Interaction of hydrophobic ions with amphiphile monolayers at the air—water interface

1. Monolayers of stearylamine and dioctadecyldimethylammonium

V. L. Shapovalov

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4, ul. Kosygina, 117334 Moscow, Russian Federation.
Fax: 007 (095)938 2156. E-mail: KINET@GLAS.APC.ORG

The interaction of monolayers of stearylamine (SAM) and dioctadecyldimethylammonium (DODA) at the air—water interface with hydrophobic ions in the water phase was investigated by using the techniques of two-dimensional pressure isotherms and the surface electrostatic potential. In both cases the interaction with tetraphenylborate anions results in the formation of mixed monolayers whose properties sharply differ from those of the original monolayers. The effect of subphase composition on the formation of mixed monolayers has been studied. A qualitative description of the interaction under study has been given. A model including the phase inhomogeneity of the mixed monolayer and the formation of multilayer structures from the areas of the "surface salt" has been suggested. The strong effect of hydrophobic ions on the monolayers is not only due to Coulomb interaction; their hydrophobic properties also play an important role.

Key words: monolayers, air—water interface; surface electric potential; hydrophobic ions; surface salt.

The Langmuir—Blodgett (LB) method, the formation of monomolecular layers at the air—water interface with their subsequent transfer to solid surfaces, has been widely used for several tens of years to create two-dimensional and three-dimensional organized molecular structures.[1,2] LB films are promising materials for chemical and biological sensors, nonlinear optical elements, devices of molecular electronics etc.[1,2] Monolayers of amphiphile molecules at the air—water interface, on one hand, serve as direct precursors of LB films and, on the other hand, are the simplest model of biological membranes and are used to investigate various physicochemical processes in these membranes.[3]

Abundant evidence in the literature shows that the physical state of the initial monolayer at the water subphase—air interface largely determines the properties of the LB films formed as the monolayer is transferred to the solid surface as well as the possibility of realization of such process.[1,4] The state of the monolayer for many amphiphiles depends on the ionic composition of the subphase and is often determined by interaction of ions with the monolayer.[4] In biological membranes, there is a large number of diverse ions in their environment. Moreover, many functions of these membranes are due to interactions with the surrounding ions.

Unlike most other microheterogeneous structures, the monolayers at the water surface are macroscopic objects. Thanks to this, many of their parameters can be measured by direct procedures.[2]

By now, the effect of many inorganic (hydrophilic) cations[4] and several anions[5] on the properties of typical monolayers has been studied in considerable detail. A series of interesting works devoted to the interaction of ionic organic dyes[6,7] and of polyelectrolytes[8] with monolayers at the water surface has appeared in recent years.

Depending on the chemical nature of the head groups of the amphiphile that forms the monolayer and on the type of ions in the subphase, their interaction can include versatile processes: the formation of a double electric layer, dissociation (or protonation) of the head groups, the formation of coordination bonds, *etc.* By considering one or another of them, one can successfully qualitatively describe changes in the properties of the monolayer in the presence of ions. In this case, the reverse effect of ions bound to the monolayer on the charge state of its head groups must be significant, which has not been taken into account in most works known to us.

Along with the above mentioned types of ions, the so called "hydrophobic ions" are of extreme interest from the viewpoint of their possible interaction with amphiphilic monolayers at the water surface. These ions include small, strongly hydrophobic ions of high symmetry, *e.g.*, the anion BPh_4^- and the cation PPh_4^+; owing to their high symmetry they have no surface-active properties. Previously,[9,10] they have been used for imparting a deliberately chosen electrostatic potential to the droplets of "oil in water" type microemulsions.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1701—1707, July, 1996.

As far as we know, systematic studies on the interaction between hydrophobic ions and the monolayers of amphiphilic molecules at the air—water interface have not yet been conducted. The present work is devoted to an experimental study of such interaction in model systems using the methods of two-dimensional pressure (π—A) and of the surface electrostatic potential isotherms (φ—A) (A is the area per molecule).

