

Coupled Diffusion by Proton Exchange in Aqueous Solutions of Acetic Acid + Triethylamine

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Nernst–Planck equations are used to calculate ternary interdiffusion coefficients (D_{ik}) for aqueous solutions of a molecular weak acid and base that react as follows: $B + HA \rightleftharpoons BH^+ + A^-$. The D_{ik} coefficients provide a convenient description of diffusion by relating the fluxes of the total acid and base components to the gradient in the concentration of each component: $J_1 = -D_{11}\nabla C_1 - D_{12}\nabla C_2$; $J_2 = -D_{21}\nabla C_1 - D_{22}\nabla C_2$. Cross-coefficients D_{12} and D_{21} measure the coupled fluxes of acid and base caused by local equilibrium of the proton exchange reaction and by the diffusion-induced electric field that adjusts the speeds of the diffusing BH^+ and A^- ions to prevent charge separation. The contribution to each D_{ik} coefficient from the migration of the BH^+ and A^- ions in the electric field is evaluated to help interpret the concentration dependence of the diffusion behavior. Strongly coupled diffusion is predicted in cases where a gradient in the acid is formed in an alkaline solution of excess base, or *vice versa*. The accuracy of the predictions is tested by using Taylor dispersion to measure D_{ik} coefficients for aqueous solutions of acetic acid + triethylamine at 25 °C.

Introduction

The interdiffusion of weak acids and bases is important in a surprising range of processes, including ion exchange,¹ active transport in biological systems,^{2–4} and the chemical absorption of industrial gases (for example, the reversible absorption of CO_2 and H_2S by aqueous amines).^{5–7} The work reported here is a study of coupled interdiffusion in solutions of a molecular weak acid (HA) and weak base (B) that react by proton exchange.



One of the interesting features of this system is the formation of ionic products from molecular reactants. The reacted acid and base must therefore diffuse together to prevent charge separation. Additional coupling is provided by local equilibrium of the proton exchange reaction.

Previous studies have shown that ternary Fick equations

$$J_1(\text{total acid}) = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \quad (2)$$

$$J_2(\text{total base}) = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \quad (3)$$

provide an accurate and convenient description of acid/base interdiffusion by relating measurable fluxes of total (reacted + unreacted) acid and base components to the gradients in the concentration of each component.^{8,9} In this paper Nernst–Planck equations are used to predict the ternary interdiffusion coefficients (D_{ik}) for aqueous solutions of acid HA and base B. To help understand the complicated diffusion behavior of these systems, the electrostatic contribution to each D_{ik} coefficient made by the migration of BH^+ and A^- ions in the diffusion-induced electric field is estimated. Dissociation of the acid (HA

$\rightleftharpoons H^+ + A^-$) and hydrolysis of the base ($B + H_2O \rightleftharpoons BH^+ + OH^-$) are included in the analysis.

The accuracy of the predictions is tested by measuring D_{ik} coefficients for aqueous solutions of acetic acid (1) + triethylamine (2). This system was chosen because the mobilities required for the Nernst–Planck calculations are available^{10–12} for aqueous acetate and triethylammonium ions and for acetic acid and triethylamine molecules. Also, binary diffusion coefficients reported previously for aqueous acetic acid^{12,13} and triethylamine¹¹ may be compared with the present ternary results.

Experimental Section

Solutions were prepared by dissolving weighed amounts of reagent-grade acetic acid and triethylamine (> 99.5% purity, Caledon Laboratories) in distilled, deionized water in calibrated volumetric flasks. Ternary mutual diffusion coefficients of the solutions were measured at 25 °C by the Taylor dispersion (peak-broadening) method. At the start of each run a 20- μ L sample of solution was injected into a laminar carrier stream of slightly different composition at the entrance to a Teflon dispersion tube (length 3524 cm, inner radius 0.0473₈ cm). Sample retention times were typically 8000–9000 s. The D_{ik} coefficients were evaluated by least-squares analysis of the refractive index profiles across pairs of dispersed sample peaks¹⁴ (one generated by an initial concentration gradient in acetic acid, the other by an initial gradient in triethylamine). Details of the equipment and procedure have been described.^{14,15}

