

THE INFLUENCE OF ACCOMPANYING COMPONENTS ON THE SORPTION OF MOLYBDATE ANIONS FROM AQUEOUS SOLUTIONS ON DISPERSED ICE SURFACE

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The ice surface in the natural environments of the Earth may influence natural processes due to activity of the quasi-liquid film that is formed on the surface of ice crystals. Sorption of molybdate anions ($4 \cdot 10^{-5}$ mol/L) from water solutions by the surface of dispersed ice particles is investigated. Supporting electrolyte is KCl (11.75 g/100 g of water) with addition of magnesium chloride with concentration not greater than 10^{-2} mol/L or ethanol with concentration not greater than 10^{-1} mol/L. The temperature is -5.1 °C. It has been demonstrated that increase of the content of magnesium chloride promotes sorption of molybdate anions. In contrast, increase of the content of alcohol lowers it. Different effects of added substances may be due to the different degrees of the influence of magnesium chloride ions and undissociated organic substance of the water structure in the quasi-liquid film on the nature of dissolution of the other substances in it. The polar ethanol molecules can interact also with the surface of dispersed particles of ice.

Ice, quasi-liquid film, sorption, molybdate anion, magnesium ion, ethanol

INTRODUCTION

It has been shown in the review paper by J.G. Dash and his colleagues [Dash *et al.*, 2006] that practically every solid substance is characterized by a disordered (quasi-liquid) state on the surface of the crystals, which is displayed at the temperatures close to its melting point in the volume, and only in the presence of the solid phase of this substance. The latter detail accounted for naming this phase non-autonomous, i.e., existing only in the ensemble with the crystal's volume phase [Urusov *et al.*, 1997]. The non-autonomous phase of water with increased mobility of molecules emerging on the ice surface was quantified by V.I. Kvlividze and his team [Kvlividze *et al.*, 1974], who studied ice that bordered on air, fluoroplastic (polytetrafluorethylene), and other materials.

Thus, the presence of quasi-liquid film on the ice surface in the range of temperatures below its melting point is a well-known fact. The components of the natural environment may be subjected to indirect impact of this film, which may be displayed, for example, in the flow of glaciers [Makarov and Fedoseev, 1989] and in formation of geochemical halos of dispersion of soluble chemical substances in the snow cover originating from buried ore bodies or sources of anthropogenic contamination [Makarov *et al.*, 1990], etc. In this regard, interest for the study of physical and chemical properties of ice surface has recently grown. For example, in the study by Y. Tasaki and T. Okada [2008], the possibility of using dispersed ice even as an immobile phase in chromatography is considered, when dissolution of the components of the mobile phase in quasi-liquid film is one of the main mechanisms of their fixation during their separation. In ad-

dition, research is expanding relating to the behavior of the ice surface in relation to chemical substances of a different nature under the temperature conditions in which snow particles are generated (see, for example, the papers by Jedlovsky [Jedlovsky *et al.*, 2008; Szóri and Jedlovsky, 2014]).

Participation of quasi-liquid film in the natural processes occurring in frozen and glacial systems may be attributed to the film's dissolving properties. As known, the self-diffusion coefficient of water molecules in quasi-liquid film is only by an order of magnitude lower than that in common water [Ushakova, 1975]; therefore, we could suppose the film to be able to sorb water-soluble substances. That was established for certain organic acids and alcohols dissolved in hydrophobic solvents (toluene, hexane) [Nechaev *et al.*, 1981]. Under these conditions, quasi-liquid film of ice is not 'perturbed' by the influence of the contacting solvent. During interaction of the formic, acetic and halogen-containing acetic acids, of ethanol and methanol with dispersed ice, their transition was observed from the organic layer into the surface quasi-liquid layer of ice. It turned out that those substances were best adsorbed on ice which were not only well-soluble in water but also had a relatively high coefficient of partition between water and the organic layer [Nikolsky, 1965]. Thus, sorption of substances was caused by their dissolution in the quasi-liquid film. As the content of such substances, for example, trichloroacetic acid, increased, partition melting of dispersed ice in the system was observed, with the volume phase of the water solution of the substance formed¹. Quasi-liquid film was also shown to

¹ In contrast to the solution in quasi-liquid film, the volume phase of a water solution may be separated and exist separately.

disappear after prolonged (2–2.5 months) exposure to the temperatures below $-40\text{ }^{\circ}\text{C}$ and to reappear when higher negative temperatures were reached (-2 , -5 , $-10\text{ }^{\circ}\text{C}$). It has been noted that duration of the period till re-appearance of the film essentially depends on temperature and increases as the temperature decreases. Therefore, it is evident that the surface film of ice manifests solvent properties, and its condition depends on the environmental conditions. Both at cooling and at heating, the system reaches the equilibrium state after a certain period of time, conditioned by the value of the temperature at which the experiment is held.

