Solvent-Jump Relaxation Kinetic and Equilibrium Studies of the Reaction of NOCI with n-BuOH¹

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The kinetics and mechanism of the reaction between NOCl and *n*-BuOH is investigated at 5 and 22 °C in CCl_4 -HOAc mixtures, ranging from pure CCl_4 to 75% v/v HOAc. In the solvent mixtures, the use of the solvent-jump relaxation method is demonstrated on this reaction which is insensitive to concentration-jump but is perturbable by a sudden change of the reaction medium. The experimental relaxation amplitudes are in agreement with the ones calculated theoretically, and the ratios of the rate constants k_1/k_{-1} agree with the equilibrium constants K determined photometrically. The variation of the thermodynamic and activation parameters is discussed as a function of solvent composition.

Introduction

Although nitrosyl chloride NOCl is one of the strongest oxidizing agents, the kinetics of its reactions in solution has not been studied extensively.² As an intermediate, NOCl has been shown to be an important N-nitrosating agent in the diazotization of primary aromatic amines in aqueous³ and methanolic⁴ solutions, as well as in methanol-carbon tetrachloride mixtures.⁵

In the present paper we report solvent-jump relaxation kinetic, relaxation amplitude, and equilibrium spectrophotometric studies of the reaction

NOCl +
$$n$$
-BuOH $\stackrel{k_1}{\underset{k_{-1}}{\leftarrow}} n$ -BuONO + HCl (1)

in a series of mixtures of CCl_4 and acetic acid (HOAc) as solvents at 5 and 22 °C. The work was undertaken to investigate the effects of the solvent on the rate and mechanism of the reaction, as well as to demonstrate for the first time the applicability of the sudden change of the reaction medium as perturbation in relaxation kinetic studies.

In solvent-jump experiments⁶ an equilibrium solution is suddenly mixed with the same or with another solvent. If the system is sensitive to the change of the total concentration and/or to the change of the medium, the perturbation will cause a relaxation to new equilibrium concentrations. Thus, it is a relaxation experiment⁷ where the chemical potential of all species is directly and internally altered during perturbation. Similarly to other relaxation experiments, the primary information obtained in solvent-jump studies is usually the spectrum of relaxation times and the relaxation amplitudes. For a given equilibrium, the relaxation time τ is an explicit function of the rate constants k_i involved, and the relaxation amplitude, $\Delta \xi$ (which is a measure of the enforced equilibrium shift during the relaxation), is given by⁶

$$\frac{\Delta \xi}{\frac{\ln (K_1/K_2) - (\ln n) \sum \nu_i - BI_1^{1/2} (\epsilon_2^{-3/2} n^{-1/2} - \epsilon_1^{-3/2}) \sum \nu_i z_i^2}{\sum \nu_i^2 / n_{i1} + \sum (\ln \gamma_{i2}) (\sum \nu_i^2 z_i^2 / 2 \sum n_{i1} z_i^2)}}$$
(2)

Hence, the change of the extent of reaction, $\Delta \xi$, is a function of the dilution ratio *n*, the equilibrium constants in the initial (K_1) and final (K_2) media of given dielectric constants (ϵ_1 and ϵ_2 , respectively), as well as the stoichiometric coefficients⁸ ν_i , initial mole numbers n_{i1} , final ac-

tivity coefficients γ_{i2} , and charges z_i , of the species present in the reaction mixture. The value of B is a function of

$$B = 4.204 \times 10^{6} \, (\text{K})^{3/2} \, (\text{mol}/\text{L})^{-1/2} \, T^{-3/2} \tag{3}$$

the temperature T only which is kept constant during the experiment. As expected, eq 2 predicts a successful perturbation by solvent-jump (i.e., a nonzero $\Delta \xi$) even for equilibria where only nonionic species ($z_i = 0$) are present, and/or for equilibria with $\sum v_i = 0$, if $K_1 \neq K_2$ is satisfied. Reaction 1 is an example for both these cases, where the change of the reaction medium during perturbation is solely responsible for the relaxation.

Experimental Section

Chemicals. The solvents CCl_4 (Baker Analyzed reagent) and glacial acetic acid (Fisher ACS grade) were dried and distilled over P_2O_5 . Nitrosyl chloride was obtained from the Matheson Co., analyzed by the Addison–Thompson method,⁹ and purified from N_2O_4 with solid potassium chloride containing 3–5% surface water.¹⁰ The gas then was dried over anhydrous CaCl₂ (Figure 1). 1-Butanol (Fisher Spectranalized reagnet) was dried for several hours with CaO and subsequently distilled.

