

Coupled Diffusion in Aqueous Weak Acid + Alkanolamine Absorbents

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Taylor dispersion and differential refractometry are used to measure ternary interdiffusion coefficients (D_{ik}) for aqueous solutions of acetic acid + triethanolamine (TEA) and aqueous solutions of oxalic acid + TEA at 25 °C. The D_{ik} coefficients give the coupled fluxes of acid and TEA driven by the gradient in the concentration of each solute. Ternary Fick equations with variable D_{ik} coefficients are integrated numerically to calculate accurate concentration profiles and the moving reaction front produced by the interdiffusion of TEA and acetic or oxalic acid. Ternary diffusion coefficients are also used to predict the rate of dissolution of oxalic acid in 1.00 mol dm⁻³ aqueous TEA, a process analogous to the absorption of a diprotic acid gas by an alkanolamine absorbent. The diffusion of oxalic acid drives a significant counterflow of TEA. The resulting buildup of TEA at the surface of the dissolving acid increases the interfacial concentration of TEA from 1.00 to 1.20 mol dm⁻³, which in turn increases the solubility of the acid by 0.20 mol dm⁻³. Nernst–Planck equations are used to predict D_{ik} coefficients for aqueous weak acid + alkanolamine solutions. The fluxes of these solutes are shown to be strongly coupled by the electric field that is generated by the diffusing ions.

Introduction

The diffusion of dissolved gases in chemical absorbents is important in hydrogenation processes, the operation of electrochemical gas sensors, the hemoglobin-assisted transport of oxygen for metabolic processes, and the reversible and selective absorption of industrial acid gases (CO₂, H₂S, SO₂) by aqueous alkanolamine solutions. Fick's binary equation

$$J = -D\nabla C \quad (1)$$

is frequently used to describe the diffusion of a reacting gas, where J , D , and ∇C denote the flux, the apparent diffusion coefficient, and the gradient in the concentration of total (reacted plus unreacted) dissolved gas. Values of D were reported recently for CO₂ and H₂S in aqueous methyldiethanolamine solutions (Pani et al., 1997a,b; Rowley et al., 1997).

Binary equations can provide a useful and convenient model of diffusion in multicomponent solutions. Experiment and theory show, however, that the interdiffusion of solutes is coupled (Cussler, 1976; Tyrell and Harris, 1984). In general, a gradient in the concentration of solute 1 will produce a flux of solute 2, and vice versa. Diffusion in a three-component solution, such as aqueous CO₂ (1) + alkanolamine (2) + H₂O, is therefore described by the coupled Fick equations

$$J_1(\text{solute 1}) = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \quad (2)$$

$$J_2(\text{solute 2}) = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \quad (3)$$

where ternary diffusion coefficient D_{ik} gives the molar flux of solute i produced by the gradient in the concentration of solute k . Cross-coefficients D_{12} and D_{21} are especially

important for ionic or chemically reacting solutes (Cussler, 1976). In fact, it is not uncommon for D_{12} or D_{21} to be larger than the main diffusion coefficients, D_{11} and D_{22} . One mole of a diffusing solute can therefore cotransport or countertransport more than 1 mol of another solute.

Ternary D_{ik} coefficients were reported recently for aqueous solutions of acetic acid (HA) + triethylamine (NEt₃) (Curtis and Leaist, 1998), which react as follows: HA + NEt₃ ⇌ A⁻ + ⁺HNEt₃. At one composition each mole of diffusing triethylamine countertransported 0.65 mol of acetic acid. Nernst–Planck (NP) equations were used to show that the fluxes of acetic acid and triethylamine are strongly coupled by the diffusion-induced electric field that drives coupled flows of the ionic reaction products, A⁻ and ⁺HNEt₃.

These considerations suggest that coupled diffusion might play a significant role in the absorption of acid gases by aqueous alkanolamine absorbents. An obvious way to explore this possibility would be to measure D_{ik} coefficients for CO₂, H₂S, or SO₂ in aqueous alkanolamine solutions. In practice, however, ternary diffusion measurements require a series of solutions with small but precisely known composition differences. The preparation of these solutions would be extremely difficult for volatile solutes such as CO₂, H₂S, or SO₂.

To provide reliable data for the diffusion of weak acids in alkanolamine solutions, we report here D_{ik} coefficients for aqueous acetic acid + triethanolamine (TEA) solutions and aqueous oxalic acid + TEA solutions. The vapor pressures of these systems are relatively low, so accurate ternary diffusion measurements are feasible. The measured diffusion coefficients are used to calculate accurate concentration profiles for the coupled interdiffusion of TEA and acetic or oxalic acid. The D_{ik} coefficients are also used to calculate the rate of dissolution of oxalic acid in aqueous triethanolamine, a process analogous to the absorption of an acid gas by an alkanolamine absorbent. To help

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understand coupled diffusion in these solutions, NP equations are used to predict the D_{ik} coefficients as well as the electrostatic contribution to each coefficient from the migration of ions in the diffusion-induced electric field.

Experimental Section

The diffusion coefficients reported in this paper were measured at (25.0 ± 0.1) °C by the Taylor dispersion method (Leaist, 1991b). A Rheodyne model 50 injection valve was used to introduce 20 mm³ samples of solution into laminar carrier streams of slightly different composition. The broadened distribution of the dispersed solutes was monitored by a Gilson model 131 differential refractometer at the outlet of a Teflon capillary tube (length 3524 cm, inner radius 0.0473₈ cm). Sample retention times ranged from 7 to 9 ks. Refractometer voltages were measured at 5 s intervals by a Hewlett-Packard model 34401A digital voltmeter.

Solutions were prepared by dissolving weighed amounts of reagent-grade acetic acid, oxalic acid, and TEA (Caledon Laboratories) in distilled, deionized water in volumetric flasks. The purity of the solutes (>99%) was checked by titration against standardized HCl or NaOH solutions. Uncertainties in the concentrations were less than 0.3%.

Binary Diffusion Measurements. Diffusion in binary aqueous solutions of oxalic acid or TEA was measured by injecting solute at concentration $C + \Delta C$ into carrier solutions at concentration C . Binary diffusion coefficients (D) were evaluated by fitting the equation

$$V(t) = V_0 + V_1 t + (t/t_R)^{1/2} V_{\max} \exp\left(-\frac{12D(t-t_R)^2}{r^2 t}\right) \quad (4)$$

to the measured refractometer voltages. r is the inner radius of the dispersion tube, t_R the retention time, and V_{\max} the peak height relative to the baseline voltage $V_0 + V_1 t$. The term $V_1 t$ allows for small linear drifts in the detector signal (<2% of V_{\max}).

