Dissolution equilibria of arsenic pentafluoride in anhydrous hydrogen fluoride

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Abstract

Dissolution equilibria of arsenic pentafluoride in anhydrous hydrogen fluoride have been quantitatively examined by measuring the scattering intensity of the Raman spectra of the corresponding species in the solution at ambient conditions. For the superacid formation reaction, $2HF + AsF_5 \rightleftharpoons H_2F^+ + AsF_6^-$, $K_1 \ (= [H_2F^+][AsF_6^-]/[HF]^2[AsF_5])$ has been determined to be $\sim 2 \times 10^{-5} \ mol^{-1} \ kg$, and dinucleation reaction of the anion, $AsF_6^- + AsF_5 \rightleftharpoons As_2F_{11}^-$, $K_2 \ (= [As_2F_{11}^-]/[AsF_6^-][AsF_5])$ to be $\sim 8 \times 10^{-1} \ mol^{-1} \ kg$, respectively.
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1. Introduction

Lewis acidity and complex formation have been studied on many fluoroacids in anhydrous hydrogen fluoride (HF) superacid systems [1]. Among them, the most systematically studied from early times is the SbF_5–HF system [2,3]. By the conductivity and ^{19}F-NMR measurements, Gillespie and his co-workers found the dissolution of SbF_5 occurred in the following manner (Eqs. (1) and (2)) and succeeded to explain the decrease of the conductivity by the formation of fluorine-bridged polynucleus anions with low-mobility [3].

$$2HF + SbF_5 \rightleftharpoons H_2F^+ + SbF_6^- \tag{1}$$

$$SbF_6^- + nSbF_5 \rightleftharpoons Sb_{n+1}F_{5n+6}^- \tag{2}$$
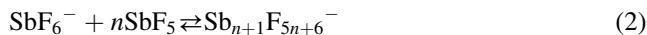
Concerning AsF_5–HF system, they found again by the conductivity measurement at $-83.6°C$, that the formation of the dinucleus anion was dominant in HF even at a low-concentration [4].

$$2HF + 2AsF_5 \rightleftharpoons H_2F^+ + As_2F_{11}^- \tag{3}$$
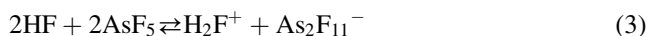
O'Donnell and his co-workers measured the conductivity and Raman spectra of AsF_5–HF system at and near room temperature [1,4]. They found significant amount of molecular AsF_5 in addition to AsF_6^- and $As_2F_{11}^-$ in the solution, the concentration of the last species being increased at the expense of the former two along with the reduction of temperature.

$$2HF + AsF_5 \rightleftharpoons H_2F^+ + AsF_6^- \tag{4}$$

$$AsF_6^- + AsF_5 \rightleftharpoons As_2F_{11}^- \tag{5}$$
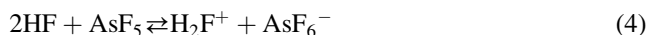
The aim of the present study is to give a quantitative view to the dissolution equilibiria of AsF_5 in HF observed by the previous workers described above.

2. Experimental

2.1. Reagents

AsF_5 was prepared by reacting elemental arsenic (Nacalai Tesque, purity 99%) and fluorine (Daikin Industries Ltd., purity 99.7%) in a Monel metal reaction vessel, and then purified by trap-to-trap distillation. Impurities such as AsF_3 were not detected by IR spectroscopy of the sample gas (0.01 MPa) introduced in a gas cell with AgCl windows. KF (Nacalai Tesque, purity 98%) was vacuum-dried at 200°C. HF (Daikin industries Ltd., purity 99% or more) was dried over K_2NiF_6 (Ozark-Mahoning) to remove trace of water. $KAsF_6$ was prepared by the reaction of KF with excess AsF_5 in HF. The X-ray powder diffraction or IR spectroscopy of the dried sample did not detect impurities such as KF·nHF.

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2.2. Analyses

An FEP tube with an outer diameter of 9.5 mm and a wall thickness of 1.3 mm was used for a sample cell. The tube was equipped with a Whitey valve made of PFA. A Kel-F tube was occasionally substituted for it to avoid the overlap of the peaks of the samples and those from the container. The volatile materials were transferred to the tube by condensation through a metal vacuum line. The amount of the material was mainly determined by weighing the tube disconnected from the line. The Raman spectra were obtained with the aid of FTS-175C FT Raman spectrometer (Bio-Rad) using a Nd-YAG laser (1064 nm). The laser power was 1200 mW, and the resolution was 4 cm^{-1}. An intermittent irradiation was made in order to keep the ambient temperature of the sample during the data collection of 256 times.