The stock solution of NOCl was prepared by bubbling the gas through CCl₄. This solution was diluted with CCl₄ or/and HOAc to obtain the desired initial NOCl concentration and solvent composition. The reverse sequence of solution preparation (i.e., bubbling NOCl through HOAc and subsequent dilution with CCl₄) could not be practiced because of chemical reaction between acetic acid and NOCl at high local concentrations of NOCl during the bubbling. However, at a NOCl concentration of 4.0×10^{-1} M or below, no reaction takes place between NOCl and HOAc, as tested photometrically and in the stopped flow apparatus.

The NOCl concentration of the stock solutions was determined photometrically immediately before each kinetic measurement. Although the main absorption band of NOCl ($\lambda_{max} = 473$ nm in pure CCl₄) shows a hypsochromic shift with increasing mole fraction of HOAc ($\lambda_{max} = 464$ nm in pure acetic acid), it follows Beer's law in every solvent mixture. All photometric measurements in the equilibrium as well as kinetic experiments were done at $\lambda = 470$ nm. The molar decadic extinction coefficient ϵ_{470} of NOCl at this wavelength varies with the solvent composition (Figure 2). In order to establish the ϵ_{470} values, the NOCl concentration of the stock solutions was initially

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Figure 1. Schematic diagram of the NOCI purification and solution preparation apparatus.



Figure 2. Molar decadic extinction coefficient ϵ_{470} of NOCl at $\lambda = 470$ nm as a function of solvent composition. In pure HOAc ϵ decreases with time, indicating reaction between NOCl and the solvent. The value extrapolated to zero time is given in this figure.

determined by Mohr titration of the chloride ions following the hydrolysis of NOCl.

Equilibrium Measurements. The equilibrium constant K of reaction 1 was determined photometrically at several different solvent compositions (ranging from pure CCl₄ to 90% acetic acid by volume) by using a Gilford Instrument Model 250 spectral photometer. The results are shown in Figure 3.

Kinetic Measurements. The stopped-flow apparatus used in the solvent-jump experiments has been described previously.¹¹ Its optical path length, dead volume, and smallest experimental total liquid volume are 2 cm, $55 \ \mu$ L, and 0.2 mL, respectively. The optical detection system has a minimum time constant of 0.2 ms. The mixing ratio of solutions was 1:1 or 1:10 by volume, depending on the solvent composition of the reaction medium desired (which ranged from 0 to 75% by volume of HOAc). The temperature was controlled to ± 0.5 °C. In the experiments below ambient temperature, a stream of dry air kept the windows of the observation cell free of moisture condensation. The progress of reaction was followed at $\lambda = 470$ nm, where only NOCl absorbs.

In the solvent-jump experiments, equilibrium 1 was established always in pure CCl₄ (solution I) which was suddenly mixed with CCl₄–HOAc mixtures (solution II) to yield certain final solvent compositions. In order to achieve fast and complete mixing (in 1 ms), solution II always contained at least 17.5% v/v CCl₄ as structure breaker for the acetic acid.¹² Including all experiments, the equilibrium concentration of NOCl and *n*-BuOH was varied over the ranges of 3.83×10^{-1} to 5.2×10^{-3} M and 6.75×10^{-1} to 4.9×10^{-3} M, respectively. Single relaxation





Figure 3. Equilibrium constant *K* of reaction 1 at 5 (Δ) and 22 °C (O) as a function of solvent composition. Uncertainties in the numerical values are typically ±11%, as average deviations from the mean.



Figure 4. A typical solvent-jump relaxation curve of reaction 1 in a CCl₄-HOAc mixture (75% CCl₄ v/v) at 5 °C. The equilibrium concentrations are 8.1 × 10⁻² M for NOCl and 1.8 × 10⁻¹ M for *n*-BuOH. Vertical scale: 10 mV/division; horizontal scale: 10 ms/division. Increasing light intensity (λ = 470 nm) is toward the top of the page.

was observed in all cases, and the relaxation times τ measured varied from 3.8 to 120 ms.