Experimental

The studies of monolayers were carried out on an installation consisting of a rectangular Langmuir trough (250×100×8 mm), an electronic balance with a Wilhelmi plate made of the filter paper (of 10 mm width), an electrometer for measuring the surface potential (Kelvin method, gilded working electrode of 10 mm diameter), and an IBM-AT computer equipped with a multichannel analog-to-digital converter. A three-electrode scheme (with an Ag/AgCl electrode as reference electrode and a metal auxiliary electrode) was used for measuring the surface potential. The φ—A isotherms were recorded relative to the potential of the subphase surface before spreading of the monolayer.

The subphase was prepared using double-distilled water, additionally purified from surfactant impurities by passage through a column with activated carbon. In most experiments, the ionic strength of the subphase was kept close to $I = 10^{-2}$ mol L^{-1} using NaCl additives. Acetate, borate, and Tris buffer solutions were used to obtain different pH values; the concentration of the buffer ions did not exceed 10^{-3} mol L^{-1}. The pH-value was monitored both before and after measurements. All starting solutions were prepared from reactants of grade not worse than "analytically pure"; they were passed through a column with activated carbon to pre-purify them from surfactant impurities.

Freshly prepared $5 \cdot 10^{-4}$—10^{-3} M solutions of stearylamine and dioctadecyldimethylammonium bromide (not less than 98 % base substance) in distilled chloroform were used for deposition of monolayers. Measurements of π—A and φ—A isotherms were started 2 min after spreading of the monolayer. The compression rate of the monolayer was ~50 Å^2 per molecule per minute. The choice of such a high rate was caused by the necessity to maintain constant pH in the near-surface layer of the subphase contacting the atmosphere during the whole experiment, since several systems under study were extremely sensitive to pH. Because of the high compression rate of the monolayer there was a potential danger of obtaining isotherms strongly differing from equilibrium isotherms.[11] Therefore, not only the compression, but also the expansion of the monolayer was recorded in all cases. The observed hysteresis (associated with deviation of the system from equilibrium), as a rule, did not exceed several percent. The exceptions were only the experiments carried out at the lowest concentrations of hydrophobic ions (< 1 μmol L^{-1}) and strong interaction of the ions with the monolayer. The establishment of the monolayer—subphase equilibrium under these conditions is connected with the diffusion of hydrophobic ions over distances ~1 mm, therefore the hysteresis sometimes amounted to 10—20 %.

Results and Discussion

Interaction of the stearylamine monolayer with hydrophobic anions. The isotherms of two-dimensional pressure (π—A) of the stearylamine monolayer (SAM) at the subphase—air interface (Fig. 1) in the pH range from 8 to 12 remain unchanged and are characterized by nearly constant and very low pressure (π < 0.2 mN m^{-1}) at the values of the area per molecule exceeding 30 Å^2. This region corresponds to the condensed monolayer—two-dimensional gas equilibrium. A sharp increase in the two-dimensional pressure π begins when the monolayer is compressed to A = 23 Å^2, which corresponds to the complete transition of the monolayer to the condensed state. Further compression is followed by a rapid increase in the two-dimensional pressure and ends in the collapse of the monolayer. A region of a smooth increase in π appears on the π—A isotherm as the subphase pH decreases to 7, while the two-dimensional gas pressure in the region of A > 30 Å^2 increases to 1 mN m^{-1}.

