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Mutual Diffusion Coefficients for Binary Aqueous Solutions of Arsenous, Arsenic, and Malonic Acids

Derek G. Leaist*

Department of Chemistry, St. Francis Xavier University, P.O. Box 5000, Antigonish, Nova Scotia, Canada B2G 2W5

Prompted by interest in reaction-diffusion waves in arsenous acid−iodate and Belousov−Zhabotinsky systems, mutual diffusion coefficients (D) are measured for binary aqueous solutions of arsenous, arsenic, and malonic acids at 25 °C and concentrations from (0.00012 to 0.020) $\text{mol}\cdot\text{dm}^{-3}$. Arsenous acid, a relatively weak acid (pK_{1a} 9.2), diffuses in molecular form in this composition range with $D \approx 1.11\cdot10^{-5}\ \text{cm}^2\cdot\text{s}^{-1}$. Arsenic and malonic acids (pK_{1a} 2.3 and 2.8, respectively) dissociate appreciably, causing D to increase sharply with increasing dilution due to the unusually large mobility of aqueous H^+ ions. Differential D values for solutions of these acids are determined by extrapolating diffusion coefficients measured from Gaussian dispersion peaks to zero concentration difference between the injected solution and the flow solution. Using a simple modification of conventional dispersion equipment, differential diffusion coefficients are measured directly from small-Δc error-function dispersion profiles generated from step-function initial conditions. Analysis of the concentration dependence of D, including electrophoretic and activity coefficient terms, provides estimates of the diffusion coefficients of the molecular and ionic forms of the acids. The integral mutual diffusion coefficient defined by $c^{-1}\int_0^c D(c)\text{d}c$ is identified as the concentration-weighted average of the diffusion coefficients of the molecular and ionic forms of the acids.

Introduction

Propagating chemical fronts and pulses can be generated in solution by combining diffusion and chemical reactions with a feedback mechanism, such as autocatalysis.[1−7] Propagating fronts, such as shock waves, leave behind solution at equilibrium.[1−5] Chemical pulses[1,2,6,7] generally display a wider range of behavior. Because the solution returns nearly to its initial state after the passage of a pulse, another pulse or train of pulses can follow, producing remarkable spatial structures, such as spirals and target patterns.

Propagating reaction-diffusion fronts have been investigated for aqueous iodate−arsenous acid,[3,4] iron(II)−nitric acid,[8,9] chlorate−sulfite[10] and iodate−sulfite[11] systems. The iodate oxidation of arsenous acid is particularly well understood.[3] Fronts in this system can be initiated by iodide ions. Reaction with iodate ions

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

produces iodine for the oxidation of arsenous acid to arsenic acid

$$3H_3AsO_3 + 3I_2 + 3H_2O = 3H_3AsO_4 + 6H^+ + 6I^-$$

and additional iodide ions for chemical feedback. Reliable rate constants for these reactions have been reported.[12] In addition, diffusion coefficient data are available for I_2, I^-, IO_3^-, and H^+ species.[13−15] However, diffusion coefficients for aqueous arsenous and arsenic acids do not appear to have been measured. To provide data for modeling iodate−arsenous acid propagating fronts, mutual diffusion coefficients (D) for binary aqueous solutions of arsenous and arsenic acids are reported in this paper. Diffusion coefficients for these acids could find additional application in studies of the transport of arsenical pollutants in groundwater.[16,17]

Propagating chemical pulses have been thoroughly investigated for Belousov−Zhabotinsky (BZ) solutions.[1,2,6,7] These systems frequently contain aqueous bromate and bromide salts, a metal catalyst (such as cerium ions or ferroin), and malonic acid or a similar organic substrate. To provide data for modeling BZ pulses, mutual diffusion coefficients for aqueous malonic acid are also reported here. Diffusion coefficients for aqueous malonic acid are of additional interest in studies of groundwater and brines where malonic acid leached from organic matter is an important acidifier and chelating agent for the transport of aluminum and other metal ions.[18]

Arsenous acid, H_3AsO_3, a relatively weak acid (pK_{1a} 9.2 at 25 °C),[17,19−21] diffuses in molecular form at the compositions used in the present study. In contrast, arsenic and malonic acids (pK_{a1} 2.27 and 2.85, respectively)[16,18,21] dissociate appreciably

$$H_3AsO_4 = H^+ + H_2AsO_4^-$$

$$(HOOC)_2CH_2 = H^+ + HOOCH_2COO^-$$

which can produce sharp increases in D owing to the unusually large mobility of aqueous H^+ ions.[15] We use modified Taylor dispersion procedures[22,23] to measure well-defined differential mutual diffusion coefficients for these solutions. The results are analyzed to determine diffusion coefficients for the molecular and ionic forms of the acids.

Experimental Procedure

A Teflon dispersion tube (length (L) = 3000 cm, internal radius (r) = 0.0380_6 cm) was wrapped in the form of a helix (diameter = 70 cm) and held at (25.00 ± 0.05) °C in a

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* Corresponding author. Phone: (902) 867-5372. Fax: (902) 867-2414. E-mail: dleaist@stfx.ca.