As expected, no relaxation was observed in pure concentration-jump experiments, where the equilibrium solution I was diluted with the original solvent. Therefore, in pure CCl_4 as solvent, the reactants NOCl and *n*-BuOH had to be directly mixed in the stopped flow apparatus, and the rate of approach to the equilibrium was measured.

Results and Discussion

Since the equilibrium constant K of the reaction is larger in pure CCl_4 than in the solvent mixtures, the increase of the HOAc content of the medium during solvent jumps is shifting the equilibrium toward the side of NOCl. This is in accord with the relaxation signals observed (Figure 4).

The reciprocal relaxation time measured for reaction 1 is given by

$$\tau^{-1} = k_1 (\bar{C}_{\text{NOCl}} + \bar{C}_{n-\text{BuOH}}) + k_{-1} (\bar{C}_{\text{HCl}} + \bar{C}_{n-\text{BuONO}})$$
(4)

where \bar{C}_i are the equilibrium concentrations in the final reaction mixtures. On the basis of eq 4, the rate constants k_1 and k_{-1} can be determined from a minimum of two measurements of τ and the known values of \bar{C}_i . On the



Figure 5. Forward and reverse rate constants of reaction 1 as a function of solvent composition: k_1 at 5 (Δ) and 22 °C (O), and k_{-1} at 5 (Δ) and 22 °C (\oplus).

average, six data pairs were used for the calculation of $k_{\pm 1}$ and the resulting mean values are listed in Table I, together with the equilibrium constants. The equilibrium constants determined photometrically, $K_{\rm opt}$, are in good agreement with the ratios of the forward and reverse rate constants $K_{\rm kin} = k_1/k_{-1}$.

constants $K_{kin} = k_1/k_{-1}$. As compared to pure CCl₄, the rate constants first decrease with increasing mole fraction of HOAc, reaching a minimum at about 75% v/v CCl₄ (mole fraction of CCl₄ ~ 0.6) except for k_{-1} at 22 °C, where the minimum is at about 50% v/v (Figure 5). Beyond the minimum, the forward rate constants change only slightly, but the reverse rate constants show a pronounced increase as the acetic acid content of the solvent is further increased. On the basis of the kinetic results, in pure CCl₄ the reaction can be described by a single step where the activated complex



(I) is formed by the simple addition of the reactants. Although, orbital symmetry arguments do not favor a four-centered activated complex, the formation of such a configuration with a nonzero activation energy (see Table II) is allowed for polar complexes. With growing mole fraction of HOAc in the solvent, all four species in (1) are solvated to an increasing extent by the polar acetic acid. This first may lower the direct encounter frequency of the reactants.

At high enough acetic acid concentration (above 25% v/v HOAc), the structure of the activated complex may change predominantly to II where HOAc becomes part of



the complex. The six-centered structure lowers the acti-

and Equilibrium Constants of the Reaction of NOCl with n-BuOH in CCl ₄ -HOAc Mixtures as a Function of Solvent Composition and Temperature ^a	22	75 50 25	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
		100	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
	5	25	0.125 ± 0.018 0.86 ± 0.076 0.15 0.15 ± 0.026
		50	$\begin{array}{c} 0.089 \pm 0.011 \\ 0.58 \pm 0.018 \\ 0.15 \\ 0.15 \\ 0.1 \pm 0.0095 \end{array}$
		75	$\begin{array}{c} 0.055 \pm 0.011 \\ 0.53 \pm 0.067 \\ 0.1 \\ 0.09 \pm 0.006 \end{array}$
		100	0.424 ± 0.025 0.78 ± 0.046 0.54 0.505 ± 0.071
TABLE I: Rate Constants	temp, °C	solv compn, vol % CCl4	$\begin{array}{c} k_{1} \left[\mathrm{M}^{-1} \mathrm{s}^{-1} \right] \times 10^{-3} \\ k_{-1} \left[\mathrm{M}^{-1} \mathrm{s}^{-1} \right] \times 10^{-3} \\ k_{\mathrm{kin}} (= k_{1} / k_{-1}) \\ k_{\mathrm{opt}} \end{array}$

Error limits are given in terms of mean deviation from the mean. The values given for K_{kin} are the ratios of the mean values of the rate constants.

