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# Stoichiometry of Langmuir-Blodgett Multilayers of Docosylammonium Arsenate

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The stoichiometry of Langmuir-Blodgett multilayers of docosylammonium arsenate has been studied by means of neutron-activation analysis. The content of arsenic in the multilayer systems has been determined at different pH's and concentrations of arsenate in the aqueous subsolution, and the number of anions per docosylamine molecule,  $\theta$ , has been evaluated. The results show that the counterion inclusion is stoichiometric and that it is due to electrostatic interaction between the positively charged ammonium groups of the monolayer and arsenate anions of the subsolution. From the  $\theta/\text{pH}$  and  $\theta/C_0$  dependences, it follows that the divalent counterions  $\text{HAsO}_4^{2-}$  are predominantly present in the multilayers.

## Introduction

The Langmuir-Blodgett (LB) films built-up of fatty acids and their soaps have been studied for a long time.<sup>1</sup> Although the multilayers of primary amines and ammonium salts are analogous to them in many of their features,<sup>2</sup> they have been considerably less investigated. Petrov, Kuhn, and Möbius<sup>3</sup> and Petrov and Kuhn<sup>4</sup> have studied the conditions for irreversible transfer of octadecylamine monolayers from solutions containing salts of polyvalent acids. It has been established that formation of good multilayers of octadecylamine, from aqueous solutions of sodium phosphate, arsenate, chromate, and sulfate, is possible in a narrow pH range around the neutral point. Under the same pH, ionic strength, surface pressure, and other experimental conditions the chlorine anions do not ensure the irreversibility of the monolayer transfer. From these results, it follows that the polyvalent anions are likewise essential for the formation of Langmuir-Blodgett films of cationic surfactants as  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , etc. for building of multilayers of fatty acids.<sup>5</sup> In this connection, the determination of the counterion content in the multilayers is the first and necessary step in clarifying of their role in the formation of Langmuir-Blodgett molecular assemblies.

The amount of phosphorus, arsenic, and chromium in the corresponding multilayers of octadecylammonium salts has been determined by means of neutron-activation analysis.<sup>6</sup> It has been found that the ratio of the numbers of anions to amine molecules is considerably above the stoichiometric one for the arsenate and chromate anions. Unfortunately, the "piston oil" method applied in these experiments did not allow control of the stability of the monolayer being transferred. The determination of the amount of octadecylamine on the solid substrate was also more complicated; it has been evaluated from earlier data<sup>4</sup> about the area per molecule on the air/water interface and

the transfer coefficients characterizing the density of the monolayers on the solid substrate. These data have important biological implications; therefore, because of the possible errors in this determination and due to some uncertainties about the standards for neutron-activation analysis (volatility of  $\text{AsCl}_3$  and  $\text{CrCl}_3$  used), these results should be proved under more definite conditions and with a more precise experimental technique. ( $\text{HPO}_4^{2-}$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{CrO}_4^{2-}$  have the same tetrahedral structure, but their biological activity is rather different. The first anion is one of the most important constituents of living organisms, and the second and the third ones are toxic.)<sup>7</sup>

By means of an automatic film balance, recording the reduction of the monolayer area caused by the deposition, the system octadecylamine/phosphate was studied in more detail.<sup>8</sup> From the neutron-activation analysis of phosphorus in the multilayers it was concluded that the interaction between monolayer and counterions is stoichiometric. The results showed also that predominantly the divalent phosphate anions interact with the ammonium head groups.

All these investigations were limited to a narrow pH interval around the neutral point because of the high solubility of the octadecylammonium salts in the acidic pH region and an entrainment of a liquid film of the subsolution ("wet deposition") in the strongly alkaline range. In this paper we have used docosylamine hydrochloride (due to its higher stability<sup>9</sup>) as a homologue with a longer hydrocarbon chain, having considerably lower solubility. This has permitted an extension of the pH interval where the multilayers can be built-up by  $\sim 2$  pH units toward the lower pH values. As Adam<sup>9</sup> pointed out, the free base gives results identical with those of the hydrochloride. Aqueous subsolutions containing  $\text{KH}_2\text{AsO}_4$  or  $\text{Na}_2\text{HAsO}_4$  were used. Neutron-activation analysis has been applied due to its high sensitivity in determination of arsenic.<sup>10</sup> However, this method does not give direct information about the valence of the anions included in the Langmuir-Blodgett systems.

