

# Use of the Unique Properties of Fluoropolymers in the Design of New, Highly Effective, Ecologically Friendly Technologies for the Fine Purification of Hydrogen Halides and Their Aqueous Solutions

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**ABSTRACT:** A number of properties of fluoropolymers in aqueous solutions of hydrogen halides were investigated. The results enable fluoropolymers to be used in the purification of hydrogen halides and their aqueous solutions. The hydrophobicity of fluoropolymers and their diffusion permeability enable production of hydrogen halides of low moisture content. A second unit for hydroionic convection is based on hydroionic repulsion (determined by the hydrophobic properties of the fluoropolymer) and ionic elimination. The two units enable the highly effective, ecologically safe manufacture of highly pure hydrogen halides and their aqueous solutions to be carried out with minimum feedstock, cooling water, and power consumption. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1383–1387, 2001

**Key words:** fluoropolymer; hydrogen halides; diffusion permeability; hydroionic convection; physicochemical

## INTRODUCTION

The modern industrial production of a wide range of high-purity hydrogen halides and their aqueous solutions is traditionally based on distillation in polytetrafluoroethylene (PTFE) equipment. These processes have limited potential for satisfying demand and have resulted in their being made a target for product purity and ecologically safe production. This is due, in particular, to the elimination of a contaminated finely dispersed liquid phase by steam<sup>1</sup> and to the diffusion of hydrogen halides through the equipment walls

and housing.<sup>2</sup> In addition, existing manufacturing methods are energy-intensive and expensive.

Attempts at minimizing the contaminating effect of drop elimination by using slow evaporation does not give the desired effect of extensive purification of aqueous solutions due to the phenomenon of ionic elimination. Moreover, increasing within reasonable limits the thickness of the apparatus walls and housing had no positive effect in the case of contact with highly concentrated solutions of hydrogen halides. Thus, a wall material with appropriate physicochemical properties participates directly in the purification process, enhancing the effects mentioned above. An extensive study of the properties of "hydrogen halide fluoropolymer" systems led the present authors to the idea of using the above undesirable effects for

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the purposes of fine purification. Various analytical monitoring methods were used, notably emission spectra analysis using ICP conductively compiled plasma. The measurements were carried out at a purity level of a  $10^{-6}$ – $10^{-8}$  wt %. The experimental error was  $\pm 30\%$ .

## EXPERIMENTAL

The system upon which the new technology is based consists of a fine purification block containing two units: (1) diffusion permeability and (2) hydroionic convection. It must be emphasized that the system uses the physicochemical properties of hydrogen halides and of their aqueous solutions as well as those of the fluoropolymers. It is potentially highly effective (the target product purification is 1–2 orders of magnitude higher than with existing technology), ecologically safe (the concentrations of toxic substances in air and waste water are lower than the permissible limits), and nonintensive material (minimum feedstock, cooling water, and power consumption). The proposed technology has no analog in world practice. F-4MB is pure copolymer tetrafluoroethylene and hexafluoropylene.

## DIFFUSION PERMEABILITY UNIT

The use of diffusion permeability for the purposes of fine purification and drying of hydrogen halides required the replacement of PTFE by other materials that have a number of advantages. Quantitative estimation of the physicochemical stability in various “fluoropolymer–fluid” systems was first carried out by a technique proposed by Ryabchenko et al.<sup>3</sup>

Experimental data revealed that the fusible fluoropolymers F-4MB, F-50, and F-2M and unfusible F-4 have the best physicochemical stability in the given media. However, the use of fusible specimens has the advantage of enabling high-quality thin films to be prepared with a minimum number of structural defects.

At the same time, films of fusible fluoropolymer grades have rather low diffusion permeability, which complicates their use in fine purification.<sup>4,5</sup> Therefore, it was necessary to increase the diffusion permeability of the film to improve process efficiency.

It is known that diffusion permeability  $P_j$  is a product of the diffusion coefficient  $D$  and the max-

imum solubility  $C_s$  of the hydrogen halide in a layer of the fluoropolymer:

$$P_j = DC_s$$

A study was made of the dependence of diffusion on the process temperature and on the concentration of aqueous solutions of hydrogen halides. The diffusion coefficient changed with the temperature according to the Arrhenius law:

$$D_t = D_{t_0} \exp(\Delta A_a/RT)$$

where  $D_t$  and  $D_{t_0}$  are the diffusion coefficients for the two experimental temperatures, and  $\Delta A_a$ , the activation energy of the process in kcal. The dependence of  $D$  on the concentration of aqueous solutions of halogen hydrides can be ignored.