a

TABLE II: Standard Thermodynamic Quantities and Activation Parameters as a Function of Solvent Composition (Energies in kcal/mol⁻¹, Entropies in eu)^a

solvent 100% CCl ₄ $\Delta H^{\circ} = 8 \pm 0.8$ $\Delta G^{\circ}_{295} = -0.13 \pm 0.056$ $\Delta S^{\circ}_{295} = 27.6 \pm 2.5$	$E_{a} = 14.3 \pm 0.36$ $\Delta H_{1}^{+} = 13.7 \pm 0.36$ $\Delta G_{1}^{+} = 12.8 \pm 0.77$ $\Delta S_{1}^{+} = 2.9 \pm 1.2$	$\begin{array}{l} {}_{-1}E_{a} = 6.1 \pm 1.4 \\ \Delta H_{-1} = 5.5 \pm 1.4 \\ \Delta G_{-\frac{1}{2}} = 12.9 \pm 0.025 \\ \Delta S_{-1} = -25.3 \pm 5 \end{array}$	$b \\ \Delta H_{1}^{+} - \Delta H_{-1}^{+} = 8.2 \\ \Delta G_{1}^{+} - \Delta G_{-1}^{+} = -0.1 \\ \Delta S_{1}^{+} - \Delta S_{-1}^{+} = 28.2$
solvent 75% v/v CCl ₄ $\Delta H^{\circ} = -2.5 \pm 0.73$ $\Delta G^{\circ}_{295} = 1.6 \pm 0.08$ $\Delta S^{\circ}_{295} = -13 \pm 2.1$	${}_{1}E_{a} = 3.5 \pm 1.6$ $\Delta H_{1}^{+\pm} = 2.9 \pm 1.6$ $\Delta G_{1}^{\pm} = 14.7 \pm 3.2$ $\Delta S_{1}^{\pm} = -40 \pm 5.5$	$\begin{array}{c} _{-1}E_{a} = 4.6 \pm 1 \\ \Delta H_{-1} ^{\pm} = 4 \pm 1 \\ \Delta G_{-1} ^{\pm} = 13.3 \pm 2.1 \\ \Delta S_{-1} ^{\pm} = -31 \pm 3.7 \end{array}$	$\Delta H_{1}^{+} - \Delta H_{-1}^{+} = 1.1$ $\Delta G_{1}^{+} - \Delta G_{-1}^{+} = 1.4$ $\Delta S_{1}^{+} - \Delta S_{-1}^{+} = -9$
solvent 50% v/v CCl ₄ $\Delta H^{\circ} = -2.2 \pm 1.4$ $\Delta G^{\circ}_{295} = 1.5 \pm 0.15$ $\Delta S^{\circ}_{295} = -12 \pm 4.2$	${}_{1}E_{a} = 1.13 \pm 0.22$ $\Delta H_{1}^{+} = 0.54 \pm 0.22$ $\Delta G_{1}^{+} = 14.6 \pm 0.51$ $\Delta S_{1}^{+} = -47 \pm 1$	$\begin{array}{c} {}_{-1}E_{a} = 3.2 \pm 0.57 \\ \Delta H_{-1} \stackrel{\pm}{=} 2.6 \pm 0.57 \\ \Delta G_{-1} \stackrel{\pm}{=} 13.3 \pm 1.2 \\ \Delta S_{-1} \stackrel{\pm}{=} -36 \pm 2.1 \end{array}$	$\Delta H_{1}^{\ \pm} - \Delta H_{-1}^{\ \pm} = -2.06$ $\Delta G_{1}^{\ \pm} - \Delta G_{-1}^{\ \pm} = 1.3$ $\Delta S_{1}^{\ \pm} - \Delta S_{-1}^{\ \pm} = 11$
solvent 25% v/v CCl ₄ $\Delta H^{\circ} = -1.4 \pm 0.16$ $\Delta G^{\circ}_{295} = 1.2 \pm 0.09$ $\Delta S^{\circ}_{295} = -9 \pm 0.24$	${}_{1}E_{a} = 0.3 \pm 0.38$ $\Delta H_{1}^{+\pm} = -0.29 \pm 0.38$ $\Delta G_{1}^{\pm} = 14.4 \pm 0.03$ $\Delta S_{1}^{\pm} = -50 \pm 1.3$	$\begin{array}{c} {}_{-1}E_{a} = 2.1 \pm 0.63 \\ \Delta H_{-1} = 1.4 \pm 0.63 \\ \Delta G_{-1} = 13.2 \pm 1.3 \\ \Delta S_{-1} = -40 \pm 2.2 \end{array}$	$\Delta H_{1}^{\ \pm} - \Delta H_{-1}^{\ \pm} = -1.1$ $\Delta G_{1}^{\ \pm} - \Delta G_{-1}^{\ \pm} = 1.2$ $\Delta S_{1}^{\ \pm} - \Delta S_{-1}^{\ \pm} = -10$

