

Hydration and Ion Pairing in Aqueous Sodium Oxalate Solutions

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Dielectric spectra have been measured for aqueous sodium oxalate solutions up to the saturation concentration ($0.04 \leq c [\text{mmol L}^{-1}] \leq 0.25$) at 25°C over the approximate frequency range $0.2 \leq \nu [\text{GHz}] \leq 20$. The spectra exhibit a process at about 1 GHz associated with the presence of ion pairs, in addition to the dominant solvent relaxation process at about 18 GHz. Detailed analysis of the solvent dispersion amplitude indicates that the oxalate ion is highly hydrated but that its solvation sheath is "fragile", decreasing quickly with increasing solute concentration. The $\text{NaOx}(\text{aq})^-$ ion pair is shown to be of the double-solvent-

separated (2SIP) type, with an infinite dilution association constant $K_A = 1.04 \pm 0.02$. Analysis of the ion-pair relaxation time as a function of solute concentration gave rate constants for the formation ($k_{12} = (7.3 \pm 0.4)10^9 \text{ L mol}^{-1} \text{ s}^{-1}$) and dissociation ($k_{21} = (6.7 \pm 0.5)10^8 \text{ s}^{-1}$) of the ion pair. These values are reasonably close to the diffusion-controlled values predicted by the Eigen theory, consistent with a 2SIP structure for the ion pair.

KEYWORDS:

complex formation · dielectric relaxation · ion hydration · ion pairs · liquids

The binding between sodium and nonmacrocylic carboxylate ions is generally thought to be extremely weak.^[1, 2] Nevertheless, there is mounting evidence that such weak interactions become significant under appropriate circumstances. In particular, there is a considerable interest in the interactions between sodium and oxalate ions (Ox^{2-} , $\text{C}_2\text{O}_4^{2-}$). For example, the solubility of calcium oxalate, the major component of human kidney stones, has been shown to be influenced by the formation of weak $\text{Na}^+/\text{Ox}^{2-}$ ion pairs in urine.^[3, 4] On the industrial scale, under typical conditions encountered in the Bayer process (used for the extraction of alumina from bauxitic ores) the total sodium ion concentration can be very high ($\approx 6\text{M}$) and the concentration of oxalate, which arises from the decomposition of organic matter in the ore, may be appreciable.^[5] Under such conditions, even a very small association constant can result in significant ion-pair formation, which may have appreciable effects on process chemistry and kinetics,^[1, 6] and on physicochemical properties such as density and viscosity.^[7] However, in spite of these potential impacts, ion-pair formation between sodium and oxalate ions is poorly characterized, largely because of the difficulties of quantifying such weak interactions.

In this regard, dielectric relaxation spectroscopy (DRS), which is a powerful technique for investigating the thermodynamics, kinetics, and structures of ion pairs in electrolyte solutions,^[8, 9, 10] should be especially helpful. DRS involves the measurement of the complex dielectric permittivity of a sample [Equation (1)]:

$$\hat{\epsilon}(\nu) = \epsilon'(\nu) - i\epsilon''(\nu) \quad (1)$$

as a function of the frequency ν of an applied electromagnetic wave, where $\epsilon'(\nu)$ is the relative permittivity and $\epsilon''(\nu)$ is the

dielectric loss. For an electrolyte solution, only the total loss is measurable [Equation (2)]:

$$\eta''(\nu) = \epsilon''(\nu) + \frac{\kappa}{2\pi\nu\epsilon_0} \quad (2)$$

where $\kappa/(2\pi\nu\epsilon_0)$ represents the conductivity contribution from the electrolyte and ϵ_0 is the permittivity of free space. The conductivity term, which dominates at low frequencies, may be evaluated by separate measurement or, as shown previously,^[11, 12] by careful fitting of the dielectric data.

In earlier papers it has been shown that, provided a careful calibration and measurement protocol is followed, reliable dielectric spectra up to 20 GHz can be obtained for electrolyte solutions using a commercially-available vector network analyzer. Such spectra have proven to be very informative about the extent and nature of ion pairs formed in the aqueous solutions of a number of weakly associating electrolytes.^[9, 13–15] The present paper presents dielectric spectra for aqueous sodium oxalate (Na_2Ox) solutions at concentrations (c) up to saturation ($c \leq 0.25 \text{ mol L}^{-1}$) and at frequencies up to 20 GHz.

