KINETICS OF ION EXCHANGE. VII.*
MEASUREMENTS
IN THE FILM DIFFUSION REGION

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From the oscillometrically measured exchange half times the film diffusion data of a number of cations, organic bases on Dowex 50W X 16 with respect to the H^+ ion, as well as data of anions and anions of organic acids on Dowex 1 X 8 with respect to the OH^- ion have been calculated, the total concentration of external solution being $5 . 10^{-3}$ val/l. Integral kinetic data may be interpreted by means of the Nernst–Planck equation or transport coefficients in the ternary system. Effect of some variables as, for example, concentration of the external solution, charge, mobility, hydration, and selectivity of ions on the kinetics of exchange in individual systems has been discussed.

In solutions having normalities of 10^{-2} or lower, the diffusion of ions through a liquid film of thickness δ, surrounding the ion-exchanger particle, is the slowest and from the kinetic point of view most decisive process. The theories aiming at a quantitative interpretation of the kinetics of the film diffusion start partly from the Nernst–Planck equation[1–3], partly from the connection between the diffusion flow and thermodynamic forces involving transport coefficients[4–6]. Since the diffusion coefficient comprises the transport coefficients, both theories connect with each other, the competence of the latter being confirmed by separate differential kinetic measurements[5–7]. For the most part, only the systems alkali metals–H^+ ion[5,6,8] or ethylammonium–H^+ ion[7] have been measured experimentally. By using electrodeless high-frequency oscillometer arrangement[9], the number of systems have been so much enlarged that it was possible to make a comparison of the film diffusion rate of several groups involving related substances from the point of view of their physico-chemical properties, and to discuss the results on the basis of the theories suggested.

THEORETICAL

The total flow J_i (mol cm^{-2} s^{-1}) of the ion i consists of the diffusion component and the component raised by an electric field characterized by electric potential φ. The combination of both leads to the Nernst–Planck equation having the form

$$J_i = -D_i \left(\text{grad } \bar{c}_i + z_i C_i \textbf{F}/RT \text{ grad } \varphi \right), \tag{1}$$

where D_i and C_i are the diffusion coefficient and concentration of the ion i, respectively, $\bar{c}_i$ is the concentration of the i ion in the film, z_i denotes its charge, $\textbf{F}$ is the Faraday constant, R the gas constant, and T is the absolute temperature. The flow of the ion can be expressed on the basis of irreversible thermodynamics[10] by summation of the product of phenomenologic (transport) coefficients l_{ij} and thermodynamic forces X_j

$$J_i = \sum_{j=1}^{n} l_{ij} X_j \quad i = l, ..., n \tag{2}$$

while the phenomenologic coefficients are governed by the Onsager reciprocal relations

$$l_{ij} = l_{ji} \tag{3}$$

and the ternary system is formed by an ion, counterion, and water as solvent. Here, the gradient of the electrochemical potential $\tilde{\mu}_j$ appears as thermodynamic force. From relations (1) and (2) a connection between the diffusion and transport coefficients follows.

The electric potential φ consists of a sum of electrostatic potential ψ and the surface potential of the phase boundary χ. Its gradient can be expressed by

$$\text{grad } \varphi = \text{grad } \psi + \text{grad } \chi, \tag{4}$$

an electric field with an intensity ε of the opposite direction being produced by the electrostatic potential gradient

$$\text{grad } \psi = -\varepsilon. \tag{5}$$

By combining equations (1), (4), and (5) we obtain

$$J_i = -D_i \left[\text{grad } \bar{c}_i + z_i C_i \textbf{F}/RT \left(-\varepsilon + \text{grad } \chi \right) \right]. \tag{6}$$

