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Determination of the Ratio of Contact to Solvent-Separated Ion Pairs in $ZnSO_4$ in Methanol via High-Field Conductometric Measurements

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Received October 25, 1978

High-field conductometric measurements of the ratio of contact to solvent-separated ion pairs have been made on the system $ZnSO_4$ in methanol ($K = 5.8 \times 10^4$). The method used has quite general applicability for such determination and is one of the few such generally useful methods. The method is based on the dynamic response of the system to a short high-field pulse. Under most conditions the ion-pair interconversion cannot take place during the pulse and then the electrolyte behaves as if it contained only a free ion outer-sphere complex equilibrium.

The general Eigen mechanism[1] for metal ion substitution reactions has been very successful in treating kinetic data involving numerous ions and diverse types of ligands. In this mechanism we have (for a symmetrical electrolyte)

$$M^{n+} + X^{n-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M,,X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M,X \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} MX$$

where M,,X is a doubly solvent-separated ion pair (anion and cation each retaining a solvation shell), M,X is a solvent-separated ion pair, and MX is the contact pair. In the usual case, the final process refers to the desolvation of the cation. The rate constant k_3 is on the order of magnitude of the rate of solvent exchange which for many systems leads to a relaxation time for the system on the order of 10^{-4} s or more. In the analysis of the data, the second step is often omitted and the first step is treated as a fast preequilibrium. The equilibrium constant for this step is then evaluated by means of the Fuoss equation.[2] For a two-step mechanism the slower relaxation time is given by

$$\tau_s^{-1} = k_f\Phi + k_r$$

$$\Phi = \theta/(\theta + K^{-1})$$

$$\theta = \bar{M}^{n+} + \bar{X}^{n-}$$

with a superscript bar indicating an equilibrium concentration. k_f and k_r are the forward and reverse rate constants for ion-pair interconversion. Clearly the value of k_f obtained will be affected by errors in the calculations of K^{-1}. In addition, the validity of the neglect of the anion desolvation process is suspect since discrete anion desolvation processes have been found in nonaqueous[3,4] and aqueous solutions.[5] It was therefore of considerable interest to obtain an experimental method to check the validity of this procedure by direct measurement of the outer-sphere complex formation constant. The method employed is based on the application of high electric field pulses to the electrolyte and observation of the conductometric change observed due to the second Wien effect.[6] This effect is the enhanced dissociation of weak electrolytes in high fields.

Theory

If we again neglect anion desolvation momentarily and write the Eigen scheme as

$$M^{n+} + X^{n-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M,X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MX$$

the *fast* relaxation time will be given by the expression

$$\tau_1^{-1} = k_1\theta + k_{-1} + k_2 + k_{-2}$$

If we limit discussion only to those ions whose rate of solvent exchange (or more objectively, the rate of ligand substitution) is relatively slow—10^{-4} s or longer—then we can neglect k_2 and k_{-2} compared to the first terms. This is due to the fact that k_1 is almost always diffusion controlled or nearly so and thus $k_1 \approx 10^{10}$ M^{-1} s^{-1}. For a weak electrolyte with a total association constant, K_T, very large we have

$$K_T = K_1(1 + K_2)$$

where $K_{1(2)}$ is the association constant for the first (second) step and $\theta = 2(C_T/K_T)^{1/2}$ with C_T the total concentration of electrolyte. Then

$$\tau_1^{-1} = 2k_1(C_T/K_T)^{1/2} + k_{-1}$$

or

$$\tau_1^{-1} = k_1[2(C_T/K_T)^{1/2} + K_1^{-1}] \tag{1}$$

Suppose K_T and K_1 are each on the order of 10^4 M^{-1} while C_T is about 10^{-4} M. Then τ_1 is about 2.5×10^{-7} s. Suppose we apply a pulse of high voltage to this solution. According to the theory of the second Wien effect there will be a relative change in conductance

$$\frac{\Delta\Lambda}{\Lambda} = \frac{1-\alpha}{2-\alpha}\frac{9.64}{DT^2}E \tag{2}$$

with E the applied field in kV and α the degree of dissociation at zero field. If the field is applied as a step function, the conductance will lag behind the field and will reach its equilibrium value after roughly five relaxation times. For the system we have described there are two relaxation times, one at 2.5×10^{-7} s and the other $\tau_{11} > 10^{-4}$ s. If the field is applied as a pulse with a pulse width τ_p chosen such that $5\tau_1 < \tau_p \ll \tau_{11}$, then the first step and only the first step will equilibrate in the field and the conductance change due to that process alone will be measured. On the time scale of the microsecond field pulse, the second process will appear to stand still and hence contribute nothing to the dynamic conductance change. Measurement of the relative change in conductance as a function of field enables one to calculate α, the degree of dissociation of the first step alone at zero field, by eq 2. This in turn enables one to calculate K_1, the outer-sphere complex formation constant by the relationship

$$K_1 = (1-\alpha)/\alpha^2 C_T \gamma_\pm^2$$

The activity coefficient term can be calculated by the usual Debye–Hückel equation.