The investigation of the dependence of the maximum solubility  $C_s$  of the electrolyte in the fluoropolymer on the concentration of the solution of hydrogen halide  $C_e$  has resulted in its mathematical description as a hyperbola:

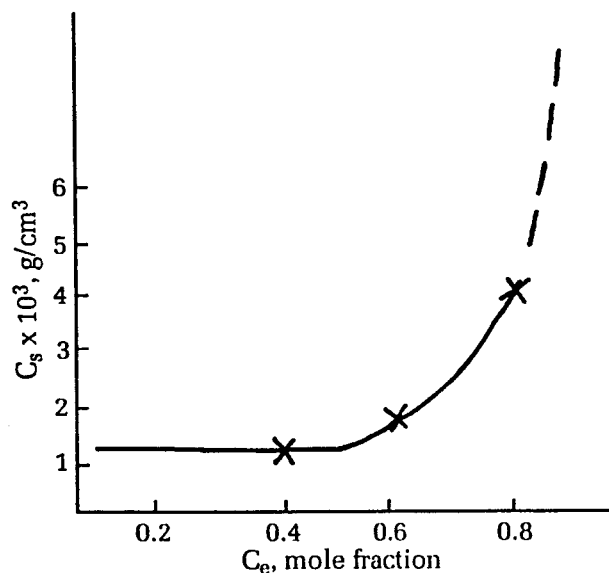
$$C_s = C_{sa} - (C_e - C_a)/(b - C_e)$$

where  $C_a$  is the concentration of the azeotropic “hydrogen halide–water” composition,  $C_{sa}$ , the solubility of the electrolyte in the fluoropolymer at the azeotropic concentration;  $b$ , the maximum concentration of moist halogen hydride; and  $C_e$ , the concentration of the halogen hydride under investigation. In practice, the values of  $b$  differ from unity by a 0.01–0.04 weight fraction of moisture.

The results for the case of an aqueous solution of a hydrogen fluoride–fluoropolymer F-4MB system are given in Figure 1. According to the experimental data, the temperature dependence of  $C_s$  can be ignored.

The permeability parameters in a “hydrofluoric acid–fluoropolymer F-4MB” system are given in Table I for various temperatures and initial concentrations. The experimental data in Table I reveal that a mathematical description of the effect of the temperature and the initial concentration,  $C_k$ , of the aqueous solution of hydrogen fluoride on the diffusion permeability through the fluoropolymer F-4MB is described by the equation

$$P_j(T, C_k) = P_j(T_0, C_a) \times C_{sa} \times 0.6/(0.95 - C_k) \exp \times [1.25E_a/R \times \Delta(1/T)]$$



**Figure 1** Dependence of hydrogen fluoride solubility  $C_s$  in layer of fluoropolymer F-4MB on concentration of initial solution  $C_e$ . Vertical axis:  $C_s \times 10^3$  (g/cm<sup>3</sup>); horizontal axis:  $C_e$  (mol fraction).

where  $\Delta(1/T) = 1/T_0 - 1/T$ . Similar results were obtained for other systems of the same type.

The phenomenon of the separation of aqueous solutions of hydrogen halides was observed during the study of the diffusion permeability. This is shown by a hydrogen halide concentration gradient, which increases toward the contacting fluoropolymer wall. The subsequent process was caused primarily by diffusion of anhydrous hydrogen halide as opposed to that of the aqueous phase (several orders of magnitude greater).

The above makes it possible to optimize the process in order to achieve the desired productivity of 10–30 t/year. The process requires diffusion elements with a sufficiently large surface area (up to 10 m<sup>2</sup>) and a minimum thickness of the mass exchange wall of 1–10  $\mu\text{m}$ .

## HYDROIONIC CONVECTION UNIT

The second component of the block for fine purification of an aqueous solution of hydrogen halide is the hydroionic convection unit. This is to provide fine purification of a thin film of a downflowing liquid, losing hydrogen halide by slow evaporation (without boiling). Elimination of hydrated microimpurity ions (hydroionic clusters) from the surface layer of the liquid film occurs at the same time. As previously shown, fine purification of the

aqueous solution of halogen hydride relies on two effects: ionic elimination from the surface of the fluid and hydroionic repulsion. Ionic elimination (ignoring hydroionic repulsion) depends on the ion hydration ( $\xi$ ) and the ion charge ( $\rho$ ).