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Results and Discussion

Ion Hydration

The major process apparent in the spectra (Figure 1), at around 18 GHz and virtually independent of the solute concentration, is readily assigned to solvent water with a relaxation time $\tau_s \approx 8$ ps. The dielectric permittivity of the solvent, ϵ_s , is given as a function of the solute concentration in Figure 2. These data show the usual nonlinear decrease with increasing Na_2Ox concentration, consistent with extensive ion–solvent interactions.

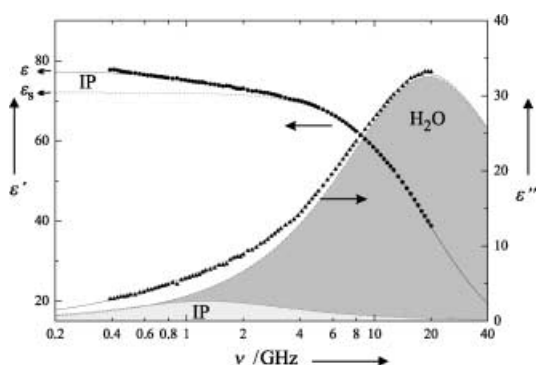


Figure 1. Dielectric permittivity, $\epsilon'(\nu)$, and loss, $\epsilon''(\nu)$, spectra of saturated aqueous Na_2Ox solutions ($c \approx 0.25 \text{ mol L}^{-1}$) at 25°C , including the contributions attributed to the ion pair (IP) and the solvent (H_2O).

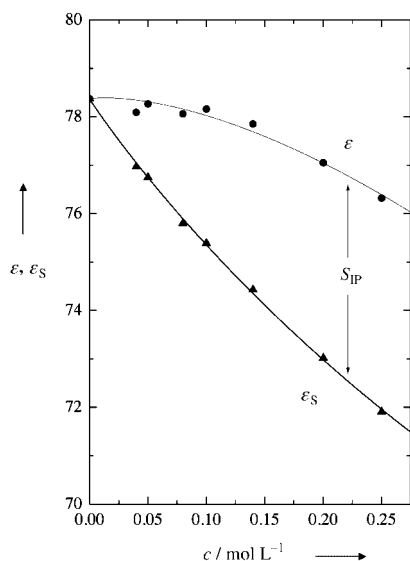


Figure 2. Dielectric permittivity of the solution, ϵ , and of the solvent, ϵ_s , as a function of electrolyte concentration, c , in aqueous Na_2Ox solutions at 25°C .

Ion hydration numbers can be obtained from the solvent dispersion amplitude, $S_s = \epsilon_s - \epsilon_\infty$, using the procedure described in detail previously.^[11, 9] Briefly, this involves correction of the observed dispersion amplitude for kinetic depolarization, which is associated with the movement of the solvated ions in the applied field. The kinetic depolarization is calculated by using the Hubbard–Onsager continuum model,^[16, 17] assuming “slip” boundary conditions for the transport of the ions; this is

consistent with previous findings.^[9, 11–13] If we assume that the Kirkwood factor g_k for the solvent is independent of the solute concentration, then the number of “irrotationally bound” solvent molecules $Z_{\text{ib}}^{\text{slip}}(c)$, hereafter just Z_{ib} , can be obtained from the expression in Equation (3):

$$Z_{\text{ib}} = \frac{c_s^0 - c_s^{\text{ap}}}{c} \quad (3)$$

where c_s^0 is the analytical concentration of the solvent, c is the electrolyte concentration, and c_s^{ap} is the number of (rotationally) “free” solvent molecules. This last quantity is calculated from the Cavell equation [Eq. (8)],^[18, 19] normalized with respect to the pure solvent [Equation (4)]:

$$c_s^{\text{ap}} = \frac{2\epsilon(c) + 1}{2\epsilon(0) + 1} \times \frac{\epsilon(0)}{\epsilon(c)} \times \frac{(1 - \alpha_s f_s(c))^2}{(1 - \alpha_s f(0))^2} \times \frac{c_s^0(0)}{S_s(0)} \times S_s(c) \quad (4)$$

where α_s is the polarizability and f_s the reaction field factor of water.