For the new knowledge to be applicable to the natural water-containing systems, it is necessary to investigate the properties of the surface on the boundary between ice and water solution. The presence of the phase boundary ‘ice–water solution’ is possible, if there is salt (background electrolyte) in the water system, in the amount corresponding to the phase diagram ‘salt–water’ [Nikolsky, 1965]. Such a diagram reflects dependence of the temperature of formation of the solid phase (ice or salt) on the composition of the water solution as the temperature changes. Based on the general rules regarding co-existence of phases and considering the results of investigating sorption of organic substances from hydrophobic solvent by ice, we believe that all the more so, a transition layer should exist on the surface of ice particles.

The hydrogen ion exponent, pH, is known to be an important characteristic of an aqueous medium; therefore, the influence of pH on the sorption of molybdate anions by ice was investigated [Fedoseeva and Fedoseev, 2010]. The composition of these ions does not vary in the broad range of the medium acidity; therefore, they can be used as an indicator reflecting any changes at the boundary between the solution and the ice (background electrolyte–potassium chloride) that occur under the influence of pH.

Sorption of molybdate anions grew as the pH of the medium increased and decreased as the temperature decreased (from -1.7 to $-5.2\text{ }^{\circ}\text{C}$) within the range of temperatures close to the melting point of ice. The nature of the dependence of the sorption of the investigated anions on pH could be explained by the effect of the concentration of hydroxyl ions which penetrate into the quasi-liquid film of ice, through its thickness. Passing from the solution into the film as a solving medium, these ions, due to their strong ‘structuring’ effect on water [Ryabukhin, 2002], apparently contribute to additional melting of the ice layers adjacent to the film. As the film thickness increased, the amount of the sorbed molybdate anions grew, accordingly.

The conclusion regarding the essential influence of the hydroxide-anions on the water structure was stated in the analysis of the enthalpy changes in the formation of aqueous solutions of different inorganic

compounds [Nikolsky, 1965]. To obtain a series of solutions with different pH values, in [Fedoseeva and Fedoseev, 2010] potassium hydroxide was used. For this compound, the enthalpy change when dissolving in water has a negative value (-53.86 kJ/mol), indicating a strong structuring effect of ions on water. The main role in it should be played by hydroxide-anions. Large-size potassium ions are poorly hydrated; therefore, their influence on the enthalpy of dissolution is small. Additional experiments were carried out to verify the thesis of the influence of water-structuring substances added to the system.

THE TECHNIQUE OF THE SORPTION EXPERIMENTS APPLIED

After analyzing the enthalpy changes following dissolution of different compounds in water, magnesium chloride and ethanol were selected, capable of influencing the structure of water. In the dissolution of the former compound, the enthalpy change was -151.5 kJ/mol , the enthalpy change for the second compound was -11.195 kJ/mol [Nikolsky, 1965]. The amounts of magnesium chloride or ethanol were chosen as for their concentrations to be low, in order to avoid distortion of the condition of the system ‘water–background electrolyte’. As the latter, also potassium chloride was used, with concentration corresponding to the temperature of the system under investigation ($-5.1\text{ }^{\circ}\text{C}$) [Nikolsky, 1965].

The technique of conducting the sorption experiment consisted in the following. Solutions with background electrolyte, which contained molybdate anions and the added magnesium chloride or ethanol, were placed into the underground laboratory of the Permafrost Institute, where the air temperature was maintained to be negative throughout a year ($\leq -5.5\text{ }^{\circ}\text{C}$). After an experimentally established interval of time, sufficient for reaching temperature equilibrium (4 hours), pieces of ice 5 g in mass prepared from distilled water were added to the control and experimental solutions (25 mL), in order to reach phase equilibrium. After 24 hours, the amount of 5 g of dispersed ice was added to the solutions. As dispersed ice, samples of snow were used sampled outside the city in leeward areas after a heavy snowfall. It is to be noted that after sampling, snow samples were kept under the new temperature and moisture conditions of the underground laboratory for a period of not less than a month.

Then, 24 hours after, the control solution and the solutions under study were separated from the solid phase and analyzed for the presence of molybdate anions using the photometric method [Lurye, 1984]. The amount of molybdenum absorbed by dispersed ice was determined from the difference of concentrations in the control solution and the solution under study for each original concentration of added magnesium chloride or ethanol. The equilibrium content

of the latter in the solutions was not analyzed. It should be noted that the results of sorption studies involving addition of magnesium chloride or ethanol to the system have been partly published (for MgCl_2) [Fedoseeva et al., 2015]; however, they should be considered in totality, due to different influence of the added components.

THE RESULTS OF THE SORPTION EXPERIMENTS AND DISCUSSION

The results of the sorption experiments testify that, as the concentration of magnesium ions in the original solution increases, the amount of molybdenum adsorbed on the surface of the ice particles grows, which agrees well with the proposed description of the influence of added salt (Fig. 1). It seems that the magnesium cations, also coming into the quasi-liquid film, cause a change in the structure of this film. The extent of the influence of the components on the structure of water may be characterized by the value of the hydration number [Afanas'ev and Ustinov, 2011], which is 32.4 for magnesium chloride. This is much higher than for the background electrolyte (15.5) with KCl concentration established according to the experimental conditions. It follows that in the presence of magnesium chloride, melting of the adjacent layers of volume ice² adjacent to the film should also take place. At the newly established equilibrium, the thickness of the transition film and, accordingly, sorption of molybdenum ions grow.