A quantitative description of the effect can be carried out using an exponential function. The exponent will be proportional to the product  $\xi\rho$ . The proportionality constant lies within the range  $1-5 \times 10^{-2}$ . The effect of using ionic elimination for the purposes of fine purification of the fluid is insignificant; the degree of purification for hydrohalic acids varies from 0.1 to 0.3.

The effect of hydroionic repulsion naturally arising at contacts in a fluoropolymer aqueous HX system was employed to increase substantially the removal of ionic impurities. It is caused by the hydrophobic properties of the fluoropolymer surface and can be described by the equation

$$\psi = K_h(\delta)(1 + \cos \theta_k)/(1 + \cos \theta_{\text{water}})$$

where  $\psi$  is the hydroionic regulation;  $K_h(\delta)$ , the constant of hydroionic repulsion, which decreases significantly with distance  $\delta$  from the surface of the fluoropolymer;  $\theta_k$ , the degree of wetting of the fluoropolymer surface by the aqueous solution of halogen hydride (acid); and  $\theta_{\text{water}}$ , the degree of wetting of the fluoropolymer surface by water. In practice, the ratio  $(1 + \cos \theta_k)/(1 + \cos \theta_{\text{water}})$  varies from 2 to 4.

Preliminary research revealed that the wetting of various structural fluoropolymers by aqueous solutions of the same hydrogen halide is similar (it differs by  $\pm 10\%$ , which does not exceed the experimental error). If the experimental conditions ensure that the value of  $K_h(\delta)$  is close to

**Table I** Influence of Electrolyte Temperature and Concentration on Diffusion Permeability Coefficient  $P_j$  (g cm<sup>-1</sup> s<sup>-1</sup>) in Hydrofluoric Acid-Fluoropolymer F-4MB System

$C_{\text{HF}}$ (Mol Fraction)	$P_j \times 10^{15}$ at 23°C	$P_j \times 10^{14}$ at 70°C	$P_j \times 10^{13}$ at 100°C
0.4	3.0	1.2	2.4
0.5	5.4	1.6	4.2
0.6	6.8	1.7	5.4
0.7	9.7	2.4	6.6
0.8	16.4	4.0	13.0
0.85	24.4	6.3	13.4
0.9	48.8	12.0	14.4

**Table II** Dependence of  $\psi$  on  $\theta_k$  for Various Concentrations of Aqueous Solutions of Hydrofluoride at  $\delta = 150 \mu\text{m}$ 

$C_k$ (Mol Fraction)	0.4	0.6	0.8	0.95
$\theta_k$	81	72	68	53
$\psi$	2.8	3.2	3.3	3.9

unity at a liquid film thickness of 100–200  $\mu\text{m}$ , then  $\psi = (1 + \cos \theta_k)/(1 + \cos \theta_{\text{water}})$ . The dependence of hydroionic repulsion  $\psi$  on the degree of wetting  $\theta_k$  for various concentrations of aqueous solutions of fluoropolymers is given in Table II.

The overall effect of hydroionic convection in the fine purification of an “aqueous solution of the hydrogen fluoride–fluoropolymer F-4MB” system at the specific liquid film thickness is described as

$$\lg(C_{g0}/C_g) = 1/2.3[(1-5) \times 10^{-2} \xi \rho + (1 + \cos \theta_k)/(1 + \cos \theta_{\text{water}})]$$

where  $\lg(C_{g0}/C_g)$  is the degree of purification of the aqueous solution of halogen hydride by hydroionic convection;  $C_{g0}$ , the average concentration of the impurity in the initial hydrohalic acid; and  $C_g$ , the average concentration of the impurity in the purified acid.

The proposed term “average impurity” ( $N_g$ ) implies the average sum of the 10 most strictly limited microimpurities—Ca, Mg, Na, Fe, Mn, Cr, Ni, Si, Al, and Co:

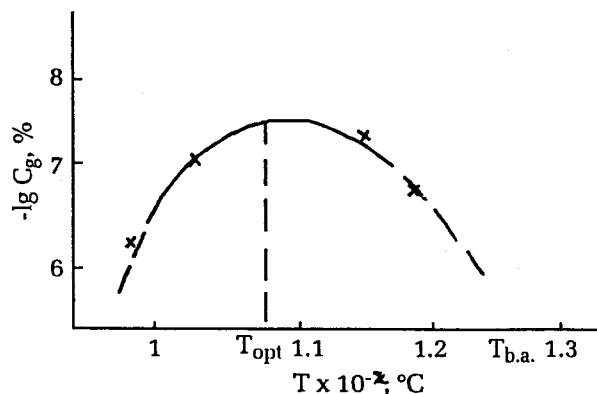
$$C_g = 1/x \sum_{i=1}^n C_i$$

where  $x$  is the amount of limited impurities, and  $i$ , the index of the impurity.