The values of Z_{ib} calculated in this way for Na_2Ox decrease linearly with increasing solute concentration, as given by Equation (5):

$$Z_{\text{ib}} = (15.1 \pm 0.7) - (19 \pm 4)c \quad (5)$$

Given that $Z_{\text{ib}}(\text{Na}^+, c=0) = 4.5 \pm 0.2$ and is virtually constant over the present concentration range,^[9, 11] it follows that [Eq. (6)]:

$$Z_{\text{ib}}(\text{Ox}^{2-}) = (6.1 \pm 1.1) - (19 \pm 4)c \quad (6)$$

The infinite dilution value of ≈ 6 suggests that Ox^{2-} is reasonably well solvated in water (although rather less so than SO_4^{2-} ^[9] or CO_3^{2-} ^[13]). More surprising is the very large concentration dependence of $Z_{\text{ib}}(\text{Ox}^{2-}, c)$. Thus, in a saturated Na_2Ox solution, $Z_{\text{ib}}(\text{Ox}^{2-}, 0.25 \text{ M}) = 2.3$, which seems low for a doubly charged anion and suggests that the solvation sheath around the oxalate ion is unusually “fragile”. The solvation number of the related carbonate ion also displays a considerable concentration dependence^[13] at low concentrations [$c \leq 1.5 \text{ mol L}^{-1}$; Eq. (7)], but eventually levels off at the rather high value of ≈ 7 .

$$Z_{\text{ib}}(\text{CO}_3^{2-}, c) \approx 13 - 7c \quad (7)$$

This may indicate that the rigid, nonspherical oxalate ion does not fit easily into the water structure and thus binds less strongly to the water molecules in its vicinity.

Ion Pairing

The minor, slower relaxation process centered on ≈ 1 GHz (Figure 1) is attributed to the presence of an $\text{NaOx}^-(\text{aq})$ ion pair. The dielectric permittivity of the Na_2Ox solutions, ϵ , is given as a function of $c(\text{Na}_2\text{Ox})$ in Figure 2. The ion-pair dispersion amplitude $S_{\text{IP}} = \epsilon - \epsilon_s$ seems to be approaching a plateau with increasing solute concentration, as has been observed for other $\text{NaX}^-(\text{aq})$ ion pairs,^[9, 13] but does not reach this plateau before the solubility limit.

Providing the dipole moment of the ion pair, μ_{IP} is known, the ion-pair concentrations in these solutions, c_{IP} , can be determined from the modified Cavell Equation (8)

$$c_{\text{IP}} = \frac{3(\varepsilon + (1 - \varepsilon)A_{\text{IP}})}{\varepsilon} \times \frac{k_{\text{B}}T\varepsilon_0}{N_{\text{A}}} \times \frac{(1 - \alpha_{\text{IP}}f_{\text{IP}})^2}{\mu_{\text{IP}}^2} \times S_{\text{IP}} \quad (8)$$

where N_{A} and k_{B} are the Avogadro and Boltzmann constants and T is the (Kelvin) temperature.^[18, 19] The quantities α_{IP} , A_{IP} and f_{IP} are the polarizability, the cavity-field factor and the reaction-field factor of the ion pair, respectively.

Values of μ_{IP} calculated for various possible ion-pair structures are listed in Table 1. Dipole moments for contact (CIP) and solvent-shared (SIP) ion pairs were calculated using the program Gaussian 94 at the PM3 level. For both the CIP and SIP there are two possible “chelating” structures (Figure 3), corresponding to

Table 1. Properties of the various models for the bidentate NaOx^- (aq) ion-pair species: dipole moment, μ_{IP} (in D, $1\text{D} = 3.33564 \times 10^{-12}\text{ C m}$); association constant, K_{A} [with parameters b_{β} and c_{β} obtained for Equation (8)] and the rotational correlation time, τ'_{IP} (in ps, estimated using Equation (15) for ion-pair rotation with stick boundary conditions).