One can use the results of K_1 to calculate the ratio of solvent-separated to contact ion pairs. The value of K_T can be obtained by conventional techniques which allow both steps to equilibrate. We then have

$$(K_T - K_1)/K_1 = K_2$$

Thus this technique provides a powerful method to determine

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the ratio of solvent-separated to contact ion pairs.

In principle we have an internal consistency check on the results. If τ can be measured as a function of C_T, then a plot τ^{-1} vs. θ gives k_1 as slope and K_1/k_1 as intercept. If the latter can be evaluated accurately, we have an independent check on the value of K_1. Experimentally this was not possible in our case due to severe electrical ringing which prevented measurement of τ.

As for the influence of an anion desolvation step, we must consider the fact that all such processes to date have shown relaxation time in the ultrasonic region, that is with $\tau < 100$ ns.[7] Thus anion desolvation will probably be fast compared to ion-pair formation and the relaxation time observed in the microsecond region will be given by the expression

$$\tau^{-1} = k_1\theta + (k - 1)/(1 + K_{AD})$$

where K_{AD} is the ratio of desolvated anion pairs to solvated ones. The ratio of slope to intercept will be

$$K^* = K_1(1 + K_{AD})$$

Since both anion desolvation and ion pairing will equilibrate in the field pulse, the value of K obtained from the relative change in conductance will correspond to K^*. It is important to note that if $K_{AD} \gg 1$ the use of the Fuoss equation to evaluate stopped-flow or Joule heating T-jump kinetic results will lead to anomalously large rate constants for ligand substitution since $K^* \gg K_{Fuoss}$. Hence the use of the pulsed field technique to directly measure K^* will be very useful in any case of anomalously fast substitution kinetics.

Experimental Section

The system studied was $ZnSO_4$ in methanol. The instrument used was a conductometric detection E-jump which has been previously described in detail.[8] Briefly it consisted of two cells, sample and reference, which have adjustable electrode spacing. The reference cell contains a strong electrolyte to cancel first Wien effects. The references used were $NaBPh_4$ in methanol or in water–ethylene glycol mixtures. The latter is especially convenient for matching the low sample conductivities with a reasonable concentration of electrolyte so that adsorption is not a problem as occurs with 10^{-5} M concentration. The reference cell electrode spacing is adjusted to give an exactly matched resistance at zero field. It is not possible to match both zero-field conductance and capacitance. The mismatch of the latter gave rise to serious ringing during the first microsecond of the pulse which precluded measurements of the relaxation time. However, since the pulse (obtained by a cable discharge) was 9 μs long, the limiting value of the conductance change was easily determined. The value of K was independent of reference solution used. The range of fields used were from 8 to 25 kV/cm. No variation of K with field was observed outside experimental errors. The value of K_T was determined by using conventional conductance methods. Hydrated zinc sulfate was dissolved in anhydrous methanol for all measurements. The concentrations used were from 0.5 to 1.0 × 10^{-3} M. Added water in small amounts had no noticeable effects.

Table I

$\Delta\Lambda/\Lambda$, %	E, kV/cm	$(1-\alpha)/(2-\alpha)$	α
$C = 1.6 \times 10^{-4}$ M $ZnSO_4$ in MeOH, $\epsilon = 32.63$			
12.0	28	0.164	0.80
8.14	24	0.130	0.85
5.7	20	0.109	0.86
$C = 5.0 \times 10^{-4}$			
16.0	25	0.24	0.69

Results and Discussion

Data are shown in Table I. The mean value of K_1 obtained from high-field methods was $(1.3 \pm 0.2) \times 10^3$ M^{-1}. The conventional low-field conductance value gave 7.5×10^6 M^{-1}. The ratio of solvent-separated to contact pairs was therefore 5.8×10^3. This result should be compared to the value of K_{Fuoss} for a 2:2 electrolyte obtained by Lovas et al.[9] which is 980 M^{-1} using a size parameter of 1.35 nm estimated from hydrodynamic radii. The precision of the results is not very high since changes in conductance were obtained by measurements of voltage changes from oscilloscope photographs. The accuracy of the results suffers from the fact that $ZnSO_4$ in methanol contains some triple ions (i.e., $Zn(SO_4)_2^{2-}$) which contribute to the observed conductance leading therefore to errors in $\Delta\Lambda/\Lambda$. However, the population of such triple ions is very small and the concentration independence of K shows that the effect of these species is negligible.

Acknowledgment. The authors would like to thank the Scientific Affairs Office of the North Atlantic Treaty Organization for a travel grant which made this work possible. P.H. wishes to thank the U.S. Department of Energy for support under Grant No. ER-78-S-02-4945 during the final stages of this project.

Registry No. $ZnSO_4$, 7733-02-0.

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