Ternary Diffusion Measurements. D_{ik} coefficients for the ternary solutions [e.g., oxalic acid (1) + TEA (2) in water] were measured by injecting solutes at concentration $C_1 + \Delta C_1$, $C_2 + \Delta C_2$ into carrier streams of composition C_1 , C_2 . The ternary dispersion profiles were analyzed by fitting the equation

$$V(t) = V_0 + V_1 t + (t/t_R)^{1/2} V_{\max} \left[W_1 \exp\left(-\frac{12D_1(t-t_R)^2}{r^2 t}\right) + W_2 \exp\left(-\frac{12D_2(t-t_R)^2}{r^2 t}\right) \right] \quad (5)$$

to pairs of sample peaks, one generated by an initial gradient in acetic or oxalic acid and the other generated by an initial gradient in TEA. The D_{ik} coefficients were calculated from the fitted values of D_1 and D_2 (the eigenvalues of the D_{ik} matrix) and the normalized weights ($W_1 + W_2 = 1$) of the exponential terms. Details of the calculations have been reported (Deng and Leaist, 1991).

Results and Discussion

Binary Diffusion in Aqueous Solutions of Oxalic Acid, Acetic Acid, and TEA. In this section binary diffusion data for aqueous oxalic acid, acetic acid, and TEA are summarized briefly before the more complicated coupled diffusion of the solutes is discussed. The values of D at

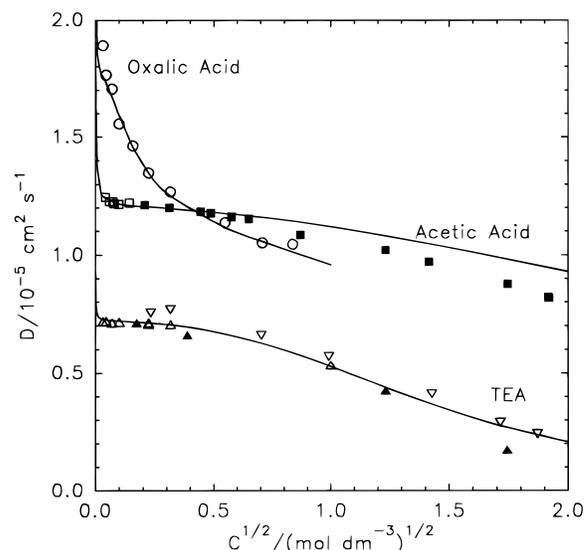


Figure 1. Binary diffusion coefficients of oxalic acid, acetic acid, and TEA solutions at 25 °C plotted against the square root of the concentration of each solute. Oxalic acid: ○, this work; Acetic acid: □, Leaist and Lyons (1984); ■, Vitagliano and Lyons (1956). TEA: △, this work; ▽, Hikita et al. (1980); ▲, Thomas and Furzer (1962). The solid curves give the D values predicted by the NP equations.

Table 1. Binary Diffusion Coefficient of Aqueous Oxalic Acid Solutions at 25 °C

$C/\text{mol dm}^{-3}$	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$C/\text{mol dm}^{-3}$	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$
0.005	1.71	0.100	1.27
0.010	1.52	0.300	1.14
0.025	1.46	0.500	1.05
0.050	1.35	0.700	1.05

each composition were reproducible within $\pm 0.01 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The estimated accuracy of the diffusion measurements is 1 to 2%.

(a) Aqueous Oxalic Acid. Binary diffusion in aqueous solutions of oxalic acid was measured 4 to 6 times at carrier-stream concentrations ranging from 0.005 to 0.700 mol dm⁻³. Table 1 gives the average value of D determined at each composition. These values are plotted against the square root of the total oxalic acid concentration in Figure 1. The plotted curve for oxalic acid gives the concentration dependence of D predicted by the NP treatment developed in the Appendix.

The sharp increase in D evident at low concentrations is caused by the partial dissociation of molecular oxalic acid (H_2L) to hydrogen oxalate (HL^-), oxalate (L^{2-}), and highly mobile hydrogen ions. Although aqueous oxalic acid diffuses in different chemical forms, the association/dissociation reactions ($\text{H}_2\text{L} \rightleftharpoons \text{H}^+ + \text{HL}^-$, $\text{HL}^- \rightleftharpoons \text{H}^+ + \text{L}^{2-}$) are sufficiently rapid compared to diffusion to maintain reaction equilibrium at each point along the diffusion path. As a result of the local equilibrium and electroneutrality restrictions, oxalic acid diffuses through the solutions as a single "total" solute component. Similar considerations apply to the other solutes used in the present study.

(b) Aqueous Acetic Acid. Accurate D values for aqueous acetic acid measured previously by Gouy interferometry (Vitagliano and Lyons, 1956) and a conductometric technique (Leaist and Lyons, 1984) are also plotted in Figure 1. Aqueous acetic acid ($K_a = 1.75 \times 10^{-5}$) is a weaker acid than oxalic acid ($K_{a1} = 0.053$) (Robinson and Stokes, 1959). Consequently, the sharp increase in D caused by dissociation occurs at lower concentrations for acetic acid.

Table 2. Binary Diffusion Coefficient of Aqueous TEA Solutions at 25 °C

$C/\text{mol dm}^{-3}$	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$C/\text{mol dm}^{-3}$	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$
0.001	0.71	0.010	0.71
0.002	0.71	0.050	0.70
0.005	0.71	0.100	0.70

Table 3. Ternary Diffusion Coefficients of Aqueous Acetic Acid (C_1) + Triethanolamine (C_2) Solutions at 25 °C

C_1^a	C_2^a	D_{11}^b	D_{12}^b	D_{21}^b	D_{22}^b
0.005	0.095	0.83	0.00	0.15	0.68
0.025	0.075	0.84	-0.02	0.14	0.67
0.045	0.055	0.83	-0.01	0.12	0.70
0.051	0.049	1.00	-0.18	0.08	0.73
0.055	0.045	1.15	-0.42	0.00	0.80
0.075	0.025	1.16	-0.39	0.00	0.85
0.085	0.015	1.15	-0.42	-0.01	0.89
0.095	0.005	1.17	-0.70	-0.01	0.98

^a In units of mol dm^{-3} . ^b In units of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

(c) Aqueous TEA. In previous studies, diaphragm cells (Hikita et al., 1980) and Gouy interferometry (Thomas and Furzer, 1962) were used to measure binary diffusion in aqueous TEA solutions. As shown in Figure 1, the diaphragm-cell results are about 7% larger than the optical results. In an attempt to resolve this discrepancy, we used Taylor dispersion to remeasure diffusion in aqueous TEA solutions. The results are summarized in Table 2. Figure 1 shows that the dispersion results are in close agreement (2% or better) with the previously reported interferometric D values for aqueous TEA solutions. This comparison provides a measure of support for the dispersion results since interferometric diffusion measurements are usually very accurate ($\pm 0.2\%$).

