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Coadsorption of carbofuran and lead at the water/silica interface. Possible impact on environment

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Abstract

Despite its extremely weak adsorption at the water/silica interface, carbofuran can, however, induce the coadsorption of metallic salts, like, for example, lead nitrate, and thus enhance its adsorption. We quantitatively studied this phenomenon with a depletion method and under concentration conditions close to the environmental ones. Heavy metal salt was found to positively adsorb, whereas carbofuran relative adsorption is generally slightly negative. This study provides evidence that considering these facts is of paramount importance in environmental prospects. *To cite this article: G. Elmanfe et al., C. R. Chimie 9 (2006).*

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Résumé

En dépit de sa très faible adsorption à l'interface eau/silice, le carbofurane peut cependant induire la coadsorption de sels métalliques, comme, par exemple, le nitrate de plomb, et ainsi augmenter son adsorption. Nous avons étudié quantitativement ce phénomène avec la méthode des restes et dans des conditions de concentration proches de celles rencontrées dans l'environnement. Nous avons constaté que le sel de métal lourd présente une adsorption (relative) positive, alors que l'adsorption du carbofurane est dans l'ensemble légèrement négative. Ces résultats montrent que la prise en compte de ces mécanismes est de première importance dans la prévision des comportements environnementaux. *Pour citer cet article : G. Elmanfe et al., C. R. Chimie 9 (2006).*

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1. Introduction

We recently contributed to elucidate how adsorption film containing two sorts of non-volatile pollutants, as hydrocarbons or carbofuran and lead salt [1,2], can lead to a dissemination of both of them in the atmosphere.

This is particularly intriguing because, instead of adsorbing at the water surface whenever there is no co-adsorbate, the ionic salt is even depleted [3–5]. It is worth examining other possible interfaces because of the increasing occurrence of situations where both types of pollutants (organic pesticides and metallic salts) are present together. This is exemplified by pools in industrials or agricultural wastelands, rivers close to mines and exploited fields, metal-polluted effluents flowing to fields further to mine accidents.

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This report deals with the adsorption of carbofuran and lead on a model of soil, namely silica suspension. Indeed, carbofuran adsorption has been extensively studied [6–8], but its coadsorption with salts has been considered only at the solution/air interface [2,9]. Thus, besides the layout of ions, our concern, here, will be the very specific behaviour of water. Indeed, this behaviour, being known to be of first importance at the air–water interface, needs to be carefully considered at an aqueous–solution/silica interface, given the particular affinity of silica for water.

2. Experimental

2.1. Chemicals

Carbofuran, certified for laboratory use and 99.5% pure, was supplied by Dr Ehrenstorfer, GmbH (Augsburg, Germany). Its solubility limits are available in the literature: for example, it is 320 mg kg^{-1} (certificate of analysis) at $25 \text{ }^\circ\text{C}$ in pure water.

Nearly saturated solutions of carbofuran were, first, prepared at the temperature chosen for the study and then diluted. A certain quantity of known weight and estimated to be less than the soluble one was, first, mixed with the chosen weight of purified water, then gently agitated in a thermoregulated oven for 15 days, the duration required for a complete dissolution of crystals [7,8]. All the prepared solutions were stored in the dark to prevent carbamate decomposition. Spontaneous pH was checked to fall within 4.7 and 5.5 and be far from the basic pH that induces decomposition.

Water was purified on a milliQ device from Millipore. Lead nitrate of analytical grade (more than 99.9% pure) was from Merck.

Silica was Degussa Aerosil 200 prepared by pyrogenation. Its specific area measured by BET adsorption isotherms for nitrogen was $196 \text{ m}^2 \text{ g}^{-1}$. According to the supplier, silica particles had a mean diameter of about 15 nm and carried 3 OH groups per nm^2 . To always operate in the same surface conditions, Aerosil 200 was dried at $195 \text{ }^\circ\text{C}$ during 1 week.