| | CIP | | SIP | | 2SIP |
|---------------------|----------------|-----------|----------------|----------------|----------------|
| | “end-on” | “side-on” | “end-on” | “side-on” | |
| μ_{IP} | 18.8 | 12.9 | 34.5 | 30.4 | 51.8 |
| K_{A} | 330 ± 50 | ∞ | 28.1 ± 1.4 | 42 ± 3 | 10.9 ± 0.5 |
| b_{β} | -5.7 ± 1.0 | – | -2.5 ± 0.2 | -2.7 ± 0.3 | -2.1 ± 0.2 |
| c_{β} | 4.4 ± 1.3 | – | 1.5 ± 0.3 | 1.7 ± 0.3 | 1.2 ± 0.2 |
| τ'_{IP} | 40 | | 80 | | 140 |

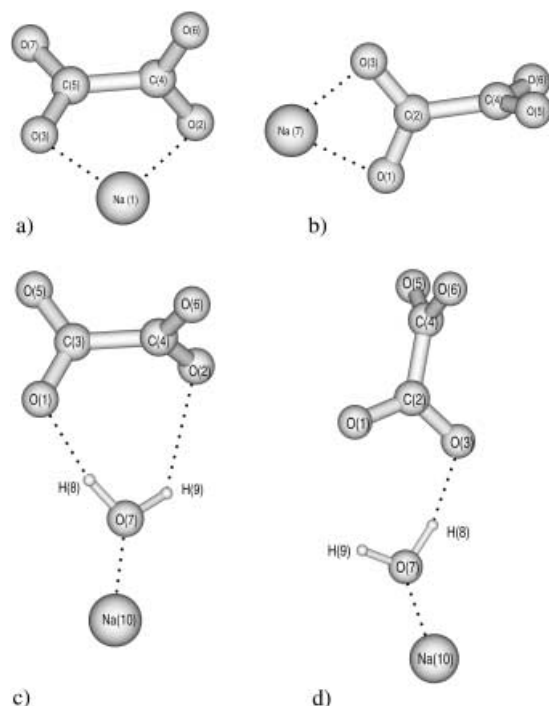


Figure 3. Structures of contact (CIP: a, b) and solvent-shared (SIP: c, d) bidentate ion pairs obtained with Gaussian 94 at the PM3 level. The ion pairs with the “side-on” oxalate ion (a; c) are less stable by ≈ 3.4 and $\approx 6.0\text{ kJ mol}^{-1}$, respectively, than the “end-on” structures (b and d).

“end-on” and “side-on” orientations of the oxalate ion.^[20] For the chelated structures Gaussian 94 indicated that the “end-on” configuration was slightly more stable than the “side-on” (by $\approx 3.4\text{ kJ mol}^{-1}$ for CIP and $\approx 6.0\text{ kJ mol}^{-1}$ for SIP). In addition, Gaussian gave D_{2d} (staggered) symmetry for the isolated anion and Ox^{2-} in the ion pairs, consistent with vibrational spectroscopic data for solutions.^[21] For the double solvent separated-ion pair (2SIP), μ_{IP} was calculated using the ionic radius of sodium, $r(\text{Na}^+) = 98\text{ pm}$,^[22] the average radius of the oxalate ion obtained from Gaussian 94, $r(\text{Ox}^{2-}) = 200\text{ pm}$, and the radius of the water molecule of 142.5 pm .^[23]

The factors f_{IP} and A_{IP} can be calculated from geometric data [Equations (15) and (16) of ref. [9]]. The polarizability of Na^+ , $\alpha(\text{Na}^+) = 4\pi\varepsilon_0 \times 0.149 \times 10^{-30}\text{ m}^3$ was taken from ref. [24]. The polarizabilities of Na_2Ox and Ox^{2-} in aqueous solution were obtained as described in ref. [25] from the molar refraction [Eq. (9)]

$$[R] = \frac{(1-x)M(\text{H}_2\text{O}) + xM(\text{Na}_2\text{Ox})}{\rho} \frac{(n_{\text{D}}^{25})^2 - 1}{(n_{\text{D}}^{25})^2 + 2} \quad (9)$$

where x is the mole fraction of the electrolyte and M is its molar mass, using the data of Table 2. The values $\alpha(\text{Na}_2\text{Ox}) = 4\pi\varepsilon_0 \times (7.10 \pm 0.03)10^{-30}\text{ m}^3$ and $\alpha(\text{Ox}^{2-}) = 4\pi\varepsilon_0 \times 6.80 \times 10^{-30}\text{ m}^3$ were obtained. In the application of Equation (8) it is reasonably assumed that dipole–dipole correlations between ion pairs are negligible.