Hydrolysis ($\text{B} + \text{H}_2\text{O} = \text{BH}^+ + \text{OH}^-$) can produce a significant increase in the diffusion coefficients of dilute aqueous amines (Leaist and Lu, 1997) owing to the exceptional mobility of the hydroxide ions. Aqueous TEA, however, is a relatively weak base (Robinson and Stokes, 1959). At the lowest TEA concentration used in the present study, only about 2% of the total TEA is hydrolyzed and the resulting increase in D is very small.

Ternary Diffusion in Aqueous Acetic Acid (C_1) + TEA (C_2) Solutions. Diffusion coefficients were measured four to eight times for each ternary carrier solution and then averaged. Sharp changes in the D_{ik} coefficients can occur at the transition from acidic to alkaline solution compositions (Curtis and Leaist, 1998). To avoid possible ambiguities in the fitted diffusion coefficients caused by variations in the coefficients across the dispersion profiles, acidic solutions ($C_1 > C_2$) were injected into acidic carrier solutions and alkaline solutions ($C_1 < C_2$) were injected into alkaline carrier solutions. Solute concentrations in the injected solutions and the carrier solutions differed by $0.100 \text{ mol dm}^{-3}$ or less. In this range the D_{ik} coefficients were independent of the initial concentration differences within the precision of the measurements, $\pm(0.01 \text{ to } 0.03) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The results for solutions containing $0.100 \text{ mol dm}^{-3}$ total acetic acid + TEA are summarized in Table 3. In Figure 2 the measured D_{ik} coefficients are plotted against the solute fraction of acetic acid: $f_1 = C_1/(C_1 + C_2)$. The solid curves give for comparison the D_{ik} values predicted by the NP treatment developed in the Appendix. Although NP equations are exact only for infinitely dilute solutions, the measured and predicted D_{ik} coefficients are in close agreement.

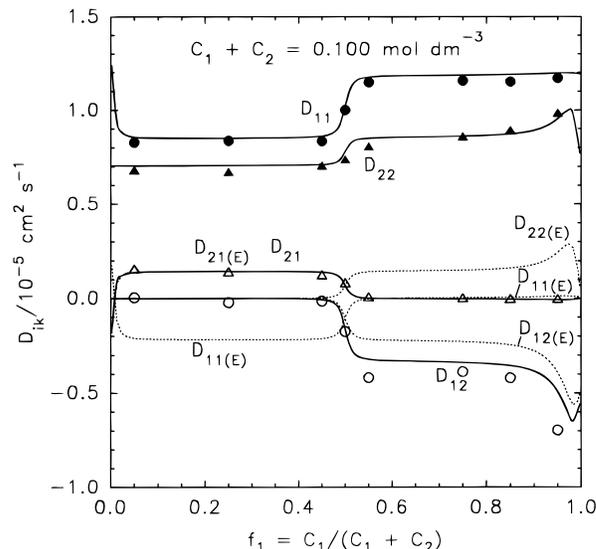


Figure 2. Ternary diffusion coefficients of aqueous acetic acid (C_1) + TEA (C_2) solutions at 25 °C plotted against the solute fraction of acetic acid for solutions containing $0.100 \text{ mol dm}^{-3}$ total solute. Measured D_{ik} values: ●, ○, △, ▲. Predicted D_{ik} values: —. Predicted electrostatic $D_{ik(E)}$ contributions: - - -.

The dashed curves in Figure 2 are the predicted electrostatic contributions to the ternary diffusion coefficients. Specifically, $D_{ik(E)}$ gives the flux of solute i caused by the electric field generated by the gradient in the concentration of solute k . It is noteworthy that the electrostatic contributions account for the bulk of the concentration dependence of the ternary diffusion coefficients, including the remarkably sharp changes in the D_{ik} coefficients at the equivalence point of the $\text{HA} + \text{TEA} = \text{A}^- + \text{TEAH}^+$ neutralization reaction ($f_1 = 0.50$).

The results for the acetic acid + TEA solutions are qualitatively similar to the results obtained previously for aqueous acetic acid + triethylamine solutions (Curtis and Leaist, 1998). In that study the mechanism for the coupled diffusion of a monoprotic weak acid and weak base is discussed in detail.

(a) Interdiffusion of $0.100 \text{ mol dm}^{-3}$ Acetic Acid and $0.100 \text{ mol dm}^{-3}$ TEA. To illustrate the coupled diffusion of a weak acid and an alkanolamine, Figure 3 shows concentration profiles for the interdiffusion of $0.100 \text{ mol dm}^{-3}$ acetic acid and $0.100 \text{ mol dm}^{-3}$ TEA across a sharp initial boundary. The profiles were calculated by using a finite difference procedure (Leaist, 1987) to integrate the time-dependent diffusion equations

$$\frac{\partial C_i(z, t)}{\partial t} = -\frac{\partial J_i}{\partial z} = \frac{\partial}{\partial z} \left[D_{i1} \frac{\partial C_1(z, t)}{\partial z} + D_{i2} \frac{\partial C_2(z, t)}{\partial z} \right] \quad (6)$$

The variable D_{ik} coefficients employed in the calculations were evaluated by linear interpolation of the measured values plotted in Figure 2.

The time-dependent concentration profiles for the interdiffusing acetic acid and TEA are plotted against the Boltzmann variable $z t^{-1/2}$. This convenient transformation allows concentration profiles at any time t to be evaluated from a single plot, even though the D_{ik} coefficients change along the diffusion path (Robinson and Stokes, 1959; Leaist, 1991a).

