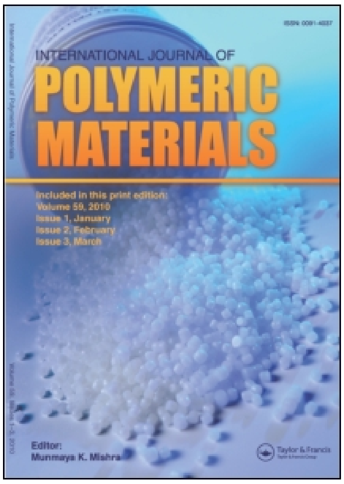

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Diffusion of Aggressive Media in Hydrophilic Polymers

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To cite this Article Zimina, L. A. , Madyuskin, N. N. , Polishchuk, A. Ya. , Iordansky, A. L. and Zaikov, G. E.(1992) 'Diffusion of Aggressive Media in Hydrophilic Polymers', International Journal of Polymeric Materials, 16: 1, 185 — 193

To link to this Article: DOI: 10.1080/00914039208035422

URL: http://dx.doi.org/10.1080/00914039208035422

Intern. J. Polymeric Mater., 1992, Vol. 16, pp. 185–193
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Printed in the United Kingdom

Diffusion of Aggressive Media in Hydrophilic Polymers

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The simultaneous sorption and diffusion of acid and salt in polyvinylalcohol are considered under conditions of polymer swelling. Obtained data on water sorption by PVA show an anomalous mechanism of the transport of solvent in this kind of polymer. The analysis of equilibrium sorption of an acid-salt mixture shows that interactions of polymer OH groups with hydrogen ions of hydrogen chloride lead to a decrease in salt solubility in the polymer. The theory of Donnan equilibrium was used to solve the problem of the sorption of the acid-salt mixture as well as to create the boundary conditions for a proposed mathematical model of the transport of the buffer mixture.

Methods of determining parameters of the buffer mixture transport in hydrophilic polymers have been created and physicochemical characteristics of investigated multicomponent system are calculated on the basis on these methods.

KEY WORDS Diffusion, hydrophilic polymers

INTRODUCTION

The transport and sorption processes in systems, consisting of polymer, solvent and electrolytes, define working parameters of polymer materials, such as chemical stability, electroconductivity, relative strain and mechanical modulus. The theoretical aspects of electrolyte transport have been investigated in detail for one-component diffusion,[1–3] but the transport of electrolyte mixtures has received little discussion.[4,5] Taking into account the great importance of this process for many practical cases, the present research deals with complex analysis of sorption and diffusion processes in multicomponent systems (hydrophilic polymer—water—aqueous solutions and acid and salt).

We consider two electrolytes KCl and HCl having anions of the same name. Both electrolytes are sorbed by polyvinylalcohol, which was the model of the neutral hydrophilic polymer.[6] Simultaneous sorption and diffusion of acid and salt in polymers were observed very often, for instance, in membranes for dialysis, hemodialysis and ultrafiltration. The productivity of these membrane devices is defined by the hydrophilic character of the polymer and their selectivity is defined by the content of ionogenically charged groups.

EXPERIMENTAL

The PVA films named "POVAL FILM" and produced in Japan are investigated. The thickness and weight of films consequently vary from 35 μ to 75 μ, and from 0.07 g to 0.15 g. Concentration of each electrolyte in the polymer is measured by original laboratory methods using Cl-selected and glass electrodes. The range of electrolyte concentration in water varies from 0.1 to 0.8 N for each compound. The dependence of electroconductivity on log C_{KCl} is linear. The concentration of water in the polymer is measured by McBain balance. All experiments are carried out at 23°C.

RESULTS AND DISCUSSION

Obtained data on water sorption by PVA show the anomalous mechanism of the transport of solvent in this kind of polymer. Structural transmission in a matrix produced by the sorption of solvent changes kinetic parameters of relaxation and convective processes and, therefore, influences the mechanism and velocity of the transport of electrolytes in the polymer.

The equilibrium sorption of each electrolyte in the presence as well as in absence of another one is represented in Figures 1 and 2. Figure 1 illustrates that the sorption isotherms for all mixtures have linear initial part, positively diverge from line at $C_{HCl} > 0.3$ mol/l and rather weakly depend on KCl concentration.

