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RECENT EXPERIMENTAL WORK ON SOLUTE REDISTRIBUTION AT THE ICE/WATER INTERFACE. IMPLICATIONS FOR ELECTRICAL PROPERTIES AND INTERFACE PROCESSES

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Résumé.- Nous avons étudié la ségrégation de NaF, HCl, NaCl, NH_4F et AFGP à l'interphase eau/glace. Le coefficient de distribution de NaF diminue de 2×10^{-1} (à la concentration initiale de la solution mère de 10^{-6} mol/l) à 3×10^{-3} (à 10^{-2} mol/l). Par contre, celui des deux chlorures reste constant à 3×10^{-3} entre les concentrations initiales de 5×10^{-6} mol/l et 5×10^{-4} mol/l. À la concentration de 10^{-6} mol/l de la solution mère, le coefficient de distribution de NH_4F est fortement dépendant du pH de la solution liquide. AFGP est le plus soluble des dopants connus de la glace. Le coefficient de distribution est voisin de l'unité. Si le liquide n'est pas agité, des traces d'AFGP dans la solution mère augmentent le coefficient de distribution de HCl à cause d'instabilités des champs de flux de la chaleur et du dopant.

Abstract.- Redistribution of NaF, HCl, NaCl, NH_4F, and AFGP at the ice/water interface have been investigated under near-equilibrium constrained growth conditions. The distribution coefficient of NaF declined from 2×10^{-1} (at 10^{-6} N initial liquid concentration) to 3×10^{-3} (at 10^{-2} N). By contrast, the distribution coefficient of the two chlorides was 3×10^{-3} and invariant with initial liquid concentrations in the range 5×10^{-6} N to 5×10^{-4} N. At 10^{-6} N concentration of the mother solution, the distribution coefficient of NH_4F was found to be strongly pH dependent. AFGP is the most highly soluble of known impurities in ice, with a distribution coefficient close to unity. In unstirred solutions, traces of AFGP in the mother solution caused an increase in the distribution coefficient of HCl due to instabilities in the flux fields of heat and solute.

We report on new measurements of redistribution of trace amounts of ionic solutes (NaF, HCl, NaCl, NH_4F) and of AFGP (antifreeze glycoprotein) at the ice/water interface under near-equilibrium conditions of phase transformation. Concentration dependence of the distribution coefficient was of primary concern because it reflects solute interactions with the ice lattice, such as formation of point defects [1], microstructures [2], dislocations [3], and vacancies [4]. Conductivity and dielectric relaxation spectrum of ice are controlled by these phenomena [5].

THEORY

The interfacial distribution coefficient for a trace solute at the phase boundary between a liquid and a solid solution at thermodynamic equilibrium is defined as

$$k_o = C_S/C_L,$$

where C_S and C_L are solute concentrations on the solid and liquid side of the interface, respectively, for a particular position of the latter. If the two solutions in contact are "ideal" or "ideal dilute" [6], the distribution coefficient is independent of concentration but the converse is not necessarily true. Solutions of ionic compounds in water, even dilute ones, tend to depart from ideality,

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especially in the solid phase. Solute specificity of such departures is of interest for the interpretation of electrical measurements.

Solute fractionation processes at the ice/water phase boundary easily depart from equilibrium due to the development of unsteady diffusion fields of heat and solutes at the dynamic interface. Departures from equilibrium mask solute concentration effects.To minimize the effects of such interface instabilities on solute redistribution, very low freezing rates and stirring of the liquid solutions are recommended for this type of study.

Fractionation at the ice/water interface of ionic solutes (chlorides and fluorides) discussed in this paper causes a preferential rejection of the cation and development of an electrical field at the phase boundary, the freezing-potential effect [7]. For this reason, the distribution measurements here reported refer exclusively to the anion, and a subsidiary question was whether ion separation affects anion redistribution.

METHODS

The Bridgman method was used to grow nearly monocrystalline ice columns of 3.8 cm diameter and 20-25 cm length at a freezing rate of 1.9 mm/h [8]. Except as noted, the liquid solution was continually stirred at 300 rpm in a plane 4-6 cm from the interface. After freezing about three fourths of the solution, the supernatant liquid phase was separated. Its volume and solute content were measured and used as a check on solute mass balance. From the solid column, successive 5 mm or 10 mm portions (for chloride and fluoride solutions, respectively) were melted off. Measurements of solute content were obtained as a function of freezing length. Computational methods have been described elsewhere [9].