In the diffusion of the ion i through the film, both the concentration gradient of the i ion in the film and gradient of the interphase potential χ at the interface ion-exchanger-film will be then effective in the same direction. Vector ε of the electric

field intensity, raised by unequal ion mobilities, will then act in the opposite direction. Considering the diffusion process in terms of a combination of the diffusion through a liquid with the subsequent interaction with the solid phase surface, the terms grad $\bar{c}_i$ and grad ψ will be then the driving forces during the diffusion through liquid, whereas interaction with an ion-exchanger will be determined by the magnitude of the interphase surface potential χ. For the diffusion through the liquid phase (film), the Nernst–Einstein equation is valid showing relation between the diffusion coefficient of the ion i, its mobility l_i and the charge z_i

$$D_i = \frac{li\,RT}{z_i F^2}.\tag{7}$$

Besides, the diffusion coefficient is directly dependent on the mobility and indirectly dependent on the degree of the ion hydration[11].

Assuming integral diffusion through the liquid film, the first two members in relation (6) will become effective to a great extent, *i.e.* the rate of diffusion should be governed by valency and mobility of the ion. The third member of relation (6) comprises in the potential χ the extent of the interaction of ion concentrations in both phases. The concentration ratio of ions in both phases changes continuously with the change in the ion-exchanger phase. The change in the ratio is different with each ion pair, but its effect on the integral kinetics of the film diffusion may be assessed, if dependence of the course of equilibrium data on the ion-exchanger phase composition is known. The course is given by a difference between the values of equilibrium coefficients on both ends[12] ($x_i = 0$, $x_i = 1$), where x_i is the mol ratio of the ion i in the ion-exchanger phase.

EXPERIMENTAL

Reagents and solutions. The $5 . 10^{-3}$ val/l solutions of chlorides or nitrates of the cations Li^+, Na^+, NH_4^+, K^+, Rb^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cu^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Al^{3+}, La^{3+}, and Th^{4+} as well as of hydrochlorides of organic bases such as methylamine, dimethylamine, ethylamine, diethylamine, triethanolamine, piperidine, cyclohexylamine, benzyl-amine, α-naphthylamine, *m*-toluidine, *m*-phenylendiamine, and benzidine were prepared by dissolution of purest reagents in distilled water. In a similar way, the $5 . 10^{-3}$ val/l solutions of sodium or potassium salts of the anions F^-, Cl^-, Br^-, J^-, BrO_3^-, NO_2^-, NO_3^-, CNS^-, SO_3^{2-}, CO_3^{2-}, SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, $S_2O_5^{2-}$, $[SiF_6]^{2-}$, PO_4^{3-}, and $[Fe(CN)_6]^{3-}$ as well as sodium formate, acetate, oxalate, malonate, tartrate, benzoate and terephthalate were prepared.

Ion-exchange resins and apparatus. The strongly acidic as well as basic styrene–divinylbenzene copolymers Dowex 50W X 16 and Dowex 1 X 8 were employed. The diameter and capacity $\bar{C}$ of the former substance in the H-cycle were $6.5 . 10^{-2}$ cm and 2·08 val/l, respectively. For the latter substance in the Cl-cycle, the parameters were $5.8 . 10^{-2}$ cm and 1·12 val/l, respectively. Prior to the measurements, the cation or anion exchange resins were pretreated by a manifold conversion from the sodium cycle to the hydrogen one, or from the chloride cycle to the hydroxide one. A fully swollen, washed, and sucked cation exchanger in the H-cycle, or anion exchanger

in the OH-cycle were taken for the kinetic measurements. All the kinetic measurements were made with use of oscillotitrator OK 302 operating at a frequency of 140 MHz and at a constant temperature of 25°C.

RESULTS AND DISCUSSION

The film diffusion region is very advantageous for apparatus operating at high frequency, for the relative sensitivity of the method increases with the decreasing concentration of the solution. It was therefore possible to work with half a sensitivity than in the gel diffusion region, the precision being maintained the same. At first, it was necessary to determine a certain equivalent ratio between ions in the ion-exchanger and those in the solution. This ratio must be kept on an approximately constant value; otherwise, the ion-exchange half times $t_{1/2}$ are not constant, particularly when the ratio in question is too high (Fig. 1). The most advantageous value to keep was approximately 1 : 1, which corresponded to an introduction of about 0·5 ml of the cation exchanger or 1·0 ml of anion exchanger into the whole volume of 200 ml of the $5 . 10^{-3}$ val/l solution.