On the other hand, sorption of KCl by PVA films depends on the equilibrium content of HCl; moreover, we have seen the exchange of the character of the curve

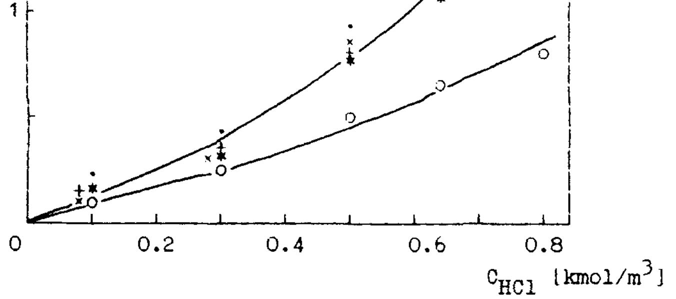

FIGURE 1 Equilibrium sorption of hydrochloric acid by PVA in the presence of KCl (●, experimental data; –, calculated curves). KCl concentrations: 0 (●), 0.1 (×), 0.3 (+), 0.5 (*), 0.8 (o) mol/l.

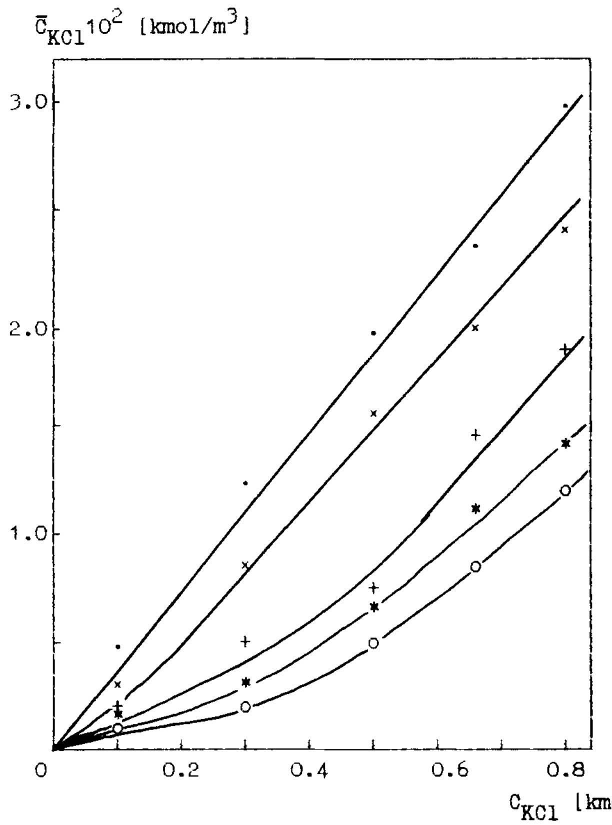

FIGURE 2 Equilibrium sorption of potassium chloride by PVA in the presence of HCl (●, experimental data; –, calculated curves). HCl concentrations: 0 (●), 0.1 (×), 0.3 (+), 0.5 (*), 0.8 (○) mol/l.

and its slope. The addition of acid leads to a decrease in salt content in PVA, i.e., its exclusion.

The effect of the decrease in KCl concentration may be explained by the reduction of water activity in the polymer due to the interaction of H_2O molecules with acid molecules. But this explanation may be correct only for results of HCl sorption, and it is impossible to explain the fall of KCl solubility by a decrease in water activity because the water content in PVA is quite independent of ion force: $\phi_w = 0.653$ ($C_{HCl} = 0.1$ mol/l), $\phi_w = 0.639$ ($C_{HCl} = 0.8$ mol/l).