Usually, only aqueous solutions of hydrohalic acids with a concentration  $C_{g0}$  within the range  $10^{-6}$ – $10^{-8}$  wt % (or  $10^{-8}$ – $10^{-10}$  weight fraction) undergo fine purification at the final stages. It was shown that a similar dependence exists for other hydrohalic acids:

$$\lg(C_{g0}/C_g) = 1/2.3[K_{i,e} \xi \rho + (1 + \cos \theta_k)/(1 + \cos \theta_{\text{water}})]$$

where  $K_{i,e}$  is the constant of ionic elimination.

**Figure 2** Dependence of concentration of ionic impurity  $-\lg C_g$  in purified solution of hydrobromic acid of azeotropic nature on process temperature. Vertical axis:  $-\lg C_g$  (%); horizontal axis:  $t \times 10^{-2}$  ( $^{\circ}\text{C}$ ).

The value of  $K_h(\delta)$  does not depend significantly on the liquid film thickness  $\delta$  up to 100  $\mu\text{m}$  [ $K_h(\delta) = 1$ ]. An increase in the liquid film thickness above 100  $\mu\text{m}$  results in a sharp weakening of hydroionic repulsion, that is, to a substantial reduction in  $K_h(\delta)$  [ $K_h(\delta) \leq 1$ ].

The overall effect of hydroionic convection was quantitatively evaluated by correlating the equilibrium concentrations of contaminating ions in the initial solution with their concentration in the solution after fine purification. This effect was investigated for a fixed area of evaporation ( $10^5 \text{ cm}^2$ ) at the optimum evaporation temperature of ionic clusters for various acids. Experimental results revealed that the degree of purification for various solutions of halogen hydrides and fluoropolymers varies from 1 to 1.5.

The dependence of the concentration of ionic microimpurities in a purified solution of hydrobromic acid at an azeotropic composition on the process temperature is shown in Figure 2. The optimum process temperatures for aqueous solutions of halogen hydrides at azeotropic compositions are given in Table III.

**Table III** Optimal Temperatures of the Process for Azeotropic Aqueous Solutions of Halogen Hydrides at Azeotropic Composition

$t$ ( $^{\circ}\text{C}$ )	2HF* 3H <sub>2</sub> O	HCl* 8H <sub>2</sub> O	HBr* 6H <sub>2</sub> O	HI* 5H <sub>2</sub> O
$\Delta t$ ( $^{\circ}\text{C}$ )	11.4	8.6	26.0	27.0
$t_{\text{opt}}$ ( $^{\circ}\text{C}$ )	103	102	108	108

The generalized results of the research showed that the optimum temperatures  $t_{\text{opt}}$  (°C) for all hydrohalic acids can be approximated by the following equation:

$$t_{\text{opt}} = 100 + 0.3\Delta t$$

where  $\Delta t = t_{\text{b.a.}} - t_{\text{b.w.}}$  ( $t_{\text{b.a.}}$  is the boiling point of the azeotropic solution of halogen hydride, °C;  $t_{\text{b.w.}}$  is the boiling point of water, °C).

Increasing the process temperature to the optimum results in an increase in the degree of purification. Further increase in the temperature leads to a sharp decrease in the degree of purification on account of the degradation of the hydroionic clusters and unproductive elimination of water.

The dimensions of the hydroionic convection devices were determined on the basis of experimental results. The results obtained in this research were used in the design of effective equipment for a unit operating by hydroionic convection.

The units of the block for the fine purification of hydrohalic acids (based on the use of physicochemical effects in "structural fluoropolymer-aqueous solution of halogen hydride" systems) should be complemented by a number of other units; for example, a unit for microfiltration (to remove heterogeneous impurities—microparticles), a unit for absorption (for preparation of aqueous solutions of acids of the given concentration), and other units to complete the process.

The role of the transport unit, consisting of a composite container with an internal layer prepared from a fluoropolymer, for the storage and delivery of highly pure products to the consumer, should be pointed out.<sup>6</sup> In accordance with the results of the carried-out investigations, it is declared that fluoropolymers may be used both as constructive materials and as an active component of the deep purification processes of hydrohalogens and corresponding water solutions. An enormous increase of the purification process efficiency is observed. Thus, the use of fluoropolymers in technology for the fine purification of hydrohalic acids has made it possible to develop highly effective, ecologically friendly technologies with minimum feedstock, cooling water, and power consumption that meet all modern requirements.

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