3. Results and discussion

Since the Raman spectroscopy measures a part of the light scattered from the sample, quantitative measurements are generally not easy. If the scattering is isotropic, the strength of the light is expressed by the following equation [5]:

$$I \propto I_0 T(v) v^4 A(v)^{-1} \alpha(v)^2 c \qquad (6)$$

where I, and I_0 are strength of the scattered and incident beam, respectively. T the transmittance of the spectrometer, A the absorption strength of the sample, and α the polarizability related to the Raman scattering are the functions of the Raman shift and v the frequency. This equation implies that the strength of the scattered light from the sample is proportional to the concentration, c, if the other conditions are fixed. Examples of quantitative analyses are found in the literatures [6]. This technique is advantageous for the measurements of the samples that must be kept in an air-tight fluoropolymer tube with a valve, following the change in the concentration of the species in the solution.

Figs. 1 and 2 show the Raman spectra of AsF$_5$–HF solution in an FEP and a Kel-F tube, respectively with the comparison of those of the container without the sample. The peaks were found at 685, 704, and 733 cm^{-1}, ascribed to AsF$_6^-$ (O_h, $v1$), As$_2$F$_{11}^-$, and AsF$_5$ (D_{3h}, $v1$), respectively [5]. It was necessary to use both FEP and Kel-F tubes since the former gave a peak at 731 cm^{-1} which overlapped with that of AsF$_5$, and the peak from the latter at 668 cm^{-1} overlapped with that of AsF$_6^-$, respectively.

Raman spectrum of KAsF$_6$–HF solution gave only the AsF$_6^-$ peak at the same wavenumber found for AsF$_5$–HF solution.

$$KAsF_6 \rightarrow K^+ + AsF_6^- \qquad (7)$$

Fig. 3 shows the relative Raman intensity against the dose of AsF$_6^-$ in HF. Although, the intensity is usually normalized
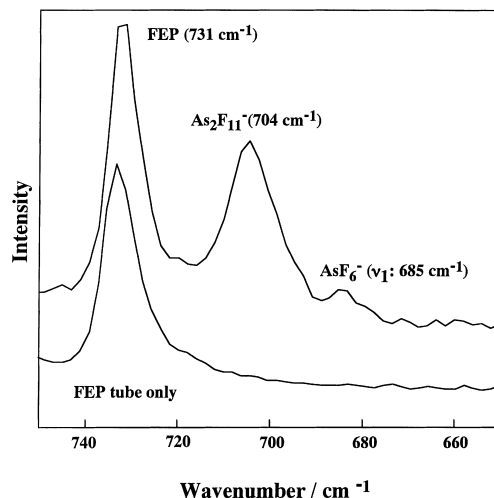

Fig. 1. Raman spectrum of AsF$_5$–HF solution (2.5 mol kg^{-1}) in an FEP container.

by the internal standard dissolved in the solution in the experiment of this kind, it was difficult to find a suitable standard soluble in the sample solution without affecting the chemical equilibrium. Therefore, normalization of the intensity was made by using that from the container. A linear relation is observed in the concentration range of lower than 0.1 mol kg^{-1} HF. From the saturation of the intensity, the solubility of KAsF$_6$ in HF is determined to be 0.095 mol kg^{-1} HF (2.1 g in 100 g HF). Dissolution equilibrium was achieved by stirring the solution by a magnetic stirrer for 20–30 min at room temperature, which was monitored by the change of the peak intensity after KAsF$_6$ powder was introduced in HF.

The calibration line for As$_2$F$_{11}^-$ is more difficult to obtain because there is no stable As$_2$F$_{11}^-$ salts at room temperature and the concentration cannot be fixed due to the shift of equilibrium according to Eq. (5) which occurs after dissolving the salts in HF. In the present study, we determined the
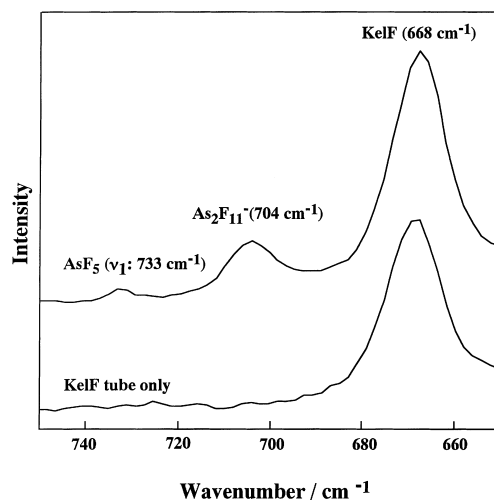