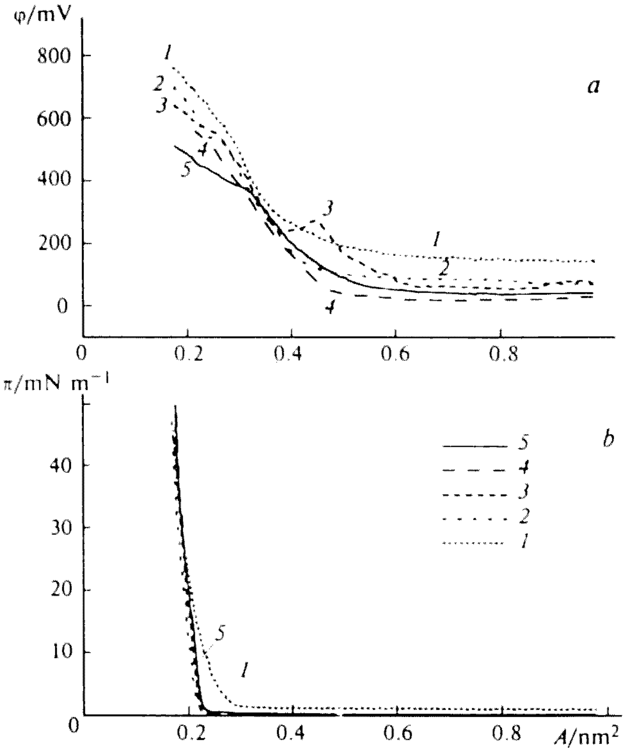

Fig. 1. The φ—A (*a*) and π—A (*b*) isotherms of the SAM monolayer at the surface of an aqueous subphase containing no hydrophobic ions at different pH values: 7.0 (*1*), 8.3 (*2*), 9.5 (*3*), 10.7 (*4*), 11.8 (*5*). $I = 10^{-2}$ mol L^{-1}, T = 297 K (φ is the surface potential, π is the two-dimensional pressure, A is the area per molecule).

The isotherms of the surface electrostatic potential (φ—A) (Fig. 1) in the region of the coexistence of both gas and condensed phases are characterized by poor reproducibility caused by the phase inhomogeneity of the monolayer. This points to the fact that the characteristic sizes of the areas occupied by the separate phases are comparable with the diameter of the working electrode (10 mm). Nevertheless, there is a general trend for φ to increase with monolayer compression, associated with the increase in the portion of the surface occupied by the condensed phase in this region. The φ—*A* isotherms become reproducible when the region of the condensed state of the monolayer is reached; here, a regular increase in potential as *A* decreases (*i.e.* as the number of amphiphile molecules per unit area of the monolayer increases) is well seen. There is a pronounced increase in φ as the pH of the subphase decreases in the whole range of pH under study. This is associated with the increasing degree of protonation (α) of the head amino groups of SAM; in the range $7 < \mathrm{pH} < 12$ α never reaches one of its limiting values, *i.e.*, the monolayer is always partially protonated.

The unexpectedly broad pH region where changes in α are observed, occurs for the following reasons. To a first approximation, the degree of protonation of the head amino groups of the monolayer is determined by the local concentration of protons in the immediate vicinity of these groups:

$$\log(\alpha/(1-\alpha)) = \mathrm{p}K_i - \mathrm{pH}_i.$$

If the volume of the subphase adjacent to the monolayer contains a double electric layer, this value can appreciably differ from the proton concentration within the bulk of the subphase:

$$\mathrm{pH}_i = \mathrm{pH} - e\Delta\varphi/kT\ln 10,$$

where e is the charge of an electron, *k* is the Boltzmann constant, *T* is temperature, Δφ is the potential difference between the area of the head groups and the bulk of the subphase, *i.e.*, the potential of the double electric layer. The Δφ value depends on the surface charge density of the monolayer $\sigma = -\alpha e/A$ and on the ionic strength of the subphase, which determines the thickness of the double electric layer. The change in Δφ is a main reason for the surface potential to decrease as pH increases; it amounts to 240 mV at $A = 20$ Å^2 per molecule. Starting from this value, one can easily estimate the variation of pH_i. In the pH range under study (4.7 units) this change is merely 0.7. In view of this, the dependence of α on pH does not appear unusual; moreover, if one takes into account the direct effect of the protonated head groups on their nearest neighbors (the dependence of $\mathrm{p}K_i$ on α), it could result in more appreciable retardation of the increase in α as pH decreases.

It follows from the above consideration that as the monolayer expands (retaining its phase homogeneity), the protolytic transformation of the head groups (protonation or dissociation) should occur in more narrow pH range due to the fact that σ and Δφ depend more weakly on α as *A* increases. In the limiting case of a rarefied two-dimensional gas, the dependence of α on pH should be of the same character as in solution. Unfortunately, this result can not be demonstrated with the SAM monolayer because it is phase-inhomogeneous in almost the whole range of *A* under study.

The π—*A* and φ—*A* isotherms of the SAM monolayer suffer marked changes when low concentrations of hydrophobic $\mathrm{BPh_4}^-$ anions are introduced into the subphase (apart from the supporting electrolyte (10^{-2} mole L^{-1} NaCl) and the buffer); the changes increase as the $\mathrm{NaBPh_4}$ concentration increases (Fig. 2) and as pH decreases (Fig. 3). At the highest $\mathrm{NaBPh_4}$ concentrations and the lowest pH the rise of π begins even at A = 80 Å^2, whereas the limiting pressure on monolayer compression is merely about 20 mN m^{-1}. A decrease in the pressure of the two-dimensional gas should also be noted (the right part of the π—*A* isotherms in Fig. 2). A decrease in φ on the φ—*A* isotherms in the whole range of *A* is observed, whereas the maximum values of φ do not exceed 150 mV. The increase in π is followed by an increase in φ when the monolayer is compressed; since π reaches its limiting value the surface potential remains nearly constant.