There were 10^{17} particles in 1 g of Aerosil. Most of the experiments were carried out on silica samples of 0.4 g mixed with about 20 cm^3 of solution, or 0.2 g for 10 cm^3 . A rough calculation showed that the shortest distance between two particles in solution varied between 64.0 and 40.4 nm, distances sufficient to avoid capillary condensation.

The silica porosity, measured by BET adsorption with different gases was very low, the mean radius of pores was 66.88 \AA (mesoporosity), and the microporos-

ity was almost absent. According to the supplier, the distribution of particle diameters has a maximum at $d = 100 \text{ \AA}$ and the particles are almost spherical. All the tests we have been able to do (with other types of silica, several very different adsorption values) showed that there was no interference, during centrifugation, between adsorption (molecules fixed on the surface) and the trapping of molecules between the packed silica particles.

2.2. Pb speciation in the studied samples

The Pb^{2+} ion is known to very easily form complexes [10]. This process is highly dependent on the solution pH. In the samples of concern here and prepared with de-ionised water, the most probable ligands were likely carbofuran, NO_3^- ion, CO_3^{2-} and HCO_3^- ions issued from dissolution of atmospheric CO_2 . In water equilibrated with CO_2 (pH 5.5), addition of carbofuran and lead nitrate slightly elevated or lowered the pH by 1 or 2 tenths, depending on the salt concentration, whereas the solutions of pure carbofuran were at pH 7. According to the literature, such a pH is incompatible with the formation of a nitrate complex or that of a hydroxide [10]. The polarographic analysis described hereafter showed no appreciable formation of Pb^{2+} –carbofuran complex; as Pb^{2+} and NO_3^- were the only ionic species to be considered, the use of the equations given hereafter is thus justified.

2.3. Adsorption isotherm measurement

We used the classical depletion method to measure adsorption isotherms. Samples of silica powder (0.4 g) were weighed into centrifuge tubes before addition of 18 g of an aqueous solution of either carbofuran alone, or lead nitrate alone, or a mixture of both and smooth agitation during the time required for equilibrium. Previous determinations of this duration by adsorption kinetics experiments drove us to let adsorption develop for 40 h, a time sufficient to reach equilibrium for the three systems. During agitation, the samples were kept in a thermoregulated oven, at $25 \text{ }^\circ\text{C}$; this temperature was known at more or less 0.2 K. Prior to adsorption determination, silica powder was removed from the suspensions by centrifugation at $2000 \times g$ in a FirLabo centrifuge till getting a clear supernatant, which was then titrated.

Carbofuran was titrated at 276 nm with a KONTRON Uvikon 930 spectrophotometer; this wavelength corresponds to a peak on the spectrum. Let n^0 be the total number of moles in the sample, x_2^0 be the initial

mole fraction of the solute, and x_2 be the equilibrium mole fraction of the supernatant after adsorption; then, the relative adsorption of solute 2 with respect to the solvent 1 is:

$$\Gamma_{2,1} = (1/x_1) n^0(x_2^0 - x_2)/m S \quad (1)$$

where S is the specific area of silica, m is the mass of silica, and x_1 is the mole fraction of water in the supernatant.

Lead nitrate was analysed by Differential Pulse Polarography (DPP) on a Hanging Mercury Drop Electrode (HMDE) [11]. To avoid interactions of metallic ions with carbonate and hydroxyl ions and to play the supporting electrolyte role, 15 μl of 10^{-2} nitric acid were added to the sample before analysis. Other working conditions were as follows: a 50-mV pulse height and a 50-ms pulse duration. Before measurements, the solutions were always purged for 15 min with a nitrogen stream saturated with water vapour to remove oxygen.

