

Proposition of two layered ionic structures, with xy disorder but z-ordered, in a quasi-liquid system

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Recibido el 10 de diciembre de 2001; aceptado el 20 de abril de 2005

Boundary layers at the liquid-solid interface of increasing concentrations of CuSO_4 aqueous solutions in contact with glass have been studied. An orderly sequence of Cu^{2+} - SO_4^{2-} - Cu^{2+} - SO_4^{2-} solvated ionic sub-layers parallel to the glass are formed, being the first one electrostatically anchored to the surface. Cu^{2+} EPR line intensity, and NMR proton relaxation T_2 studies show outstanding similarities, which can be explained by the presence of different stages of ionic organization with the concentration, at the semi-liquid boundary layers. At a critical concentration C_m , two stable local layers (of two sub-layers each) of ions are proposed to be present. In them, the ions in the xy, parallel to the wall plane are randomly distributed, but with the proposed order in z perpendicular to the wall axis.

Keywords: Boundary layers; EPR; NMR; ionic order; magnetic ordering.; CuSO_4 .

Se han estudiado las capas límites en la interfase líquido-sólida formadas por concentraciones crecientes de soluciones acuosas de CuSO_4 , en contacto con una superficie de vidrio. Se forma una secuencia ordenada de iones solvatados Cu^{2+} - SO_4^{2-} - Cu^{2+} - SO_4^{2-} de sub-capas paralelas a la pared, estando la primera anclada electrostáticamente a la superficie. Estudios de las intensidades de línea de RPE de los iones Cu^{2+} , así como estudios de la relajación T_2 de los protones mediante RMN, muestran comportamientos similares, que pueden ser explicados por la presencia de distintos estadios en la organización de los iones con la concentración, en las capas límites. A cierta concentración crítica C_m , se propone la presencia de organizaciones locales y estables de dos capas de iones (con dos sub-capas cada una), dichos iones están dispuestos al azar en el plano xy definido por la pared, y con el orden propuesto en el eje z perpendicular a la misma.

Descriptores: Capas límites; RPE; RMN; orden iónico; orden magnético; CuSO_4 .

PACS: 73.30.+y; 75.10.-b; 87.64.Hd

1. Introduction

In a CuSO_4 aqueous solution in contact with a glass surface, in the liquid-solid interface, the so called boundary layers are formed. They are an arrangement of solution ions in which they lose their mobility and follow an order attending to an electrostatic equilibrium [1,2]. Usually, all references to orderly layers are related to their electrochemistry condition, in which a negatively charged metallic electrode is in contact with the solution; the electric field around it induces an ionic order forming up to three layers [3]. In our study, we have a glass surface in which a finite and equal number of positive and negative charged centers are present. The surface charges are originated by the glass dipoles, randomly distributed in its bulk, and in which some of them have one of its charged ends, showing up at the surface. When a low

CuSO_4 salt concentration solution is present, the solvated salt ions are widely scattered and temporarily attached to the surface, but due to the collisions with the liquid phase ions, they can return to the solution. At this stage, no constant pattern of electrostatically attached ions is obtained, even though the number and distribution of the available electrical dipolar centers on the surface is spatially constant. At a concentration of 800 mg/L, the Cu^{2+} ions and the negative ones (OH^- and SO_4^{2-}) are distributed in such a way on the surface that distances among them obey to an electrostatic and magnetic equilibrium, and therefore become attached in a random but spatially and timely constant pattern in the glass plane xy. At larger concentrations, between 800 and 1408 mg/L, the experiments of non resonant microwave absorption in CuSO_4 aqueous solutions show the formation of a new layer [4]. This is a different case than the one treated by electrochemistry. In