Chloride concentrations were determined by using solutions spiked with Chlorine-36 and measuring activity in a refrigerated scintillation counter.

Fluoride was determined with a biochemical method [10] based on the inhibitory effect of fluoride on the hydrolysis of ethyl butyrate in the presence of pork-liver esterase. Carbon-14 labelled ethyl butyrate was used to increase the sensitivity of the method, and one of the hydrolysis products, water-soluble butyric acid, was separated and measured in the liquid scintillation counter.

AFGP was determined by the Lowry method [11]. To compare results from columns grown with and without AFGP, a multiple regression study was carried out [12]. The multiple regression procedure involved two stages. In the first stage, a cutoff value was determined for the point where stability was attained in the growth rate of each individual ice column. This is critical in unstirred columns where initial growth was always unsteady. The second stage used the data for samples beyond the cutoff point since it is the intercept of this curve (in the logarithmic domain) that is related to the distribution coefficient. Regression was then used to estimate slopes and intercepts and to carry out various statistical tests about the slopes and intercepts. The model used for regression was

$$\log \varphi_S = a + b \log \varphi_L,$$

where φ_S and φ_L are normalized solute concentrations of solid and liquid at the interface (Fig. 3).

SODIUM FLUORIDE

The distribution coefficient exhibits a marked concentration dependence in the range of initial NaF concentrations in the liquid between 10^{-6} N and 10^{-2} N (Fig. 1). A logarithmic straight-line fit to central values of our data yields

$$\log k = (-3.276 \pm 0.300) - (0.447 \pm 0.069) \log C_o ,$$

at the 95% confidence level and a correlation coefficient of -0.968, in reasonable agreement with some earlier work [8, 13].

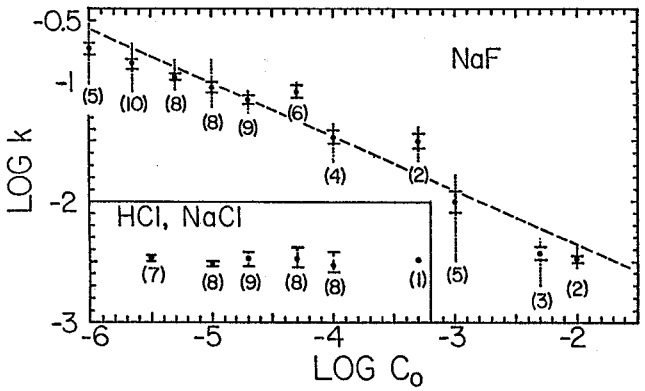

Fig. 1.- Concentration dependence of the distribution coefficient. = normality of the mother solution. Indicated in parentheses below each data point is the number of ice columns studied for each concentration. Solid bars indicate the 95% confidence intervals of k-values determined for all columns grown from a particular solute species and concentration. Dotted lines: range of extreme k-values measured for a particular fluoride concentration. Dashed line: simple straight-line least-squares fit through central k-values at each fluoride concentration.

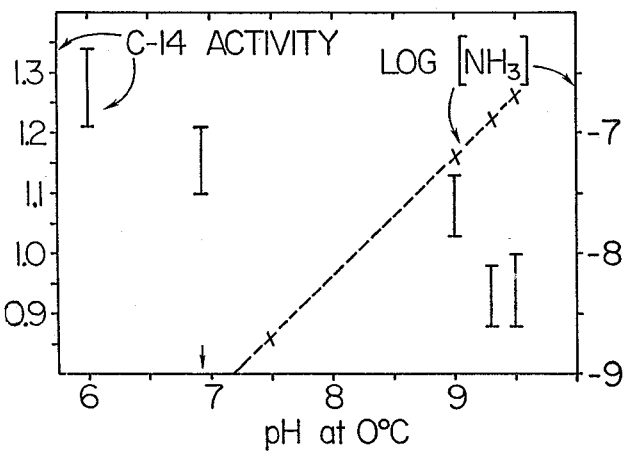

Fig. 2.- C-14 activity (arbitrary units) in ice vs. pH of 10^{-6} N ammonium fluoride mother solution. Each vertical line shows the activity range measured in one ice column. Dashed line: calculated normality of NH_3 in mother solution. C-14 activity is inversely and nonlinearly related to fluoride concentration. pH was controlled with HCl or NaOH, respectively. Arrow: estimated pH of 1×10^{-6} N NH_4F solution without additives.