Fig. 2. Raman spectrum of AsF$_5$–HF solution (2.5 mol kg^{-1}) in a Kel-F container.
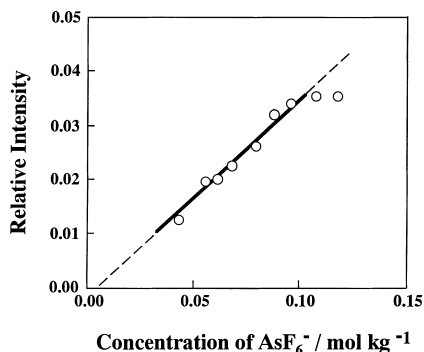
Fig. 3. Raman intensity against the concentration of $As_2F_6^-$ in HF.

concentration of $As_2F_{11}^-$ in the following manner, dissolving known amount of $KAsF_6$ and AsF_5 to HF.

$$KAsF_6 \rightarrow K^+ + AsF_6^- \qquad (7)$$

$$2HF + AsF_5 \rightleftarrows H_2F^+ + AsF_6^- \qquad (4)$$

$$AsF_6^- + AsF_5 \rightleftarrows As_2F_{11}^- \qquad (5)$$

Here, the initial concentrations of AsF_6^- and AsF_5 are known. The concentration of $As_2F_{11}^-$ cannot be determined directly at equilibrium state. However, now we are able to determine the concentration of AsF_6^- at equilibrium state by measuring the Raman intensity with the aid of the calibration line obtained above. The concentration of $As_2F_{11}^-$ at equilibrium state was approximated to be a difference of AsF_6^- concentration at initial and equilibrium state. This approximation is based on an assumption that the formation of AsF_6^- by the reaction (4) is negligibly small compared with that formed by the dissociation of $KAsF_6$ in HF (7). In order to satisfy this condition, the initial amount of AsF_5 to be dissolved in HF was controlled to be as small as possible. Fig. 4 shows the relative Raman intensity of $As_2F_{11}^-$ peak against the estimated concentration of $As_2F_{11}^-$ obtained by changing the initial concentration of AsF_5 and AsF_6^- in HF. Proportionality between the intensity and the concentration was again observed although the deviation was larger. The amount of $As_2F_{11}^-$ was determined as a decrease of AsF_6^- from the initial concentration. The maximum concentration examined is 0.055 mol kg^{-1} HF. This is because the dose of
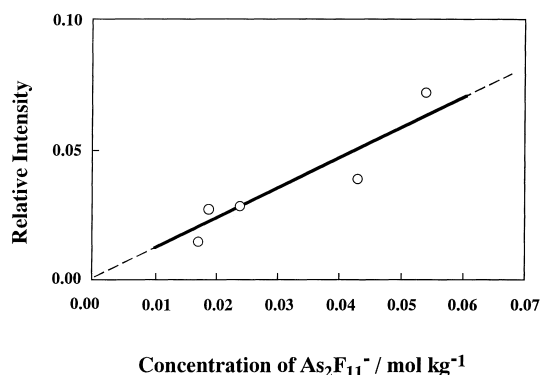
AsF_5 was minimized in order to fulfill the requirement described above. When the initial concentration of AsF_5 significantly exceeded 0.5 mol kg^{-1} HF, such an approximation for the concentration of $As_2F_{11}^-$ was not appropriate anymore.

Thus, the proportionality was confirmed between the relative Raman intensity and the concentration of AsF_6^- and $As_2F_{11}^-$. Determination of the concentration of these fluoroarsenate species in HF was made assuming this proportionality is valid even at higher concentration region.

The concentration of AsF_5 was determined by subtracting the concentrations of AsF_6^- and $As_2F_{11}^-$ from the initial concentration of AsF_5. The charge neutrality expressed by the following equation gives the concentration of H_2F^+.

$$[H_2F^+] = [AsF_6^-] + [As_2F_{11}^-] \ (mol \ kg^{-1} \ HF) \qquad (8)$$

The concentration of HF, [HF] is 50 mol kg^{-1} by definition.