3. Results and discussion

3.1. Adsorption of lead nitrate alone

Fig. 1 shows the adsorption isotherm of lead nitrate on silica from aqueous solutions at 25 °C. Conversely to the case of solution/air interfaces and despite the still rather small adsorption, the salt is positively adsorbed instead of being depleted [2,9]. At this stage and on condition to agree with the classical explanation by Wagner–Onsager–Samaras, this positive adsorption is induced by the difference between the dielectric con-

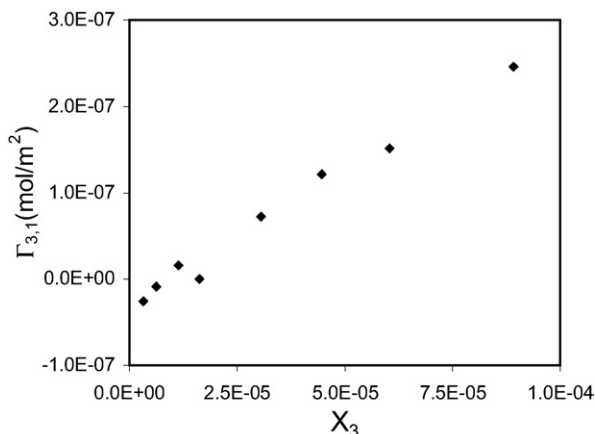


Fig. 1. Adsorption isotherm of lead nitrate (3) onto silica from aqueous solutions at 25 °C. Adsorptions are Gibbs relative adsorptions with respect to water (1). Concentrations are those of supernatant after equilibrium.

stant of silica and that of the air. One should remind that the profile of an ion i , at the interface between an aqueous solution (w) and the air (a), along an axis z perpendicular to the interface is [4]:

$$c_i(z) = c_i(\infty) \exp\left(-\left[\frac{\epsilon_w - \epsilon_a}{\epsilon_w + \epsilon_a}\right]\{\exp\kappa a\}/(1 + \kappa a)\right) \{Z^2 e^2 [\exp(-2\kappa z)]/16 \pi \epsilon_0 \epsilon_w z\}/k_B T \quad (2)$$

Then, the Gibbs excess is given by:

$$\Gamma_i = \int_{\text{GP}}^{\infty} [c_i(z) - c_{i\infty}] dz = c_{i\infty} \int_{\text{GP}}^{\infty} [\{c_i(z)/c_{i\infty}\} - 1] dz \quad (3)$$

where GP is the coordinate of the Gibbs plane.

On condition to identify the surface salt content as $\Gamma_{\text{Pb}^{++}}$ and whatever the bulk concentration, its concentration profile given by Eq. (4) is of the form displayed on Fig. 2. Indeed, the dielectric constant of silica, the medium where the image charge appears, is lower than that of water, like in the case of contact with air. Then, one gets:

$$\Gamma_3 = \Gamma_s = \Gamma_{\text{Pb}^{++}} < 0$$

Then, the water (w) excess at the silica/solution interface in presence of salt (s) is:

$$\Gamma_1 = \Gamma_w = (x_w/x_s)(\Gamma_{s,w} - \Gamma_s) > 0 \quad (4)$$

because $\Gamma_{3,1} = \Gamma_{s,w} > 0$ and $\Gamma_3 = \Gamma_s < 0$.

So, the surface layer contains a lot of water.

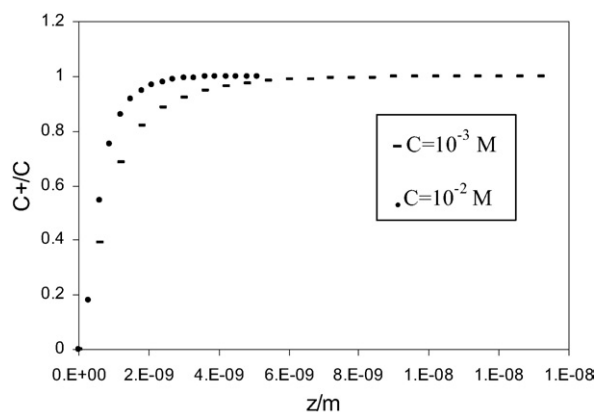


Fig. 2. Pb^{++} surface concentration profiles at the aqueous solution/air interface according to relation (2) and for bulk concentrations 10^{-3} and 10^{-2} M [4]. Profiles depend on the ion charge and on bulk concentration, but their integration according to Eq. (3) leads always to negative surface excesses. The same variation is obtained whenever the dielectric constant of the ion-containing medium is greater than that of the image-containing medium.