Using the c_{IP} values obtained from the Cavell Equation (8) enables calculation of the ion-pairing constant [Equation (10)].

$$\beta = \frac{c_{\text{IP}}}{(2c - c_{\text{IP}})(c - c_{\text{IP}})} \quad (10)$$

The value of $K_{\text{A}}(\text{NaOx}^-)$, the standard state (infinite dilution) ion-pairing constant, is obtained by fitting these results to a Guggenheim-type Equation (11):

$$\log\beta = \log K_{\text{A}} - \frac{2A_{\text{DH}}|z_+z_-|\sqrt{I}}{1 + \sqrt{I}} + b_{\beta}I + c_{\beta}I^{3/2} \quad (11)$$

where $A_{\text{DH}} = 0.5110\text{ dm}^{3/2}\text{ mol}^{-1/2}$ for Na_2Ox solutions in water at 25°C and $I = 1/2\sum c_i z_i^2 = 3c - 2c_{\text{IP}}$ is the actual ionic strength.

The $K_{\text{A}}(\text{NaOx}^-)$ values and the empirical parameters b_{β} and c_{β} obtained in this way for the various types of ion pairs are given in Table 1. Although no high quality study of the thermodynamics of ion association in the $\text{Na}^+/\text{Ox}^{2-}$ system as a function of I is available in the literature, some estimates have been made of the ion-pairing constant. The most notable of these estimates, based on solubility measurements, is by Finlayson et al.^[26] who give $\log K_{\text{A}} \approx 1.1$, which has been confirmed by Singh.^[3] This value, and comparison with similar systems,^[9, 13] suggest that the K_{A} values required for both CIP and SIP are unrealistically large (S_{IP} even yields $c_{\text{IP}} > c$ for the “side-on” CIP).

The stability constants derived assuming a 2SIP are plotted in Figure 4 as a function of the ionic strength, I . The 2SIP-derived value of $\log K_{\text{A}} = 1.04 \pm 0.02$ is in excellent agreement with the result of Finlayson and Roth.^[3, 26] Furthermore, the value of $\beta(\text{NaOx}^-) \approx 0.11$, which can be calculated by using Equation (11) for a hypothetical $I = 1\text{ mol L}^{-1}$ Na_2Ox solution, compares favorably with the values of $\beta(\text{NaOx}^-) \approx 0.14$ and 0.10 obtained

Table 2. Concentration, c (in mol L^{-1}), density, ρ (in g cm^{-3}), effective conductivity, κ_e (in $\Omega \text{ m}^{-1}$), and refractive index, n_D^{25} of sodium oxalate solutions in water at 25°C , together with the dielectric relaxation parameters: τ_{IP} , τ_s (in ps); ϵ , ϵ_s , ϵ_∞ ; and the variance, σ^2 , obtained from fitting a sum of two Debye equations, Equation (16), to $\epsilon''(\nu)$.

| c | ρ | κ_e | ϵ , n_D^{25} | ϵ | τ_{IP} | ϵ_s | τ_s | ϵ_∞ | σ^2 |
|--------|--------------------------|------------|-------------------------|------------|--------------------|-----------------------|----------------------|----------------------|------------|
| 0 | 0.997043 ^[34] | 0 | 1.33280 | – | – | 78.37 ^[11] | 8.26 ^[11] | 5.65 ^[11] | |
| 0.0400 | – | 0.721 | – | 78.09 | 162 | 76.97 | 8.08 | 5.38 | 0.009 |
| 0.0501 | 1.00253 | 0.878 | 1.33408 | 78.27 | 168 | 76.75 | 8.22 | 5.85 | 0.011 |
| 0.0800 | – | 1.31 | – | 78.06 | 147 | 75.80 | 8.02 | 5.47 | 0.012 |
| 0.1001 | 1.00794 | 1.58 | 1.33515 | 78.16 | 145 | 75.39 | 8.11 | 5.47 | 0.022 |
| 0.1400 | 1.01203 | 2.10 | 1.33620 | 77.85 | 129 | 74.43 | 8.10 | 5.50 | 0.019 |
| 0.2002 | 1.01861 | 2.82 | 1.33731 | 77.05 | 108 | 73.02 | 8.00 | 5.14 | 0.031 |
| 0.2502 | 1.02386 | 3.37 | 1.33838 | 76.32 | 96.2 | 71.91 | 7.99 | 5.21 | 0.030 |

