Maryland. Drs. Majid Jahangiri and R. T. Jacobsen provided us with the Helmholtz function for ethylene.

Registry No. Ethylene, 74-85-1; methane, 74-82-8; butane, 106-97-8; isobutane, 75-28-5; isopentane, 78-78-4.

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Diffusion Coefficient of Aqueous Benzoic Acid at 25 °C

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A conductometric technique has been used to measure precise binary diffusion coefficients for aqueous benzoic acid solutions at concentrations from 0.0003 to 0.0153 mol dm^{-3} at 25 °C. As the concentration drops, dissociation of benzoic acid molecules increases the overall rate of diffusion of the solute. The concentration dependence of the measured diffusion coefficients is in good agreement with predicted behavior and yields 0.900 (±0.006) × 10^{-9} m^2 s^{-1} for the limiting diffusion coefficient of the undissociated aqueous benzoic acid molecule. The new diffusion data can be used to model dissolution of the acid, a standard procedure for determination of mass-transfer coefficients.

Introduction

Mass transfer between solid surfaces and moving fluids finds important applications in extraction, leaching, drying, ion exchange, and adsorption processes. Rate constants for these processes are frequently determined by measuring dissolution of test pieces of solid benzoic acid (*1–6*). This material is easily cast or pressed into tubes, plates, spheres, or cylinders. Its solubility in water lies in a convenient range, and the solutions can be analyzed accurately by titration with standardized base. Interfacial resistance to dissolution of the acid appears to be negligible (*2*).

Interpretation of benzoic acid dissolution rates requires solubility, viscosity, and diffusion data. Although accurate solubilities and viscosities have been reported (*7*), the diffusion data usually employed were obtained by the porous diaphragm cell method before reliable stirring (*8*) and calibration (*9*) procedures were developed. Because the solubility of benzoic acid in water is relatively low (0.0275 mol dm^{-3} at 25 °C (*7*)), the diaphragm cell measurements were made at low ionic strengths where adsorption on the diaphragm can lead to significant errors (*10*). The concentration dependence of the diffusion coefficient and the concentrations at which the measurements were made were not specified.

More recently, an optical technique, Mach-Zehnder interferometry, was used to measure diffusion of aqueous benzoic acid (*11*). But since solute concentrations are low and the changes in refractive index are correspondingly small, optical diffusion experiments are difficult to apply to benzoic acid solutions and the data lack precision. The reported linear concentration dependence of the diffusion coefficient is neither supported by theory nor observed for other weak acids (*12–14*).

These considerations prompted us to use the Harned conductometric method (*15*) to determine precise diffusion coefficients for benzoic acid. In this technique flow of solute is followed by measuring changes in electrical conductance along a column of diffusing electrolyte. Precise conductivity measurements can be made down to very low concentrations. Consequently, Harned's technique is the method of choice for studies of diffusion of dilute electrolytes.

Experimental Section

Procedure. The cells used in this work had cylindrical diffusion channels (1.278 cm diameter, 3.050 (±0.002) cm depth) which were machined from high-density polyethylene. Pairs of circular platinum electrodes (0.1 cm diameter) were cemented with epoxy into the cell walls at levels one-sixth and five-sixths of the channel height. The cells were initially filled with pure water or dilute benzoic acid solutions and sealed with lightly greased glass plates. To begin a run a known volume of stock benzoic acid solution was injected into the lower end of the solution chamber by using a calibrated precision syringe. Electrical resistances were measured every 10 000 s for 5 days with a General Radio Model 1689 automatic ac bridge. The bridge was interfaced with a Hewlett Packard Model 3488A switch unit and a Hewlett Packard Model 216 computer for data acquisition and analysis. The diffusion cells were held in a water thermostat controlled at 25.00 (±0.01) °C.