Figure 3 shows that the concentration profiles for the interdiffusion of acetic acid and TEA are asymmetric. On the TEA-rich side of the diffusion boundary, for example, the concentration gradients are steeper because D_{11} and

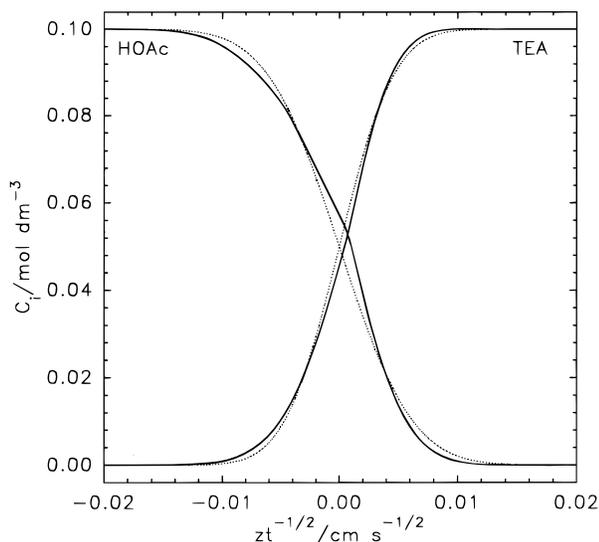


Figure 3. Concentration profiles for the interdiffusion of 0.100 mol dm⁻³ acetic acid (C_1) and 0.100 mol dm⁻³ TEA (C_2): —, ternary profiles calculated using variable D_{ik} coefficients; - - -, pseudo-binary profiles. Initial conditions: $C_1(z < 0, 0) = C_2(z > 0, 0) = 0.100$ mol dm⁻³; $C_1(z > 0, 0) = C_2(z < 0, 0) = 0$.

D_{22} are smaller in this region. The equivalence point for the HA + TEA = A⁻ + TEAH⁺ neutralization reaction occurs at $C_1 = C_2 = 0.0528$ mol dm⁻³ and $zt^{-1/2} = +0.720 \times 10^{-3}$ cm s^{-1/2}. At time t , therefore, the reaction front advancing into the TEA solution is located at $z = (0.720 \times 10^{-3}$ cm s^{-1/2}) $t^{1/2}$.

Figure 3 includes for comparison pseudo-binary concentration profiles (dashed curves) for the hypothetical uncoupled interdiffusion of acetic acid and TEA. These symmetrical error-function profiles (Robinson and Stokes, 1959) were calculated by integrating the time-dependent diffusion equations with $D_{12} = D_{21} = 0$. D_{11} and D_{22} were set equal to 1.20×10^{-5} and 0.70×10^{-5} cm² s⁻¹, the respective binary diffusion coefficients of oxalic acid and TEA at 0.050 mol dm⁻³, the mean concentration of each solute along the diffusion path. The pseudo-binary reaction front is stationary at the initial diffusion boundary ($z = 0$) where $C_1 = C_2 = 0.0500$ mol dm⁻³.

Ternary Diffusion in Aqueous Oxalic Acid (C_1) + TEA (C_2) Solutions. (a) 0.100 mol dm⁻³ Total Oxalic Acid + TEA. The results for the oxalic acid + TEA solutions are summarized in Table 4. In Figure 4 the D_{ik} coefficients for the solutions containing 0.100 mol dm⁻³ total oxalic acid + TEA are plotted against the solute fraction of oxalic acid. Sharp increases in both D_{11} and D_{22} are evident near $f_1 = 0.50$. At this composition the cross-coefficients D_{12} and D_{21} are large and negative, about -1.5×10^{-5} and -0.9×10^{-5} cm² s⁻¹, respectively. Coupled diffusion is much weaker in the solutions containing excess TEA relative to oxalic acid.

The solid curves plotted in Figure 4 give the D_{ik} coefficients predicted by the NP equations. Sharp changes in the D_{ik} coefficients are predicted at the first and second equivalence points of the oxalic acid (1)-TEA (2) neutralization reactions: H₂L + TEA = HL⁻ + TEAH⁺ ($f_1 = 0.50$) and H₂L + 2TEA = L²⁻ + 2TEAH⁺ ($f_1 = 0.33$).

The dashed curves in Figure 4 are the predicted electrostatic contributions to the ternary diffusion coefficients. Once again the $D_{ik(E)}$ values account for the unusual concentration dependence of all four D_{ik} coefficients, including the sharp minima and maxima at $f_1 = 0.50$. Moreover, the predicted cross-coefficients and correspond-

Table 4. Ternary Diffusion Coefficients of Aqueous Oxalic Acid (C_1) + Triethanolamine (C_2) Solutions at 25 °C

C_1^a	C_2^a	D_{11}^b	D_{12}^b	D_{21}^b	D_{22}^b
0.010	0.090	0.72	0.00	0.09	0.68
0.020	0.080	0.71	0.02	0.05	0.67
0.035	0.065	1.02	-0.16	0.06	0.70
0.040	0.060	1.01	-0.25	0.01	0.73
0.048	0.052	2.00	-1.13	-0.54	0.80
0.052	0.048	2.36	-1.54	-0.94	0.85
0.053	0.047	2.14	-1.33	-0.78	0.89
0.056	0.044	1.95	-1.12	-0.62	0.98
0.065	0.035	1.78	-0.74	-0.42	0.80
0.075	0.025	1.49	-0.62	-0.19	0.85
0.085	0.015	1.31	-0.60	-0.07	0.89
0.100	0.000	1.21	-0.52	0.00	0.98
0.050	0.500	0.44	0.32	0.06	0.64
0.200	0.500	0.56	0.03	-0.02	0.65
0.400	0.500	0.95	-0.23	0.02	0.67
0.600	0.500	1.34	-0.73	-0.39	1.10
0.800	0.500	1.13	-0.66	-0.25	1.00
1.000	0.500	1.06	-0.63	-0.20	0.94
1.200	0.500	1.03	-0.45	-0.17	0.81
0.050	1.000	0.51	0.01	0.15	0.54
0.300	1.000	0.44	0.05	0.02	0.50
0.400	1.000	0.45	0.07	-0.02	0.57
0.900	1.000	0.81	-0.18	-0.06	0.62
1.000	1.000	0.95	-0.31	-0.20	0.71
1.200	1.000	0.93	-0.45	-0.25	0.85
1.500	1.000	0.86	-0.44	-0.19	0.79
1.800	1.000	0.73	-0.35	-0.13	0.72

^a In units of mol dm⁻³. ^b In units of 10⁵ cm² s⁻¹.