Results

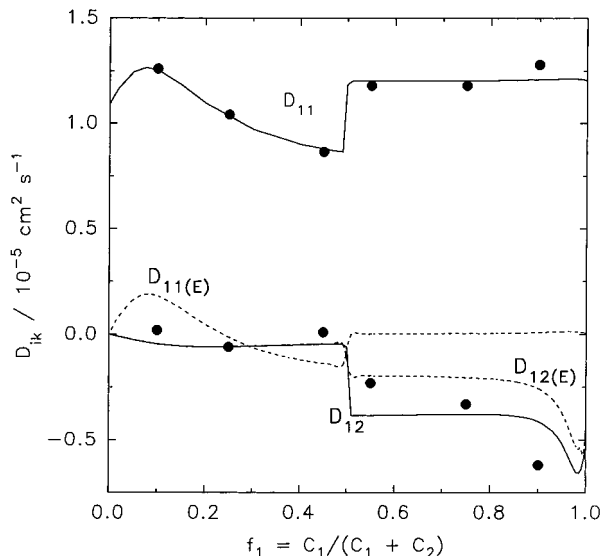
Ternary interdiffusion coefficients were measured 6–8 times for each acetic acid (1) + triethylamine (2) carrier solution and averaged. The results are summarized in Table 1. The standard deviations of the measured D_{ik} coefficients were typically $(0.02 \text{ to } 0.03) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Previous work has shown that sharp changes in diffusion coefficients can occur at the boundary between acidic and

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TABLE 1: Ternary Diffusion Coefficients of Aqueous Acetic Acid (1) + Triethylamine (2) Solutions at 25 °C^a

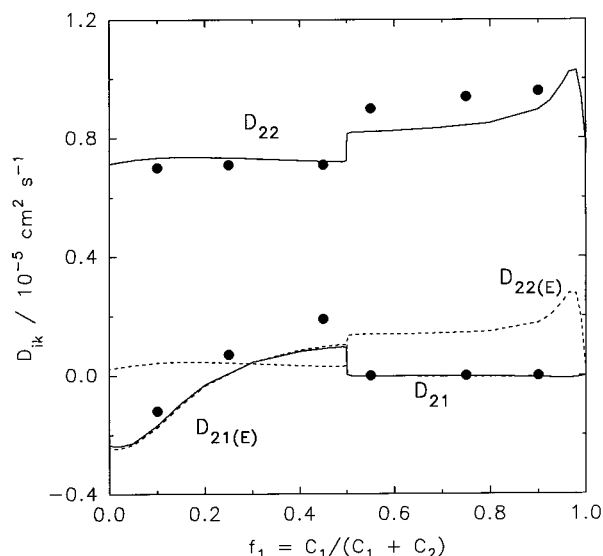
C_1	C_2	D_{11}	D_{12}	D_{21}	D_{22}
0.010	0.090	1.26	0.02	-0.01	0.70
0.025	0.075	1.04	-0.06	0.07	0.71
0.045	0.055	0.86	0.01	0.19	0.71
0.055	0.045	1.18	-0.23	0.00	0.90
0.075	0.025	1.18	-0.33	0.00	0.94
0.090	0.010	1.28	-0.62	0.00	0.96
0.100	0.300	0.84	0.03	0.15	0.66
0.180	0.220	0.98	0.05	0.19	0.78
0.220	0.180	1.10	-0.24	0.00	0.83
0.300	0.100	1.13	-0.33	0.00	0.88

^a Units: D_{ik} in $10^{-5} \text{ cm}^2 \text{ s}^{-1}$; C_i in mol L^{-1} .**Figure 1.** Ternary diffusion coefficients, D_{11} and D_{12} , of the acetic acid component in aqueous acetic acid (1) + triethylamine (2) solutions plotted against the solute fraction of acetic acid for solutions containing 0.100 mol L^{-1} total solute. Key: (●) measured values; (—) predicted values (eqs 13–16); (---) predicted electrostatic contributions (eqs 17 and 18).

alkaline solution compositions.^{8,9} To avoid possible difficulties in the fitting procedure caused by strong variations in the diffusion coefficients across the dispersion profiles, acidic solution samples ($C_1 > C_2$) were always injected into acidic carrier solutions and alkaline solution samples ($C_1 < C_2$) were always injected into alkaline carrier solutions. The concentration of acetic acid or triethylamine in the injected solutions and carrier solutions differed by $\leq 0.100 \text{ mol L}^{-1}$. These solutions gave D_{ik} coefficients that were independent of the initial concentration differences within the precision of the experiment.