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thermostat. A peristaltic pump (Gilson MiniPuls 3) produced steady laminar flows of solution with retention times (t_R) of $(1.5 \pm 0.1)\cdot 10^4$ s. Dispersion profiles were monitored by a refractometer detector (Agilent model 1100) at the tube outlet. To minimize bubble formation along the flow path, a 2 bar backpressure regulator was connected to the outlet line of the detector.

Gaussian Dispersion Profiles. In the pulse-injection mode, the most frequently used Taylor dispersion procedure,[24] small samples of solution (volume $(\Delta v) = 0.020$ cm^3) containing solute at concentration $c + \Delta c$ were introduced into carrier solutions of composition c through a six-port Teflon valve (Rheodyne model 50) connected between the pump outlet and the inlet of the dispersion tube. Initial concentration differences from 0.002 mol·dm^{-3} to 0.010 mol·dm^{-3} were used.

Radial diffusion and axial convection along the dispersion tube shape the initial δ-function concentration pulses for the injected solute into broadened distributions that closely resemble Gaussian concentration profiles[24] of variance $r^2t_R/24D$. Diffusion coefficients were evaluated by fitting the equation

$$V(t) = V_\infty + V_1 t + \Delta V_{\max}(t_R/t)^{1/2} \exp[-12D(t - t_R)^2/r^2 t] \quad (1)$$

to the measured detector voltages, $V(t)$, using the least-squares fitting parameters D and t_R, the peak height $\Delta V_{\max}$, the baseline voltage V_∞, and the baseline slope V_1.

The operation of the equipment was checked by measuring dispersion profiles for aqueous glycine. Replicate injections of solution samples containing 0.035 mol·dm^{-3} of glycine into a 0.025 mol·dm^{-3} glycine carrier solution gave $(1.061 \pm 0.008)\cdot 10^{-5}$ cm^2·s^{-1} for the mutual diffusion coefficient, in acceptable agreement with the accurate value $1.055\cdot 10^{-5}$ cm^2·s^{-1} for 0.025 mol·dm^{-3} of aqueous glycine interpolated from Gouy diffusion measurements.[25]

Error-Function Dispersion Profiles. Additional diffusion measurements were made using a modified Taylor procedure and error-function (erf) dispersion profiles.[23,26] The error-function profiles were generated from step-function initial conditions prepared by using a two-way three-port switching valve (Rheodyne model 5301) connected to the pump inlet. A solution of composition $c - (\Delta c/2)$ was drawn into the pump through one of the valve inlet ports. At time $t = 0$, the valve was switched to select the other inlet port to begin feeding the solution of composition $c + (\Delta c/2)$ to the pump. After waiting for a suitable period of time ($>10(r^2t_R/24D)^{1/2}$) to avoid overlapped profiles, the valve was switched back to the previous setting to generate the return profile with a leading solution of composition $c + (\Delta c/2)$ and a trailing solution of composition $c - (\Delta c/2)$. The error-function profiles measured at the tube outlet were analyzed by fitting the equation

$$V(t) = V_\infty + V_1 t + \frac{\Delta V_{\max}}{2}\operatorname{erf}\left(\sqrt{\frac{12D}{t}}\,\frac{t - t_R}{r}\right) \quad (2)$$

to the detector voltages.

A study of Taylor dispersion in a Fourier ring[27] has shown that dispersion in peristaltic pumps is inherently low due to the pinching of short segments of solution by the pump rollers. Dispersion in the pump was further reduced to negligible levels by using a short length (15 cm) of narrow-bore peristaltic tubing (inner radius = 0.040 cm). Check runs using error-function profiles for the interdiffusion of 0.024 mol·dm^{-3} of glycine and 0.026 mol·dm^{-3} of glycine solutions gave $(1.059 \pm 0.005)\cdot 10^{-5}$ cm^2·s^{-1} for the mutual diffusion coefficient of 0.025 mol·dm^{-3} of aqueous glycine, in close agreement with the pulse-injection and Gouy results.

Table 1. Mutual Diffusion Coefficients of Aqueous Arsenous Acid at 25 °C

c	D	c	D
10^{-3} mol·dm^{-3}	10^{-5} cm^2·s^{-1}	10^{-3} mol·dm^{-3}	10^{-5} cm^2·s^{-1}
0.489	1.113	10.1	1.107
1.21	1.114	12.4	1.105
3.09	1.110	14.8	1.106
5.65	1.105		

A two-way switching valve at the pump inlet can also be used in pulse-injection mode to generate Gaussian profiles. At the flow rates used in the present study, for example, switching to a solution of composition $c + \Delta c$ and then switching back to a solution of composition c after an interval of about 20 s corresponds to the injection of a 0.020 cm^3 sample of solution containing solute at excess concentration Δc relative to the carrier solution.