## Methods and Materials

The hydrochloride form of n-docosylamine was synthesized by Dr. M. Mladenova (Institute of Organic Chemistry, Sofia)

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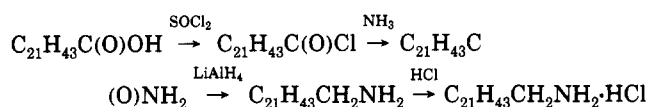
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from behenic acid (Merck, additionally recrystallized) according to following scheme:



The salt, with a melting point of 122–127 °C, was characterized by its IR spectrum and via thin-layer chromatography. Along with its elementary analysis (73.05% C, 10.33% H, 4.00% N), these techniques showed that the product is pure.

The aqueous subsolutions were prepared by dissolution of  $\text{KH}_2\text{AsO}_4$  or  $\text{Na}_2\text{HAsO}_4$  (of AR purity grade) in doubly distilled water. pH was adjusted by addition of NaOH or  $\text{HNO}_3$ , also of AR purity.

Thin polyethylene foils (1.1 mg/cm<sup>2</sup>) mounted on glass frames were used as solid substrates. After completion of the deposition, circles with area of 2 cm<sup>2</sup> were cut from the polyethylene, irradiated, and analyzed. Polyethylene is an appropriate matrix for neutron-activation analysis since it consists of nonactivatable light elements. The foils were cleaned in mixtures of ethanol and doubly distilled water, rinsed with doubly distilled water, and dried by an infrared lamp.

The standards for neutron-activation analysis were prepared from As(V) compounds in order to prevent possible losses due to the volatility of the As(III) compounds. Stock solutions (1.0 mg/mL) were obtained by dissolution of  $\text{As}_2\text{O}_3$  (Merck) in a minimum amount of warm concentrated HCl (Merck) and subsequent oxidation of As(III) to As(V) in an excess of 30%  $\text{H}_2\text{O}_2$ . Parallel standard solutions of  $\text{KH}_2\text{AsO}_4$  were used as well, and they gave the same results.

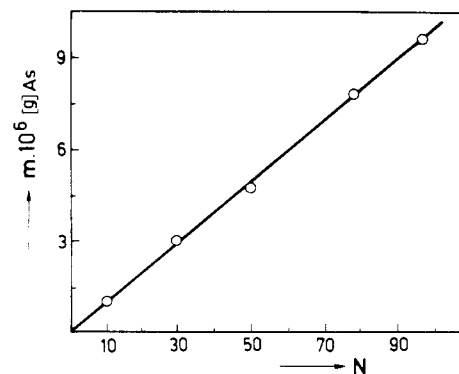
The monolayers were spread onto the air/water interface as a  $1 \times 10^{-3}$  M solution of docosylamine hydrochloride (DCA) in benzene/ethanol mixture (10:4 v/v).<sup>9</sup> (Depending on pH, the monolayer will consist of docosylammonium ions and (or) neutral docosylamine molecules. For the sake of convenience we shall use the abbreviation DCA for all cases.) The deposition was carried out at a constant surface pressure of 30 dyn/cm and a constant velocity of dipping and withdrawal,  $V = 0.22$  cm/s, providing a "dry" monolayer transfer. The sequential immersions and emersions of the solid substrates were performed immediately, without any time interval between the up and down trips. All measurements were done at room temperature.

On average 50 layers were built-up on the polyethylene substrates. The maximum possible number of "dry" layers were deposited in the strongly acidic and strongly alkaline regions. Polyethylene capsules, containing samples and standards, were irradiated together for 12 h in a neutron flux of  $2 \times 10^{12}$  n/cm<sup>2</sup>s intensity at the research nuclear reactor IRT-2000, Sofia.

The quantitative determination of As via neutron-activation analysis was based on the nuclear reaction  $^{76}\text{As}(n,\gamma)^{76}\text{As}$ . The generated radionuclide  $^{76}\text{As}$  has a half-decay life of 26.3 h. After a "cooling" period of 1 day, the induced radioactivity of the samples and the standards was measured for 100–200 s. The determination of  $^{76}\text{As}$  was carried out by its  $\gamma$ -lines at energies of 558 and 657 keV. The spectrometry was performed with a germanium detector Canberra with an energetic resolution of 1.8 keV and registration efficiency of 15% for the  $\gamma$ -line of  $^{60}\text{Co}$  at an energy of 1332.5 keV. The detector was connected to a 4096-channel amplitude analyzer Canberra 35 Plus. The amount of arsenic in the samples was evaluated from the areas of the two  $\gamma$ -peaks according to corresponding standard straight lines. A correction for the activity of a "blank" sample was introduced, taking into account the possible content of arsenic in the polyethylene foil. This correction did not exceed  $8 \times 10^{-8}$  g for a total amount of arsenic in the samples of over  $1 \times 10^{-6}$  g.