The concentrations of AsF_5, AsF_6^- and $As_2F_{11}^-$ were determined changing the initial concentration of AsF_5. Checking the total pressure and IR spectrum of the gas above the solution, the initial concentration was adjusted so that the amount of AsF_5 in the vapor negligibly small compared to that dissolved in the solution. From the average, equilibrium constants for the superacid formation reaction (4), $K_1 = [H_2F^+][AsF_6^-]/[HF]^2[AsF_5]$ and dinucleation reaction of the anion (5), $K_2 = [As_2F_{11}^-]/[AsF_5][AsF_6^-]$ were determined to be $\sim 2 \times 10^{-5}$ and $\sim 8 \times 10^{-1}$ mol^{-1} kg, respectively. Using these values, concentration changes of these species in HF were evaluated as a function of the initial AsF_5 concentration, in other words, the doze of it in HF (Figs. 5 and 6). As shown in Fig. 5, AsF_5 is estimated to be dominant in HF at room temperature above the AsF_5 doze of more than 0.1 mol kg^{-1} HF, which agrees with the result obtained by O'Donnell et al. [7]. However, AsF_6^- becomes
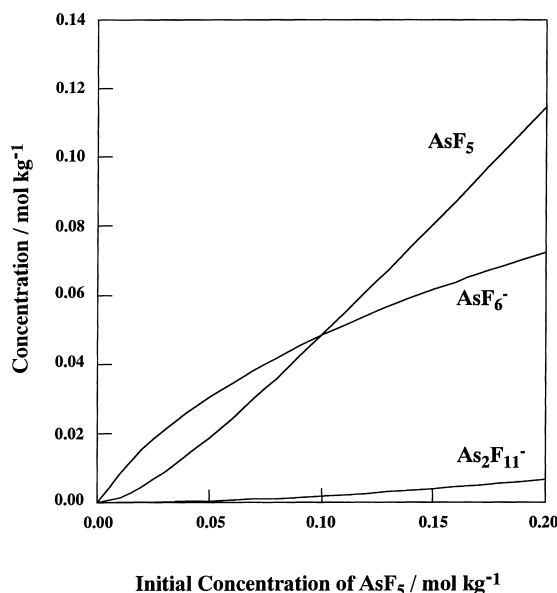

Fig. 4. Raman intensity against the concentration of $As_2F_{11}^-$ in HF solution.

Fig. 5. Calculated concentration of AsF_5, AsF_6^- and $As_2F_{11}^-$ in HF solution. Initial concentration of AsF_5: 0.0–0.2 mol kg^{-1}.
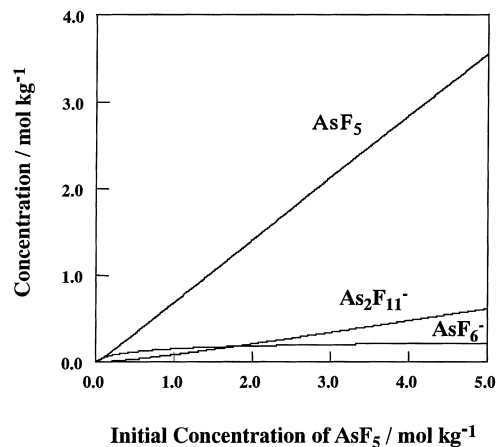
Fig. 6. Calculated concentration of AsF_5, AsF_6^- and $As_2F_{11}^-$ in HF solution. Initial concentration of AsF_5: 0.0–5.0 mol kg^{-1}.

the dominant species in the range of lower than 0.1 mol kg^{-1} HF, according to the equilibrium constants obtained above. The concentration of AsF_6^- exceeds that of $As_2F_{11}^-$, which is reversed above 1.8 mol kg^{-1} HF of initial doze of AsF_5 (Fig. 6). Unlike the case at low-temperatures such as $-83.9°C$ [4], $As_2F_{11}^-$ never becomes dominant species in HF at ambient temperature.

In the case of SbF_5–HF system, most of the antimony species exist in the form of SbF_6^- in the concentration range of lower than 6.2 mol kg^{-1} HF (11 mol%) [3]. SbF_6^- and $Sb_2F_{11}^-$ co-exist in the range of 6.2–14.1 mol kg^{-1} HF (11–22 mol%), concentration of the latter increasing with the increase of the SbF_5 doze. Above 14.1 mol kg^{-1} HF, complexes such as $Sb_3F_{16}^-$ are formed, whereas polynucleus anions other than $As_2F_{11}^-$ are not found in the case of AsF_5–HF system according to the Raman spectroscopy. This difference is considered to be due to the difference of the amount of free HF molecule in the solution. In the case of

SbF_5–HF system, most of the antimony species exist in the form of anion forming hydrogen bonding with HF. According to Gillespie et al. [3], almost no free HF molecules are present in the 6.2 mol kg^{-1} HF solution, HF being consumed by the formation of H_2F^+ and solvation to fluoroanimonate anions. However, in the case of AsF_5–HF system, the ionized arsenic species are much less, therefore the amount of free HF molecule is large. It is more advantageous for fluoroarsenate anion to be stabilized in the solution by forming hydrogen bonds with free HF molecules than forming polynucleus anions as in the case of SbF_5–HF system.

Acknowledgements

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