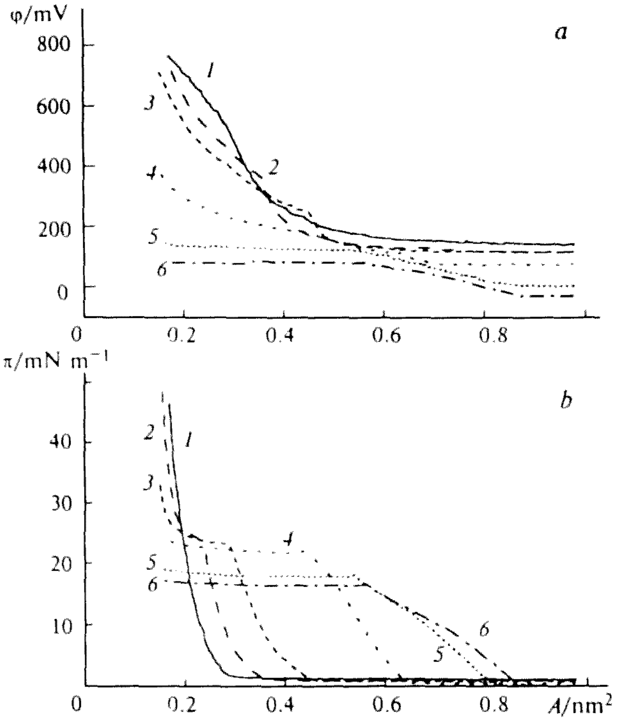

Fig. 2. The φ—*A* (*a*) and π—*A* (*b*) isotherms of the SAM monolayer at the surface of an aqueous subphase containing different amounts of hydrophobic anions. $\mathrm{NaBPh_4}$ concentrations, mol L^{-1}: 0 (*1*), $3\cdot10^{-7}$ (*2*), $1\cdot10^{-6}$ (*3*), $3\cdot10^{-6}$ (*4*), $1\cdot10^{-5}$ (*5*), $1\cdot10^{-4}$ (*6*). $I = 10^{-2}$ mol L^{-1}, T = 297 K, pH = 7.0.

The observed picture is in good agreement with the formation of a mixed monolayer at high concentrations of $\mathrm{NaBPh_4}$ and at low pH values; the monolayer consists of almost completely protonated SAM molecules and of an approximately equivalent amount of $\mathrm{BPh_4}^-$ ions (the "surface salt"). This model follows from the large area per SAM molecule and the low surface potential as well as from the weak sensitivity of the π—*A* and φ—*A* isotherms to small changes in the subphase composition. The penetration of the $\mathrm{BPh_4}^-$ anions in the SAM monolayer is due not only to Coulomb interaction with protonated head groups, but also to the decreasing energy of the monolayer—subphase system because these