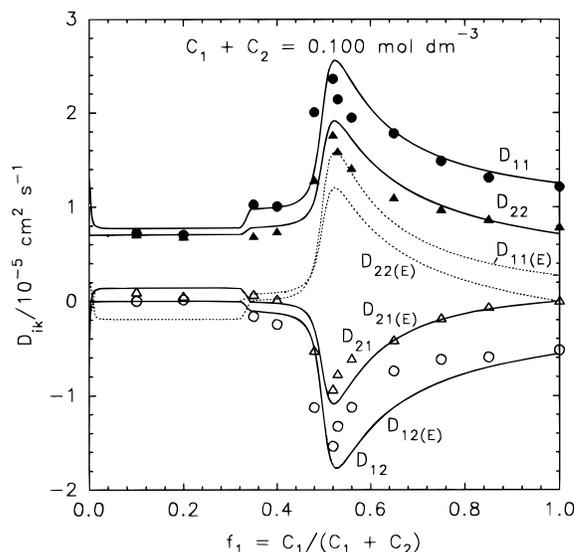


Figure 4. Ternary diffusion coefficients of aqueous oxalic acid (C_1) + TEA (C_2) solutions at 25 °C plotted against the solute fraction of acetic acid for solutions containing 0.100 mol dm⁻³ total solute. Measured D_{ik} values: ●, ○, △, ▲. Predicted D_{ik} values: —. Predicted electrostatic $D_{ik(E)}$ contributions: - - -.

ing electrostatic contributions are identical: $D_{12} = D_{12(E)}$ and $D_{21} = D_{21(E)}$. Therefore, at the level of approximation used here, the fluxes of the oxalic acid and TEA components are coupled entirely by the migration of HL⁻, L²⁻, and TEAH⁺ ions driven by the diffusion-induced electric field.

The first dissociation of oxalic acid [pK₁ = 1.27 (Robinson and Stokes, 1959)] produces significant concentrations of H⁺ ions in solutions containing a molar excess of oxalic acid relative to TEA ($f_1 > 0.50$). In this composition region a gradient in the concentration of oxalic acid generates an electric field to slow the exceptionally mobile H⁺ ions in order to maintain electroneutrality across the solution. The

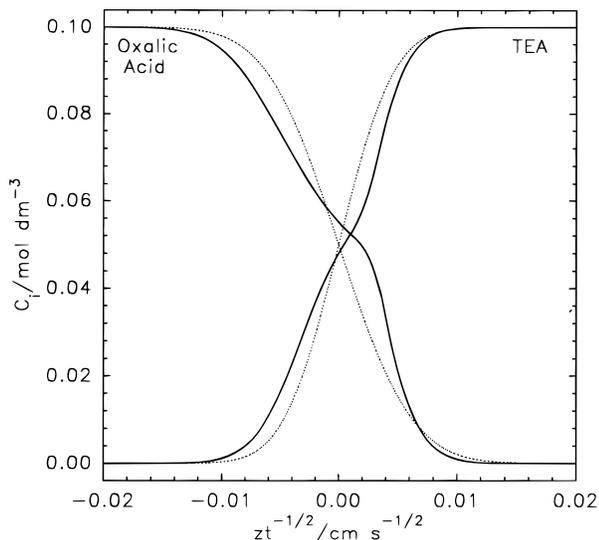


Figure 5. Concentration profiles for the interdiffusion of 0.100 mol dm⁻³ oxalic acid (C_1) and 0.100 mol dm⁻³ TEA (C_2): —, ternary profiles calculated using variable D_{ik} coefficients; - - -, pseudo-binary profiles. Initial conditions: $C_1(z < 0, 0) = C_2(z > 0, 0) = 0.100$ mol dm⁻³; $C_1(z > 0, 0) = C_2(z < 0, 0) = 0$.

electric field has two important effects: (i) HL⁻ ions are driven “down” the oxalic acid gradient; (ii) TEAH⁺ ions are driven in the opposite direction, “up” the oxalic acid gradient. The electrostatically enhanced transport of oxalic acid (as HL⁻ ions) and the counterflow of the TEA component (as TEAH⁺ ions) are responsible for the increase in D_{11} and the negative D_{21} values, respectively. These effects are most pronounced near the equivalence point at $f_1 = 0.50$ where essentially all of the oxalic acid and TEA components exist as HL⁻ and TEAH⁺ ions.

When a gradient in the concentration of TEA is formed in a solution containing excess acid ($f_1 > 0.50$), H⁺ ions diffuse rapidly up the TEA gradient to replace the H⁺ ions consumed by the protonation of TEA. In this case the electric field required to slow the H⁺ ions drives TEAH⁺ ions down the TEA gradient. In addition, HL⁻ ions are driven in the opposite direction, up the TEA gradient. This electrostatic transport mechanism is responsible for the large positive D_{22} values and large negative D_{12} values near $f_1 = 0.50$.

Aqueous oxalic acid is ($pK_1 = 1.27$) is more completely dissociated than acetic acid ($pK = 4.75$) at a given concentration. In view of the important role played by H⁺ ions in the diffusion behavior, the concentration dependence of the D_{ik} coefficients for the oxalic acid + TEA solutions (Figure 4) is therefore more dramatic than for the acetic acid + TEA solutions (Figure 2).

(b) Interdiffusion of 0.100 mol dm⁻³ Oxalic Acid and 0.100 mol dm⁻³ TEA. Concentration profiles for the interdiffusion of oxalic acid and TEA are plotted in Figure 5. The profiles are strongly asymmetric owing to the pronounced concentration dependence of the D_{ik} coefficients.

Coupled diffusion produces significant counterflows of oxalic acid and TEA at compositions near $f_1 = 0.50$. The resulting buildup of solute in the diffusion boundary leads to an equivalence point of the H₂L + TEA = HL⁻ + TEAH⁺ reaction at $C_1 = C_2 = 0.0524$ mol dm⁻³. At time t the moving reaction front is located at $z = (1.00 \times 10^{-3} \text{ cm s}^{-1/2})t^{1/2}$.

Concentration profiles for the hypothetical uncoupled interdiffusion of oxalic acid and TEA are also plotted in

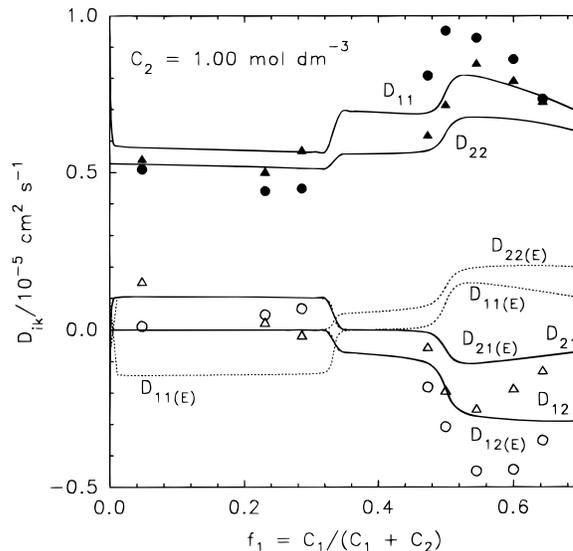


Figure 6. Ternary diffusion coefficients of aqueous oxalic acid (C_1) + TEA (C_2) solutions at 25 °C plotted against the solute fraction of acetic acid for solutions containing 1.00 mol dm⁻³ total solute. Measured D_{ik} values: ●, ○, △, ▲. Predicted D_{ik} values: —. Predicted electrostatic $D_{ik(E)}$ contributions: - - -.