this paper, we are proposing the existence of ionic order in the boundary layers in absence of an external electric potential. Studies of electrical and magnetic changes in the boundary layers for the cases of NaCl and CuCl_2 , using a microwave cavity and observing its frequency changes when increasing the concentration [5], lead to further studies including the slipping of the fluid at the walls to assure we are in presence of an interface phenomenon, and not in a bulk property [4]. However, only one reliable reference on the subject for ionic organized boundary layers, in form of an electronic report, was available [6]. As we have said, only two consecutive layers are present at a moderate concentration, about 1408 mg of salt per solution liter, each one formed by two sub-layers of ions. The first sub-layer, mainly composed of Cu^{2+} and OH^- ions is followed by a next one of SO_4^{2-} , and hydrogen bridges. In the sub-layer, close to the glass, the Cu^{2+} ones are immobilized by negative charges, the ones of the surface, and the corresponding to the neighboring SO_4^{2-} . This restriction in the degree of freedom of each molecule due to the wall, also influences his magnetic dipolar moment, providing a preferred orientation axis to align the $m_S = \pm 1/2$ states. Further, statistical averaging favors the lowest magnetic and electric energy configuration. For typical distances between boundary layer ions of 3.10^{-8}cm , the electrical dipolar interactions energy among them, $p^2/r^3 \sim 1\text{ eV}$ [7] is larger than the fluctuation energy $kT \sim 0.02\text{ eV}$, that will not be able to disorder them easily. On the other hand, the paramagnetic disordered phase, whose exchange energy interaction ranges in the order of $kT_C \sim 0.0002\text{ eV}$ (extrapolated from the solid case), is not present in those closest to the wall layers. The finite number of attachment sites in the wall, enables us to expect observable saturation effects in function of a solute concentration, and to relate these effects to the filling of layers. The first layer ($p^2/r^3 \sim 1\text{ eV}$), clearly the most stable one, is filled minimizing both, the electric and magnetic energies, and similarly does the second layer, although in it Cu^{2+} ions are less attached ($p^2/r^3 \sim 0.1\text{ eV}$) to their equilibrium positions. In fact a critical concentration, C_m , is observed and can be understood by the filling of both layers.

2. Experimental

In order to minimize the undesired information of the bulk of the salt solutions, and maximize the one from the liquid-solid interface, the EPR and NMR experiments were performed embedding packs of glass beads of 250 microns in diameter in 15 increasing concentrations of aqueous CuSO_4 solutions at 25°C , and taking the spectra of them. In both cases, EPR and NMR, we got the effect of the bulk and the one of the interface overlapped in the resulting spectra. However, the effect of the bulk was expected to be shown as a monotonous increasing mean value at the baseline, and the effect at the layers, as deviations from it. As a proof, we performed the EPR experiments in (a) a tube of internal diameter $D_1=0.114\text{ cm}$, filled with the glass beads, (b) in the same tube without the beads, and (c) in a tube of internal diameter of

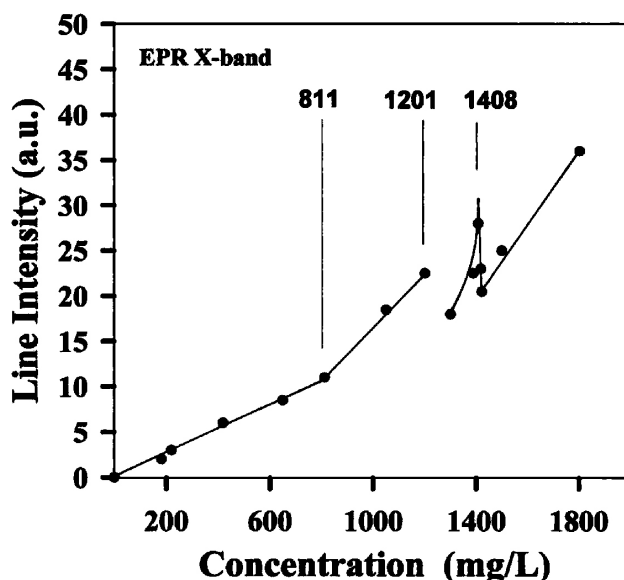


FIGURE 1. Variation of the EPR intensities lines I_{PP} with the Cu^{2+} concentration, mainly at the boundary layers. The three different zones of the curve suggest the Cu^{2+} layers.