^a The uncertainties in the numerical values are associated with the extreme values of the rate constants. ^b $\Delta X_1^{*} - \Delta X_{-1}^{*}$ are reported as the differences of the mean values.

vation energy $E_{\rm a}$ and the activation entropy ΔS^* drastically for the forward, and moderately for the reverse reaction (Table II). The specific rates increase again in this range of solvent composition, as shown in Figure 5.

The activation parameters and the standard thermodynamic quantities are listed in Table II. In the calculation of the thermodynamic quantities the standard state of the solute is considered to be the hypothetical state of 1 M solution under 1 atm pressure having the properties of infinite dilution. In this case, if $C_i \rightarrow 0$, then the activities $a_i \rightarrow C_i$, and the change of the standard molar enthalpy of the reaction ΔH° becomes equal to ΔH^{∞} (change of the molar enthalpy at infinite dilution) which can be calculated from d ln $K/dT = \Delta H^{\circ}/RT^2$. Further we have $\Delta G^{\circ} = -RT \ln K$, and $\Delta G^{\circ} \equiv \Delta H^{\circ} - T\Delta S^{\circ}$.

The Arrhenius activation energy ${}_{\pm 1}E_a$ for the forward and reverse reaction was obtained from the least-squares fitted linear plot of ln $k_{\pm 1}$ vs. T^{-1} . Since $E_a = \Delta H^* + RT$, the entropy of activation can be calculated from the equation as given by the transition-state theory. Obvi-

$$k_{\pm 1} = \frac{kT}{h} \exp(-\Delta H_{\pm 1}^*/RT) \exp(\Delta S_{\pm 1}^*/R)$$
 (5)

ously, since $K = k_1/k_{-1}$, then $\Delta H^{\circ} = \Delta H_1^{\dagger} - \Delta H_{-1}^{\dagger}$, and $\Delta G^{\circ} = \Delta G_1^{\dagger} - \Delta G_{-1}^{\dagger}$ and $\Delta S^{\circ} = \Delta S_1^{\dagger} - \Delta S_{-1}^{\dagger}$. The agreement between the quantities determined optically and kinetically is shown in Table II.

Although the activation energy decreases monotonically with increasing polarity of the solvent, the presence of a minimum in the rate constants (Figure 5) can be rationalized by entropy effects. Apparently, the exponential entropy factor in (5) first decreases faster than the enthalpy factor increases. The decreasing value of the activation entropies $\Delta S_{\pm 1}^{+}$ indicates that the activated complex and/or the medium around it becomes more organized on the addition of acetic acid. Beyond the minimum, the enthalpy factor becomes predominant.

The relaxation amplitudes measured experimentally at 5 °C were compared with the theoretical ones calcuated by using a simplified form (6) of eq 2 (Figure 6). The ΔC_i 's at 22 °C were too large to satisfy certain assumptions made in the derivation⁶ of eq 2, therefore, the theoretical relaxation amplitudes could not be calculated at this temperature.

Assuming that only neutral species (including ion pairs) are present in our solvents of low dielectric constant¹³ (ϵ_{CCL_4} = 2.238 and ϵ_{HOAc} = 6.15 at 20 °C), z_i s are zero in (2). Since



Figure 6. Comparison of the experimental (symbols) and the theoretical (curves) relaxation amplitudes at 5 °C as a function of the equilibrium concentration of NOCI and the solvent composition (\oplus , 75% v/v CCI₄; \blacksquare , 50%, \blacktriangle , 25%). The theoretical curves were calculated for the given experimental conditions.