Materials. Stock solutions of arsenous and arsenic acids were prepared by ion exchange of aqueous solutions of sodium meta-arsenate (BDH AnalaR $NaAsO_2$, purity > 99 %) or disodium hydrogen arsenate heptahydrate (Mallinckrodt $Na_2HAsO_4{\cong}7H_2O$, purity > 99 %), respectively, on 50 cm columns of analytical-grade resin beads (Amberlite IR 120H, 25 to 50 mesh). The concentrations of the stock acids were determined by iodine and thiosulfate titrations following standard procedures.[28] Solutions for the diffusion measurements were prepared in calibrated volumetric flasks from distilled deionized water and weighed amounts of acid stock solution or reagent-grade (Sigma, > 99 % purity) malonic acid or glycine.

Results and Discussion

Arsenous Acid. Gaussian profiles were used to measure mutual diffusion coefficients for aqueous arsenous acid. The results are summarized in Table 1 for carrier-stream concentrations from 0.0005 mol·dm^{-3} to 0.015 mol·dm^{-3}. Dissociation of the acid is negligible (< 0.1 %) at these compositions. As a result, the concentration dependence of D is weak (see Figure 1). Also, the measured values of D were independent of the initial concentration differences and therefore represent differential mutual diffusion coefficients at each carrier-stream concentration. Linear extrapolation gives $(1.112 \pm 0.004)\cdot 10^{-5}$ cm^2·s^{-1} for the limiting diffusion coefficient of molecular arsenous acid at infinite dilution.

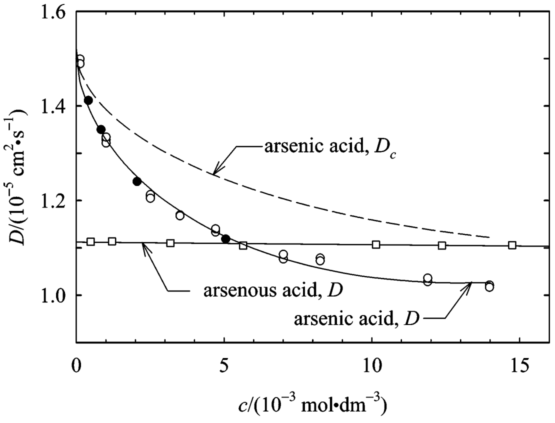

Figure 1. Diffusion coefficients of binary aqueous solutions of arsenous acid and arsenic acids: D, mutual diffusion coefficients from Gaussian (●) and error-function (□, ○) profiles; D_c, concentration-weighted average diffusion coefficient of the molecular and ionic forms of arsenic acid (— — — —).

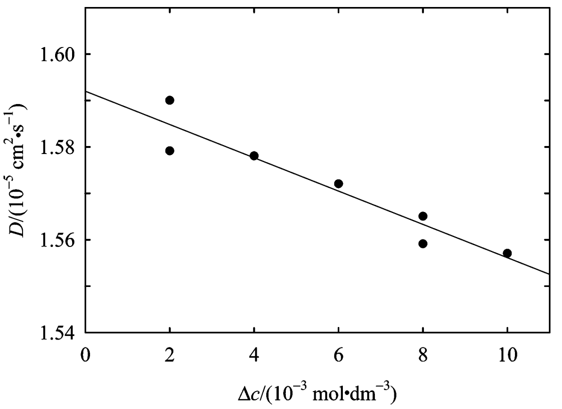

Figure 2. Diffusion coefficients calculated from Gaussian dispersion profiles measured for a 0.000253 mol·dm^{-3} malonic acid carrier solution plotted against the initial concentration difference used to generate the profiles.

Arsenic and Malonic Acids. The substantial composition dependence of D for solutions of arsenic and malonic acids caused the diffusion coefficients calculated from Gaussian dispersion to increase with increasing dilution of the injected solution samples, even for the smallest practicable initial concentration differences. Differential mutual diffusion coefficients were evaluated for each carrier solution by linear extrapolation of the fitted coefficients[22] to $\Delta c = 0$. A representative extrapolation is illustrated in Figure 2. The differential mutual diffusion coefficients obtained by extrapolation are designated by $\Delta c = 0$ and listed in Tables 2 and 3.

Gaussian dispersion profiles are not optimized for the measurement of strongly composition-dependent diffusion coefficients. The average concentration of diffusing solute changes continuously, from $c + (\Delta c/2)$ at $t = 0$ to c in the limit $t \to \infty$. In addition, strong dilution[24] of the injected solution samples with the carrier solution, by factors of $\approx (r^3 L/\Delta v)(12 D t_R/\pi^3)^{-1/2}$, requires initial concentration differences that are typically 1 to 2 orders of magnitude larger than the concentration differences measured across the dispersion peaks at the tube outlet.