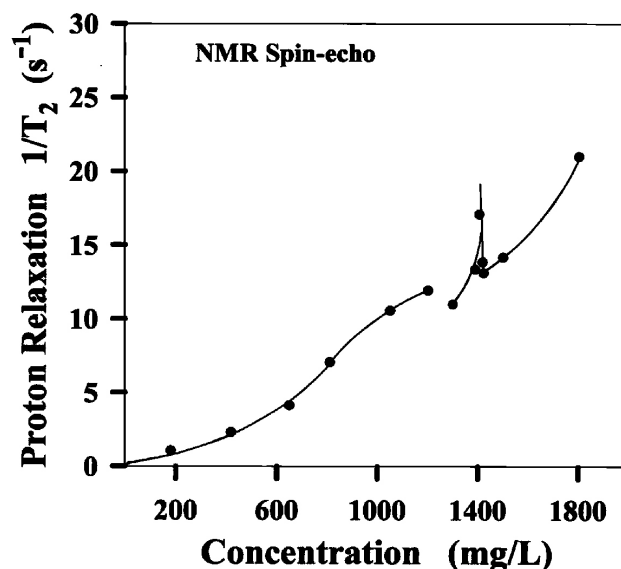


FIGURE 2. Variations of the T_2 proton relaxation time, in terms of the solution concentration. The maximum at $C_m = 1408\text{ mg/L}$ suggests a magnetic local order.

$D_2=0.136\text{ cm}$. The surface to volume S/V ratios being: 166.6 cm^{-1} ; 35.3 and 29.4 cm^{-1} , respectively. As expected, the larger the bulk, the baseline increased its derivative, although the curve structure, due to the layers, was still visible, even though at lower concentrations tended to average at the baseline.

- a) EPR experiments: A rectangular cavity operating in the mode TE102 was used in a X-band Varian E-Line, EPR spectrometer. The spectra showed a similar width and g values, but different I_{PP} intensities whose results are displayed in Fig. 1 for the case (a).

If the paramagnetic centers are agglomerated, for instance in the case of the crystal of the corresponding salt, then there will be two competing effects: on one hand, as in the case of the bulk of the paramagnetic CuSO_4 solution, the dipolar interaction will cause a widening of the spectral line. On the other hand, in a crystal, the dipolar moments will be close enough to produce a wave function overlapping that will narrow the spectral lines by the exchange interaction. The possibility of a closely packed concentration of Cu^{2+} ions at the surface, is suggested by the I_{PP} of the EPR signal in our experiments. In that fraction, the exchange interaction among the closest neighbors may be important. In the more dilute fraction in the surface site, only dipolar interaction would be present. It can be observed that between 150 and 800 mg/L, there is a smooth increase in the spectra intensities that has been attributed to the appearing of the first layer. Between 800 and 1200 mg/L, the increasing rate is larger and is attributed to the partial formation of an unstable second layer which collapses at 1200 mg/L. From 1299 to 1408 mg/L, a reordering takes place until a new equilibrium is established when both layers are complete at $C_m = 1408$ mg/L, and the proposed structure is formed. After this level in the concentrations, the newly arriving ions weaken again the structure, and a new third layer starts to be formed, as shown in the last part of the graphic of Fig. 1.

- b) NMR experiments: The proton T_2 relaxation time of the system was measured using the Carr-Purcell-Meiboom-Gill pulse sequence [8]. The obtained data reveal an exponential decay for the protons, corresponding to the presence of local order.

Such a behavior which is remarkably similar as the one obtained in the Cu^{2+} electron paramagnetic resonance shown in Fig. 1, is also shown in Fig. 2. It should be remarked that the T_2 relaxation, is more efficient if the protons are in presence of a strong local field due to the organization of electronic magnetic dipolar moments, and less efficient if they are randomly oriented.

3. Conclusions

The similarity among EPR and NMR experiments can be explained by the presence of local ordered structures. In the xy-plane parallel to the glass surface, the ions are randomly attached to the surface. In the first sub-layer, where the populations of Cu^{2+} ions is large, its electrical dipole, anchored to the surface, favors a privileged direction for the magnetic dipole. This situation makes possible a collective classical magnetic interaction between them, which superposed to the dominant electrical ionic order favors the explanation of the experimental results. We believe that what we have mentioned gives a relevant support to the existence of the proposed two layered local structure, ordered in the z-direction (of $\text{Cu}^{2+} - \text{SO}_4^{2-} - \text{Cu}^{2+} - \text{SO}_4^{2-}$ solvated ions) occurring in the semi-liquid boundary layers at a $C_m = 1408$ mg/L concentration of aqueous CuSO_4 solution in the liquid-glass interface [4].

Acknowledgements

We want to thank Prof. Alfredo Zambrano for his EPR spectra calculations using his Flipper Program System. This research was sponsored by the Research Grant CDCH-03.11.2799.92; D.M. thank adnj-2.03 support.

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