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Tracer Diffusion of Cr^{3+} Ions in Agar Gel Media Containing Transition-Metal Sulfates†

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This paper deals with the determination of tracer diffusion coefficients of Cr^{3+} ions in agar gel media containing $MnSO_4$, $CuSO_4$, $CoSO_4$, $NiSO_4$, and $ZnSO_4$. The diffusion coefficients in various electrolytes were measured over the electrolyte concentration range ($5\cdot10^{-7}$ to 10^{-2}) M using the zone diffusion technique at 25 °C. The resulting values are compared with theoretical values obtained using Onsager's theory, and the observed deviations are explained qualitatively on the basis of various interactions occurring in the ion−gel−water system.

1. Introduction

Tracer diffusion of various uni-[1−3] and bivalent[4−6] ions in different supporting electrolytes under different experimental conditions has been reported by this laboratory. In our previous paper, we reported a study of the activation energy and obstruction effect for tracer diffusion of Cr^{3+} ions in agar gel media containing different electrolytes.[7] The present paper deals with the effect of electrolyte concentration on coefficients for diffusion of Cr^{3+} ions in agar gel media containing various transition-metal sulfates. The diffusion coefficients were measured in 2.5 % agar gel at 25 °C using the zone diffusion technique. The experimental diffusion coefficients thus obtained are compared with theoretical values obtained using the Onsager−Gosting−Harned equation in order to see the applicability of Onsager's theory to diffusion in a gel medium.

2. Experimental Section

Tracer diffusion of Cr^{3+} ions in different supporting electrolytes, namely, $MnSO_4$, $CuSO_4$, $CoSO_4$, $NiSO_4$, and $ZnSO_4$, was studied over the electrolyte concentration range ($5\cdot10^{-7}$ to 10^{-2}) M in 2.5 % agar gel at 25 °C. The diffusion coefficients were determined using labeled ^{51}Cr ions and the zone diffusion technique,[6,8] the details of which are discussed in earlier papers.[2,8] ^{51}Cr ($t_{1/2} = 24.7$ days) was obtained from BARC (Mumbai, India). The diffusion was allowed to proceed for 24 h, after which the diffusion column was assayed by measuring the activity of ^{51}Cr at 320 keV using a NaI (Tl) detector coupled with a single channel analyzer. The diffusion coefficients were then calculated from plots of log(activity) versus (distance)^2, and the values presented are averages of four independent measurements with a precision of ± 0.5 %.

3. Results and Discussion

Theoretical values of the diffusion coefficient for tracer diffusion of Cr^{3+} ions were calculated using the Onsager−Gosting−Harned[9,10] equation:

$$D_j^* = \frac{RT\lambda_j^0}{|Z_j|F^2} - \frac{\lambda_j^0|Z_j|F^2}{3N\varepsilon}\cdot 2.694\cdot 10^{16}\cdot\sqrt{\frac{4\pi}{\varepsilon RT}}\cdot\left[1-\sqrt{d(\omega_j)}\right]\cdot\sqrt{\sum_i C_i Z_i^2} \qquad (1)$$

where D_j^* is the diffusion coefficient of the diffusing tracer ion j, R is the gas constant (8.314 $J\cdot K^{-1}\cdot mol^{-1}$), F is the Faraday constant (96 500 $C\cdot mol^{-1}$), ε is the dielectric constant of water (78.5), T is the absolute temperature (298 K), λ_j° is the limiting conductance of j, Z_j is the charge of j, $d(\omega_j)$ is the mobility function for j, C_i is the charge on ion i, and N is Avogadro's number.