3.2. Adsorption of carbofuran alone

Adsorption of a single solution of carbofuran is rather well-known [6–8]. The adsorption isotherm obtained in this study and displayed on Fig. 3 is consistent with our previous experimental data [7,8]. The finding of a very low adsorption due to the negative Gibbs relative adsorption does not mean that the surface layer is devoid of carbofuran, but indicates that this layer is richer in water than bulk. This explains why carbofuran is quoted in the literature as “non-adsorbed” (implied “on soils”). The physico-chemical reason for that is that the organic molecule, which has affinity with the interface with air, considered as hydrophobic [7,8], is far less attracted by the silica surface, known to be covered with water molecules, particularly in aqueous suspensions.

3.3. Co-adsorption of carbofuran and lead

Figs. 4 and 5, respectively, display relative adsorptions of lead nitrate and carbofuran, with respect to the concentrations of both components. The concentrations given on the axes are the equilibrium data, i.e. the supernatant concentrations once adsorption equilibrium had been reached. Fig. 4 shows an increase of salt adsorption with both salt and carbofuran concentrations; on the other hand, Fig. 4 highlights the weakness of carbofuran adsorption together with the lack of strong variations.

A comparison of Fig. 4 with Fig. 1 shows that lead nitrate adsorption is favoured by the presence of carbofuran: indeed, for the same bulk content, the relative

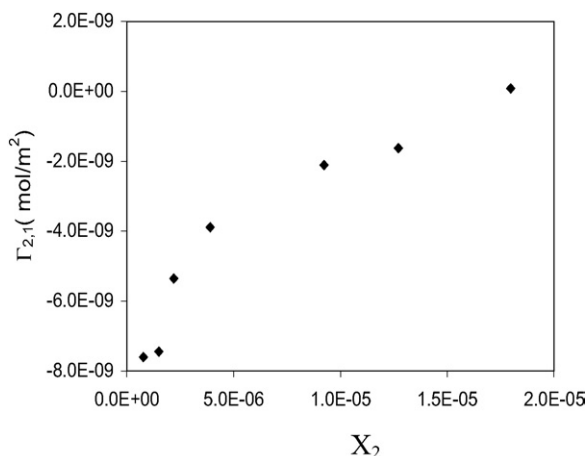


Fig. 3. Adsorption isotherm of carbofuran (2) from aqueous solution onto silica at 25 °C. Adsorptions are Gibbs relative adsorptions with respect to water (1). Concentrations are those of supernatant after equilibrium.

adsorption values are approximately twice the initial ones. An examination of Fig. 5 obtained with data collected in the same run of experiments (co-adsorption) indicates that the relative adsorption of carbofuran is still negative, but its absolute value is larger, which means a lower relative adsorption in presence of salt. This experimental result is very intriguing. Indeed, the solubility of the organic compound is reduced by the presence of salt in the solution, and theoretical and experimental demonstrations have shown that, at the air–solution interface, it usually results in an enhancement of the organic molecule adsorption [1,2,8].

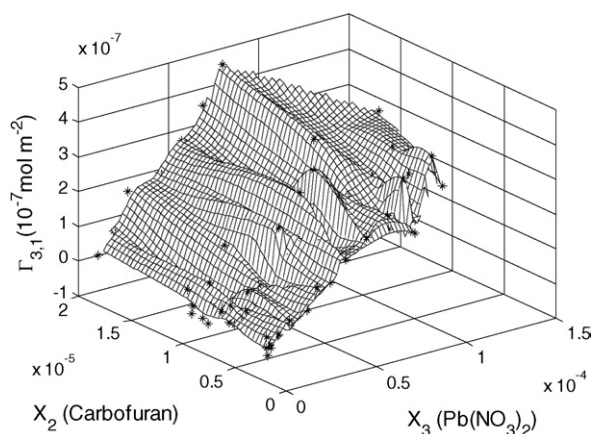


Fig. 4. Adsorption isotherm of lead nitrate from a mixture of lead nitrate (3) and carbofuran (2) in water (1) onto silica at 25 °C. Concentrations are those of supernatant after equilibrium, both in carbofuran and salt.