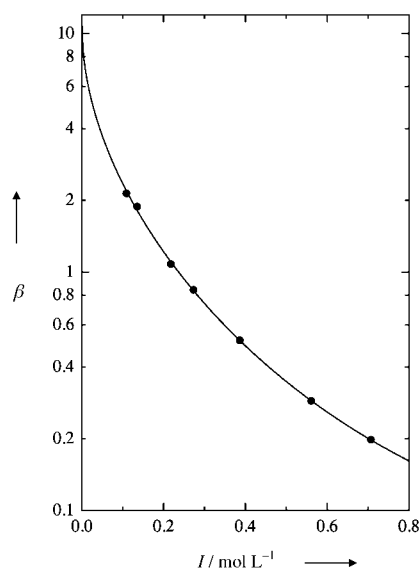
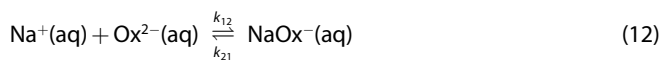


Figure 4. The stability constant, β , of the $\text{NaOx}^-(\text{aq})$ ion pair as a function of ionic strength, I , in aqueous Na_2Ox solutions at 25°C .

at $I=1 \text{ mol L}^{-1}$ in KCl and CsCl media, respectively, from potentiometric measurements of the protonation constants of H_2Ox .^[27]

Ion-Pair Relaxation Time

The relaxation times of the ion pair, τ_{IP} , are summarized in Table 2. The values obtained show a strong decrease with concentration, which is indicative of a significant kinetic contribution.^[28] If a single-step equilibrium for the formation of the ion pair is assumed [Equation (12)]



then the observable relaxation rate is [Equation (13)]

$$\tau_{\text{IP}}^{-1} = (\tau'_{\text{IP}})^{-1} + (\tau_{\text{ch}})^{-1} \quad (13)$$

where τ'_{IP}^{-1} is the rotational correlation time of the ion pair and τ_{ch} is the chemical relaxation rate. The latter is given by Equation (14)

$$(\tau_{\text{ch}})^{-1} = k_{21} + 2k_{12}(3c - 2c_{\text{IP}}) \quad (14)$$

where k_{12} and k_{21} are, respectively, the rate constants for the formation and dissociation of the ion pair.

A plot of $1/\tau_{\text{IP}}$ against I (Figure 5) is linear, which indicates the formation of only one ion pair.^[28] The slope of this plot gives $k_{12} = (7.3 \pm 0.4)10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. Combination of this value with K_A yields $k_{21} = (6.7 \pm 0.5)10^8 \text{ s}^{-1}$, which corresponds to an ion-pair

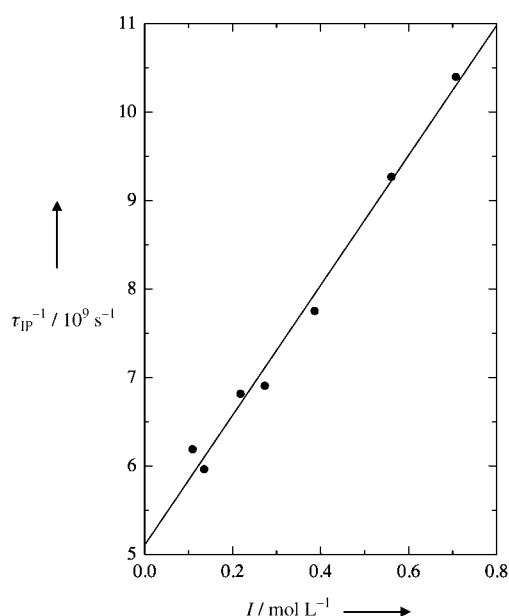


Figure 5. Ion-pair relaxation rate, τ_{IP}^{-1} , as a function of ionic strength, I , in aqueous Na_2Ox solutions at 25°C .