The presence of ethanol in the original solution within the same range of concentrations had the opposite result (Fig. 1). As the concentration of alcohol increases, sorption of molybdenum ions decreases. This explanation is based on analysis of reference data [Nikolsky, 1965] on solubility of salts in a water-alcohol mixed solvent, which indicates that solubility of salts with an expressed ion bond drops as the content of alcohol increases. On the contrary, heavy metal salts, in which bonds have a significant degree of covalence, get dissolved much easier as the fraction of alcohol rises. Thus, the presence of alcohol in the quasi-liquid film of ice ensures manifestation of certain 'phobicity' in relation to ions of inorganic substances.

It seems that polar hydroxyl groups $-\text{OH}$ of the alcohol molecule ($\text{C}_2\text{H}_5\text{OH}$), similarly to hydroxyl ions, should to a certain extent violate the equilibrium at the boundary of the quasi-liquid film of ice with its solid phase, resulting in the increase of the film thickness. In the figure (curve 2), increased amount of adsorbed molybdenum is observed at low concentration of ethanol in the original solution. However, the hydrophobic part of the molecule (C_2H_5-) prevents the growth of thickness of the film of ion sub-

stances. It can be seen that at higher concentrations of alcohol sorption of the molybdate anions is much lower. According to the literature data [Vezhnikov, 2011], the hydrophobic interactions of substances in aqueous solutions energetically contribute to recovery of the structure of water. Hence, the presence in the system of soluble undissociated compounds with hydrophilic and hydrophobic groups in a molecule may exert different influence, depending on concentration, on the condition of the quasi-liquid film at the 'ice-solution' boundary.

The behavior of snow particles after sorption also generally indicates different influences of magnesium chloride and ethanol on the quasi-liquid film in the sorption experiments and on the system as a whole. In the presence of magnesium chloride, snow particles in the aqueous solution of KCl are separated, i.e., they are hydrophilic. In the presence of ethanol, they are aggregated, which may be observed from hydrophobization of the surface of snow particles due to adsorption of alcohol molecules on it. It is clear that adsorption may take place due to formation of hydrogen bonds between the hydroxyl groups of the molecules of alcohol and water in the quasi-liquid film. Hydrophobic ethyl (C_2H_5-) groups turn out to be directed at the aqueous solution, which results in aggregation of snow particles in the aqueous medium. These assumptions require testing in similar experiments using different organic substances. The possibility of sorption of low-molecular alcohols from the organic layer by quasi-liquid film of ice is shown in [Fedoseeva et al., 1977]. According to literature data, adsorption of alcohols on the ice surface has been studied only from the gas phase and at rather low (213–243 K) temperatures (see, for example, the study by M. Kerbrat [Kerbrat et al., 2007]).

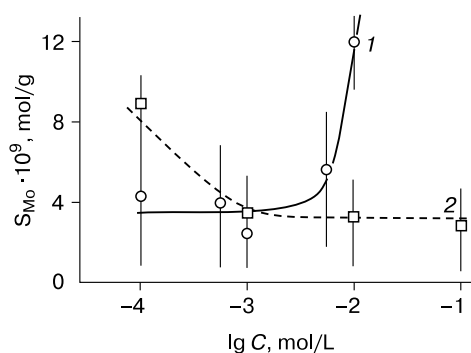


Fig. 1. Dependence of sorption of molybdate anions (S_{Mo}) upon the surface of dispersed ice on the original concentration (C) of MgCl_2 (1) or ethanol (2) added to the solution.

Temperature -5.1°C ; background electrolyte – KCl; concentration of MoO_4^{2-} is $4 \cdot 10^{-5}$ mol/L.

² Volume ice is ice having orderly structure, characteristic of this phase in volume (in contrast to the disorderly layer on the surface, which exists only in the presence of volume ice crystals).

CONCLUSIONS

It has been shown by the example of sorption of molybdate anions that, firstly, the so-called quasi-liquid transition film exists on the surface of ice which borders on the aqueous solution containing background electrolyte, and, secondly, the film manifests adsorbing properties, the character of which may vary depending on the properties of soluble components co-existing in the system and their concentration. Given the substances which do not dissociate but have a polar and non-polar group, adsorption of their molecules on the boundary separating the ice particles from the aqueous solution is possible. The hydrophobic character of the surface of the particles thus acquired prevents migration of the ions of inorganic substances into the film.

The results of the previously conducted nature experiments on the study of migration of the gold ions from the underlying substrate into the snow cover may serve as confirmation of the practical significance of the studies of the physical and chemical properties of the quasi-liquid film of ice under different conditions [Makarov *et al.*, 1990]. These data have been interpreted based on the new knowledge of the physical and chemical properties of the surface of dispersed ice obtained by the time [Nechaev *et al.*, 1981], as well as of the character of the adsorption affinity between different complexes of gold and the surface of certain mineral components of soils, which is described in detail in a monograph [Fedoseeva, 2003]. The results of this study testify that the role of the transition film on the boundary between ice and aqueous solution in migration of soluble substances in the natural environment may essentially vary depending on the composition of the pore solution.

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Received August 10, 2016