Figure 5. These pseudo-binary profiles were calculated by setting D_{11} and D_{22} equal to the binary D values for oxalic acid and TEA at 0.050 mol dm⁻³: (1.35×10^{-5} and 0.70×10^{-5}) cm² s⁻¹. Also, D_{12} and D_{21} were set equal to zero. The concentrations in the pseudo-binary profiles differ significantly from those in the more accurate ternary profiles, by more than 50% at some locations. The predicted pseudo-binary reaction front is stationary at $z = 0$ where $C_1 = C_2 = 0.0500$ mol dm⁻³.

(c) Dissolution of Oxalic Acid in 1.00 mol dm⁻³ Aqueous TEA. The dissolution of oxalic acid in an aqueous TEA solution is analogous to the absorption of a diprotic acid gas by an aqueous alkanolamine solution. To study the role of coupled diffusion in the dissolution of oxalic acid in 1.00 mol dm⁻³ aqueous TEA, ternary diffusion coefficients were measured for solutions containing 0.05 to 1.8 mol dm⁻³ oxalic acid and 1.00 mol dm⁻³ TEA. The measured and predicted D_{ik} coefficients are plotted in Figure 6. Because these solutions are more concentrated than the 0.100 mol dm⁻³ solutions (Figure 4), the predictions are less reliable.

Dissolution profiles were calculated by integrating the time-dependent diffusion equations subject to the mixed boundary conditions

$$c_{\text{H}_2\text{L}}(z=0, t) = c_{\text{H}_2\text{L}(\text{sat})} \quad (7)$$

$$J_2(z=0, t) = -[D_{21}\partial C_1/\partial z + D_{22}\partial C_2/\partial z]_{z=0} = 0 \quad (8)$$

The solubility equilibrium H₂L(s) ⇌ H₂L(aq) provides the first boundary condition by fixing the interfacial concentration of molecular oxalic acid at the saturation value, $c_{\text{H}_2\text{L}(\text{sat})}$. The second boundary condition states that TEA cannot diffuse into the solid oxalic acid phase. [Analogous equations have been used to analyze the absorption and diffusion of SO₂ and Cl₂ in multicomponent solutions (Leaist, 1986, 1988).]

The diffusion coefficients used to calculate the dissolution profiles were evaluated by interpolation of the measured D_{ik} values plotted in Figure 5. Titration of saturated solutions gave $C_{1\text{sat}} = c_{\text{H}_2\text{L}(\text{sat})} + c_{\text{HL}^-} + c_{\text{L}^{2-}} = 2.01$ mol dm⁻³ for the solubility of total oxalic acid in 1.00 mol dm⁻³ TEA.

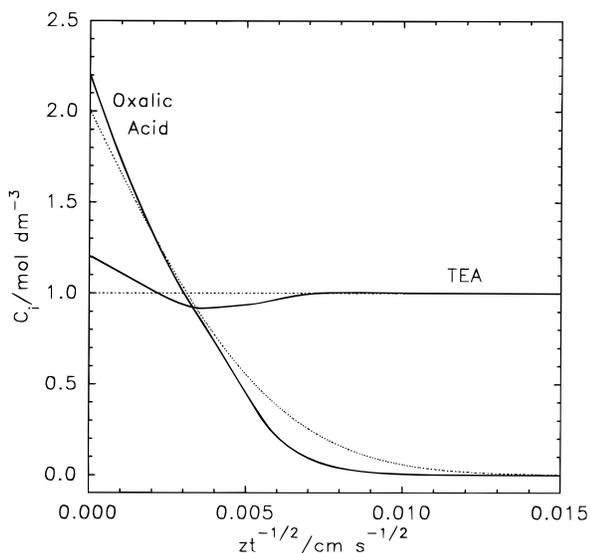


Figure 7. Concentration profiles for the dissolution of oxalic acid into 1.00 mol dm⁻³ aqueous TEA solution: —, ternary profiles calculated using variable D_{ik} coefficients; ---, pseudo-binary profiles. Initial conditions: $C_1(z > 0, 0) = 0$, $C_2(z > 0, 0) = 1.00$ mol dm⁻³. The surface of the dissolving acid is assumed to be stationary (at $z = 0$) in order to simulate the absorption of an acid gas into an aqueous alkanolamine solution.

With this result, the equations for electroneutrality and the dissociation equilibria (eqs 20–24) can be solved to give $C_{\text{H}_2\text{L}(\text{sat})} = 0.96$ mol dm⁻³.

After each time step in the numerical integration, eq 8 together with the equations for electroneutrality ($c_{\text{H}^+} + c_{\text{TEAH}^+} = c_{\text{HL}^-}$) and dissociation equilibrium ($K_1 = c_{\text{H}^+}c_{\text{HL}^-}/c_{\text{H}_2\text{L}(\text{sat})}$) were solved iteratively for the interfacial concentrations of the H⁺, TEAH⁺, and HL⁻ ions. The solution at the surface of the dissolving acid is acidic. Consequently, the interfacial concentrations of OH⁻, L⁻, and molecular TEA can be neglected, which gives $C_1(z = 0, t) = c_{\text{H}_2\text{L}(\text{sat})} + c_{\text{HL}^-}$ and $C_2(z = 0, t) = c_{\text{TEAH}^+}$ for the interfacial concentrations of the total oxalic acid and TEA components.

The concentration profiles for the dissolution of oxalic acid in a 1.00 mol dm⁻³ TEA solution are plotted in Figure 7. At time t , the $\text{H}_2\text{L} + \text{TEA} = \text{HL}^- + \text{TEAH}^+$ reaction front is located at $z = (3.28 \times 10^{-3} \text{ cm s}^{-1/2})t^{1/2}$, where $C_1 = C_2 = 0.924$ mol dm⁻³.

Cross-coefficient D_{21} is large and negative for the acidic solution near the surface of the solid acid. Consequently, the diffusion of oxalic acid into the TEA solution produces a significant counterflow of TEA (from right to left in Figure 7). TEA cannot diffuse into the solid acid. The resulting buildup of TEA at the surface of the solid acid raises the interfacial concentration of TEA to 1.20 mol dm⁻³, which is 20% higher than the bulk 1.00 mol dm⁻³ TEA concentration. The 0.20 mol dm⁻³ increase in the interfacial TEA concentration caused by coupled diffusion produces a corresponding increase in the solubility of total oxalic acid in the interfacial solution. In this case the interfacial concentration of total oxalic acid is 2.21 mol dm⁻³, which is 10% higher than the 2.01 mol dm⁻³ solubility of the total acid in the bulk 1.00 mol dm⁻³ TEA solution.