Molar ratios of acetic acid to triethylamine ranging from 1:10 to 10:1 were used to explore the composition dependence of the diffusion behavior. In Figures 1 and 2 the D_{ik} coefficients for the solutions containing 0.100 mol L^{-1} total acetic acid + triethylamine are plotted against the solute fraction of acetic acid, $f_1 = C_1/(C_1 + C_2)$.

Figure 1 shows the diffusion coefficients of the acetic acid component, D_{11} and D_{12} . For the acidic solutions that contain excess acetic acid relative to triethylamine ($f_1 > 0.50$), the main diffusion coefficient of the acetic acid component (D_{11}) is similar to the binary diffusion coefficient reported previously¹² for 0.100 mol L^{-1} aqueous acetic acid: $D = 1.20 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. However, diffusion of the acid is not a pseudo-binary process because the large, negative D_{12} values indicate that the triethylamine concentration gradient drives a substantial coupled flow of acetic acid, from lower to higher triethylamine concentrations.

**Figure 2.** Ternary diffusion coefficients D_{22} and D_{21} of the triethylamine component in aqueous acetic acid (1) + triethylamine (2) solutions plotted against the solute fraction of acetic acid for solutions containing 0.100 mol L^{-1} total solute. Key: (●) measured values; (—) predicted values (eqs 13–16); (---) predicted electrostatic contributions (eqs 17 and 18).

As the solute fraction of acetic acid drops below 0.50, D_{11} decreases and then increases. Also, the values of D_{12} become very small. This result suggests that the coupled transport of acetic acid “switches off” in alkaline solutions. It is impossible for the gradient in the concentration of triethylamine to drive a coupled flow of acetic acid in a solution free of acetic acid. Consequently, D_{12} must vanish as $f_1 \rightarrow 0$.

In Figure 2 the diffusion coefficients of the triethylamine component (D_{21} and D_{22}) are plotted against the solute fraction of acetic acid. For the alkaline solutions ($f_1 < 0.50$), the values of the main diffusion coefficient of the triethylamine component (D_{22}) are close to the binary mutual diffusion coefficient¹¹ of 0.100 mol L^{-1} aqueous triethylamine: $D = 0.70 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. At low solute fractions of acid, the diffusion of the acetic acid component drives a substantial countercurrent coupled flow of triethylamine. As the solute fraction of acetic acid rises above 0.50, there is a sharp increase in D_{22} . Also, D_{21} drops to zero. Though not plotted, the diffusion coefficients for the solutions containing 0.400 mol L^{-1} total acetic acid + triethylamine show similar behavior.

Discussion

Previous work has shown that limiting ionic conductivities and binary diffusion data can be used to predict multicomponent diffusion coefficients.^{15–18} In this section equations are developed to predict the interdiffusion coefficients of aqueous solutions of a weak acid HA and weak base B. The results are used to interpret the diffusion behavior of aqueous solutions of acetic acid + triethylamine.

Concentrations of the Solute Species. The first step is to calculate the concentrations of the A^- and BH^+ ions and the unreacted HA and B molecules. This calculation will allow the ternary diffusion coefficients measured for the total acid and base components to be related to the transport of actual solution species. Unless the acid is very weak, solutions of excess acid ($C_1 > C_2$) will also contain significant concentrations of H^+ ions produced by dissociation of the molecular acid: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$. Similarly, the hydrolysis reaction $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$ might produce significant concentrations of OH^-

ions in solutions of excess base ($C_2 > C_1$). These considerations suggest that six different solute species should be included in the analysis; that is, HA, B, BH⁺, A⁻, H⁺, and OH⁻.

Given the concentrations of total (reacted + unreacted) acid and base components

$$C_1(\text{total acid}) = c_{\text{HA}} + c_{\text{A}^-} \quad (4)$$

$$C_2(\text{total base}) = c_{\text{B}} + c_{\text{BH}^+} \quad (5)$$

the concentrations of the species can be evaluated by solving the equations (eqs 6–9) for charge balance and equilibrium of the dissociation reactions.