 $\sum v_i$ is also zero for reaction 1, eq 2 simplifies in our case to

$$\Delta \xi = \frac{\ln (K_1/K_2)}{\sum \nu_i^2 / n_{i1}}$$
(6)

that was used to calculate the theoretical values of $\Delta \xi$. In order to be able to compare $\Delta \xi$'s with experimentally observed signal amplitudes ΔI (differences in mV on the oscilloscope traces), $\Delta \xi$'s must be converted to ΔI , or vice versa. The relationship between the two quantities is given by

$$\Delta \xi = nV \log \left(1 - \Delta I / I_{\rm s}\right) / \nu_{\rm i} \epsilon_{\rm i} l \tag{7}$$

where the volume V is 1 L, I_a is the signal amplitude after the relaxation (usually set to 400 mV in trial runs), ν_i is the stoichiometric coefficient, ϵ_i the molar decadic extinction coefficient of the observed species i (NOCl), l the optical path length in cm, and n the dilution ratio.

As shown in Figure 6, the measured amplitudes are, within experimental error, in agreement with the calculated ones, corroborating the kinetic and equilibrium spectrophotometric results on the reaction.

The method used in this study should be applicable to many systems with relaxation times in the millisecond (or longer) range. For example, combined with other types of detection (such as conductance, circular dichroism, fluorescence, etc.), conformational changes of globular proteins could be investigated this way.

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Kinetics of Ion Exchange. A Radiochemical Study of Rb^+-H^+ and Ag^+-H^+ Exchange on Zirconium Arsenophosphate

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This communication reports a study of the kinetics of ion exchange of Rb⁺ and Ag⁺ on the H⁺ form of zirconium arsenophosphate by the "limited bath technique". The slow step which determines the rate of exchange at concentrations ≥ 0.1 M is diffusion through the exchanger particles. The values of interdiffusion coefficients, energy of activation, and entropy of activation have been calculated. The data obtained have been compared with those on organic resins and other inorganic ion exchangers. The rates of exchange for Rb⁺ and Ag⁺ on zirconium arsenophosphate have been found to approach to those on some organic resins and inorganic ion exchangers.

Introduction

The rate-controlling step in ion exchange is diffusion either through the exchanger particle (particle diffusion) or an adherent liquid layer (film diffusion) and under an intermediate range of conditions both mechanisms may contribute to the rate-determining step.¹ Of the various types of ion-exchange processes, particle-diffusion-controlled exchange has been studied thoroughly and has adequate theoretical understanding. It is observed that, in a process where an ion A is exchanged with an ion B in solution, there occurs an electric coupling of the opposite fluxes of the two ions, so that the rate of interdiffusion is dependent on the state of conversion of exchanger from form A to form B, and the diffusion coefficient in the exchanger is not constant with time. However, an approximate indication of the rate may be obtained if an average constant mobility is assumed (constant-diffusivity model). In isotopic exchange this assumption is of course very nearly correct. The particle-diffusion equation developed by Boyd et al.¹ for isotopic exchange was found to be valid for binary ion exchange also, at higher concentrations in which the composition of the external solution is assumed to be constant and not time dependent.

Studies on the kinetics of ion exchange are mostly directed toward organic resins and thus leaving their inorganic counterparts still to be exploited. Some of the im-

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portant contributions in this direction may be cited by mentioning the work on synthetic zeolites,² zirconium phosphate,³⁻⁵ hydrous zirconium oxide,⁶ zirconium antimonate,⁷ tin antimonate,⁸ tantalum arsenate,⁹ and iron antimonate.¹⁰ Most of these studies have been directed toward the investigation of the diffusion coefficients, since it can describe the mobility of the ion in the exchanger and, in addition, it might give a clue to the "degree of openness"

of the channels through which diffusion takes place.¹¹ Recently zirconium arsenophosphate (ZAP)¹² has been synthesized in chemical laboratories and was found to possess good ion-exchange properties. The material showed appreciable resistance toward high temperature. chemical attack, and ionizing radiations. The practical utility of the material was shown by achieving several metal ion separations of analytical and radiochemical interest. The present communication reports our findings on the kinetics of Rb+-H+ and Ag+-H+ exchange systems on the material. The rate of exchange of Cs⁺ was found to be too slow to obtain any meaningful results.

Experimental Section

ZAP was prepared at pH ~ 2 by the method reported elsewhere.¹² The diameters of the particles of two different sieved fractions were measured with a micrometer microscope for 100 particles of each fraction. The mean radii were 2.16×10^{-2} and 6.35×10^{-3} cm (within ~4% error).

The ion-exchange capacity measured at pH 2 by the radiometric method for Rb⁺ and Ag⁺ was found to be 1.26 and 1.17 mequiv/g, respectively.

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