The mobility function $d(\omega_j)$ in eq 1 is a function of concentration, valence, and limiting ionic conductance of ions in the solution. In the derivation of eq 1, the ions were treated as point charges, which is justifiable at very low concentrations only. At higher concentrations, one has to take into consideration the sizes of the ions present in the solution, as they are reasonably close to each other. Taking this into account, Stokes et al.[11] made an empirical correction to the Onsager−Gosting−Harned equation by replacing $\sqrt{C}$ by $\sqrt{C}/[(1 + A'\sqrt{C})(1 + A'\sqrt{C}/\sqrt{2})]$, in which $A'\sqrt{C} = \kappa a$, where a is the closest distance of approach of oppositely charged ions and κ is the reciprocal radius of the ionic atmosphere. The values of the various parameters involved in eq 1 for the calculation of the theoretical diffusion coefficient for the different ions are recorded in Table 1. Substituting these values into eq 1 gives the following limiting law expressions for the diffusion coefficient of Cr^{3+} ions ($D_{Cr^{3+}}$, in $m^2\cdot s^{-1}$) in the different electrolytes at 25 °C:

Table 1. Values of Different Parameters for the Calculation of Theoretical Diffusion Coefficients for Tracer Diffusion of Cr^{3+} Ions in Different Systems

	electrolyte				
parameter	$ZnSO_4$	$NiSO_4$	$CoSO_4$	$MnSO_4$	$CuSO_4$
$\lvert Z_1\rvert$	3	3	3	3	3
$\lvert Z_2\rvert$	2	2	2	2	2
$\lvert Z_3\rvert$	2	2	2	2	2
$\lambda_1^0/10^{-4}\cdot S\cdot m^2\cdot mol^{-1}$	67	67	67	67	67
$\lambda_2^0/10^{-4}\cdot S\cdot m^2\cdot mol^{-1}$	52.8	54.0	55	53.5	53.6
$\lambda_3^0/10^{-4}\cdot S\cdot m^2\cdot mol^{-1}$	802.0	80.0	80.0	80.0	80.0
$d(\omega_j)$	0.591	0.594	0.596	0.593	0.593
A'	1.407	1.355	3.293	1.355	1.407

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$$\text{in NiSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.177\sqrt{C} \qquad (2)$$

$$\text{in CuSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.246\sqrt{C} \qquad (3)$$

$$\text{in ZnSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.317\sqrt{C} \qquad (4)$$

$$\text{in CoSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.083\sqrt{C} \qquad (5)$$

$$\text{in MnSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.215\sqrt{C} \qquad (6)$$

Similarly, the extended limiting law expressions for $D_{\mathrm{Cr}^{3+}}$ at 25 °C take the following forms:

$$\text{in NiSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.177\frac{\sqrt{C}}{(1 + 1.355\sqrt{C})(1 + 1.355\sqrt{C}/\sqrt{2})} \qquad (7)$$

$$\text{in CuSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.246\frac{\sqrt{C}}{(1 + 1.407\sqrt{C})(1 + 1.407\sqrt{C}/\sqrt{2})} \qquad (8)$$

$$\text{in ZnSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.317\frac{\sqrt{C}}{(1 + 1.407\sqrt{C})(1 + 1.407\sqrt{C}/\sqrt{2})} \qquad (9)$$

$$\text{in CoSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.083\frac{\sqrt{C}}{(1 + 3.293\sqrt{C})(1 + 3.293\sqrt{C}/\sqrt{2})} \qquad (10)$$

$$\text{in MnSO}_4\text{:}\quad 10^{10}\cdot D_{\mathrm{Cr}^{3+}} = 5.941 - 19.215\frac{\sqrt{C}}{(1 + 1.355\sqrt{C})(1 + 1.355\sqrt{C}/\sqrt{2})} \qquad (11)$$

The theoretical values of the diffusion coefficients of Cr^{3+} ions in different supporting electrolytes at various concentrations calculated using eqs 2 to 11 are presented in Tables 2 to 6 and are shown graphically in Figures 1 to 5 as a function of the square root of electrolyte concentration. An examination of Tables 2 to 6 and Figures 1 to 5 reveals that theoretical value of $D_{\mathrm{Cr}^{3+}}$ is always less than the experimental value at all concentrations for all of the systems studied, with only a few exceptions (in $5\cdot10^{-5}$ M $\mathrm{CuSO_4}$, $1\cdot10^{-3}$ M $\mathrm{ZnSO_4}$, and $5\cdot10^{-4}$ M $\mathrm{CoSO_4}$), where $D_{\mathrm{theor}} > D_{\mathrm{exptl}}$. A minimum in the plot of $D_{\mathrm{Cr}^{3+}}$ versus $\sqrt{C}$ is a characteristic of all of the systems (Figures 1 to 5) and occurs at 10^{-3} M in the $\mathrm{NiSO_4}$, $\mathrm{MnSO_4}$, and $\mathrm{ZnSO_4}$ systems, $5\cdot10^{-5}$ M in the $\mathrm{CuSO_4}$ system, and $5\cdot10^{-4}$ M in the $\mathrm{CoSO_4}$ system; such a minima are absent in the theoretical curves.