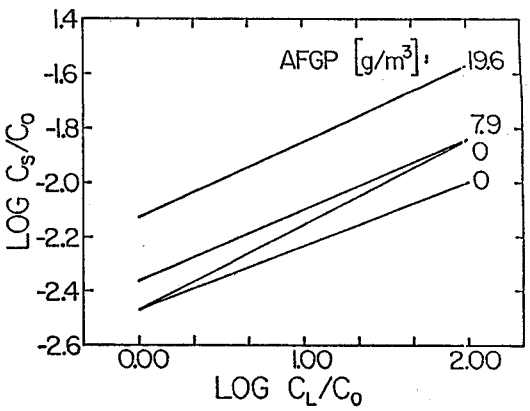

Fig. 3.- Distribution curves for ice columns grown (unstirred) from 5×10^{-5} N HCl with various additions of AFGP. C_o = initial chloride concentration in the liquid phase.

Discussion.- Because of preferential cation rejection (see above), sodium ion does not participate appreciably in the equilibrium fractionation, and the solute species in the liquid is effectively hydrogen fluoride [7]. The equilibrium distribution coefficient can be expressed as a function of solute mole fraction in the liquid, and of the number of "point defects" (n_L, n_S), such as ions, or Bjerrum defects (L_B, D_B), etc., generated by one solute unit (HF molecule) in the liquid and in the solid solution, respectively [14, 15]. According to this thermodynamic model, the equilibrium distribution coefficient varies as

$$X_L^{(n_L/n_S)-1}$$

It will be concentration-dependent if $n_L \neq n_S$, and the simplest assumptions give a slope of 1/3 for the plot of Fig. 1 (i.e.: F^- and H^+ in the liquid; F^-, L_B, and H^+ in the solid phase). Ignored in this reasoning are: concentration-dependent activity coefficients [15], effects due to interstitial solute, and effects of lattice distortion caused by the solute. Interstitialcy of fluoride, and bond-shortening, have been documented in fluoride-doped ice by studies of dislocation density [3], diffusion [16], NMR [17]. Lattice distortion may cause an increase in the point defect population in the solid thereby steepening the slope of Fig. 1. Statistical uncertainties in our data are, however, at least as large as theoretical slope differences. Uncertainties are mainly connected with the chemical analysis; they were much smaller for chloride-doped ice columns (Fig. 1). Flattening at the low and high concentration extremes (Fig. 1) has been attributed, respectively, to a buffering action by intrinsic defect concentrations, and to incomplete extrinsic (solute) defect dissociation [15].

CHLORIDES OF SODIUM AND OF HYDROGEN

The concentration range in which these solutes could be studied is limited by their much lower distribution coefficient and lower solubility limit [18] as compared to the corresponding fluorides. In contrast with the latter, the distribution coefficient is invariant with concentration in the range 5×10^{-6} N to 5×10^{-4} N (initial liquid solution concentrations). For 42 columns (half each of HCl and NaCl) we obtained $(3.2 \pm 0.2) \times 10^{-3}$. There was no significant difference between the two chlorides investigated here (Fig. 1).

Discussion.- The lower distribution coefficient and its lack of concentration dependence suggest that lattice interaction of chloride is different from that of corresponding fluorides. Conductivity and dielectric relaxation measurements of fluoride and chloride-doped ice indicate, however, similar responses of both types of impurity when comparing the same concentrations in ice [19]. This is a paradox in need of explanation. Lack of a significant difference between distribution coefficients of HCl and NaCl (the second of these solutes being subject to preferential cation rejection) tends to support a model according to which the electrical interface charge is distributed over an appreciable thickness (≤1 mm) [20]. In this case, the electrical work required to transfer a majority ion (chloride) across the phase boundary is small.

AMMONIUM FLUORIDE

The distribution coefficient is about 0.1 and roughly invariant in the concentration range 10^{-5} N to 10^{-3} N [9]. This result contradicts earlier findings [13]. At 1×10^{-6} N, however, fluoride concentration in ice dropped below the detectability limit. This effect, totally unexpected, raises the question of what are the solute species actually going into the solid phase. Adding 2×10^{-6} N NaOH (a species practically insoluble in ice) brought the distribution coefficient back up. This increases the theoretical liquid-solution pH (at 0 °C) from somewhere between 6.92 and 7.46 to above 9 (Fig. 2). The effect of this pH change on fluoride dissociation is minor but the ammonium equilibrium is shifted appreciably to a higher proportion of undissociated NH_3.