The extrapolated Gaussian results were supplemented with differential mutual diffusion coefficients measured directly from small-Δc error-function dispersion profiles. Error-function profiles are generally more suitable for the measurement of composition-sensitive diffusion coefficients[23] because the average concentration of diffusing solute remains constant across

Table 2. Mutual Diffusion Coefficients, Extents of Dissociation, Thermodynamic Factors, and Electrophoretic Corrections for Aqueous Arsenic Acid at 25 °C

10^{-3} mol·dm^{-3}		10^{-5} cm^2·s^{-1}			10^{-5} cm^2·s^{-1}		10^{-3} mol·dm^{-3}		10^{-5} cm^2·s^{-1}			10^{-5} cm^2·s^{-1}	
c	Δc	D	α	α(dln$y_\pm$/dln$c$)	$\Delta_1 + \Delta_2$	Y	c	Δc	D	α	α(dln$y_\pm$/dln$c$)	$\Delta_1 + \Delta_2$	Y
0.125	0.250	1.499	0.978	−0.0061	−0.0029	1.544	3.51	1.00	1.170	0.707	−0.0146	−0.0130	1.544
0.125	−0.250	1.489	0.978	0.0061	−0.0029	1.534	3.51	−1.00	1.168	0.707	−0.0146	−0.0130	1.542
0.407	0	1.412	0.936	−0.0097	−0.0051	1.521	4.71	1.41	1.133	0.660	−0.0147	−0.0146	1.550
0.837	0	1.350	0.885	−0.0120	−0.0071	1.530	4.71	−1.41	1.140	0.660	−0.0147	−0.0146	1.560
1.01	0.50	1.328	0.868	−0.0126	−0.0077	1.530	5.06	0	1.119	0.649	−0.0147	−0.0150	1.543
1.01	−0.50	1.322	0.868	−0.0126	−0.0077	1.522	7.01	1.03	1.077	0.596	−0.0144	−0.0169	1.543
1.01	0.50	1.334	0.868	−0.0126	−0.0077	1.537	7.01	−1.03	1.086	0.596	−0.0144	−0.0169	1.557
1.01	−0.50	1.328	0.868	−0.0126	−0.0077	1.530	8.25	1.46	1.078	0.570	−0.0143	−0.0179	1.575
1.01	0.50	1.323	0.868	−0.0126	−0.0077	1.522	8.25	−1.46	1.073	0.570	−0.0143	−0.0179	1.567
1.01	−0.50	1.334	0.868	−0.0126	−0.0077	1.537	11.9	1.70	1.028	0.511	−0.0138	−0.0203	1.564
2.06	0	1.240	0.784	−0.0141	−0.0105	1.538	11.9	−1.70	1.036	0.511	−0.0138	−0.0203	1.575
2.51	1.01	1.210	0.757	−0.0144	−0.0114	1.535	14.0	2.50	1.021	0.485	−0.0136	−0.0215	1.578
2.51	−1.01	1.213	0.757	−0.0144	−0.0114	1.538	14.0	−2.50	1.022	0.485	−0.0136	−0.0215	1.579
2.51	1.01	1.205	0.757	−0.0144	−0.0114	1.528	14.0	2.50	1.017	0.485	−0.0136	−0.0215	1.572

Table 3. Mutual Diffusion Coefficients, Extents of Dissociation, Thermodynamic Factors, and Electrophoretic Corrections for Aqueous Malonic Acid at 25 °C