Table 2. Variation of the Tracer Diffusion Coefficient of Cr^{3+} Ions with the Concentration of $\mathrm{NiSO_4}$ in 2.5 % Agar Gel at 25 °C

	$10^{10}\cdot D_{\mathrm{Cr}^{3+}}/\mathrm{m^2\cdot s^{-1}}$		
	theoretical		
conc/M	limiting law	extended limiting law	experimental
0	5.941	5.941	–
$5\cdot10^{-7}$	5.927	5.921	8.38
$1\cdot10^{-6}$	5.921	5.913	8.81
$5\cdot10^{-6}$	5.898	5.880	8.69
$1\cdot10^{-5}$	5.880	5.855	8.35
$5\cdot10^{-5}$	5.805	5.752	7.9
$1\cdot10^{-4}$	5.749	5.677	5.92
$5\cdot10^{-4}$	5.512	5.369	5.46
$1\cdot10^{-3}$	5.334	5.152	5.19
$5\cdot10^{-3}$	4.584	4.344	5.82
$1\cdot10^{-2}$	4.023	3.837	7.78

Table 3. Variation of the Tracer Diffusion Coefficient of Cr^{3+} Ions with the Concentration of $\mathrm{CuSO_4}$ in 2.5 % Agar Gel at 25 °C

	$10^{10}\cdot D_{\mathrm{Cr}^{3+}}/\mathrm{m^2\cdot s^{-1}}$		
	theoretical		
conc/M	limiting law	extended limiting law	experimental
0	5.941	5.941	–
$5\cdot10^{-7}$	5.927	5.921	6.85
$1\cdot10^{-6}$	5.921	5.913	7.44
$5\cdot10^{-6}$	5.897	5.880	6.89
$1\cdot10^{-5}$	5.880	5.855	6.11
$5\cdot10^{-5}$	5.805	5.752	5.22
$1\cdot10^{-4}$	5.748	5.676	6.46
$5\cdot10^{-4}$	5.510	5.368	6.86
$1\cdot10^{-3}$	5.332	5.152	7.25
$5\cdot10^{-3}$	4.580	4.348	8.12
$1\cdot10^{-2}$	4.016	3.849	8.03

Table 4. Variation of the Tracer Diffusion Coefficient of Cr^{3+} Ions with the Concentration of $\mathrm{ZnSO_4}$ in 2.5 % Agar Gel at 25 °C

	$10^{10}\cdot D_{\mathrm{Cr}^{3+}}/\mathrm{m^2\cdot s^{-1}}$		
	theoretical		
conc/M	limiting law	extended limiting law	experimental
0	5.941	5.941	–
$5\cdot10^{-7}$	5.927	5.921	8.52
$1\cdot10^{-6}$	5.921	5.913	9.28
$5\cdot10^{-6}$	5.897	5.880	10.51
$1\cdot10^{-5}$	5.879	5.855	10.47
$5\cdot10^{-5}$	5.804	5.751	8.82
$1\cdot10^{-4}$	5.747	5.675	8.52
$5\cdot10^{-4}$	5.509	5.331	7.01
$1\cdot10^{-3}$	5.330	5.149	5.04
$5\cdot10^{-3}$	4.575	4.343	6.63
$1\cdot10^{-2}$	4.009	3.841	6.81

Table 5. Variation of the Tracer Diffusion Coefficient of Cr^{3+} Ions with the Concentration of $\mathrm{CoSO_4}$ in 2.5 % Agar Gel at 25 °C