Apparently, this case is characterized by the other mechanism of exclusion, which is one kind of unequivalent exchange between electrolyte and ionogenic charges polymer groups (so-called "Donnan equilibrium"). The protonization of hydroxyl groups in PVA may be written in the following form:

$$\text{R—OH} + \text{H}_3 + \text{O} \overset{K_F}{\underline{\leftarrow}} \text{R—OH}_2^+ + \text{H}_2\text{O}$$

where the equilibrium constant (K_F) is defined by

$$K_F = \frac{\bar{C}_{F^+} {}^* \bar{C}_w}{\bar{C}_F {}^* \bar{C}_H} = \frac{\bar{C}_F + {}^* \bar{C}_w}{\bar{C}_H(\bar{C}_F^0 - \bar{C}_{F^+})} \tag{1}$$

where, $\bar{C}_H$ is the concentration of free form of acid, $\bar{C}_F$ and $\bar{C}_{F^+}$ are the concentrations of free and protonized groups of hydroxyls in PVA, respectively, and $\bar{C}_w$, $\bar{C}_F^0$ are the water concentration and the total concentration of hydroxyls in polymer, respectively.

Electroneutral conditions for all ions in polymer yields

$$\bar{C}_H + \bar{C}_K + \bar{C}_{F^+} - \bar{C}_A = 0 \tag{2}$$

where K and A are subscripts for K^+ and Cl^-, respectively.

Using equation (1) for obtaining the expression for $\bar{C}_F(\bar{C}_H)$, we have

$$\bar{C}_A = \bar{C}_K + \bar{C}_H{}^*[1 + K_F{}^*\bar{C}^0_{F^+}/(1 + K_F{}^*\bar{C}_H)]. \tag{3}$$

The positive charged hydroxyl groups of PVA promote to the exclusion of K^+ ions which do not interact with the polymer matrix. This Donnan mechanism of K^+ exclusion is illustrated by Figure 2.

The Donnan equation for potassium chloride may be written in the following form:

$$\bar{C}_K{}^*\bar{C}_A = K^D_{KA}{}^*C^2_{KA} \tag{4}$$

where K^D_{KA} is the Donnan constant.

Taking into account electroneutral conditions (Equation (3)), from equation (4), we obtain

$$\bar{C}^2_K + \bar{C}_H{}^*\bar{C}_K{}^*[1 + K_F{}^*\bar{C}^0_{F^+}/(1 + K_F{}^*\bar{C}_H)] = K^D_{KA}{}^*C^2_{KA}. \tag{5}$$

The solution of the quadratic equation (5) leads to an expression of dependence of sorbed K^+ ions on the system's parameters as well as on the salt and acid concentrations in the aqueous solution. The last dependencies are very important for general conclusions about transport mechanism of the investigated system:

$$\bar{C}_{KA} = \bar{C}_K = \sqrt{\bar{C}^2_H{}^*F^2/4 + K_{KA}{}^*\bar{C}^2_{KA}} - \bar{C}_H{}^*F/2$$
$$= \frac{2\bar{C}^2_{KA}{}^*K^D_{KA}}{\bar{C}_H{}^*F + \sqrt{(\bar{C}_H{}^*F)^2 + 4K^D_{KA}{}^*\bar{C}^2_{KA}}} \tag{6}$$

where $F = 1 + K_F{}^*\bar{C}^0_{F^+}/(1 + K_F{}^*\bar{C}_H)$.

Taking into account the sorption of acid in a bond ($R—OH_3^+A^-$) and free (H^+

and A^-) forms, it is very easy to show that the absence of electrostatic influences of KCl on HCl sorption leads to the equation

$$\bar{C}_{HA} = \bar{C}_H{}^*F. \tag{7}$$

Now, equation (6) may be written in a form which is convenient for analysis:

$$\bar{C}_{KA} = \bar{C}_K = \frac{2\bar{C}^2_{KA}{}^*\bar{K}^D_{KA}}{\bar{C}_H{}^*F^+ \sqrt{(\bar{C}_{HA})^2 + 4K^D_{KA}{}^*\bar{C}^2_{KA}}}. \tag{8}$$

It is obvious that equation (8) leads to an expression which is similar to the Nernst distribution:

$$\bar{C}_K = C_{KA}{}^*\sqrt{K^D_{KA}} \tag{9}$$

if the acid is absent in the polymer.

Experimental results (Figure 2) are in accordance with linear equation (9) and give us the possibility of obtaining $K_{KA} = 0.132$.