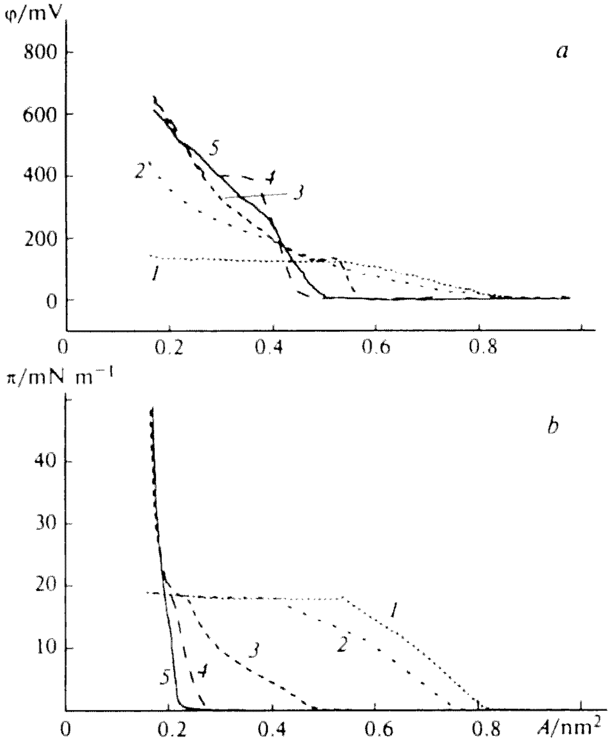

Fig. 3. The φ—*A* (*a*) and π—*A* (*b*) isotherms of the SAM monolayer at the surface of an aqueous subphase containing hydrophobic anions at different pH values: 7.0 (*1*), 8.3 (*2*), 9.0 (*3*), 9.5 (*4*), 10.7 (*5*). I = 10^{-2} mol L^{-1}, T = 297 K, [NaBPh$_4$] = 10^{-5} mol L^{-1}.

large particles, weakly interacting with water, move from the subphase volume to the monolayer area, where the density of hydrogen bonds is significantly lower (so-called hydrophobic interaction). In the monolayer region, the BPh_4^- ions can interact not only with the charged head groups of SAM, but also with its hydrocarbon radicals. This results in stabilization of the condensed mixed monolayer, which is revealed in a decrease in the two-dimensional gas pressure.

The penetration of the BPh_4^- anions into the partially protonated monolayer ($\alpha < 1$) causes a decrease in σ followed by a decrease in $\Delta\varphi$, which, in turn, must lead to a decrease in pH$_i$ and to a further increase in α. As a result, additional hydrophobic anions penetrate into the monolayer, *etc*. This is one more argument in favor of the assumed composition of the mixed monolayer at high concentrations of NaBPh$_4$ and at low pH. The composition of the monolayer does not change appreciably when it is compressed, and multilayer structures of presumably the same composition start forming after attainment of the limiting pressure. If such structures consist of odd numbers of layers in which the dipole moments have opposite directions (it seems to be realistic), the surface potential during the compression of the monolayer has to remain constant, which is observed in the experiment. The relatively low value of the limiting pressure is the result of a decrease in the energy of the interaction between the monolayer and subphase due to the large number of hydrophobic ions in monolayer.

At lower concentrations of BPh_4^- and higher pH, the π—*A* and φ—*A* isotherms are something intermediate between the isotherms of the pure SAM monolayer and the limiting mixed monolayer, and change from one direction to the other as the concentration of hydrophobic ions changes and as pH changes. The effect of the ionic strength (1—100 mmole L^{-1}) at the NaBPh$_4$ concentration of 10^{-5} mole L^{-1} and at pH = 9 appeared to be rather weak.

The family of π—*A* isotherms represented in Figs. 2 and 3 has an unusual shape, characteristic of monolayers consisting of two immiscible amphiphiles.[2] Such monolayers are a mosaic of areas occupied by isolated amphiphiles. In the process of compression, deformation of the monolayer as a whole occurs first. Upon attainment of the limiting pressure for one of the components, a collapse of pertinent areas begins, which can be seen as a horizontal section on the π—*A* isotherm. After their complete disappearance, the pressure continues to increase in accordance with the the isotherm of the second component.

Applying a similar description to the system under study, one could assume that, in this case, the monolayer consists of areas differing in the BPh_4^- anion content and degree of SAM protonation. In the process of the compression of such monolayer in the areas with a high content of hydrophobic anions, multilayer structures are formed and the fraction of surface occupied by them gradually decreases, which is followed by an increase in φ. The remaining areas contain few BPh_4^- anions; therefore, the left side regions of the π—*A* and φ—*A* isotherms at low NaBPh$_4$ concentrations and high pH look like those of the pure monolayer of SAM. However, this model in its original form seems to be poorly compatible with the existence of equibria both for the distribution of hydrophobic ions between the monolayer and the subphase bulk and for protonation of the monolayer (the monolayer areas of different composition are simultaneously at equilibrium with the subphase). In order to remove this contradiction one should assume that the areas containing strongly protonated SAM and a large number of BPh_4^- anions are only formed, when the monolayer is compressed to the limiting pressure, and are immediately formed as multilayer structures. The onset of such a process can be associated with attainment of a certain threshold surface concentration of BPh_4^- anions. We do not consider the suggested model of the phenomena occurring in the studied system to be final. Additional investigations using independent methods, for instance, visualization of the two-dimensional structure of the monolayer, are required to check the model.