lifetime $\tau'_{\text{IP}} \approx 1000 \text{ ps}$. Combination of this value with the intercept of Figure 5 gives $\tau'_{\text{IP}} = 255 \pm 8 \text{ ps}$. This value may be compared with those calculated for the various ion-pair structures using the Stokes–Einstein–Debye Equation (15)

$$\tau'_{\text{IP}} = \frac{3V_{\text{IP}}f_{\perp}C\eta}{k_{\text{B}}T} \quad (15)$$

where $\eta = 0.8904 \times 10^{-3} \text{ Pa s}$ ^[34] is the viscosity of pure water, V_{IP} is the molecular volume of the ion pair, f_{\perp} is a shape factor, and C accounts for the hydrodynamic boundary conditions for rotation.^[29]

The values of τ'_{ip} calculated for stick boundary conditions, $C = 1$ in Equation (15), are given in Table 1 (those obtained for slip conditions, where hydration is completely neglected, are unrealistically low and so will not be considered further). The values for the CIP and SIP again indicate that these structures are implausible. On the other hand, the 2SIP value of $\tau'_{ip} \approx 140$ ps is in reasonable agreement with the experimental result, the lower value being consistent with the extended solvation of the oxalate ion.

It is instructive to compare the experimental rate constants with those calculated by the theory of Eigen and Tamm^[6] for diffusion-controlled reactions. With the diffusion coefficients $D(\text{Na}^+) = 1.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ^[30] and $D(\text{Ox}^{2-}) = 0.982 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ^[31] the theory predicts $k_{12} = 31 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_{21} = 187 \times 10^8 \text{ s}^{-1}$. The experimental value of the rate constant for the formation of the ion pair, k_{12} , is about 1/4 of the diffusion controlled calculation. This value is much higher than that found for most ion-pair formation processes^[8] and suggests that very little rearrangement of the hydration shells occurs, consistent with a 2SIP product. On the other hand, the experimental ion-pair lifetime considerably exceeds the prediction of $\tau'_{ip} = \ln 2 / k_{21} \approx 37$ ps, in accordance with the rather large association constant, $K_A(\text{NaOx}^-) = 10.9$. The value for the association constant (K_A) and the relaxation time (τ'_{ip}) of the ion pair are, on the basis of the present DRS data, clearly compatible only with a 2SIP. This result is also consistent with the large hydration numbers (Z_{ib}) observed for $\text{Na}_2\text{Ox}(\text{aq})$. Similar, but not identical, conclusions have been reached from DRS studies of closely related systems such as $\text{Na}_2\text{SO}_4(\text{aq})$ ^[9] and $\text{Na}_2\text{CO}_3(\text{aq})$.^[13] It remains to reconcile these findings with a recent vibrational spectroscopic study of the alkali metal oxalate solutions.^[21] This study showed systematic differences in both the IR and Raman spectra that were ascribed to oxalate complexation. Although the authors did not address the hydration state of their species specifically, it is reasonable to assume that they were referring to CIPs (inner sphere complexes), since SIP and 2SIP cannot normally be observed from studies of ligand vibrations.^[32, 33]

The first point to make about these measurements^[21] is that they were made in mixed electrolyte solutions, in order to obtain the desired concentration ratios, and thus may not be directly comparable with the present measurements. Secondly, the effects, although systematic, are extremely small (except for solutions containing Li^+). For example, the IR peak for the symmetric C–O stretch (ν_s) of Ox^{2-} shifts by less than 0.9 cm^{-1} even at a concentration ratio, $c(\text{Na}^+)/c(\text{Ox}^{2-})$, of > 40 . Similarly, the changes in the intensity ratio of the Raman active ν_1 modes for Ox^{2-} at ≈ 1455 and $\approx 1489 \text{ cm}^{-1}$ are scarcely more in the presence of Na^+ than those for K^+ and Cs^+ , which were thought not to complex significantly.^[21] More critically, the peak at $\approx 1455 \text{ cm}^{-1}$, which was assigned to complexed Ox^{2-} ,^[21] does not show the expected dependence on cation size, nor were the other features usually apparent in the presence of CIP and SIP observed.^[32, 33] Perhaps the small effects observed (except for Li^+) are due to 2SIP but this runs counter to conventional views on vibrational spectroscopy. Clearly, further studies are required to resolve this matter.

