants on the surface of a solid carrier (adsorbent) and the ability of such surfactants to form micelles.
2. The existence of an optimal length for the hydrocarbon chain associated with the surfactant molecule on the maximal ability of the latter to adsorb on the surface of a solid carrier may be justified thermodynamically on the basis of the concept of the adsorption/micelle energetic ratio (AMER) for surfactants.
3. It has been shown that the value of AMER may be used to explain the mechanism of the influence of pH on the adsorption of surfactants on solid carrier surfaces.

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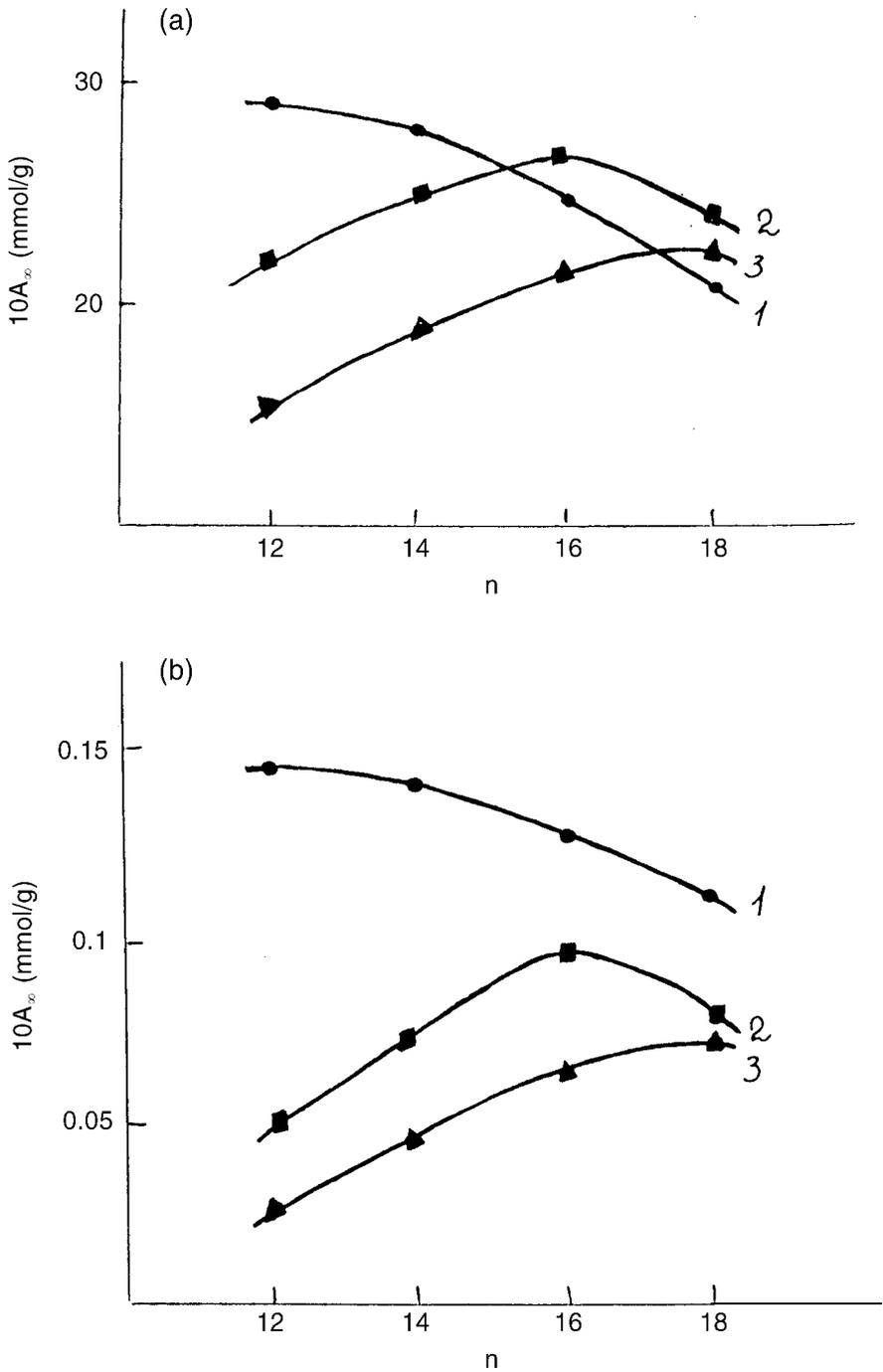
Figure 4. The influence of the number of carbon atoms (n) in the chain of the alkylammonium chloride molecule on the maximal adsorption value (A_∞) on (a) potassium manganese hexacyanoferrate(II) and (b) silicon dioxide at pH values of (1) 11, (2) 7 and (3) 3.

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