The rate of dissolution of total oxalic acid per unit surface area is given by

$$J_1(z = 0, t) = -[D_{11}\partial C_1/\partial z + D_{12}\partial C_2/\partial z]_{z=0} \quad (9)$$

From Figures 6 and 7, we calculate $D_{11} = 0.721 \times 10^{-5}$ and $D_{12} = -0.341 \times 10^{-5}$ cm² s⁻¹ for the interfacial solution

and $J_1(0, t) = (3.34 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1/2})t^{-1/2}$ for the time-dependent rate of dissolution.

The rate of dissolution is the sum of the main flux of oxalic acid driven by the oxalic acid gradient plus the coupled flux of oxalic acid driven by the TEA gradient: $-D_{11}\partial C_1/\partial z = (3.64 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1/2})t^{-1/2}$ and $-D_{12}\partial C_2/\partial z = (-0.30 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1/2})t^{-1/2}$, respectively. In this case coupled diffusion of the acid driven by the TEA gradient reduces the rate of dissolution by about 10%. This reduction nearly cancels the 10% increase in the rate of dissolution caused by the enhanced solubility of the acid discussed above.

The dashed curve in Figure 7 is the pseudo-binary dissolution profile for oxalic acid. It was calculated using the binary D value 1.05×10^{-5} cm² s⁻¹ estimated from Figure 1 for a 1.00 mol dm⁻³ oxalic solution (the mean concentration of the diffusing acid). Because coupled diffusion is assumed to be negligible ($D_{12} = D_{21} = 0$), the concentration of TEA remains uniform at 1.00 mol dm⁻³ throughout the solution. Accordingly, 2.01 mol dm⁻³ was used for the solubility of oxalic acid in the 1.00 mol dm⁻³ TEA solution. The predicted pseudo-binary rate of dissolution of the acid is $(3.67 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1/2})t^{-1/2}$.

Conclusions

Ternary diffusion coefficients have been measured for aqueous solutions of acetic acid + triethanolamine and aqueous solutions of oxalic acid + triethanolamine. The results suggest that coupled diffusion in aqueous weak acid + alkanolamine absorbents is significant, especially for solutions containing excess acid relative to alkanolamine. Sharp variations in the diffusion behavior occur when the solution composition is changed from excess acid to excess alkanolamine. These results are consistent with Nernst–Planck estimates of the ternary diffusion coefficients.

Measured ternary diffusion coefficients have been used to calculate accurate concentration profiles for the interdiffusion of aqueous weak acids and triethanolamine. These calculations can be used to locate the moving acid/base reaction front marking the transition from regions of excess acid to excess alkanolamine. The concentration profiles are asymmetric because of the changes in the diffusion coefficients across the diffusion boundary.

Ternary diffusion coefficients have been used to calculate the rate of dissolution of oxalic acid in an aqueous triethanolamine solution. Diffusion of the acid into the triethanolamine solution produces a significant counterflow of triethanolamine and a buildup of triethanolamine at the surface of the dissolving acid. The resulting increase in the solubility of the acid in the interfacial solution increases the rate of dissolution. The gradient in the concentration of triethanolamine produces a coupled flow of oxalic acid, which further changes the rate of dissolution. Coupled diffusion should have similar consequences for the absorption of an acid gas by an aqueous alkanolamine absorbent.

Appendix. Predicted Diffusion Coefficients

In this section Nernst–Planck (NP) equations are used to predict ternary diffusion coefficients for aqueous solutions of an alkanolamine and a mono- or diprotic weak acid.

NP Equations. The NP approximation (Newman, 1973) allows the flux j_s of each solute species to be separated into the “pure-diffusion” flux $j_{s(D)}$ driven by gradient ∇c_s in the

concentration of the species and the flux $j_{s(E)}$ driven by the electric field, E .

$$j_s = j_{s(D)} + j_{s(E)} \quad (10)$$

$$j_{s(D)} = -D_s \nabla c_s \quad (11)$$

$$j_{s(E)} = (F/RT) z_s c_s D_s E = - \sum_{z_s q} \frac{t_s}{z_s} z_q D_q \nabla c_q \quad (12)$$

F is the Faraday constant, R the gas constant, and T the temperature. D_s , z_s , and t_s are the diffusion coefficient, charge number, and transference number of solute species s given by

$$t_s = \frac{c_s z_s^2 D_s}{\sum_q c_q z_q^2 D_q} \quad (13)$$

Ternary D_{ik} Coefficients. The flux of each solute component can always be expressed as the sum of fluxes of solute species. The flux of the total TEA component, for example, is the sum of the fluxes of TEA molecules and TEAH⁺ ions. Each ternary diffusion coefficient can therefore be separated into pure-diffusion and electrostatic contributions (Leaist and Hao, 1993).

$$D_{ik} = D_{ik(D)} + D_{ik(E)} \quad (14)$$

$$D_{ik(D)} = \sum_s \nu_{is} D_s \frac{\partial c_s}{\partial C_k} \quad (15)$$

$$D_{ik(E)} = - \sum_s \sum_q \frac{\nu_{is} t_s z_q D_q}{z_s} \frac{\partial c_q}{\partial C_k} \quad (16)$$

$D_{ik(D)}$ gives the pure-diffusion flux of component i driven by the gradient in the concentration of electrolyte k , and $D_{ik(E)}$ gives the flux of component i driven by the electric field that is generated by the gradient in electrolyte k . The number of moles of component i transported per mole of solute species s is denoted by stoichiometric coefficient ν_{is} .