10^{-3} mol·dm^{-3}		10^{-5} cm^2·s^{-1}			10^{-5} cm^2·s^{-1}		10^{-3} mol·dm^{-3}		10^{-5} cm^2·s^{-1}			10^{-5} cm^2·s^{-1}	
c	Δc	D	α	α(dln$y_\pm$/dln$c$)	$\Delta_1 + \Delta_2$	Y	c	Δc	D	α	α(dln$y_\pm$/dln$c$)	$\Delta_1 + \Delta_2$	Y
0.124	0.248	1.674	0.926	−0.0053	−0.0025	1.809	1.38	1.25	1.324	0.632	−0.0076	−0.0070	1.830
0.124	−0.248	1.676	0.926	−0.0053	−0.0025	1.812	1.90	0	1.267	0.579	−0.0075	−0.0078	1.818
0.124	0.248	1.678	0.926	−0.0053	−0.0025	1.814	2.50	1.00	1.226	0.533	−0.0073	−0.0086	1.816
0.252	0.253	1.594	0.869	−0.0065	−0.0035	1.818	2.50	−1.00	1.231	0.533	−0.0073	−0.0086	1.824
0.252	−0.253	1.613	0.869	−0.0065	−0.0035	1.840	2.50	1.00	1.229	0.533	−0.0073	−0.0086	1.821
0.252	0.253	1.601	0.869	−0.0065	−0.0035	1.826	2.50	−1.00	1.224	0.533	−0.0073	−0.0086	1.814
0.253	0.506	1.611	0.868	−0.0065	−0.0035	1.838	3.50	1.01	1.186	0.478	−0.0070	−0.0097	1.822
0.253	−0.506	1.602	0.868	−0.0065	−0.0035	1.828	3.50	−1.01	1.188	0.478	−0.0070	−0.0097	1.825
0.253	0.506	1.595	0.868	−0.0065	−0.0035	1.820	3.50	1.01	1.188	0.478	−0.0070	−0.0097	1.825
0.253	0	1.592	0.868	−0.0065	−0.0035	1.816	3.50	−1.01	1.185	0.478	−0.0070	−0.0097	1.821
0.378	0.756	1.527	0.824	−0.0070	−0.0042	1.812	4.54	0	1.159	0.438	−0.0068	−0.0106	1.827
0.378	−0.756	1.516	0.824	−0.0070	−0.0042	1.799	4.60	1.179	1.143	0.436	−0.0068	−0.0106	1.805
0.379	0	1.518	0.824	−0.0070	−0.0042	1.802	4.60	−1.18	1.150	0.436	−0.0068	−0.0106	1.815
0.502	0.508	1.494	0.788	−0.0073	−0.0047	1.828	4.60	1.18	1.156	0.436	−0.0068	−0.0106	1.825
0.502	−0.508	1.490	0.788	−0.0073	−0.0047	1.823	7.01	0.99	1.111	0.374	−0.0064	−0.0121	1.822
0.502	0.508	1.488	0.788	−0.0073	−0.0047	1.820	7.01	−0.99	1.113	0.374	−0.0064	−0.0121	1.825
0.627	1.25	1.457	0.756	−0.0075	−0.0052	1.830	10.1	0	1.083	0.326	−0.0060	−0.0136	1.828
0.627	−1.25	1.452	0.756	−0.0075	−0.0052	1.824	11.8	1.59	1.071	0.306	−0.0058	−0.0143	1.828
0.751	1.15	1.420	0.730	−0.0076	−0.0055	1.822	11.8	−1.59	1.076	0.306	−0.0058	−0.0143	1.838
0.751	−1.15	1.418	0.730	−0.0076	−0.0055	1.819	11.8	1.59	1.074	0.306	−0.0058	−0.0143	1.835
0.803	0	1.402	0.719	−0.0076	−0.0057	1.814	15.0	1.88	1.060	0.279	−0.0055	−0.0153	1.839
1.38	1.24	1.324	0.632	−0.0076	−0.0070	1.829	15.0	−1.88	1.066	0.279	−0.0055	−0.0153	1.849
1.38	−1.24	1.327	0.632	−0.0076	−0.0070	1.833	15.0	1.88	1.055	0.279	−0.0055	−0.0153	1.830
1.38	1.24	1.328	0.632	−0.0076	−0.0070	1.834	20.1	0	1.028	0.247	−0.0052	−0.0167	1.816
1.38	−1.25	1.324	0.632	−0.0076	−0.0070	1.829							

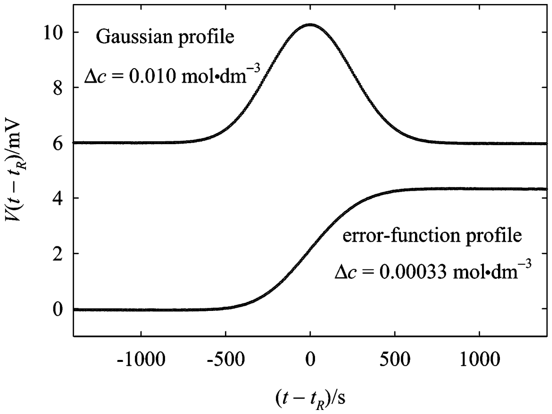

Figure 3. Dispersion profiles for aqueous malonic acid. The error function profile was generated by switching the flowing solution from a 0.000253 mol·dm^{-3} malonic acid solution to a 0.000586 mol·dm^{-3} solution at time $t = 0$. The Gaussian profile (offset vertically for clarity) was prepared by injecting a 0.020 cm^3 sample of 0.0103 mol·dm^{-3} malonic acid solution into a 0.000253 mol·dm^{-3} carrier solution.

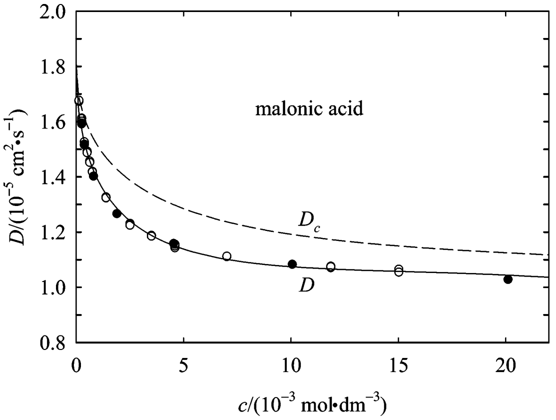

Figure 4. Diffusion coefficients of binary aqueous solutions of malonic acid: *D*, mutual diffusion coefficients from Gaussian (●) and error-function (○) profiles; D_c, concentration-weighted average diffusion coefficient of the molecular and ionic forms of malonic acid (— — — —).

these profiles and there are no dilution factors. This means that the initial concentration differences used to generate error-function profiles for arsenic and malonic acids can be about 30 times smaller than those used to generate Gaussian profiles, while maintaining similar $\Delta V_{\max}$ values and hence similar signal-to-noise ratios for the measured profiles. These features are illustrated in Figure 3.