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad K_1 = c_{\text{H}^+}c_{\text{A}^-}/c_{\text{HA}} \quad (6)$$

$$\text{BH}^+ \rightleftharpoons \text{H}^+ + \text{B} \quad K_2 = c_{\text{H}^+}c_{\text{B}}/c_{\text{BH}^+} \quad (7)$$

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_{\text{W}} = c_{\text{H}^+}c_{\text{OH}^-} \quad (8)$$

$$c_{\text{BH}^+} + c_{\text{H}^+} = c_{\text{A}^-} + c_{\text{OH}^-} \quad (9)$$

In view of subsequent approximations made in the analysis, eqs 6–8 have been simplified by assuming that the activity of water and the activity coefficients of the HA and B molecules are unity. In addition, the activity coefficients of the ions (all univalent) are assumed to equal a mean value, γ_{\pm} . These approximations are reasonable unless the solutions are very concentrated.

Predicted Ternary Diffusion Coefficients. It is difficult to measure the interdiffusion of solute species in solutions with rapid dissociation or exchange reactions. For dilute solutions, however, the Nernst–Planck approximation¹⁹:

$$j_s = -c_s(D_s/RT)\nabla\tilde{\mu}_s = -c_sD_s\nabla\ln(y_sc_s) + z_sc_sF(D_s/RT)E \quad (10)$$

can be used to estimate the flux of each species as the product of its concentration c_s , mobility D_s/RT , and driving force $-\nabla\tilde{\mu}_s$. The parameters D_s , $\tilde{\mu}_s$ and z_s are the diffusion coefficient, electrochemical potential and valence of species $s = \text{HA}, \text{B}, \text{BH}^+, \text{A}^-, \text{H}^+, \text{and OH}^-$, respectively. In eq 10, T is the temperature, R is the gas constant, F is the Faraday constant, and E is the diffusion-induced electric field.

Although there are six different solute species, only two diffusional fluxes are independent because of the constraints imposed by electroneutrality and the dissociation equilibria (eqs 6–9). The Nernst–Planck equations relating the fluxes of solute species to electrochemical potential gradients can therefore be transformed²⁰ to the much simpler equations

$$J_1(\text{total acid}) = -L_{11}\nabla\mu_1 - L_{12}\nabla\mu_2 \quad (11)$$

$$J_2(\text{total base}) = -L_{21}\nabla\mu_1 - L_{22}\nabla\mu_2 \quad (12)$$

to relate the fluxes of the total acid and base components to the gradients in their chemical potentials. Here $J_1 = j_{\text{HA}} + j_{\text{A}^-}$, $J_2 = j_{\text{B}} + j_{\text{BH}^+}$, $\mu_1 = \tilde{\mu}_{\text{HA}} = \tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{\text{A}^-}$, and $\mu_2 = \tilde{\mu}_{\text{B}} = \tilde{\mu}_{\text{BH}^+} + \tilde{\mu}_{\text{OH}^-}$. The total acid and base components are electrically neutral, so the electric field does not appear explicitly in eq 11 or 12.

Matrix equations have been developed²⁰ to estimate L_{ik} coefficients for solutions containing any number of components

and constituent species. These general equations give

$$RTL_{11} = c_{\text{HA}}D_{\text{HA}} + \frac{c_{\text{A}^-}D_{\text{A}^-}(c_{\text{BH}^+}D_{\text{BH}^+} + c_{\text{H}^+}D_{\text{H}^+} + c_{\text{OH}^-}D_{\text{OH}^-})}{c_{\text{BH}^+}D_{\text{BH}^+} + c_{\text{A}^-}D_{\text{A}^-} + c_{\text{H}^+}D_{\text{H}^+} + c_{\text{OH}^-}D_{\text{OH}^-}} \quad (13)$$

$$RTL_{12} = \frac{c_{\text{BH}^+}D_{\text{BH}^+}c_{\text{A}^-}D_{\text{A}^-}}{c_{\text{BH}^+}D_{\text{BH}^+} + c_{\text{A}^-}D_{\text{A}^-} + c_{\text{H}^+}D_{\text{H}^+} + c_{\text{OH}^-}D_{\text{OH}^-}} \quad (14)$$