Experimental diffusion coefficients accurate to 0.2–0.4% were computed from measured resistances by using linear least-squares analysis of the slope (*12*, *14*)

$$D = -\frac{a^2}{\pi^2}\frac{d}{dt}\left[\ln\,(rK_B - K_T) + \ln\left(rK_B + K_T + \frac{K_a y_\pm \Lambda}{1000\alpha K_T}\right)\right] \quad (1)$$

Here a is the height of the solution column, K_T and K_B are reciprocal resistances measured at top and bottom electrodes positions at time t, and $r = K_B/K_T$ is the ratio of electrode cell constants. Λ, $y_\pm$, and α denote respectively the molar conductance, mean molar ionic activity coefficient, and the degree of dissociation of molecular benzoic acid at the final cell concentration. Values of Λ were obtained from conductances

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Table I. Diffusion Coefficients of Aqueous Benzoic Acid at 25 °C

C, 10^{-3} mol dm^{-3}	α	$-C\ \mathrm{d}\ln y_{\pm}/\mathrm{d}C$	$\Delta_1 + \Delta_2$, 10^{-9} m^2 s^{-1}	D, 10^{-9} m^2 s^{-1}	D_{m}, 10^{-9} m^2 s^{-1}	D_{calcd},^{a} 10^{-9} m^2 s^{-1}
0.000	1.000	0.000	0.000			1.578^b
0.290	0.374	0.002	−0.005	1.053	0.899	1.054
0.406	0.328	0.002	−0.006	1.025	0.892	1.031
0.789	0.249	0.004	−0.007	0.995	0.900	0.995
1.469	0.190	0.006	−0.008	0.964	0.894	0.969
2.042	0.164	0.007	−0.009	0.953	0.894	0.959
2.918	0.140	0.008	−0.010	0.951	0.901	0.949
4.407	0.116	0.007	−0.011	0.929	0.888	0.940
5.774	0.102	0.007	−0.012	0.928	0.893	0.935
7.359	0.091	0.006	−0.013	0.933	0.902	0.931
8.941	0.083	0.006	−0.013	0.936	0.908	0.928
10.15	0.078	0.007	−0.014	0.930	0.904	0.927
11.21	0.075	0.008	−0.014	0.929	0.904	0.925
12.21	0.072	0.010	−0.014	0.918	0.894	0.924
13.21	0.069	0.011	−0.014	0.918	0.895	0.923
15.30	0.064	0.012	−0.015	0.934	0.913	0.921

^{a}Equation 4. ^{b}Calculated limiting Nernst value, eq 5.

reported by Brockman and Kilpatrick (*16*). The degree of dissociation and the activity coefficient were evaluated from the equilibrium condition

$$K_a = \alpha^2 C y_{\pm}^2/(1 - \alpha) \tag{2}$$

and the semiempirical relation (*17*)

$$\ln y_{\pm} = -1.17 I^{1/2}/(1 + I^{1/2}) \tag{3}$$

where K_a is the acid dissociation constant (6.32×10^{-5} mol dm^{-3} at 25 °C (*16*)) for the reaction $C_6H_5COOH(aq) = C_6H_5COO^-(aq) + H^+(aq)$ and $I = \alpha C$ denotes the ionic strength. At the low concentrations used in the present study the activity coefficient of the molecular acid species can be set equal to unity without significant error.

Materials. Primary standard grade benzoic acid was used without further purification. Solutions were prepared with distilled, deionized water. Cell constants were determined by calibration with aqueous potassium chloride solutions (*18*). Corrections for solvent conductance were negligible.

Results and Discussion

The experimental diffusion coefficients are summarized in Table I. Attempts to measure diffusion coefficients below 0.0003 mol dm^{-3} were unsuccessful because the density gradients were too small to stabilize the diffusion columns against convection.