Conclusions

The $\text{Na}^+/\text{Ox}^{2-}$ system represents an almost textbook case of the application of DRS to the study of weak, labile complexes in aqueous electrolyte solutions. Thus, in spite of the limited solubility of the salt and the weakness of its association, it was possible to quantify not only the extent of association but also the kinetics of formation and dissociation of the complex. In addition, the nature (2SIP) of the ion-pair formed was determined unequivocally, and useful insights into the nature of hydration of the industrially and biologically important oxalate ion were obtained. These findings nicely illustrate the fruitfulness of DRS as a technique for the study of electrolyte solutions.

Experimental and Data Analysis

The dielectric permittivity, $\epsilon'(\nu)$, and total loss, $\eta''(\nu)$, spectra were recorded with an HP 85070M dielectric probe system in the frequency range $0.2 \leq \nu \text{ GHz}^{-1} \leq 20$ at $(25.00 \pm 0.02)^\circ\text{C}$. The instrument was calibrated with air, mercury, and water as described in ref. [11], allowing an accuracy of 2% in $\epsilon'(\nu)$ and $\eta''(\nu)$ relative to the static permittivity of the sample, ϵ . For each sample, spectra were recorded using at least two independent calibrations.

Solutions were prepared volumetrically from analytical grade Na_2Ox (Ajax Chemicals, Australia) and Millipore water, without buoyancy corrections. Prior to use, Na_2Ox was dried in vacuo for at least four hours at 50°C . The densities required to calculate the water concentrations (Section 4.1) were determined with a vibrating-tube densimeter (Sodev, Model 03D) calibrated with nitrogen ($\rho = 1.1456 \times 10^{-3} \text{ g cm}^{-3}$, from van der Waals coefficients^[34]) and water ($\rho = 0.997043 \times 10^{-3} \text{ g cm}^{-3}$).^[34] Refractive indices, n_D^{25} , at the Na D line were determined with an Abbé refractometer (Atago, Japan) calibrated with aqueous sucrose solutions. The data for ρ and n_D^{25} are listed in Table 2 along with the dielectric relaxation parameters.

Each spectrum was analyzed separately to determine the slightly calibration-dependent effective conductivity, κ_e . Spectra with κ_e values departing more than $\pm 0.5\%$ from the average values summarized in Table 2 were rejected. After correction of η'' for the Ohmic loss, $\kappa_e/(2\pi\nu\epsilon_0)$, the individual complex permittivity spectra were combined and fitted to various conceivable relaxation models as described in ref. [11].

For all electrolyte solutions it was found that $\hat{\epsilon}(\nu)$ was best fitted by a superposition of a low-frequency process, assigned to ion pairs (IP) and described by the Debye equation (amplitude $S_{ip} = \epsilon - \epsilon_s$, relaxation time τ_{ip}), along with a higher frequency solvent (s) relaxation, which could also be fitted with a Debye Equation (16) (amplitude $S_s = \epsilon_s - \epsilon_\infty$, relaxation time τ_s)

$$\hat{\epsilon}(\nu) = \frac{\epsilon - \epsilon_s}{1 + i2\pi\nu\tau_{ip}} + \frac{\epsilon_s - \epsilon_\infty}{1 + i2\pi\nu\tau_s} + \epsilon_\infty \quad (16)$$

Figure 1 shows a typical dielectric spectrum for an aqueous solution of Na_2Ox , along with the individual contributions of the water and the ion pair to $\epsilon''(\nu)$. The parameters so obtained: ϵ , τ_{ip} , ϵ_s , τ_s , and ϵ_∞ are given in Table 2, together with the variance of

the fit, σ^2 . Attempts to fit the spectra with alternative relaxation models failed. Not only did such models exhibit larger σ^2 than those obtained with the 2D model, Equation (16), but systematic deviations were also apparent. In particular, it was impossible to obtain a self-consistent set of permittivities, relaxation times, and relaxation-time distribution parameters as a function of solute concentration when the solution spectra were fitted with a single Havriliak–Negami equation or any of its simpler variants.

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