The differential diffusion coefficients evaluated from the error-function dispersion profiles are listed in Tables 2 and 3 together with the initial concentration difference used to generate each profile. Figures 1 and 4 illustrate the concentration dependence of *D* for aqueous arsenic and malonic acids.

Arsenic and malonic acids are triprotic and diprotic acids, respectively. The second dissociation constants, however, are several orders of magnitude smaller than K_{1a} (see Table 5). The second and third dissociations are therefore negligible (< 1 %) at the compositions used here, allowing the acids to be treated accurately as incompletely dissociated 1:1 electrolytes ($\mathrm{HA} = \mathrm{H}^+ + \mathrm{A}^-$).

The simplest interpretation of the diffusion coefficient of a weak acid is the average of the diffusion coefficients of the molecular acid and the completely dissociated acid, D_m and $D_\pm$, weighted in proportion to the concentration of each form of the acid. Letting α denote the extent of dissociation, this approach gives

$$D_c = (1 - \alpha)D_m + \alpha D_\pm \tag{3}$$

for the concentration-weighted average diffusion coefficient, D_c. Nernst's equation[15]

$$D_\pm = \frac{2D_+D_-}{D_+ + D_-} \tag{4}$$

can be used to calculate the limiting diffusion coefficient of the completely dissociated acid as the harmonic average of the limiting diffusion coefficients D_+ and D_- of the hydrogen ion and acid anion ($\mathrm{H_2AsO_4^-}$ or $\mathrm{HOOCCH_2COO^-}$).

The concentration-weighted diffusion coefficient, though simple and intuitive, is inconsistent with the definition that mutual diffusion is driven by gradients in chemical composition.[15] To develop an expression for the mutual diffusion coefficient, the concentration weighting factors $1 - \alpha$ and α in eq 3 should be replaced with the corresponding derivatives $\mathrm{d}((1 - \alpha)c)/\mathrm{d}c$ and $\mathrm{d}(\alpha c)/\mathrm{d}c$ which are proportional to the gradients in the concentrations of the molecular and ionic forms of the acid[29] which gives

$$D = \frac{\mathrm{d}((1-\alpha)c)}{\mathrm{d}c}D_m + \frac{\mathrm{d}(\alpha c)}{\mathrm{d}c}D_\pm \tag{5}$$

for the mutual diffusion coefficient. Using the limiting relation $K_{1a} = \alpha^2 c/(1 - \alpha)$ to evaluate the derivatives, eq 5 leads to the expression

$$D = \frac{2(1-\alpha)D_m + \alpha D_\pm}{2 - \alpha} \tag{6}$$

for the mutual diffusion coefficient of an incompletely dissociated 1:1 electrolyte. The weighting factor $\mathrm{d}(\alpha c)/\mathrm{d}c = \alpha/(2 - \alpha)$ for the ionic contribution to *D* is smaller than the extent of dissociation, α. This result can be understood by noting that the extent of dissociation decreases as the acid concentration is raised, and hence $\mathrm{d}(\alpha c)/\mathrm{d}c < \alpha$. Similarly, the molecular contribution to the mutual diffusion coefficient is weighted as $2(1 - \alpha)/(2 - \alpha)$, which is larger than $1 - \alpha$.

Combining eqs 3 and 5 provides the differential relation

$$\mathrm{d}(cD_c) = D\mathrm{d}c \tag{7}$$

between the mutual and concentration-weighted diffusion coefficients. Integration and differentiation of eq 7 gives

$$D_c = \frac{1}{c}\int_0^c D\mathrm{d}c \tag{8}$$

$$D = D_c + c\frac{\mathrm{d}D_c}{\mathrm{d}c} \tag{9}$$

Interestingly, eqs 8 and 9 can be used to estimate concentration-weighted diffusion coefficients from mutual diffusion coefficients, or vice versa, without knowledge of the values of α, D_m, $D_\pm$, D_+, or D_-. Direct measurement of the concentration-weighted average of D_m and $D_\pm$ does not appear to be possible. Intradiffusion experiments employing nuclear magnetic reso-

Table 4. Fitting Parameters for Equation 10

acid	a_0	a_1	a_2	a_3
arsenic	1.521	−0.1890	−0.009152	0.006512
malonic	1.817	−0.5539	0.1388	−0.01198

Table 5. Dissociation Constants and Molecular and Ionic Diffusion Coefficients for Arsenous, Arsenic, and Malonic Acids at 25 °C

			10^{-5} $\mathrm{cm^2 \cdot s^{-1}}$			
acid	K_{1a}	K_{2a}	D_m	$D_\pm$	D_+	D_-
arsenous	$5.89 \cdot 10^{-10}$	–	1.112 ± 0.004	–	9.315	–
arsenic	$5.35 \cdot 10^{-3}$	$8.32 \cdot 10^{-8}$	0.809 ± 0.008	1.52 ± 0.02	9.315	0.83 ± 0.02
malonic	$1.41 \cdot 10^{-3}$	$2.01 \cdot 10^{-6}$	0.916 ± 0.004	1.82 ± 0.02	9.315	1.006 ± 0.120

nance or tagged arsenic atoms and malonate groups, for example, would provide the concentration-weighted average of D_m and D_-.