## Results

The dependence of the total amount of arsenic,  $m$ , on the number of the transferred DCA monolayers,  $N$ , is shown in Figure 1. The subsolution contains  $1 \times 10^{-2}$  M  $\text{KH}_2\text{AsO}_4$  and has a pH value of 5.5. Each experimental point is a result of three samples. (The same holds for all other figures.) The dependence is linear without intercept



**Figure 1.** Dependence of the total amount of arsenic,  $m$ , in the multilayers of DCA, on the number of transferred monolayers,  $N$ : aqueous subsolution  $1 \times 10^{-2}$  M  $\text{KH}_2\text{AsO}_4$ , pH 5.5.

and with a high correlation coefficient ( $r = 0.999$ ). This linearity indicates that the counterions are uniformly included in the multilayers and that every subsequent monolayer transfers the same amount of As as the others. Such a behavior suggests a stoichiometric character to the counterion inclusion.

The stoichiometry of the docosylammonium arsenate multilayers has been studied in pH range 4.0–9.0. In this interval, the transfer coefficients  $\alpha$  practically do not depend on pH and do not change with an increase in the number of deposited layers (at dipping  $\alpha_d = 0.87$ , at withdrawal  $\alpha_w = 0.97$ ). The solubility of DCA monolayers spread on an arsenate solution of pH 6.0 and concentration  $C_0 = 1 \times 10^{-2}$  M is  $7.3 \times 10^{-3}$  cm<sup>2</sup>/s (determined from the initial reduction of the monolayer area at 30 dyn/cm). Under the same conditions the octadecylamine monolayers, used in refs 6 and 8, dissolve more than 10 times faster. In addition, the solubility of the monolayers of octadecylammonium salts increases steeply below pH 6.0, while the solubility of docosylammonium arsenate monolayers is still low down to pH 4.0.

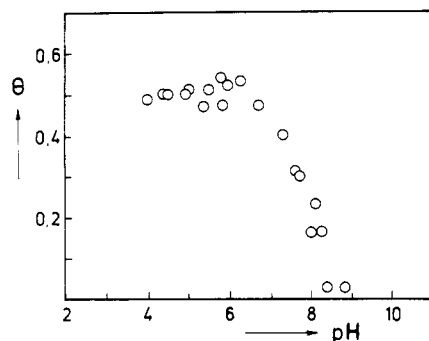
As a quantitative characteristic of the stoichiometry of the multilayers, the ratio  $\theta$  of the number of arsenic atoms,  $n_{\text{As}}$ , to the number of DCA molecules,  $n_{\text{DCA}}$ , was used:

$$\theta = n_{\text{As}}/n_{\text{DCA}} = mN_A F_L / A \Delta A_L \quad (1)$$

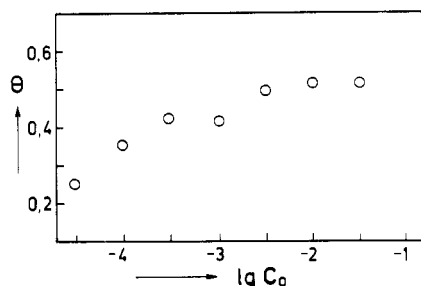
In eq 1,  $m$  is the total amount of arsenic in the multilayer,  $F_L$  the area of molecule DCA in the spread monolayer at 30 dyn/cm,  $A$  the atomic mass of As,  $N_A$  Avogadro's number, and  $\Delta A_L$  the change of the monolayer area on the liquid surface caused by the deposition.

The dependence of  $\theta$  on pH at constant concentration of  $\text{KH}_2\text{AsO}_4$  ( $C_0 = 1 \times 10^{-2}$  M) is presented in Figure 2. It shows that the multilayers do not contain arsenic above pH 9.0, probably due to the fact that the neutral amino groups do not interact with the arsenate anions. With decreasing pH,  $\theta$  increases and a maximum value of 0.52 is reached at pH  $\sim 6.0$ . For the more acidic subsolutions,  $\theta$  remains nearly constant (or decreases slightly). This particular maximum value means that one arsenate anion is bonded to not less than two molecules of DCA, a result that implies a predominant presence of the divalent form  $\text{HAsO}_4^{2-}$  in the multilayers.

The dependence of  $\theta$  on the concentration of arsenate in the subsolution at a constant pH 5.5 is presented in Figure 3. A plateau is observed above  $C_0 = 1 \times 10^{-2}$  M, with a value of  $\theta$  correlating well with that from the  $\theta$ /pH dependence from Figure 2. The existence of such a plateau also suggests a stoichiometric character to the binding of arsenate anions to the docosylammonium cations in the multilayers.