Although molecular benzoic acid, benzoate ions, and hydrogen ions diffuse in proportions that vary with total acid concentration, the restrictions of electroneutrality and local equilibrium of the dissociation reaction ensure that only one diffusional flow of solute is independent. Consequently, binary diffusion equations can be used to describe transport of the acid. The concentration dependence of the binary diffusion coefficient of a dilute 1:1 electrolyte suggested by theory (*12*, *14*, *19*) is

$$D = \frac{2(1 - \alpha)D_m + \alpha(D_{\pm} + \Delta_1 + \Delta_2)}{2 - \alpha}\left[1 + \alpha C\,\frac{\mathrm{d}\ln y_{\pm}}{\mathrm{d}C}\right] \tag{4}$$

where Δ_1 and Δ_2 are small electrophoretic terms which allow for ionic interactions, and D_m and $D_{\pm}$ designate limiting diffusion coefficients of the molecular and fully ionized forms of the acid. The latter can be evaluated from limiting ionic conductances by using Nernst's relation

$$D_{\pm} = (2RT/F^2)\lambda_+^0\lambda_-^0/(\lambda_+^0 + \lambda_-^0) \tag{5}$$

From published ionic conductances (*20*) $\lambda_+^0(H^+) = 0.034\,98$ and $\lambda_-^0(C_6H_5COO^-) = 0.003\,238$ m^2 ohm^{-1} mol^{-1}, we obtained $D_{\pm} = 1.578 \times 10^{-9}$ m^2 s^{-1} for the limiting diffusion coefficient of fully dissociated benzoic acid at 25 °C. The values of D_m listed in Table I were calculated by substituting experimental D values into the left-hand side of eq 4 and solving. Since D_m values are essentially constant over the complete concentration range, the concentration dependence of the measured D values is consistent with theory. Averaging the D_m values gives 0.900 (±0.006) × 10^{-9} m^2 s^{-1} for the diffusion coefficient of molecular benzoic acid. The diffusion coefficient of the benzoate ion is slightly smaller, 0.862×10^{-9} m^2 s^{-1} (*20*).

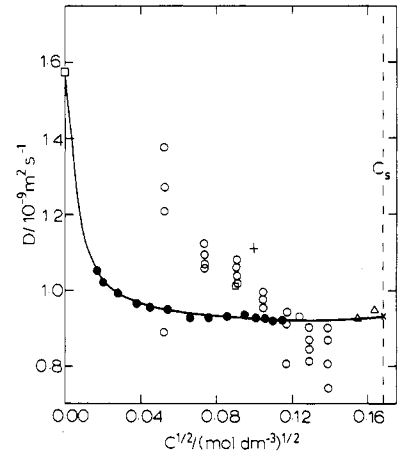

Figure 1. Comparison of measured and predicted diffusion coefficients of aqueous benzoic acid at 25 °C: solid line, eq 4; ●, present conductometric results; +, diaphragm cell data of King and Brodie; △, diaphragm cell data of Wilke et al.; □, diaphragm cell data of Lozar et al.; ×, diaphragm cell data of Vanadourongwan et al.; ○, optical data of Pradhan and Heideger.

Measured and predicted binary diffusion coefficients are compared in Figure 1. Our conductometric data are about 20% lower than the diaphragm cell value reported by King and Brodie (*21*) and about 10% lower than the value reported by Lozar et al. (*22*). A short extrapolation of the conductometric data to saturation overlaps the diaphragm cell data of Wilke et al. (*2*) and Vanadourongwan et al. (*23*) within 2%.