$$RTL_{22} = c_{\text{B}}D_{\text{B}} + \frac{c_{\text{BH}^+}D_{\text{BH}^+}(c_{\text{A}^-}D_{\text{A}^-} + c_{\text{H}^+}D_{\text{H}^+} + c_{\text{OH}^-}D_{\text{OH}^-})}{c_{\text{BH}^+}D_{\text{BH}^+} + c_{\text{A}^-}D_{\text{A}^-} + c_{\text{H}^+}D_{\text{H}^+} + c_{\text{OH}^-}D_{\text{OH}^-}} \quad (15)$$

for the solutions of acid and base considered in the present study. Expressions for the ternary diffusion coefficients are then obtained by using the identity²⁰

$$D_{ik} = \sum_{m=1}^2 L_{im}\partial\mu_m/\partial C_k \quad (16)$$

where $\partial\mu_1/\partial C_k = RT\partial\ln c_{\text{HA}}/\partial C_k$ and $\partial\mu_2/\partial C_k = RT\partial\ln c_{\text{B}}/\partial C_k$. The D_{ik} coefficients provide a more convenient description of diffusion than the Nernst–Planck equations by relating the solute fluxes to measurable concentration gradients. The number of flux equations is reduced from six to two, and evaluation of the electric field is not required.

To calculate the L_{ik} coefficients we used species diffusion coefficients derived from limiting ionic conductivities¹⁰ and binary mutual diffusion measurements^{11,12}: $D_{\text{HA}} = 1.20$, $D_{\text{B}} = 0.70$, $D_{\text{BH}^+} = 0.75$, $D_{\text{A}^-} = 1.09$, $D_{\text{H}^+} = 9.32$, and $D_{\text{OH}^-} = 5.28$ (in units of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$). The concentrations of the species were calculated by using the dissociation constants^{10,21,22} $K_1 = 1.75 \times 10^{-5}$, $K_2 = 1.93 \times 10^{-11}$ and $K_{\text{W}} = 1.03 \times 10^{-14}$. Ionic activity coefficients were estimated by using the expression¹⁰ $\gamma_{\pm} = \exp[-A|I|^{1/2}/(1 + |I|^{1/2})]$, where $A = 1.17$ at 25 °C and $I = (c_{\text{BH}^+} + c_{\text{H}^+} + c_{\text{A}^-} + c_{\text{OH}^-})/2$ is the ionic strength in units of mol L⁻¹.

Ternary diffusion coefficients calculated for the solutions containing 0.100 mol L⁻¹ total solute are plotted against the solute fraction of acetic acid in Figures 1 and 2 (solid curves). Sharp changes in the D_{ik} values are predicted at the transition from acidic to basic solutions ($f_1 = 0.50$). Maxima and minima are predicted at other compositions. Agreement with the measured coefficients is generally within $\pm 0.10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

To explain the interesting composition dependence of the diffusion coefficients shown in Figures 1 and 2, it will be helpful to estimate the electrostatic contribution²³ $D_{ik(\text{E})}$ to each D_{ik} coefficient. This contribution arises from the migration of A⁻ and BH⁺ ions driven by the diffusion-induced electric field. Specifically, $D_{ik(\text{E})}$ gives the flux of component i caused by the electric field generated by the gradient in the concentration of component k . The general equations for the $D_{ik(\text{E})}$ coefficients developed in ref 23 give

$$D_{1k(\text{E})} = t_{\text{A}^-}Q_k \quad (17)$$

$$D_{2k(\text{E})} = -t_{\text{BH}^+}Q_k \quad (18)$$

for the solutions considered here. The parameter t_s is the transference number of species s

$$t_s = \frac{c_s z_s^2 D_s}{\sum_q c_q z_q^2 D_q} \quad (19)$$

and Q_k is an abbreviation for

$$Q_k = D_{\text{BH}^+} \frac{\partial c_{\text{BH}^+}}{\partial C_k} - D_{\text{A}^-} \frac{\partial c_{\text{A}^-}}{\partial C_k} + D_{\text{H}^+} \frac{\partial c_{\text{H}^+}}{\partial C_k} - D_{\text{OH}^-} \frac{\partial c_{\text{OH}^-}}{\partial C_k} \quad (20)$$

The dashed curves in Figures 1 and 2 give the calculated $D_{\text{ik(E)}}$ values for the solutions containing 0.100 mol L⁻¹ total acetic acid + triethylamine.