	$10^{10}\cdot D_{\mathrm{Cr}^{3+}}/\mathrm{m^2\cdot s^{-1}}$		
	theoretical		
conc/M	limiting law	extended limiting law	experimental
0	5.941	5.941	–
$5\cdot10^{-7}$	5.927	5.922	10.73
$1\cdot10^{-6}$	5.921	5.914	10.82
$5\cdot10^{-6}$	5.898	5.881	10.57
$1\cdot10^{-5}$	5.880	5.857	10.71
$5\cdot10^{-5}$	5.806	5.758	8.84
$1\cdot10^{-4}$	5.750	5.688	8.22
$5\cdot10^{-4}$	5.514	5.417	5.32
$1\cdot10^{-3}$	5.337	5.240	7.83
$5\cdot10^{-3}$	4.591	4.685	7.96
$1\cdot10^{-2}$	4.032	4.413	7.19

Table 6. Variation of the Tracer Diffusion Coefficient of Cr^{3+} Ions with the Concentration of $\mathrm{MnSO_4}$ in 2.5 % Agar Gel at 25 °C

	$10^{10}\cdot D_{\mathrm{Cr}^{3+}}/\mathrm{m^2\cdot s^{-1}}$		
	theoretical		
conc/M	limiting law	extended limiting law	experimental
0	5.941	5.941	–
$5\cdot10^{-7}$	5.927	5.921	7.24
$1\cdot10^{-6}$	5.921	5.913	7.44
$5\cdot10^{-6}$	5.898	5.880	7.37
$1\cdot10^{-5}$	5.880	5.855	6.4
$5\cdot10^{-5}$	5.805	5.752	6.96
$1\cdot10^{-4}$	5.748	5.676	6.78
$5\cdot10^{-4}$	5.511	5.368	6.67
$1\cdot10^{-3}$	5.333	5.150	5.6
$5\cdot10^{-3}$	4.582	4.340	7.35
$1\cdot10^{-2}$	4.019	3.838	7.53

The observed deviations between the theoretical and experimental values of the diffusion coefficients can be

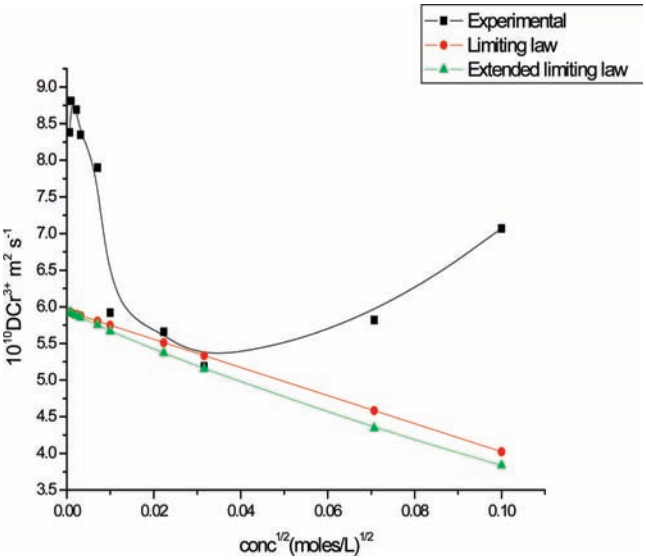

Figure 1. Variation of tracer diffusion coefficient of Cr^{3+} ions with square root of concentration of $NiSO_4$ in 2.5 % agar gel at 25 °C: ■, trend line of experimental values of diffusion coefficients; ●, theoretical line of limiting law values of diffusion coefficients; ▲, theoretical line of extended limiting law values of diffusion coefficients.