Discussion.- When ammonium fluoride is incorporated into the ice lattice, the fluoride (present as HF) is in slight excess [7]. It is proposed that cooperative incorporation of NH_3, a polar molecule and D-defect donor, relieves residual lattice strain, perhaps because it neutralizes the L-defect of HF. To verify this hypothesis, precision measurements of both fluoride and ammonium at concentrations in the ppb range, in the melted ice, are required. Such measurements have become possible with suppressor-equipped liquid ion chromatography and are being initiated in our laboratory.

These results suggest that the concentration of certain trace impurities in ice may be controlled not only by their own concentration in the liquid (or vapor) phase but also by the presence of other impurities.

ANTIFREEZE GLYCOPROTEIN

AFGP [21] is the most highly soluble of known solutes in ice. Mixtures of average molecular weight 15,000 had shown distribution coefficients of about 0.8. These results had been obtained with relatively high concentrations (5 kg/m^3) in small (10^{-6} m^3) and highly supercooled sample volumes. Our aim was to measure the distribution coefficient for similar AFGP mixture in very dilute solution (8 to 20 x 10^{-3} kg/m^3), solidified under quasi-equilibrium conditions at small supercooling. The effect of such trace amounts of AFGP on interfacial redistribution of solutes HCl and NaF was to be investigated because even at such low concentrations remarkable effects on crystal growth habits, *i.e.*, unusual crystallographic forms, have been reported [22]. Such kinetic effects are known to cause enrichment of solute impurities in faceted regions of many crystals [23].

An effective distribution coefficient was computed for each ice column by combining the volume-weighted AFGP concentrations of n ice slices and dividing the weighted average by the concentration of supernatant liquid, or

$$k_{eff} = \frac{\sum^{n} (V_i C_{Si}) \,/\, \sum^{n} V_i}{C_{L_{super}}}$$

For ice columns grown with the solution being stirred or unstirred during growth, the distribution coefficient of AFGP was 0.8 ± 0.2, *i.e.*, close to the figures reported in the literature. No effect was observed on the distribution coefficient of 2 x 10^{-5} N NaF but unstirred solutions of 5 x 10^{-5} N HCl showed a doubling of the distribution coefficient when 0, 7.9 and 19.6 x 10^{-3} kg/m^3 AFGP, respectively, were added to the freezing solution (Fig. 3).

Discussion.- The equilibrium distribution coefficient of AFGP appears to be broadly invariant in the temperature range 0 °C to -2 °C. It is independent of concentration over a range of almost three orders of magnitude. The effect of trace amounts of AFGP on the interfacial redistribution of fluoride and chloride is seen as an effect of interfacial instability rather than of crystal-kinetic effects. Adsorption of AFGP molecules at the ice surface introduced instability in the thermal and solute diffusion fields, even though only an estimated 0.003% of interface area was covered by AFGP molecules. These effects were more pronounced for the chloride because the boundary layer concentration is at least 10 times higher than for a fluoride solution of same concentration. Stirring erased the instability.

CONCLUSIONS

The quasi-equilibrium distribution coefficient of NaF in ice is strongly concentration dependent. This is attributed to thermodynamically non-ideal interactions of the solute with the ice lattice (point defects, bond-shortening,

dislocations). By contrast, no concentration dependence has been found for HCl and NaCl whose distribution coefficient is up to two orders of magnitude smaller. Yet the static conductivity and dielectric relaxation spectra for these solutes (fluoride and chloride) are broadly identical and show the same concentration dependence indicating similar effects on electrically active point-defect distributions.

Ammonium fluoride in 10^{-6} N solution shows a pH dependent distribution coefficient. The pH dependence is tentatively attributed to a lattice-strain reducing role of the polar molecule NH_3.

Effects of AFGP on redistribution of HCl and NaF in these experiments are attributed to interface-kinetic rather than crystal-growth kinetic factors.

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COMMENTS

T. KURODA

The concentration of antifreeze glycoprotein at ice/solution interface is extremely small. Nevertherless can such small amount of AFGP inhibit the growth of ice ?

Answer :

Actually, what has been observed at these low concentrations is not so much an inhibition of the overall growth velocity than second-order effects on the growth kinetics, such as development of unusual crystal faces (Knight et al. loc. cit.) or interface roughening (as infered from the results of this paper).

J.M. WARMAN

I was wondering if you had looked at the dielectric properties of the ice samples grown from the glycoprotein solutions.

Answer :

No yet. We hope to do this in the future.