Gradient in Acetic Acid (1). Diffusion driven by the gradient in the acetic acid component is relatively simple for acidic solutions that contain excess acetic acid relative to triethylamine ($f_1 > 0.50$). These solutions contain three important solute species: HA, BH⁺, and A⁻. (Only trace amounts of H⁺ ions are present because the dissociation of acetic acid is very weak.) Figure 3 shows the gradients in the concentrations of the solute species formed by a 0.010 mol L⁻¹ cm⁻¹ gradient in the total acetic acid component at $f_1 = 0.75$. The mean concentration of the acetic acid component is 0.075 mol L⁻¹ and the concentration of the triethylamine component is fixed at 0.025 mol L⁻¹ in this example. It is clear from Figure 3 that the gradient in the acetic acid component produces an essentially identical gradient in the molecular acetic acid species. The main diffusion coefficient of the total acetic acid component, D_{11} , is therefore closely approximated by D_{HA} (1.20×10^{-5} cm² s⁻¹, in Figure 1) for acidic solutions. The gradient in the concentration of the acetate ion and the acetate flux are negligible, so the acetate ion does not make a significant contribution to D_{11} in acidic solutions. The dominance of molecular transport along the acetic acid gradient is reflected by the negligibly small values of the electrostatic term $D_{11(\text{E})}$ for $f_1 > 0.50$.

In acidic solutions, virtually all of the triethylamine component exists as triethylammonium ions (BH⁺) ions. Because the gradient in HA molecules does not produce a gradient in the concentration of BH⁺ ions nor an electric field that would drive ionic flows, cross-coefficient D_{21} is negligible for acidic solutions.

Transport produced by the acetic acid gradient is very different in the alkaline solutions that contain excess triethylamine relative to acetic acid ($f_1 < 0.50$) because the acetic acid component diffuses as acetate ions, not acetic acid molecules. For example, the tracer diffusion coefficient of the acetic acid component in supporting triethylamine solutions equals the diffusion coefficient of the acetate ion: as $f_1 \rightarrow 0$, $D_{11} \rightarrow D_{\text{A}^-}$ (the intercept 1.09×10^{-5} cm² s⁻¹ in Figure 1). Because the transport number of the acetate ion vanishes in this limit, the electric field plays no role in the tracer diffusion of the acetate ion: $D_{11(\text{E})} \rightarrow 0$ as $f_1 \rightarrow 0$.

About 8% of the total triethylamine component is hydrolyzed to BH⁺ and OH⁻ ions in a 0.100 mol L⁻¹ triethylamine solution. The important solute species at low fractions of acetic acid (<0.3) are therefore B, BH⁺, A⁻, as well as OH⁻ ions. Figure 4 shows the concentration gradients in these species produced by a 0.010 mol L⁻¹ cm⁻¹ gradient in the acetic acid component at $f_1 = 0.10$. In this case, the average concentration of the acetic acid component is 0.01 mol L⁻¹ and the concentration of the total triethylamine component ($C_2 = c_{\text{B}} + c_{\text{BH}^+}$) is constant at 0.09 mol L⁻¹. Figure 4 illustrates that in alkaline solutions the

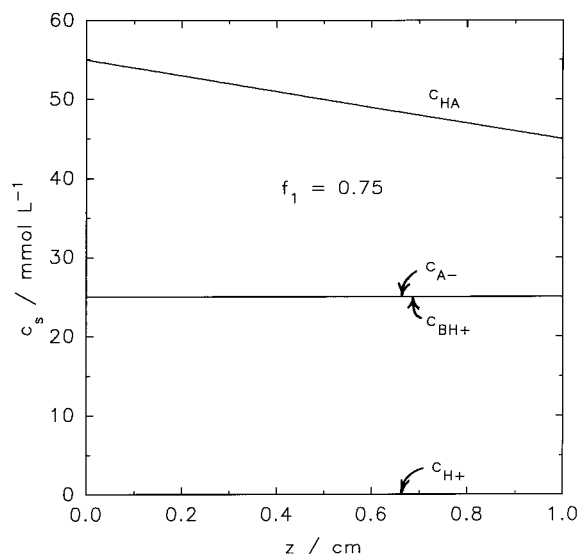


Figure 3. Gradients in the concentrations of the solute species formed by the gradient $\nabla C_1 = 0.010$ mol L⁻¹ cm⁻¹ in the concentration of the acetic acid component in acidic solutions ($f_1 = 0.75$). The average concentration of the acetic acid component along the diffusion path is 0.075 mol L⁻¹. The concentration of the triethylamine component is constant at 0.025 mol L⁻¹.