In mass-transfer investigations which employ dissolution of solid benzoic acid the concentration of diffusing acid varies from the saturation value C_s near the solid/liquid interface to a lower value, C_b, in the bulk solution. Transport of acid over this range of composition is described by the integral diffusion coefficient

$$\bar{D} = (C_s - C_b)^{-1}\int_{C_b}^{C_s} D\,\mathrm{d}C \tag{6}$$

Figure 2 shows values of $\bar{D}$ calculated by numerical integration of eq 6. Because $\bar{D}$ varies by less than 1% over the range of integration, it is an excellent approximation to assume that

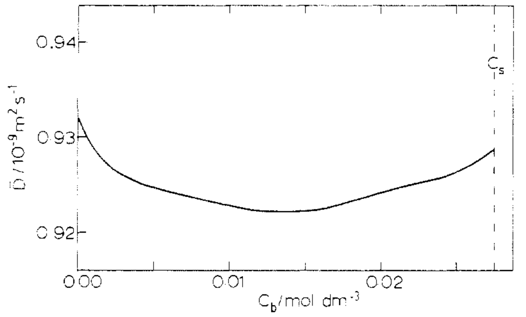

Figure 2. Integral diffusion coefficients of aqueous benzoic acid at 25 °C calculated from eq 6.

mass-transfer coefficients for dissolution of benzoic acid are independent of acid concentration.

Glossary

a	cell height, m
C	total acid concentration, mol dm^{-3}
C_b	bulk concentration, mol dm^{-3}
C_s	saturation concentration, mol dm^{-3}
D	binary diffusion coefficient, m^2 s^{-1}
$\bar{D}$	integral diffusion coefficient, m^2 s^{-1}
D_m	limiting molecular diffusion coefficient, m^2 s^{-1}
$D_\pm$	limiting ionic diffusion coefficient, m^2 s^{-1}
F	Faraday constant, C mol^{-1}
I	ionic strength, mol dm^{-3}
K_a	dissociation constant, mol dm^{-3}
K_B	bottom reciprocal resistance, ohm^{-1}
K_T	top reciprocal resistance, ohm^{-1}
k_B	bottom electrode cell constant, m^{-1}
k_T	top electrode cell constant, m^{-1}
R	gas constant, J K^{-1} mol^{-1}
r	cell constant ratio
T	temperature, K
t	time, s
$y_\pm$	mean molar ionic activity coefficient
α	degree of dissociation
Δ_1	first order electrophoretic correction, m^2 s^{-1}
Δ_2	second order electrophoretic correction, m^2 s^{-1}
Λ	molar conductance, m^2 ohm^{-1} mol^{-1}
λ_+^0	limiting cation molar conductance, m^2 ohm^{-1} mol^{-1}
λ_-^0	limiting anion molar conductance, m^2 ohm^{-1} mol^{-1}

Registry No. Benzoic acid, 65-85-0.

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Physical Properties of *N*-Methylpyrrolidinone as Functions of Temperature

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The relative permittivity, viscosity, and refractive index of the cyclic amide *N*-methylpyrrolidinone (NMP) were determined at various temperatures ranging from 251 to 353 K. Linear functions were derived to describe the changes in the physical properties with temperature. The values obtained were compared to data available in the literature for NMP and other cyclic amides. The rate of diffusion control, the activation energies of diffusion and viscous flow, and the Kirkwood correlation factor were calculated.

Introduction

The cyclic amide *N*-methylpyrrolidinone (NMP) is an excellent dissociating solvent (*1*, *2*) suitable for use in electrochemistry (*3*), organic synthesis requiring dipolar aprotic media (*4*), and polymer membrane casting (*5*). Our current investigations indicate that NMP is also a good solvent in which to study aromatic radical anions and their electron-transfer reactions using pulse radiolysis (*6*). However, there is an absence of data on the temperature dependence of the physical properties of this solvent except for its density (*7*).

Experimental Section

NMP (Aldrich) was purified by refluxing over calcium hydride for 6 h followed by distillation under vacuum. The solvent was then redistilled under vacuum from freshly prepared sodium-potassium alloy.

Capacitance and conductance measurements were obtained in duplicate at 10^4 Hz using a Wayne Kerr Universal Bridge B221A, AF Signal Generator S121, and Waveform Analyser A321 in conjunction with a glass cell containing platinum electrodes. The temperature of the cell was adjusted by circulating water from a thermostated water bath through the outer glass