**Figure 2.** Dependence of the ratio,  $\theta$ , of the number of arsenic atoms to the number of molecules of DCA in the multilayers on the pH of the subsolution at constant arsenate concentration  $C_0 = 1 \times 10^{-2}$  M.



**Figure 3.** Dependence of the ratio,  $\theta$ , of the number of arsenic atoms to the number of molecules of DCA in the multilayers on the arsenate concentration in the subsolution,  $C_0$ , at constant pH 5.5.

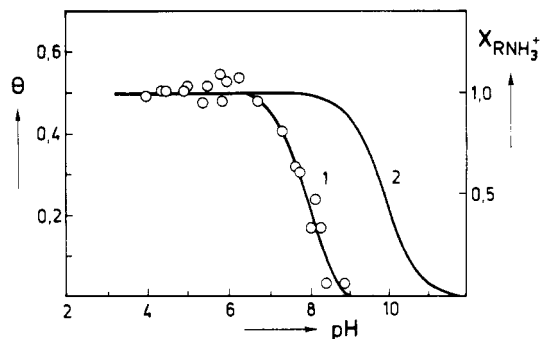
### Discussion

**Stoichiometry of the Multilayers.** The linear trend of the dependence  $m$  vs  $N$  (Figure 1) means that the ratio anion/amine,  $\theta$ , does not change with increasing number of deposited monolayers. This suggests a stoichiometric character to the inclusion of arsenate counterions. The value of  $\theta = 0.51$  evaluated from the slope, as well as the maximum values of the  $\theta$ /pH and  $\theta/C_0$  dependences, does not confirm the overstoichiometric inclusion of arsenate counterions in octadecylamine multilayers reported in ref 6; the latter is probably due to erroneous preparation of the standards for the neutron-activation analysis from the volatile  $\text{AsCl}_3$ . Since the experimental conditions in this investigation were especially chosen to always ensure "dry" monolayer deposition, all results have not been affected by a hydrodynamic inclusion of counterions through an entrainment of a liquid film of the subsolution.

The pH of the subsolution regulates the ionic equilibrium in the monolayer:



The  $\theta$ /pH dependence, experimentally obtained in this study, is compared with the pH variation of the molar fraction,  $X_{\text{RNH}_3^+}$ , of the charged form of the amine in Figure 4.  $X_{\text{RNH}_3^+}$  was evaluated from the equilibrium protonation constant of nonadecylamine,  $\text{p}K_a = 9.9$ , determined by Betts and Pethica.<sup>11</sup> The comparison shows that no binding of arsenate anions occurs above pH 9.0, although a substantial part of the monolayer molecules are still protonated. This could be due to a reduction of the concentration of the charged ammonium groups and the inability of simultaneous neutralization of two of them by one divalent anion. Under these circumstances, a portion of the  $\text{HAsO}_4^{2-}$  counterions could form negatively charged

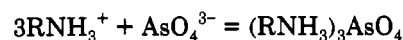
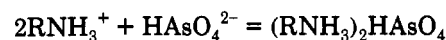


**Figure 4.** Experimental dependence  $\theta$ /pH (open circles and curve 1) and pH dependence of the molar fraction of the charged form of a long-chain amine,  $X_{\text{RNH}_3^+}$  (curve 2).

products of the type  $[\text{RNH}_3^+(\text{HAsO}_4^{2-})]^-$  with the monolayer, whose concentration will increase with pH and will lead to reversal of the charge of the liquid/gas and solid/liquid interfaces. [Similar effects have been observed with monolayers of dissociated stearic and oleic acids at 30 dyn/cm, interacting with  $\text{Ca}^{2+}$ . The smaller density of the oleic acid monolayers (due to the double bond) prevented formation of a disoap and led to a charge reversal.<sup>12,13</sup>] The electrostatic repulsion will decrease the adhesion between the hydrophilic groups of the last transferred layer and the layer being deposited and thus will impede the multilayer formation.