Interaction between the dioctadecyldimethylammonium monolayer and hydrophobic anions. In contrast to the SAM monolayer, the dioctadecyldimethylammonium

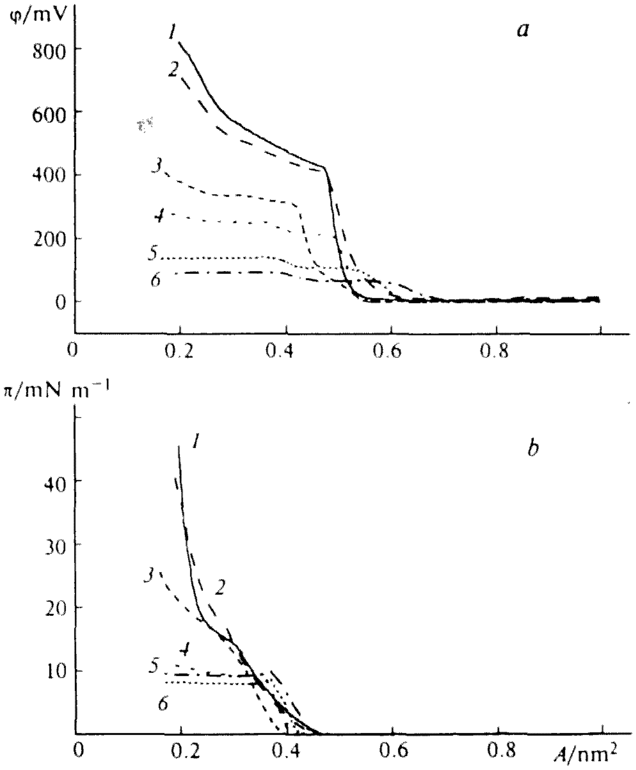

Fig. 4. The φ—A (*a*) and π—A (*b*) isotherms of the DODA monolayer at the surface of an aqueous subphase containing different amounts of hydrophobic anions. NaBPh$_4$ concentrations, mol L^{-1}: 0 (*1*), $1 \cdot 10^{-7}$ (*2*), $1 \cdot 10^{-6}$ (*3*), $3 \cdot 10^{-6}$ (*4*), $1 \cdot 10^{-5}$ (*5*), $1 \cdot 10^{-4}$ (*6*). $I = 10^{-2}$ mol L^{-1}, $T = 297$ K, pH = 7.0.

(DODA) monolayer has a constant positive charge on the head groups that is not dependent on pH, which simplifies the analysis of its interaction with hydrophobic ions. It is also phase-inhomogeneous at large A, which can be seen from the very low pressure of the two-dimensional gas (Fig. 4). Therefore, the φ—A isotherms in the $\pi < 1$ mN m^{-1} region contain no direct information on the monolayer structure despite their satisfactory reproducibility. In contrast to the SAM monolayer which is closely packed even at small π, the DODA monolayer is very "loose": the increase in π, which indicates the completion of the transition in the condensed phase, begins even at A equal to 115 Å^2 per molecule, while fairly close packing of the hydrocarbon chains is attained only at $\pi > 40$ mN m^{-1} (25 Å^2 per each chain). The surface potential of the condensed monolayer is very high even at large A and increases as the density of packing increases.

The π—A and φ—A isotherms of the DODA monolayer undergo significant changes, increasing as the concentration of the hydrophobic anions increases as small concentrations of NaBPh$_4$ are introduced into the subphase in addition to the supporting electrolyte. These changes, like those in the SAM monolayer, are associated with the formation of a mixed monolayer containing an appreciable number of BPh$_4^-$ anions. Formation of such monolayer reveals itself as a sharp decrease in the surface potential. However, in this case, the penetration of hydrophobic ions into the monolayer does not result in its expansion, but in its compression, which is due to its initial loose packing. At the highest concentrations of NaBPh$_4$, both π and φ remain constant after compression of the monolayer to the limiting pressure (~10 mN m^{-1}), which, by analogy with the SAM monolayer, can be explained by the formation of multilayer structures. The lower limiting pressure is in good agreement with the fact that the DODA head groups are less hydrophilic than those of SAM.