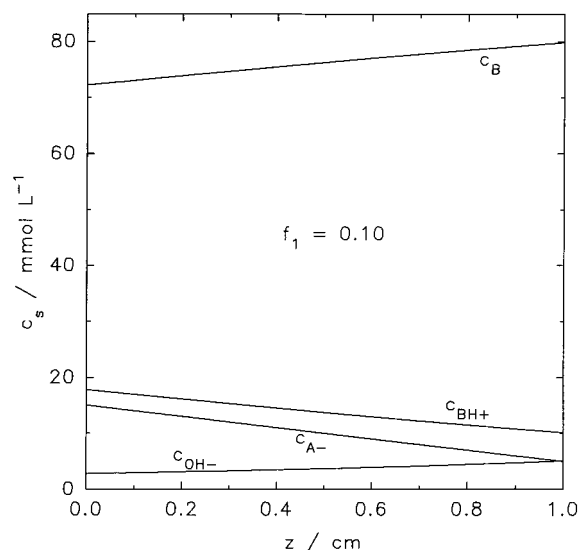


Figure 4. Gradients in the concentrations of the solute species formed by the gradient $\nabla C_1 = 0.010$ mol L⁻¹ cm⁻¹ in the concentration of the acetic acid component in alkaline solutions ($f_1 = 0.10$). The average concentration of the acetic acid component along the diffusion path is 0.010 mol L⁻¹. The concentration of the triethylamine component is constant at 0.090 mol L⁻¹.

gradient in the acetic acid component produces gradients in molecular triethylamine and triethylammonium ions of equal magnitude but of opposite sign ($\nabla C_2 = 0 = \nabla c_{\text{B}} + \nabla c_{\text{BH}^+}$). Because the diffusion coefficients of molecular triethylamine and triethylammonium ions differ by only a few percent, the fluxes of reacted and unreacted triethylamine species driven by their opposing concentration gradients nearly cancel. As a result, the gradient in the acetic acid component cannot drive a significant coupled flow of the total triethylamine component by a purely diffusive mechanism.

Figure 4 shows, however, that the acetic acid gradient produces a substantial gradient in the concentration of OH⁻ ions at low solute fractions of the acid. In view of their exceptional mobility, OH⁻ ions tend to diffuse rapidly up the acetic acid gradient, countercurrent to the acetate flux, toward the region

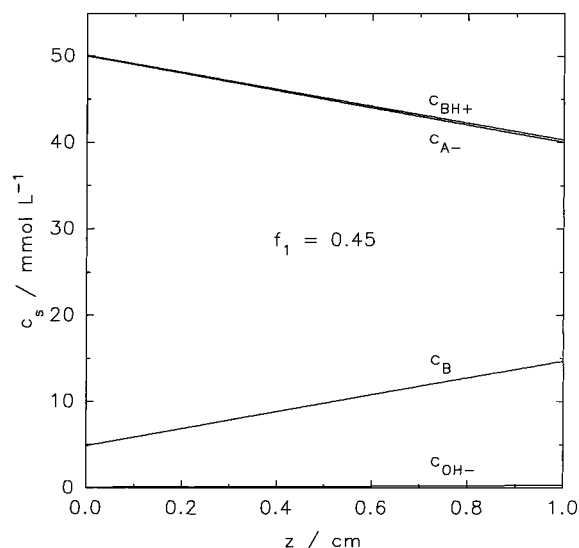


Figure 5. Gradients in the concentrations of the solute species formed by the gradient $\nabla C_1 = 0.010 \text{ mol L}^{-1} \text{ cm}^{-1}$ in the concentration of the acetic acid component in alkaline solutions ($f_1 = 0.45$). The average concentration of the acetic acid component along the diffusion path is 0.045 mol L^{-1} . The concentration of the triethylamine component is constant at 0.055 mol L^{-1} .

of lower OH^- hydroxide concentration. Charge separation is prevented by the electric field, which is generated to slow the diffusing OH^- ions (moving from right to left in Figure 4). The electric field has two other important effects. First, it drives the acetate ions down the acetate gradient (from left to right), thereby enhancing the rate of diffusion of the acetic acid component. This mechanism is confirmed by the positive values of $D_{11(\text{E})}$ and the subsequent increase in D_{11} at low values of f_1 . The electric field has the additional effect of driving BH^+ ions countercurrent to the acetate flux (from right to left). The coupled flow of BH^+ ions driven by the electric field along the acetic acid gradient accounts for the negative values of both D_{21} and the electrostatic contribution $D_{21(\text{E})}$ at low solute fractions of acetic acid.