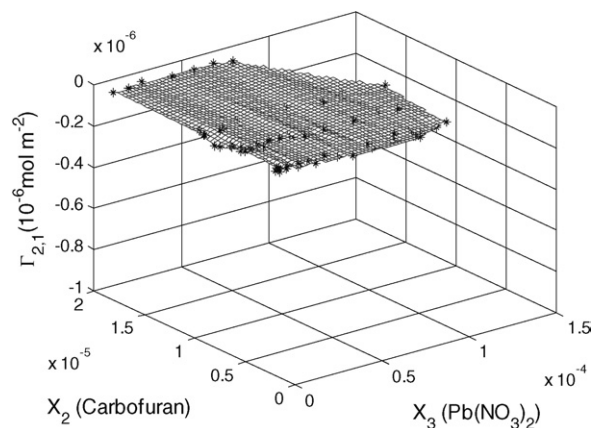


Fig. 5. Adsorption isotherm of carbofuran from a mixture of lead nitrate (3) and carbofuran (2) in water (1) onto silica at 25 °C. Concentrations are those of supernatant after equilibrium, both in carbofuran and salt.

3.4. Discussion

As clearly shown with solutions of lead nitrate alone or carbofuran alone, the surface layer in contact with silica is water-rich; this water-richness explains why ion adsorption is far much greater than at the solution/air interface: the transition between the solution and silica bulk (respectively, considered as media 1 and 2) seems to be more progressive than at the solution–air contact. We previously [1,2,9] argued that the value of the dielectric constant of a medium was affected by the existence of an organic layer between the air and a solution and that the reduction of the repulsive effect between a given ionic charge and its image could be explained by successive image-charges formed through the different interfaces (solution/organic layer, organic layer/air). Here, the situation seems to be far more complicated: indeed, the presence of organic molecules induces a consequent enhancement of ionic adsorption together with a reduction of organic adsorption. However, relation (5) indicates that the enhancement of ionic adsorption could be obtained by negative values of Γ_w .

$$\Gamma_{3,1} = \Gamma_{s,w} = \Gamma_s - (x_s/x_w) \Gamma_w \quad (5)$$

Then the enhancement of relative ionic adsorption could be explained on assuming the presence of a sufficient amount of organic molecules in the ionic layer responsible for a hydrophobic effect at the origin of the repulsion of some among the water molecules.

If one considers the effect of a negative value of Γ_w , on the Γ_{ow} relative adsorption of the organic molecule (o) with respect to water (w), according to Eq. (6):

$$\Gamma_{2,1} = \Gamma_{o,w} = \Gamma_o - (x_o/x_w) \Gamma_w \quad (6)$$

it would contribute to the enhancement of the relative adsorption of the organic molecule. But, the reverse situation was experimentally observed. Fig. 4 shows

that, in the presence of salt, the organic relative adsorption is not only reduced with respect to the adsorption in absence of salt, but also there is nearly no other variation with salt and carbofuran concentrations. The only explanation liable to conciliate both results would be to assume a particular organic concentration profile where Γ_o would be negative enough to counterbalance the negative Γ_w . Under this condition and conversely to the hypothesis at the solution–air contact, the organic molecules could go more deeply in the solution than ions with respect to the silica surface; moreover, it could be worth assuming a kind of water layer between the ionic layer and silica to take into account the hydrophilic effects (affinity of water for both ions and silica) and its electrostatic consequence on the image charge in a treatment similar to the one by Wagner–Onsager–Samaras.