To indicate the differences between D_c and D, the polynomials in $c^{1/2}$

$$D/(10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}) = a_0 + \sum_{i=1}^{3} a_i (c/10^{-3}\ \mathrm{mol \cdot dm^{-3}})^{i/2} \qquad (10)$$

were fitted to the measured mutual diffusion coefficients. The concentration-weighted diffusion coefficients for aqueous arsenic and malonic acids plotted in Figures 1 and 4 were calculated by integration of eq 10 according to eq 8

$$D_c/(10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}) = a_0 + 2\sum_{i=1}^{3} \frac{a_i}{i+2} (c/10^{-3}\ \mathrm{mol \cdot dm^{-3}})^{i/2} \qquad (11)$$

using the least-squares fitting parameters listed in Table 4. In the limit $c \rightarrow 0$, D and D_c equal the diffusion coefficient $D_\pm$ of the completely dissociated acid. At higher concentrations, D is smaller than D_c because the former is weighted less heavily in favor of the more rapidly diffusing ionic form of the acid. Equations analogous to 10 and 11 have been used previously to relate the mutual diffusion coefficients and intradiffusion coefficients for dilute solutions of nonionic associating solutes.[30]

Ideal solutions have been assumed up to this point in the analysis of the results. A more accurate account of the concentration dependence of the mutual diffusion coefficient is obtained by including electrophoretic and activity coefficient terms to allow for ionic interactions.[31−34]

$$D = \frac{2(1-\alpha)D_m + \alpha(D_\pm + \Delta_1 + \Delta_2)}{2-\alpha}\left(1 + \alpha\frac{\mathrm{d}\ln y_\pm}{\mathrm{d}\ln c}\right) \qquad (12)$$

$y_\pm$ is the mean ionic activity coefficient on the molarity concentration scale. Δ_1 and Δ_2 are the first- and second-order electrophoretic corrections to the diffusion coefficient of the dissociated acid. These terms can be evaluated with sufficient accuracy for the relatively dilute solutions used here ($\alpha c < 0.01$ $\mathrm{mol \cdot dm^{-3}}$) by solving the equations

$$K_{1a} = \frac{\alpha^2 c/(\mathrm{mol \cdot dm^{-3}})}{1-\alpha} y_\pm^2 \qquad (13)$$

$$\ln y_\pm = -1.17\frac{\sqrt{\alpha c/(\mathrm{mol \cdot dm^{-3}})}}{1 + \sqrt{\alpha c/(\mathrm{mol \cdot dm^{-3}})}} \qquad (14)$$

$$\Delta_1/(10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}) = -0.67((D_+ - D_-)/(D_+ + D_-))^2 \sqrt{\alpha c/(\mathrm{mol \cdot dm^{-3}})} \qquad (15)$$

$$\Delta_2/(10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}) = 0.075\sqrt{\alpha c/(\mathrm{mol \cdot dm^{-3}})} \qquad (16)$$

The dissociation constants used in the calculations (Table 5) were evaluated from the molal-scale dissociation constants (K_{1am}) reported in refs 16 and 18 by using[15] $K_{1a} = 0.99707K_{1am}$.

The quantity Y defined by

$$Y = D(2-\alpha)\left(1 + \alpha\frac{\mathrm{d}\ln y_\pm}{\mathrm{d}\ln c}\right)^{-1} - \alpha(\Delta_1 + \Delta_2) = 2(1-\alpha)D_m + \alpha D_\pm \qquad (17)$$

is convenient for estimating the diffusion coefficients of the molecular and ionic forms of the acids: linear extrapolation of Y against α gives $2D_m$ as the left intercept at $\alpha = 0$ and $D_\pm$ as the right intercept at $\alpha = 1$. The extrapolation of Y values calculated from the measured mutual diffusion coefficients is shown in Figure 5. The values of $D_\pm$ and D_m obtained in the manner are listed in Table 5. The values of D_- for the limiting diffusion coefficients of the acid anions were calculated using Nernst's equation and the hydrogen ion diffusion coefficient $D_+ = 9.315 \cdot 10^{-5}$ $\mathrm{cm^2 \cdot s^{-1}}$ calculated from the limiting ionic conductivity[15] 349.81 $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$.