At last, the effect of exclusion may be represented as a modified form of equation (8):

$$\bar{C}_K/C_{KA} = \sqrt{K^D_{KA}}{}^*\exp[\sinh^{-1}(\bar{C}_{HA}/2\bar{C}_{KA}{}^*\sqrt{K^D_{KA}})] \tag{10}$$

where $\bar{C}_K/C_{KA}$ is relationship between concentrations of salts in the polymer and solution.

The solid lines in Figure 2 indicate the calculated values of $\bar{C}_K$ and the points are experimental values obtained by the pH-method. Values of $\bar{C}^0_{HA}$ were obtained by sorption of individual components (Figure 1). The satisfactory coincidence of K^+ concentrations in PVA, predicted by model and measured experimentally, testifies correct utilization of Donnan equilibrium principles for neutral polymers, having charged groups.

The main diffusive and kinetic laws of the transport process in four-component system consisting of polymer, water, acid and salt were determined by mathematical modeling.

For acid/salt mixtures the system of Nernst–Planck equations may be written as

$$J_i = D_i(\nabla\bar{C}_i + \bar{C}_iF\nabla\varphi/RT) \tag{11}$$

where $i = H^+, K^+, A^-$.

Equation (11), electroneutral Equation (8) and the equation of absence of current in a system

$$J_H + J_K = J_A \tag{12}$$

enable us to obtain the expressions for the diffusion potential:

$$F\nabla\varphi/RT = \frac{(D_A{}^*(F - \bar{C}_H(F - 1)^2/C_F^0) - D_H)\nabla\bar{C}_H + (D_A - D_K)\nabla\bar{C}_K}{(D_A{}^*F + D_H)\bar{C}_H + (D_A + D_K)\bar{C}_K} \tag{13}$$

and after that cation fluxes:

$$\begin{aligned} J_H &= -D_{HH}\nabla\bar{C}_H - D_{HK}\nabla\bar{C}_K, \\ J_K &= -D_{KK}\nabla\bar{C}_K - D_{KH}\nabla\bar{C}_H \end{aligned} \tag{14}$$

where

$$\begin{aligned} D_{HH} &= D_H[D_A(2F - \bar{C}_H(F - 1)^2/C_F^0) + (D_A + D_K)\bar{C}_K]/[(D_A{}^*F \\ &\quad + D_H)\bar{C}_H + (D_A + D_K)\bar{C}_K],\ D_{KK} \\ &= D_K[2D_A + (D_A{}^*F + D_H)\bar{C}_H]/[(D_A{}^*F + D_H)\bar{C}_H + (D_A \\ &\quad + D_K)\bar{C}_K],\ D_{HK} \\ &= D_H(D_A - D_K)\bar{C}_H]/[(D_A{}^*F + D_H)\bar{C}_H + (D_A + D_K)\bar{C}_K],\ D_{KH} \\ &= D_K[(D_A(F - \bar{C}_H(F - 1)^2/C_F^0) \\ &\quad - D_H)\bar{C}_K]/[(D_A{}^*F + D_H)\bar{C}_H + (D_A + D_K)\bar{C}_K]. \end{aligned} \tag{15}$$

All coefficients D_{ii} and D_{ij} $(i, j = K, H)$ are functions of ion concentrations and that is why solutions of (14) are more simple for steady-state transport. This is the reason for our experimental measurements of steady-state fluxes (permeability). Choosing a completely dissociated acid (HA) and salt (KA) as independent components, we can write

$$\begin{aligned} -J_H &= -J_{HA} = D_{HH}\nabla\bar{C}_{HA} + D_{HK}\nabla\bar{C}_{KA}, \\ -J_K &= -J_{KA} = D_{KK}\nabla\bar{C}_{KA} + D_{KH}\nabla C_{HA} \end{aligned} \tag{16}$$

where D_{ij} is defined by thermodynamic Onzager coefficients.