Fig. 6 summarises these views about the molecular organisation, and Fig. 7 highlights schematically the result of these hypothetical arrangements on the values of the image charges finally included in the equivalent of formula (2) when the presence of organic molecules is taken into account. Fig. 7a depicts the air–solution interface, where ions are imbedded in an organic layer ($\epsilon \approx 30$ as if carbofuran was pure) in the close vicinity of the surface, and Fig. 7b shows a water layer against silica followed by an ionic layer embedded in an organic layer. Image charges were calculated according to relation (7) applied to the different interfaces:

$$q' = [(\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)] q \quad (7)$$

where an image charge q' (in medium 2, whose dielectric constant is ϵ_2) is proportional to the actual charge q (situated in medium 1, whose dielectric constant is ϵ_1). At the water/air interface, q' and q signs being alike, they create a repulsive force on the ion. At the silica/solution interface, the first image charge created at the interface between the organic layer containing the

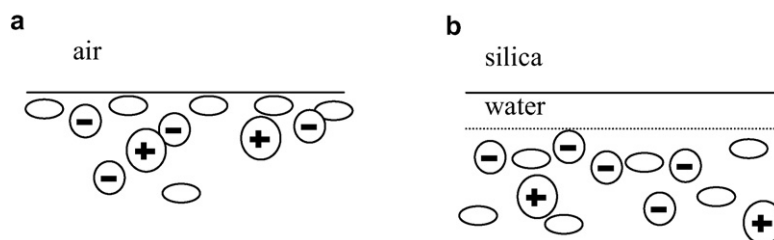


Fig. 6. Schematic representation of two different surface arrangements between carbofuran (O), Pb^{++} ions (\oplus) and anions.

(a) at the solution/air interface,
(b) at the silica/solution interface.

At the solution/air interface, organic molecules go far much closer to the surface. Interpenetration of ions and organic molecules can be imagined in a more subtle way.

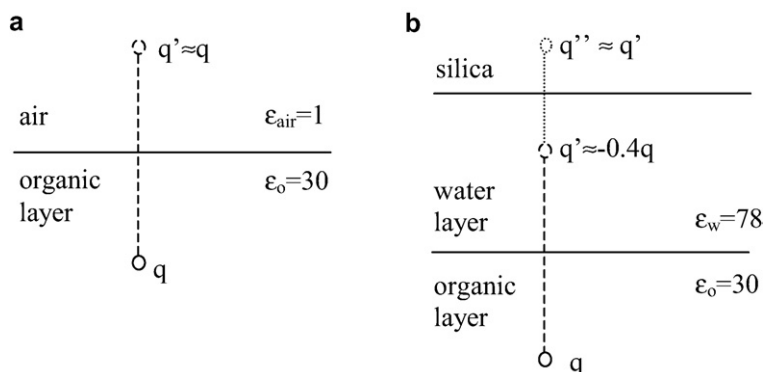


Fig. 7. Schematic calculation of an image charge according to the molecular arrangements depicted in Fig. 6. (a) at the solution/air interface, (b) at the silica/solution interface.

Image charges q' and q'' have been estimated according to formula (7).

actual ion and the water layer is then negative and attracts the ion. It is obvious that other image charges have to be taken into account like, for instance, q'' due to the interface between water and silica and whose sign is also opposite to the q one. Similarly, neither Fig. 6a nor Fig. 6b can be considered as completely realistic. However, to our opinion, the outstanding effects leading to the differences in experimental behaviours at both interfaces are contained in this first crude analysis. A full description on this basis is then worth being considered.

Finally, in the way of more or less statistical modelling, statistical simulations as done in Ref. [12] as well as quantum description of interactions [9] would be both extremely helpful. Of course, fundamental energetic data as immersion enthalpies obtained by microcalorimetry or following from adsorption studies with temperature could bring experimental confirmation to the theoretical arguments. Because of the intriguing particle arrangements in surface, kinetics measurements could also help to clarify our view of the problem.

4. Conclusion

A careful study of the coadsorption of carbofuran and lead nitrate at the interface of aqueous solutions and silica suspensions showed a spectacular enhancement of lead adsorption compared to that of solutions of salt alone at the same concentration. The observed effect is very intriguing because at the same time carbofuran adsorption seems to be more limited in mixtures than when alone in solution. Carrying out an

Onsager–Samaras-like analysis of ionic adsorption together with considerations about the likely water behaviour at an interface layer between the highly hydrophilic silica and the rather hydrophobic organic molecules provides some hints for a better understanding of this phenomenon. These results open the way to very stimulating modellings of composite interfaces and to unavoidable thermodynamical analysis and experiments.

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