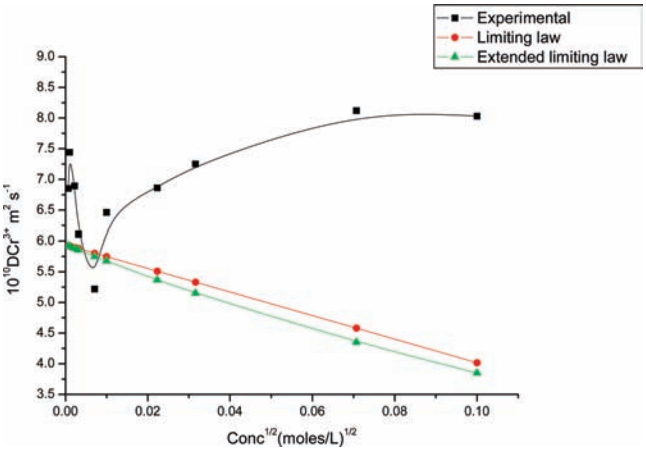

Figure 2. Variation of tracer diffusion coefficient of Cr^{3+} ions with the square root of concentration of $CuSO_4$ in 2.5 % agar gel at 25 °C: ■, trend line of experimental values of diffusion coefficients; ●, theoretical line of limiting law values of diffusion coefficients; ▲, theoretical line of extended limiting law values of diffusion coefficients.

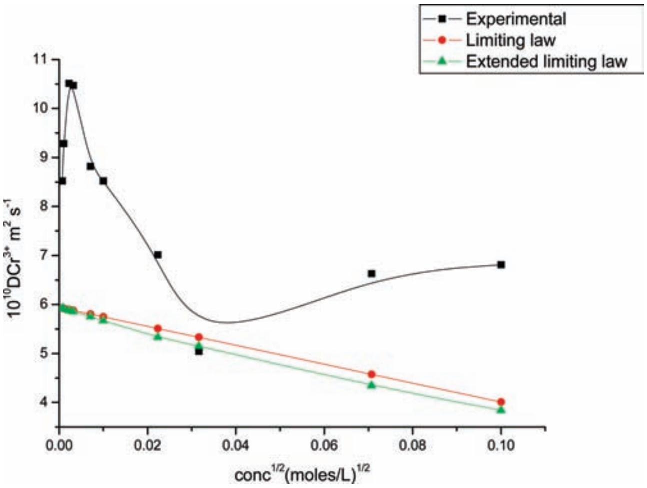

Figure 3. Variation of tracer diffusion coefficient of Cr^{3+} ions with square root of concentration of $ZnSO_4$ in 2.5 % agar gel at 25 °C: ■, trend line of experimental values of diffusion coefficients; ●, theoretical line of limiting law values of diffusion coefficients; ▲, theoretical line of extended limiting law values of diffusion coefficients.

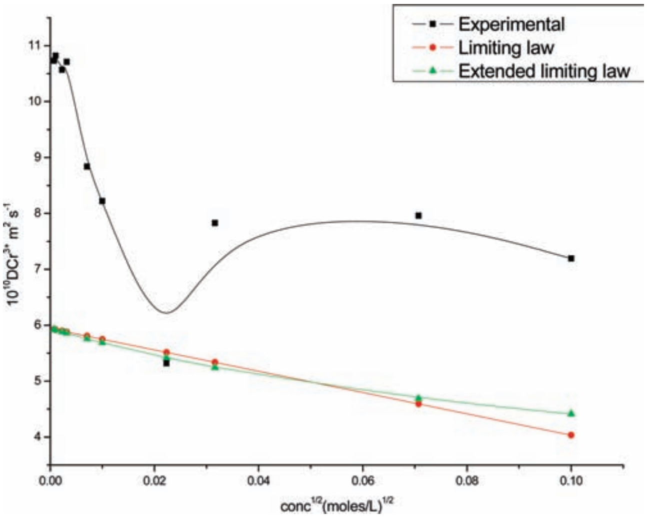

Figure 4. Variation of tracer diffusion coefficient of Cr^{3+} ions with square root of concentration of $CoSO_4$ in 2.5 % agar gel at 25 °C: ■, trend line of experimental values of diffusion coefficients; ●, theoretical line of limiting law values of diffusion coefficients; ▲, theoretical line of extended limiting law values of diffusion coefficients.