The diffusion coefficients of molecular arsenic and malonic acids are both smaller than the diffusion coefficients of the corresponding acid anion. But as illustrated by Table 6, there is no general rule for the relative diffusion coefficients of protonated and deprotonated acids. The chemical formulas for arsenous and arsenic acid are frequently written as H_3AsO_3 and H_3AsO_4, which differ by only a single oxygen atom. However, recent electrospray mass spectroscopic measurements[17] suggest that arsenous acid dissolved in water exists primarily as smaller $HAsO_2$ molecules. The present diffusion measurements would appear to support this result because the limiting diffusion of molecular arsenous acid ($1.112 \cdot 10^{-5}$ $\mathrm{cm^2 \cdot s^{-1}}$) is significantly larger than the limiting diffusion coefficient of molecular arsenic acid ($0.809 \cdot 10^{-5}$ $\mathrm{cm^2 \cdot s^{-1}}$). It is well-known, however, that the interpretation of the diffusion coefficients of small molecules and ions in aqueous solutions is complicated by hydration and by changes in the local solvent structure. Indeed, the limiting diffusion coefficient of the aqueous IO_3^- ion is about 25% *smaller*[15] than that of the IO_4^- ion (see Table 6).

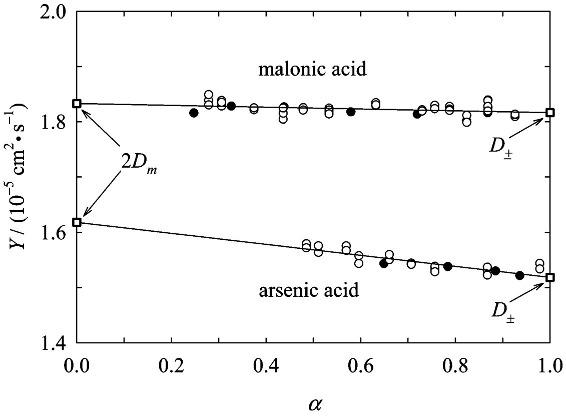

Figure 5. Plot of Y against α for binary aqueous solutions of arsenic and malonic acids.

Table 6. Limiting Diffusion Coefficients of Aqueous Acids, Deprotonated Acids, and Oxyanions at 25 °C

	D		D
species	10^{-5} $cm^2 \cdot s^{-1}$	species	10^{-5} $cm^2 \cdot s^{-1}$
H_2CO_3 [CO_2]	1.92[36]	HCO_3^-	1.185[36]
H_3PO_4	0.87[35,37]	$H_2PO_4^-$	0.860[35,37]
H_2SO_3 [SO_2]	1.45[36] (20 °C)	HSO_3^-	1.21[36] (20 °C)
H_3AsO_3 [$HAsO_2$]	1.112	$H_2AsO_3^-$ [AsO_2^-]	−
H_3AsO_4	0.809	$H_2AsO_4^-$	0.83
HCO_3^-	1.18[36]	CO_3^{2-}	0.92[36]
HSO_4^-	1.363[38]	SO_4^{2-}	1.065[38]
IO_3^-	1.080[15]	IO_4^-	1.452[15]
acetic acid	1.201[32,33]	acetate ion	1.089[32,33]
malonic acid	0.916	hydrogen malonate ion	1.006
maleic acid	0.83[39]	hydrogen maleate ion	0.98[39]
benzoic acid	0.900[40]	benzoate ion	0.862[40]
citric acid	0.657[29]	dihydrogen citrate ion	0.81[29]
NH_3 [HH_4OH]	2.08[36]	NH_4^+	1.959[15,36]
$(CH_3CH_2)NH_2$	1.13[22]	$(CH_3CH_2)NH_3^+$	1.19[22]
$(CH_3CH_2)_2NH$	0.89[22]	$(CH_3CH_2)_2NH_2^+$	0.94[22]
$(CH_3CH_2)_3N$	0.70[22]	$(CH_3CH_2)_3NH^+$	0.75[22]
−	−	$(CH_3CH_2)_4N^+$	0.870[15]
glycine	1.055[41]	glycineH^+	1.17[41]

Conclusions

Taylor dispersion equipment can be modified for the measurement of both Gaussian and error-function profiles by using a two-way switching valve and a low-dispersion pump. Error-function dispersion profiles are well suited for the measurement of composition-sensitive diffusion coefficients. Small initial concentration differences can be used (< 0.001 $mol \cdot dm^{-3}$), and the average concentration of the diffusing solute remains constant throughout each run. Gaussian and error-function profiles have been used to measure binary mutual diffusion coefficients for aqueous arsenous, arsenic, and malonic acids. Dissociation of arsenic and malonic acids causes steep increases in D with increasing dilution. Analysis of the concentration dependence of D provides estimates of the diffusion coefficients for the molecular and ionic forms of these acids and the acid anions. In addition, the concentration-weighted average of the diffusion coefficients of the molecular and ionic forms of each acid is obtained by evaluating the integral mutual diffusion coefficient.

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