$$J_i = \sum_s \nu_{is} j_s \quad (17)$$

Aqueous Oxalic Acid (C_1) + Triethanolamine (C_2) Solutions. These solutions contain seven different solute species: molecular oxalic acid (H_2L) and triethanolamine (TEA) and the following ions: hydrogen oxalate (HL^-), oxalate (L^{--}), triethanolammonium (TEAH⁺), H^+ , and OH^- . Given the concentrations of the total oxalic acid and TEA components

$$C_1(\text{total oxalic acid}) = c_{H_2L} + c_{HL^-} + c_{L^{--}} \quad (18)$$

$$C_2(\text{total TEA}) = c_{TEA} + c_{TEAH^+} \quad (19)$$

the concentrations of the solute species can be evaluated by solving the equations for electroneutrality and equilib-

rium of the dissociation reactions (Robinson and Stokes, 1959)

$$c_{TEAH^+} + c_{H^+} = c_{HL^-} + 2c_{L^{--}} + c_{OH^-} \quad (20)$$

$$H_2L \rightleftharpoons H^+ + HL^- \quad K_{a1} = c_{H^+} c_{HL^-} / c_{H_2L} = 0.053 \quad (21)$$

$$HL^- \rightleftharpoons H^+ + L^{--} \quad K_{a2} = c_{H^+} c_{L^{--}} / c_{HL^-} = 5.42 \times 10^{-5} \quad (22)$$



$$K_2 = c_{H^+} c_{TEA} / c_{TEAH^+} = 1.70 \times 10^{-8} \quad (23)$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_w = c_{H^+} c_{OH^-} = 1.01 \times 10^{-14} \quad (24)$$

In view of the NP approximation that has been made, ideal solutions are assumed. Moreover, activity coefficients have not been measured for this system.

The fluxes of the total oxalic acid and TEA components are related to the fluxes of the solute species as follows

$$J_1(\text{total oxalic acid}) = j_{H_2L} + j_{HL^-} + j_{L^{--}} \quad (25)$$

$$J_2(\text{total TEA}) = j_{TEA} + j_{TEAH^+} \quad (26)$$

and hence $\nu_{1,H_2L} = \nu_{1,HL^-} = \nu_{1,L^{--}} = \nu_{2,TEA} = \nu_{2,TEAH^+} = 1$. The remaining ν_{is} coefficients are zero for this system.

Accurate-limiting diffusion coefficients of the oxalate, hydroxide, and hydrogen ions were calculated from limiting ionic conductivities (Robinson and Stokes, 1959): $D_{L^{--}}^\circ = 0.99 \times 10^{-5}$, $D_{H^+}^\circ = 9.32 \times 10^{-5}$, and $D_{OH^-}^\circ = 5.28 \times 10^{-5}$ cm² s⁻¹. The limiting diffusion coefficient of molecular TEA, $D_{TEA}^\circ = 0.72 \times 10^{-5}$ cm² s⁻¹, was estimated by extrapolation of binary D values of aqueous TEA shown in Figure 1.

Unfortunately, neither the diffusion coefficient nor the conductivity of the TEAH⁺ ion appear to have been measured. For our purposes, however, it is sufficiently accurate to assume that the limiting diffusion coefficient of the TEAH⁺ ion is identical to that of the TEA molecule, and hence $D_{TEAH^+}^\circ = 0.72 \times 10^{-5}$ cm² s⁻¹. The error in this estimate is probably less than 5%. Similarly, the limiting diffusion coefficients of the molecular oxalic acid and hydrogen oxalate are assumed to be identical to the diffusion coefficient of the oxalate ion: $D_{H_2L}^\circ = D_{HL^-}^\circ = 0.99 \times 10^{-5}$ cm² s⁻¹.

The assumption that the diffusion coefficients of the TEA molecules and TEAH⁺ ions are identical leads to the interesting prediction that D_{21} equals $D_{21(E)}$. This result implies that the oxalic acid gradient drives a coupled flow of the TEA component by a purely electrostatic mechanism. To understand this result, suppose a gradient in the concentration of oxalic acid (1) is created in a solution containing a uniform concentration of the TEA component (2): $\nabla C_2 = 0$. Since $C_2 = c_{TEA} + c_{TEAH^+}$, the oxalic acid gradient produces gradients of equal magnitude but opposite sign in the concentration of the TEA molecules and the TEAH⁺ ions: $\nabla c_{TEA} = -\nabla c_{TEAH^+}$. If the TEA molecules and TEAH⁺ ions have identical diffusion coefficients, the diffusional fluxes of these species will be of equal magnitude but opposite sign. Hence, the pure-diffusion coupled flux of the total TEA component is zero, and $D_{21} = D_{21(E)}$. Similarly, the assumption that the diffusion coefficients of the oxalic acid species (H_2L , HL^- , and L^{--}) are identical leads to the prediction that D_{12} equals $D_{12(E)}$.

The solution viscosity increases as the concentrations of oxalic acid and TEA are raised, especially the latter. The viscosity of a 1.00 mol dm⁻³ aqueous triethanolamine solution, for example, is about 60% larger than the viscosity of pure water (Hikita et al., 1980). The well-known Stokes–Einstein relation suggests that the diffusion coefficient of a solute species is inversely proportional to η . In practice, however, this relation usually overcorrects for the viscosity changes. Better agreement for aqueous triethanolamine solutions is obtained by assuming that the diffusion coefficients are proportional to $\eta^{-2/3}$ (Hikita, 1980). Accordingly, the diffusion coefficients of the solute species were calculated by applying the empirical viscosity correction factor $(\eta/\eta_0)^{-2/3}$ to the limiting diffusion coefficients.

$$D_s = (\eta/\eta_0)^{-2/3} D_s^\circ \quad (27)$$

Relative viscosities were calculated from the equation

$$\eta/\eta_0 = 1 + 0.160C_1 + 0.040C_1^2 + 0.340C_2 + 0.254C_2^2 \quad (28)$$

which was fitted to viscosities reported for binary aqueous solutions of acetic acid and triethanolamine (Hikita et al., 1980; Washburn, 1929) with C_1 and C_2 in units of mol dm⁻³.

Aqueous Acetic Acid (C_1) + Triethanolamine (C_2) Solutions. With only minor modifications, the equations developed for oxalic acid + triethanolamine solutions can be used to predict D_{ik} coefficients for acetic acid + triethanolamine solutions. First, K_{a1} is changed to 1.75×10^{-5} for the dissociation of acetic acid (Robinson and Stokes, 1959). Second, because acetic acid is monoprotic, K_{a2} and hence α_{L^-} are set equal to zero. For the acetate ion and molecular acetic acid, we used $D^{\circ}_{HL^-} = 1.09 \times 10^{-5}$ and $D^{\circ}_{H_2L} = 1.20 \times 10^{-5}$ cm² s⁻¹ (Robinson and Stokes, 1959; Vitagliano and Lyons, 1956). Relative viscosities were calculated from the equation

$$\eta/\eta_0 = 1 + 0.110C_1 + 0.002C_1^2 + 0.340C_2 + 0.254C_2^2 \quad (29)$$

which was fitted by least-squares to reported viscosities for aqueous solutions of acetic acid and triethanolamine (Vitagliano and Lyons, 1956; Washburn, 1929). C_1 and C_2 are in units of mol dm⁻³.

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