At lower NaBPh$_4$ concentrations it is difficult to investigate the behavior of the DODA monolayer using the π—A isotherms due to the similar sizes of the areas occupied by pure and mixed monolayers. Additional obstacles are created by high compressibility of the initial monolayer (small slope of the π—A isotherm). For these reasons it is impossible to conduct as detailed an analysis as was made for the SAM monolayer. One should only note that in the weakly compressed monolayer there is a strong dependence of the content of BPh$_4^-$ ions on their concentration in the subphase that can be seen as changes in the values of φ in the initial section of the increase in π. The nonmonotonic change in A that occurs at $\pi = 5$ mN m^{-1} as the concentration of NaBPh$_4$ increases is in agreement with this conclusion: as the number of BPh$_4^-$ anions increases, the monolayer first shrinks due to Coulomb attraction (as long as there is enough free space) and then begins expanding (when there is no more free space).

Interaction between SAM and DODA monolayers and hydrophobic cations. Hydrophobic PPh$_4^+$ cations hardly interact with the SAM and DODA monolayers, whose head groups are positively charged. As can be seen from Fig. 5 the π—A isotherms of both monolayers remain nearly unchanged when PPh$_4$Cl (10^{-4} mole L^{-1}) is introduced into the subphase (in addition to 10^{-2} mole L^{-1} of NaCl and the buffer components). In this case the surface potential of the condensed monolayer decreases by several tens of mV, *i.e.*, it is shifted to the negative side, which at first sight contradicts common sense. Nevertheless, this is the change in φ that should be observed when a conventional procedure for recording the φ—A isotherms is used, if hydrophobic ions do not interact with the monolayer. The point is that the potential of the subphase surface in the absence of the monolayer is usually accepted as the "zero" value of φ. This "zero" potential measured relative to the Ag/AgCl electrode depends on the electrolyte composition of the subphase, since the ratio of the concentrations in the volume and in the surface layer is different for different ions; therefore, the surface layer has a charge. In particular, the hydrophobic ions we used are concentrated in the surface layer, which is reflected in a shift in the potential of the clean subphase surface in the direction coinciding with the sign of charge of these ions. This effect is comparatively small and depends on the

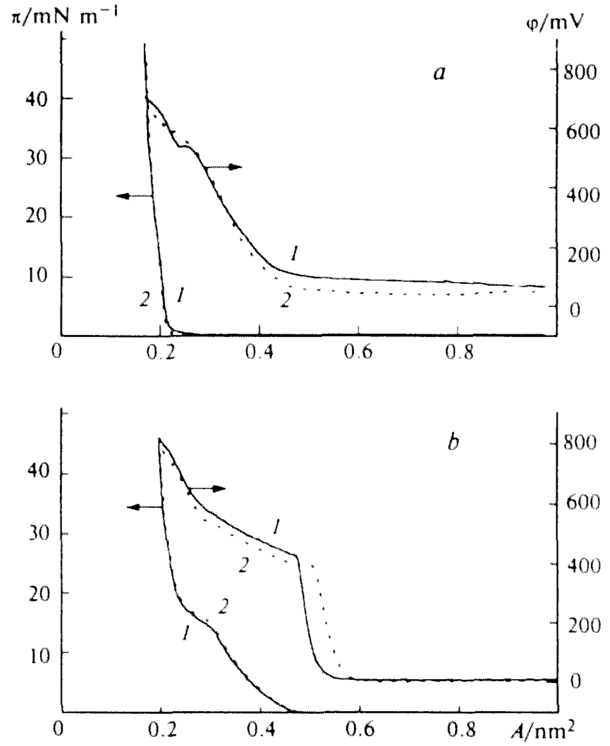

Fig. 5. The π—*A* and φ—*A* isotherms of SAM (*a*) and DODA (*b*) monolayers at the surface of an aqueous subphase containing different amounts of hydrophobic cations. PPh_4Cl^- concentrations, mol L^{-1}: 0 (*1*), $1 \cdot 10^{-4}$ (*2*). $I = 10^{-2}$ mol L^{-1}, $T = 297$ K, pH = 7.0 (DODA) and 8.3 (SAM).

concentration of hydrophobic ions, *i.e.*, the behavior of these ions is unlike that of surfactants: they behave like any other ions. When 10^{-4} mole L^{-1} of PPh_4Cl is introduced, the potential of the subphase surface (without the monolayer) is shifted to the positive side by several tens of mV. When the amphiphile monolayer appears the ions that can not penetrate therein must leave the subphase surface. Taking into account that the potential of the subphase surface without the monolayer is always taken as the zero value of φ, the recorded potential of the monolayer surface will be shifted to the negative side.