As the solute fraction of acetic acid rises toward 0.5, however, more BH^+ and A^- ions are produced by the $\text{B} + \text{HA} \rightleftharpoons \text{BH}^+ + \text{A}^-$ reaction. In this composition region, BH^+ and A^- ions become the predominate solute species, with only minor amounts of OH^- ions present. Figure 5 shows the gradients in the solute species produced by the gradient in acetic acid at $f_1 = 0.45$. Now the role of the electric field is to slow the acetate ions, which are 45% more mobile than the triethylammonium ions. By reducing the acetate flux, the electric field generated by the acetic acid gradient leads to negative values of $D_{11(\text{E})}$ and a corresponding decrease in D_{11} . As shown in Figure 1, the electrostatic contribution leads to a maximum in D_{11} in alkaline solutions near $f_1 = 0.08$.

The electric field has the additional effect of driving BH^+ ions down the acetic acid gradient (from left to right in Figure 3). This leads to positive values of $D_{21(\text{E})}$ as the solute fraction of acetic acid rises to 0.5. The dominant role played by the electric field in the coupled transport of triethylamine is illustrated by the fact that D_{21} is virtually identical to $D_{21(\text{E})}$ for alkaline solutions ($f_1 < 0.50$).

Gradient in Triethylamine (2). Diffusion caused by the gradient in the triethylamine component will not be discussed in as much detail because of the close analogy with diffusion caused by acetic acid gradient. In solutions of excess triethylamine, for example, the main effect of the triethylamine gradient is to produce a flux of triethylamine molecules. The values of

$D_{22(\text{E})}$ indicate, however, a small electrostatic enhancement of the rate of rate of diffusion of the triethylamine component. In this case, the relatively mobile OH^- ions produced by partial hydrolysis drag along the triethylammonium ions. The electric field generated by the diffusing triethylamine component also produces a weak countercurrent coupled flow of acetic acid (as acetate ions) in alkaline solutions.

Just as the gradient in the acetic acid component produces significant coupled flows of the triethylamine component in alkaline solutions, the gradient in triethylamine produces significant coupled flows of acetic acid in acidic solutions. This qualitative symmetry is not perfect, however. As already discussed, the nearly identical diffusion coefficients of the triethylammonium ions and molecular triethylamine leads to coupled flows of the triethylamine component that are driven almost entirely by the electric field. But molecular acetic acid is $\sim 10\%$ more mobile than acetate ions. When the gradient in triethylamine produces opposing gradients in molecular acetic acid and acetate ions, the pure-diffusion flux of molecular acetic acid (up the gradient in the triethylamine) slightly exceeds the pure-diffusion flux of acetate ions (accompanying the triethylammonium ions down the triethylamine gradient). This difference leads to a negative contribution to D_{12} from pure diffusion in addition to the negative electrostatic contribution $D_{12(\text{E})}$ (see Figure 1, $f_1 > 0.5$).

Conclusions

The present study shows that Taylor dispersion can be used to measure interdiffusion coefficients for solutions of acids and bases, including the cross-coefficients describing the coupled diffusion of the solutes. On one level the measured coefficients provide a useful empirical description of transport in the solutions by relating total flows of acid and base to measurable concentration gradients. With additional effort, the interdiffusion coefficients can be given a clear physical interpretation in terms of fluxes of the solute species driven by concentration gradients and by the diffusion-induced electric field. Although the treatment developed here is confined to solutions of acid HA and base B, it can be readily extended to the diffusion of polyprotic acids and bases as well as other reacting solutes. The strongly coupled interdiffusion of acids and bases has implications for practical mass transport applications, such as the chemical absorption of acid gases or the dissolution of solid acids into alkaline solutions. In particular, the sharp changes in the D_{ik} coefficients at the transition from acidic to alkaline compositions should produce sharp changes in the concentration gradients at the moving reaction front between the interdiffusing acid and base. We are currently investigating this problem.

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