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The Segregation of Sodium Ions in KCl Minute Crystals

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The surface accumulation of solute sodium ions in KCl crystallites was measured as a function of the annealing temperature, 250—450 °C. The minute crystals were baked out under 3×10^{-7} Torr, and their surface layers were dissolved successively with anhydrous ethyl alcohol. The contents of sodium and potassium were determined by instrumental neutron-activation analysis with the aid of a 50 cc-Ge(Li)-4K gamma spectrometer.

In a solid solution of ionic crystals with a common anion, quantitative measurements of the distribution coefficients of cations between the surface and the bulk are of interest in relation to the surface distortion[1)] and the surface reactivity of the solids.[2,3)] However, few experimental works have been reported even for such a simple system as alkali chloride, ACl/BCl. Kummer and his co-workers investigated the system of the Ca impurity in NaCl minute crystals[4)] by the dissolution method using acetone, and that of Cs in KCl minute crystals by isotopic exchange techniques[5)] using an acetone-solution/KCl-solid system. In these works, their attention was principally in the first surface layer of crystals in connection with the surface reactivity. According to the gas/solid-isotopic exchange reaction studied by the present authors[2,3)] and theoretical works by Benson *et al.*,[1)] the structure and properties of the surface change gradually in the range from the first layer to the fifth. With this in view, the present paper will study the accumulation of the sodium impurity in the surface layers of KCl crystals. The solubility of NaCl in KCl is rather high,[6)] for they have the same type of structure. This situation differs very much from that in the previously studied systems.[4,5)]

Experimental

Materials and Procedure. The KCl (Merck reagent, item No. 4933) used as a starting material contains 2.4 ppm of an Na impurity, as determined by radio-activation analysis. The precipitates of KCl, doped with Na amounting to 300—900 ppm, were prepared by a modified Marshall method.[7)] The precipitates were washed twice with fresh ethanol. After the supernatant ethanol phase had been replaced completely with ethyl ether, the precipitates were transferred, together with ether, into a vessel connected to a vacuum system. Both the ethanol and ethyl ether used were dehydrated with CaO baked at 1100 °C for 12 hr and then distilled *in situ.* The precipitates were carefully dehydrated and degassed by baking then in a vacuum, 3×10^{-7} Torr. The baking temperature was raised, step by step, to 450 °C over a 140 hr period and then kept at that temperature for 48 hr. The crystallites thus obtained had a surface area of about 1.5 m^2/g, as determined by krypton adsorption at 77 K and electronmicrography showed that the faces exposed were the {100} planes as well as the crystallites used by Kummer *et al.*[5)]

After pretreatment at 450 °C, the crystallites were annealed at a temperature between 250 and 450 °C for 48 hr at 3×10^{-7} Torr in order to establish the equilibrium distribution of the impurity at that temperature. Then, the surface regions of the crystals were dissolved successively with a small amount of anhydrous ethanol under atmospheric pressure. The solubility of NaCl in absolute ethanol at 20 °C is 1.149 mg/ml,[8)] while that of KCl is 1.1624 mg/ml.[9)] Because of these small solubilities, it is usually possible to remove several monolayers of the crystal surfaces in a batch-by-batch fractionation. The amounts of Na and K in each fraction were determined as follows. The alcoholic sample solution was irradiated with thermal neutrons, amounting to 1.08×10^{16} n/cm^2, by means of the TRIGA II reactor of Rikkyo University. The gamma rays of 1524.7 keV from ^{42}K and 1368.4 and 2753.6 keV from ^{24}Na in the samples concerned were measured by the use of a 50 cc-Ge(Li)-4K gamma spectrometer.

Results and Discussion

Figure 1 illustrates the relationship between the surface accumulation of sodium and the layer number as a function of the sodium concentration in the crystals. The sodium concentration in the surface region is very high as compared with that in the bulk, but far lower than the solubility limit, judging from the phase diagram of the NaCl/KCl solid solution.[6,10)] Let us define the accumulation coefficient, $C_A(n)$, by the quantity $([\mathrm{Na}]/[\mathrm{K}])_n/([\mathrm{Na}]/[\mathrm{K}])_{\mathrm{bulk}}$, where n designates

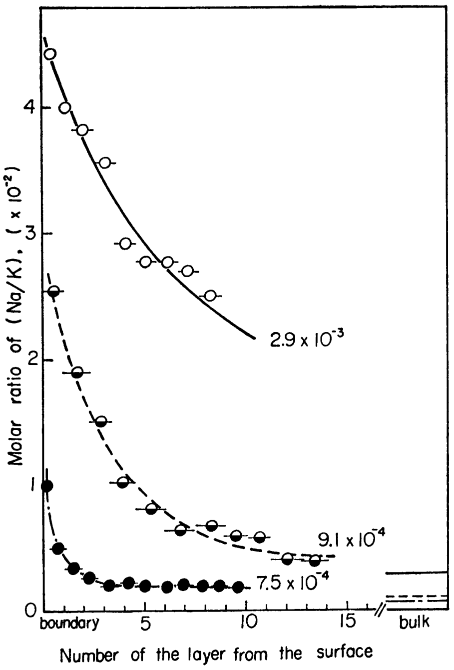

Fig. 1. The concentration dependence of the surface accumulation of sodium in potassium chloride crystallites at 300 °C.