explained qualitatively on the basis of various interactions occurring in the ion−gel−water system, as discussed in earlier reports from this laboratory.[4,12] The observed larger values of the experimental diffusion coefficients relative to the theoretically expected values over the entire concentration range in the systems studied are attributed to the dominance of gel−water interactions. At higher concentrations, however, adsorption and obstruction effects are known to decrease[6,13] with electrolyte concentration. Thus, the contribution of the diffusion-retarding effects of adsorption and obstruction is reduced at higher concentrations, and hence, the gel−water interaction becomes more prominent at these concentrations. The overall effects of all these interactions lead to larger values of the diffusion coefficients than predicted by theory at higher concentrations in all of the systems. Furthermore, Tables 2 to 6 indicate that the deviations from the theoretical values vary with concentration for a particular system and also vary from system to system. It is also evident from the figures that at higher concentrations, the experimental values are not only larger than the theoretical ones but also show a change in the trend in the plots of D_{exptl} versus $\sqrt{C}$. The measured values of the diffusion coefficients increase with concentration, and this reversal in the trend of diffusion coefficient with concentration gives rise to a minimum in the curve. The occurrence of such minima in D-versus-$\sqrt{C}$ curves has been reported by several workers both in gel[14−16] and pure aqueous media.[17−19]

The occurrence of a minimum in the D-versus-$\sqrt{C}$ plot can be explained qualitatively on the basis of Wang's model,[17] which considers the changes in the physical properties taking place at the microscopic level with increasing electrolyte concentration. Wang suggested that the ions are fully hydrated at lower concentration, so any distortion present in the solvent water immediately surrounding each hydrated ion is the same as that existing at infinite dilution; since the average distance between the ions is very large, hydration and ion−solvent interactions remain the same. Hence, the only effect of increasing electrolyte concentration in this range is to increase the long-

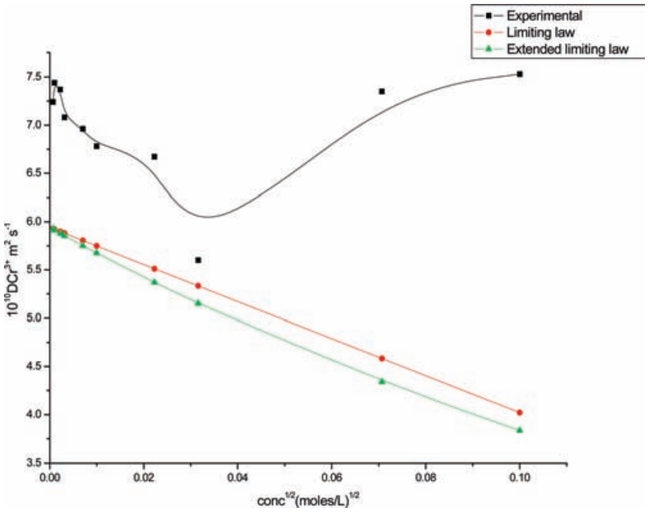

Figure 5. Variation of tracer diffusion coefficient of Cr^{3+} ions with square root of concentration of $MnSO_4$ in 2.5 % agar gel at 25 °C: ■, trend line of experimental values of diffusion coefficients; ●, theoretical line of limiting law values of diffusion coefficients; ▲, theoretical line of extended limiting law values of diffusion coefficients.

range ionic attraction (i.e., the relaxation effect), which gives a decreasing trend in D_{exptl} with increasing concentration of electrolyte in the systems studied. When the concentration of electrolyte increases, the distance and the number of water molecules between the two ions both continue to decrease, and it becomes increasingly difficult for water molecules to orient themselves and maintain the stable semicrystalline structure of water that exists at infinite dilution. Hence, the semicrystalline structure of water becomes distorted, giving a decrease in the local dielectric constant of the solvent water. This decrease in dielectric constant increases the self-energy of the ions in the normal state, while the energy of the activated state remains unaffected. Thus, the total energy barrier for diffusion of ions is reduced, leading to an increase in diffusion coefficient with increasing electrolyte concentration, as observed.

Conclusion

Agar gel provides a good stationary medium for the study of diffusion. However, a disparity between the theoretical and experimental values of the diffusion coefficients is observed, which can be explained on the basis of various interactions occurring in the ion−gel−water system.

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