Thus, strong interaction between SAM (with a pH dependent positive charge on the head groups associated with their protonation) and DODA (with a constant positive charge on the head groups) monolayers at the subphase—air interface with the hydrophobic BPh_4^- anions is observed. The interaction manifests itself in the formation of mixed monolayers whose properties drastically differ from those of the initial monolayers. At low concentrations of hydrophobic anions their content in the monolayer depends on their concentration in the subphase; it reaches a limit at higher concentrations ("surface salt") and then remains nearly constant.

In the case of the SAM monolayer the pH effect is analogous; however, the limiting state of the "surface salt" can also be attained at these pH values when the initial monolayer is only partially protonated. In order to explain the latter phenomenon a model that considers the conjugation between the penetration of hydrophobic anions into the monolayer and its protonation due to the potential jump in the double electric layer at the monolayer—subphase interface has been suggested.

The compression of mixed monolayers does not lead to the removal of hydrophobic anions and regeneration of the initial monolayer, and is followed by complicated behavior of the π—*A* and φ—*A* isotherms. The model suggested for its description includes the phase inhomogeneity of the mixed monolayer and the formation of multilayer structures from the areas of the "surface salt" during compression.

The strong effect of hydrophobic ions on monolayers is caused not only by Coulomb interaction but also by their hydrophobic properties. Nevertheless, the role of the Coulomb factor is great, which is evidenced by the absence of an effect of hydrophobic PPh_4^+ cations on the positively charged SAM and DODA monolayers even at high concentrations of these cations.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 94-03-08537). The author expresses his deep gratitude to A. Kh. Vorob'ev (M. V. Lomonosov Moscow State University) for valuable discussions, Prof. F. M. Menger (USA) for the submitted DODA specimen and encouragement, E. A. Chirkov and P. V. Protsenko for their significant contribution to refining of the experimental setup, and Prof. B. R. Shub for his generous support.

References

1. L. M. Blinov, *Usp. Fiz. Nauk*, 1988, **155**, 443 [*Russ. Phys. Rev.*, 1988, **155** (Engl. Transl.)].
2. H. Kuhn and D. Moebius, in *Investigations of Surfaces and Interfaces, Part* B, Ed. B. W. Rossiter and R. C. Baetzold. *Physical Methods of Chemistry Series*, 2nd ed., Vol. **IXB**, 375.
3. G. Schwarz and S. E. Taylor, in *The 7th Int. Conf. on Organized Molecular Films — Abstract book, Ancona*, 1995, 112; D. A. Pink, M. L. Belaya, V. Levadny, and B. E. Quinn, *Ibid.*, 113.
4. S. Bettarini, F. Bonosi, G. Gabrielli, G. Martini, and M. Pugelli, *Thin Solid Films*, 1992, **210/211**, 42.
5. R. C. Ahuja, P.-L. Caruso, and D. Moebius, *Thin Solid Films*, 1994, **242**, 195.
6. R. C. Ahuja, P.-L. Caruso, D. Moebius, G. Wildburg, H. Ringsdorf, D. Philp, J. A. Preece, and J. F. Stoddart, *Langmuir*, 1993, **9**, 1534.
7. B. W. Gregory, D. Vaknin, T. M. Kotton, and W. S. Struve, in *The 7th Int. Conf. on Organized Molecular Films — Suppl. to Abstract book, Ancona*, 1995, 42.
8. P. Stroev and M. Hva, in *The 7th Int. Conf. on Organized Molecular Films — Abstract book, Ancona*, 1995, 87.
9. V. L. Shapovalov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2245 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1756].
10. Yu. V. Il'ichev and V. L. Shapovalov, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2253 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1762].
11. T. Kato, K. Iriyama, and T. Araki, *Thin Solid Films*, 1992, **210/211**, 79.

Received January 16, 1996