In order to ensure that it was the film diffusion that occurred even in the less dissociated and sterically ambitious systems, the concentration of external solution was always $5 . 10^{-3}$ val/l, because of the transition region of these systems being shifted towards the region of higher concentration, as far as the order of magnitude is concerned[13]. It follows from Fig. 1 that at very low concentrations the exchange rates are considerably decreased. The exchange half time measured at the Na^+ concentration of $2 . 10^{-2}$ val/l is in very good accordance with the value 440 s measured in the same system on cation exchanger S X 15[8]. From the exchange half times read off graphically, the appropriate diffusion coefficients D_1 for the film diffusion were calculated using[14]

$$D_1 = 0·23 \frac{r\delta\overline{C}}{t_{1/2}C} , \tag{8}$$
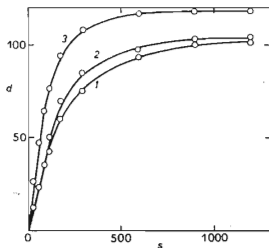

FIG. 1

Time Dependence of the Kinetics of Exchange on the Ratio of Val Amounts in the Ion-Exchanger and Solution of the Na^+–H^+ System on Dowex 50 W X 16 at a Concentration of External Solution $C = 10^{-2}$ val/l

1 Concentration ratio in the ion-exchanger and solution 1 : 1, $t_{1/2} = 150$ s; *2* 1 : 5, 130 s; *3* 5 : 1, 80 s.

TABLE I
Kinetic Data of Studied Systems

Dowex 50W X 16			Dowex 50W X 16			Dowex 1 X 8			Dowex 1 X 8		
Ion	$t_{1/2}$, s	$D \cdot 10^6$, $cm^2 s^{-1}$	Ion	$t_{1/2}$, s	$D \cdot 10^6$, $cm^2 s^{-1}$	Ion	$t_{1/2}$, s	$D \cdot 10^6$, $cm^2 s^{-1}$	Ion	$t_{1/2}$, s	$D \cdot 10^6$, $cm^2 s^{-1}$
Li^+	290	10·7	methyl-ammonium	260	12·0	F^-	360	4·2	formate	330	4·6
Na^+	175	17·8	dimethyl-ammonium	230	13·5	Cl^-	300	5·0	acetate	370	4·0
NH_4^+	180	17·2	ethyl-ammonium	350	8·8	Br^-	380	4·0	oxalate	480	3·1
K^+	200	15·5	diethyl-ammonium	340	9·1	J^-	360	4·2	malonate	490	3·0
Rb^+	170	18·2	triethanol-ammonium	450	6·9	BrO_3^-	410	3·6	tartrate	600	2·5
Tl^+	220	14·1	piperidinium	370	8·4	NO_2^-	400	3·8	benzoate	570	2·6
Mg^{2+}	340	9·1	cyclohexyl-ammonium	390	8·0	NO_3^-	270	5·6	terephthalate	650	2·3
Ca^{2+}	300	10·4	benzyl-ammonium	400	7·7	CNS^-	300	5·0			
Sr^{2+}	300	10·4	m-toluidinium	550	5·6	CO_3^{2-}	530	2·8			
Ba^{2+}	280	11·0	m-phenylene-diammonium	600	5·2	SO_3^{2-}	500	3·0			
Cu^{2+}	360	8·6	α-naphthyl-ammonium	1 800	1·7	SO_4^{2-}	600	2·5			
Pb^{2+}	350	8·9	benzidinium	2 000	1·5	CrO_4^{2-}	550	2·7			
Co^{2+}	340	9·1				MoO_4^{2-}	520	2·9			
Cd^{2+}	330	9·4				$S_2O_7^{2-}$	600	2·5			
Al^{3+}	400	7·8				SiF_6^{2-}	400	3·8			
La^{3+}	430	7·2				PO_4^{3-}	1 000	1·5			
Th^{4+}	780	4·0				$Fe(CN)_6^{3-}$	1 460	1·0			