○, ◒ and ● for the molar ratio of (Na/K) = 2.9×10^{-3}, 9.1×10^{-4} and 7.5×10^{-4}, respectively.

the numbering of the layer from the surface. Then, $C_A(n)$ may be independent of $([Na]/[K])_{bulk}$ as long as the impurity concentration is very low and far from the solubility limit. The present data may, then, be interpreted under these conditions. Figure 2 shows a typical profile of $C_A(n)$ as a function of the annealing temperature. The curves seem to converge to unity, but the rate of convergence is very low, *i.e.*, about 1/3—1/4 times that expected from the isotopic exchang reaction between chlorine gas and alkali chloride crystals.[2,3] This discrepancy may be attributed to the fact that the process of surface dissolution cannot be so well controlled as to remove strictly the specified *n*-th layer from various crystallites. The surface accumulation increases with the rise of the temperature. The value of C_A (1) is determined from the smoothed curve in Fig. 2, and its logarithms are plotted against the reciprocal of the temperature in Fig. 3. We obtain a straight line, though the figure shows some scatter of points. If an equilibrium is established, the slope of the line gives, as the enthalpy difference, ΔH, and the intercept of the coordinate at $1/T=0$ gives the entropy difference, ΔS, when sodium atoms segregate into the first layer from the bulk. We obtain $\Delta H=4.9\pm1.0$ kcal/mol and $\Delta S=13\pm1.6$ e.u. The values for both ΔH and ΔS are considerably large compared with the values predicted from the thermodynamic data of the NaCl/KCl solid solution.[6] These values cannot be explained on the basis of simple statistical thermodynamics; further detailed studies of various samples is, therefore, desired.

Next, let us discuss the rate of the eluilibriation of the impurity distribution in minute crystals of alkali chloride. According to Kummer *et al.*,[4,5] it takes longer than thirty hours to eliminate step-dislocation on the surface of KCl crystallites doped with cesium at 600 °C.[5] On the other hand, Voss *et al.*[11] proposed that the equilibrium was easily established in the system of NaCl/KCl minute crystals, even while cooling the crystals from 350 °C to room temperature. The present results support the idea that it takes a long time to attain an equilibrium distribution of the Na^+ impurity. If the latter view is true, the two curves referred to 300 and 450 °C in Fig. 2 may be reduced to the same curve.

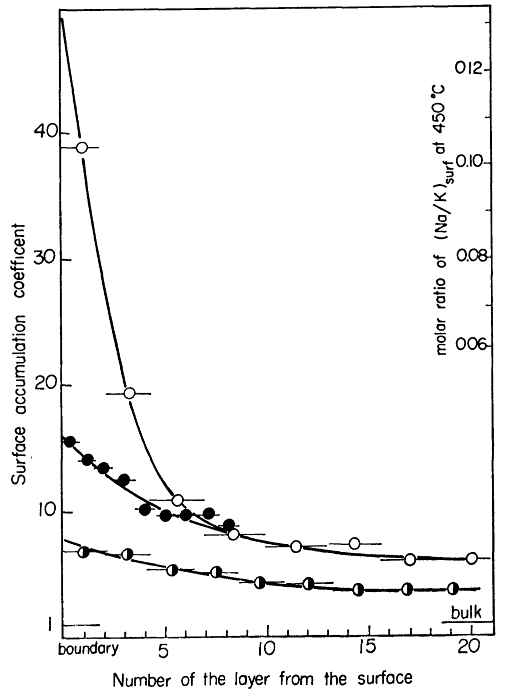

Fig. 2. The temperature dependence of the surface accumulation coefficients of sodium in potassium chloride crystallites.

○, 450 °C, 24 hr; ●, 300 °C, 24 hr and ◑, 250 °C, 48 hr.

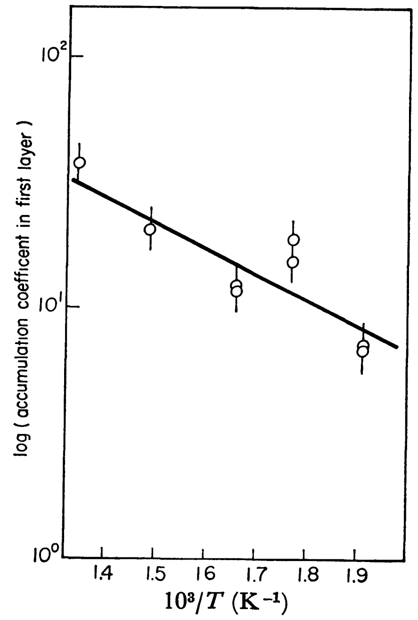

Fig. 3. Arrhenius plots of the accumulation coefficient of the surface first layer.

Finally, we must discuss the phase separation, fissures, and dislocation, the existence of which makes the analysis of the results complex. According to Barret *et al.*[6] and Tichelaar,[10] no macroscopic-phase separation takes place in the concentration range of sodium used at 250—450 °C. Even if a minute amount of NaCl crystals arises on the surface of KCl crystals during the preparation of the precipitates, it is considered that the NaCl phase is dissolved and removed by ethanol washing, as has been mentioned before. This results from the solubilities of the chlorides concerned in ethanol.[8,9] On the other hand, if crystals contain fissures and dislocations, the impurity accumulates along them as well as on the surface region; furthermore, these regions are selectively etched. Thus, fissures and dislocations remarkably disturb the study of the surface accumulation of impurities if their density is high. The present authors believe that the influence of fissures and dislocations in KCl minute crystals disapper upon the pre-baking treatment used in the present experiment. This view is supported by a comparison between the self-diffusion of Cl^- ions in large NaCl single crystals reported by Morrison *et al.*[12] and that in minute crystals reported earlier by the present authors.[3] Consequently, it can safely be concluded that the present results are a connected with the surface accumulation of impurities.

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