The above hypothesis is supported by the gradual reduction of the irreversibility of the monolayer transfer with the rise of pH in the alkaline region established in this study for multilayers of docosylammonium arsenate at pH >9.0 and in refs 4 and 6 for octadecylammonium arsenate multilayers at pH >8.0. "Dry" transfer of docosylamine without waiting between the successively transferred layers was possible up to pH 9.0. Above this value, or above pH 8.0 when multilayers of octadecylammonium arsenate were built-up, a pause of several minutes was necessary after each withdrawal of the solid substrate in order to ensure the irreversibility of the deposition.<sup>4</sup> Longer pauses and an increase of the surface pressure led to bigger dipping deposition ratios, while those on withdrawal remained equal to unity. All these facts suggest that at high pH values the deposition of octadecyl- and docosylammonium arsenate on emersion has been accompanied by entrainment of an invisible film from the subsolution. The removal of this film is a necessary condition for a good adhesion between the hydrophilic groups of the last two monolayers and thus for formation of the Langmuir-Blodgett system.

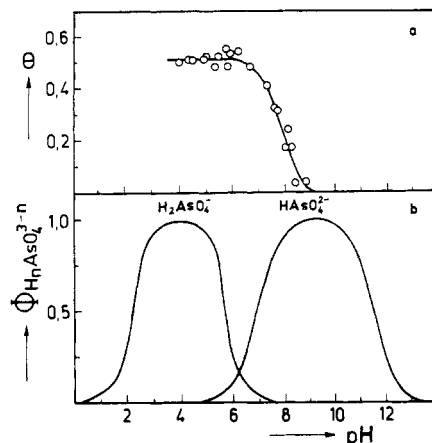
In the pH interval studied, the following stoichiometric interactions between the docosylammonium cations and the arsenate anions are possible:



The obtained maximum value of  $\theta = 0.52$  implies that it is the divalent form of the counterion  $\text{HAsO}_4^{2-}$  that is preferably bonded in the multilayers. This result is in agreement with the conclusions of the neutron-activation

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**Figure 5.** (a) Experimental dependence  $\theta$  vs pH at constant arsenate concentration  $C_0 = 1 \times 10^{-2}$  M. (b) Distribution pH diagrams of the arsenate anion forms in the subsolution,  $\Phi = [H_nAsO_4^{3-n}]/C_0$  vs pH.  $C_0 = 1 \times 10^{-2}$  M. The dissociation constants of  $H_3AsO_4$  at 25 °C were taken from ref 16:  $K_1 = 6.5 \times 10^{-3}$ ,  $K_2 = 1.1 \times 10^{-7}$ ,  $K_3 = 3.2 \times 10^{-12}$ .

analysis<sup>8</sup> and the IR spectroscopy of LB systems of octadecylammonium phosphate<sup>14</sup> and docosylammonium phosphate.<sup>15</sup> They are also in good accordance with the presence of sulfate ions in docosylamine multilayers, spectroscopically established by Gaines.<sup>2</sup>

**Surface Potential of Docosylamine Monolayers on Arsenate Solutions.** In Figure 5 the experimental  $\theta$ /pH dependence is compared with the distribution pH diagrams of the arsenate anion forms, calculated from their disso-

ciation constants.<sup>16</sup> It is seen that the maximum (or plateau) values of  $\theta = 0.5$  are observed at pH 4.5–6.5, where the concentration of  $HAsO_4^{2-}$  in the subsolution is zero or negligibly low. At the same time, the dependence  $X_{RNH_3^+}/pH$  from Figure 4 shows that  $X_{RNH_3^+}$  remains equal or close to unity up to pH 9.5. Thus, the reduction of  $\theta$  above pH 6.5 is probably due to a decrease of the divalent counterion concentration.

These facts can be explained by taking into account that the effective value of pH in the plane of the charged ammonium groups,  $pH_s$ , is shifted toward more alkaline pH in comparison with the bulk value in the aqueous subsolution,  $pH_B$ :

$$pH_s = pH_B + e\psi_0/2.3kT \quad (2)$$

$\psi_0$  is the electrostatic surface potential of the monolayer (positive for positively charged monolayers),  $e$  the elementary charge,  $k$  the Boltzmann constant, and  $T$  the absolute temperature.

The juxtaposition of the experimental  $\theta$ /pH dependence with the right-hand branch of the distribution curve of the divalent arsenate form,  $\Phi_{HAsO_4^{2-}}/pH$ , shows that they are shifted about 3.5–3.7 pH units (Figure 5). According to eq 2, such a shift corresponds to a surface potential of  $\psi_0 = 88$ –93 mV, a value that is less the one ( $\psi_0 = 115$ –120 mV) obtained for similar positively charged monolayers but on 1:1 electrolyte subsolutions.<sup>17,18</sup> This difference could be due to a partially specific character of the divalent counterion adsorption, but the more definite conclusion requires further investigation.

**Registry No.**  $2H_3C(CH_2)_{21}NH_2 \cdot (OH)_3As=O$ , 136953-66-7.

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