where r is the radius of swollen resin bead, C and $\bar{C}$ are the concentrations of ions in the solution and ion-exchanger, respectively, and δ is the thickness of the liquid film surrounding the resin bead. In this paper, $\delta = 10^{-3}$ cm was applied, this value being reported in the literature[11,14] for thoroughly mixed systems. In spite of this value being small, it is at least $2 \cdot 10^3$ times higher than the maximum radius of the ionic atmosphere at this dilution[11].

In all the systems studied, the cation and anion exchangers were at the beginning of the measurements in pure hydrogen and pure hydroxide cycles, respectively. During the exchange, an equilibrium state was attained characterized by an increase of the molar concentration of the ion i in the ion-exchanger phase up to a value close to 1. Consequently, this was a kind of integral exchange with the constant $\bar{C}/C$ ratio for all the systems involving cation as well as anion exchangers. The measured diffusion data are summarized in Table I.

System cations–H^+ ion. The half times of exchange increase with the increasing valency of the cation. With alkali metals the relatively slow diffusion rate of Li^+, which can be assigned to the high hydration and low mobility of the Li^+ ion, is dominating. A similar, even though not such pronounced position is occupied by the Mg^{2+} ion among the alkali earth metals. The kinetics of exchange of the quadrivalent thorium is slowed down relatively most markedly.

System organic base–H^+ ion. The diffusion rates of fairly small alkylamines do not differ too much from the rate of simple cyclic bases. A partial retardation occurs even with the simple conjugated system consisting of two substituents, and especially with condensed conjugated systems. The diffusion coefficient decreased with the increasing size of the organic base in the series methylamine ($d = 3 \cdot 8$ Å), cyclohexylamine ($d = 6 \cdot 0$ Å), and α-naphthylamine (d $8 \cdot 7$ Å). The size of bases is characterized by the main diameter d calculated from $d \approx \sqrt[3]{M}$, where M is the molecular weight.

System anions–OH^-. Similarly as with the cations, the kinetics of exchange is also here governed by valency of the counterion in the first place. In comparison with cations of equal valency, lower rates of diffusion are exhibited by the anions; this fact may be assigned to a decrease in the ion-exchanger phase concentration to half a value, compared with the cation exchanger. Among univalent anions, the BrO_3^- ion is the slowest, this being in accordance with its lower mobility[11]. As for the trivalent anions, the exchange is more rapid with phosphate than with complex hexacyanoferrite; from the bivalent anions, hexafluorosilicate exhibits relatively highest rates of diffusion.

System organic acids–OH^-. The rates of diffusion of the smallest acids are consistent with those of the univalent anions. The rate of diffusion decreases with the increasing steric ambition of organic acids similarly as with the decreasing mobility

of the substances. The mobilities in the series formate, acetate, and benzoate at 25°C amount to 54·6, 40·9, and 32·4 cm^2 Ω^{-1}, respectively. The diffusion data measured during the diffusion of benzoate and terephthalate through a film amount to about $1/3$ of the values measured in the diffusion of free acids in the liquid phase[15].

It should be mentioned in the conclusion that a great number of integral diffusion data had been measured, allowing mutual comparison of important systems in the film diffusion region. It has been established that the kinetics of exchange is in this region primarily dependent on valency of the ion, its mobility, hydration, and steric arrangement. The factors which influence the diffusion in the liquid phase are most decisive.

Almost in all the measured systems, the equilibrium coefficient was always greater than 1. The difference between the edge equilibrium coefficients was mostly negative, the selectivity trend within the whole concentration range was therefore similar and its resultant effect on the rate of diffusion consistent. For that reason, the selectivity changes during unidirectional integral diffusion are not so significant as in the bothway, particularly differential, kinetic measurements.

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