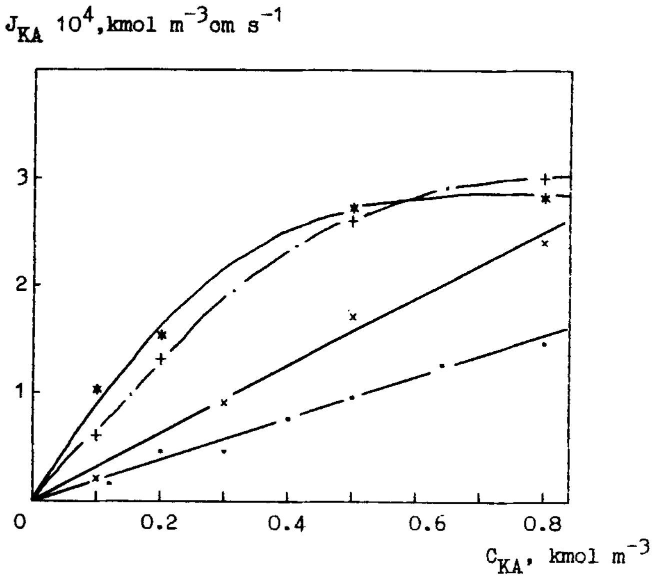

FIGURE 3 Concentration dependencies of flux of potassium chloride through PVA film in the presence of HCl. Initial concentration of HCl in solution: 0 (●), 0.1 (×), 0.3 (+), 0.5 (*) mol/l.

TABLE I

Diffusion coefficients of salt in the PVA-HCl-KCl system

$\bar{C}^0_{KCl,M}$	$\bar{C}_{HCl}$ = 0, 1 M D_{KK}*10⁶ cm²/s	D_{KH}*10⁶ cm²/s
0.1	2.25	2.25
0.2	2.75	1.25
0.3	2.50	0.75
0.4	3.25	0.75
0.5	3.25	0.75
0.6	3.75	1.00
0.7	3.75	0.75
0.8	3.75	1.00

To simplify the solutions of the diffusion equations, we used the potential function $\Phi_i(\bar{C}_i\bar{C}_j)$, which is characterized by property

$$-\partial\Phi/\partial\bar{C}_j = D_{ij}. \tag{17}$$

This function is quite similar to partial permeability $\Phi_i^0 = \int_0^{\bar{C}^0} D_{ij}\partial\bar{C}_j$, which yields in general case

$$\Delta\Phi_i = \Phi_i(\bar{C}_i^0, \bar{C}_j^0) - \Phi_i(\bar{C}_i^1 - \bar{C}_j^1) = \int_0^1 J_i dx \tag{18}$$

TABLE II

Diffusion coefficients of acid in the PVA-HCL-KCl system

	$\bar{C}_{KCl} = 0, 1$ M	
$\bar{C}^0_{HCl,M}$	$D_{HH}*10^6$ cm^2/s	$D_{HK}*10^6$ cm^2/s
0.1	5.00	1.75
0.2	5.00	1.75
0.3	5.00	2.25
0.4	5.00	2.25
0.5	7.50	2.50
0.6	8.75	3.50
0.7	12.5	4.00
0.8	15.0	4.00

and for steady-state transport

$$\Delta\Phi_i = J_i\, 1, \tag{19}$$

$$D_{ij} = \lim[\Delta\Phi_i/\Delta\bar{C}_j]_{C_k = \text{const.}} \tag{20}$$

$(i = K, H \sim m = H, K \quad i \neq m)$.

Equation (20) enables us to determine D_{ij} by experimental measurements of stationary flux (J). Really, so far as expression

$$\Phi_i(\bar{C}^0_H, \bar{C}^0_K) = \Phi_i(0, 0) + J(\bar{C}^0_H, \bar{C}^0_K)1 \tag{21}$$

follows from (18), differentiation of (21) yields

$$\partial\Phi_i/\partial\bar{C}^0_j = (\partial J/\partial\bar{C}^0_j)*1 \tag{22}$$

and graphical differentiation (Figure 3) using coordinates $J(\bar{C}^0_i)_{\bar{C}^0_j = \text{const.}} - \bar{C}^0_i$ enable us to obtain partial diffusion coefficients D_{ij}

$$D_{ij} = \tan\beta*1 \tag{23}$$

where tanβ is the slope of the dependence $J(\bar{C}^0_i)$.

The examples of values of partial diffusion coefficients, calculated by equation (23) after differentiation of dependence $J(\bar{C}^0_i)$, are represented in Tables I and II.

The proposed mathematical model, experimental methods and the methods of calculation of transport parameters can be used for similar multicomponent systems.

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