Phenomenological Relationship between the Fluidity and Tracer-Diffusion in Concentrated Electrolyte Solutions

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An attempt has been made to correlate the mobility of component species with the fluidity of the solution over a wide range of concentration in aqueous solutions. A good linear correlation was observed between the relative fluidity and the relative tracer-diffusion coefficient of Cl^- in aqueous solutions of LiCl, NaCl, $MgCl_2$, $CaCl_2$, and $NiCl_2$, particularly at higher concentrations over 2 mol kg^{-1}. The correlation for the cations was very similar to that of water in aqueous solutions of such electrolytes. The feature of these plots presents that the structural properties of concentrated electrolyte solutions are reflected on these correlations.

In recent years, much attention has been paid to physicochemical properties of concentrated electrolyte solutions; a considerable amount of experimental data have been accumulated for transport processes in aqueous electrolyte solutions of varying compositions. However, many of the features of these experimental results still remain unexplained mainly because of a lack of appropriate theories and models which can be applied up to very high concentrations.

Since very early studies of transport phenomena in solution some simple correlations have been expected and examined between the velocity of a particle and the fluidity of the medium in which the particle moves, and the examination of so-called Stokes–Einstein equation[1)] is still continuing.[2,3,4)] Many of such correlations are empirical in nature, nevertheless they are expected to be useful to gain an insight into the nature of interactions among moving particles and the structure of the solution.

In electrolyte solutions the Stokes–Einstein equation is expected to be applicable to solutions at infinite dilution or very dilute solutions where the solution is assumed to be ideal, and have been examined by using limiting values of diffusion coefficients and molar ionic conductivities at infinite dilution.[5,6)] Most of the previous studies have concerned the transport behaviour of only one component existing in the solution. In case of multicomponent solutions, however, it is important to study the transport properties of each component in the same solution. Among various transport properties only the tracer diffusion can provide the individual mobility data of each component.

In the present study, we have collected reliable tracer-diffusion data from the literature given in Table 1, and examined the correlation between the diffusion coefficients and fluidity of the solution for each individual component. Although no simple correlations may be expected between the mobility and fluidity in real solutions of finite concentrations, we have found that a substantial body of the experimental data reveals significant relationships between the mobility and fluidity in aqueous electrolyte solutions of very high concentrations.

Table 1. Sources of the Diffusion and Viscosity Data Used

Electrolyte	Tracer	Reference	
		Diffusion	Viscosity
LiCl	Li^+	(7), (8)	(29)
	Cl^-	(7), (8), (12)	
	H_2O	(8), (10)	
NaCl	Na^+	(9), (11)	(29)
	Cl^-	(12), (13)	
	H_2O	(14), (15)	
KCl	K^+	(7), (16)	(29)
	Cl^-, H_2O	(7), (12), (18)	
	H_2O	(17), (18)	
CsCl	Cs^+, Cl^-, H_2O	(18)	(29)
$MgCl_2$	Mg^{2+}, Cl^-	(19)	(29)
	H_2O	(15)	
$CaCl_2$	Ca^{2+}	(20)	(29)
	Cl^-	(20), (21)	
	H_2O	(17)	
$NiCl_2$	Ni^{2+}, Cl^-, H_2O	(22)	(26)
$CdCl_2$	Cd^{2+}, Cl^-, H_2O	(23)	(27)
CdI_2	Cd^{2+}, I^-, H_2O	(24)	(27)
R_4NBr	R_4N^+, Br^-, H_2O	(25)	(28)

The concentration dependence of tracer diffusion coefficients $D(Cl^-)$ of chloride ions in several aqueous electrolyte solutions is given in Fig. 1, in which relative diffusion coefficients as defined by $D_r(Cl^-)=D(Cl^-)/D^0(Cl^-)$ where $D^0(Cl^-)$ is the limiting diffusion coefficient calculated from the limiting ionic conductivity of Cl^- by the Nernst equation,[30)] are plotted as a function of electrolyte concentration. This figure clearly demonstrates that the rate of diffusion of chloride ion is very much affected by the cations present in the solution. In KCl and CsCl solutions chloride ions diffuse faster than in LiCl and NaCl solutions, and the rate of diffusion decreases with increasing electrolyte concentration more rapidly in solutions of divalent cations than in solutions of monovalent cations. The corresponding plot for relative fluidity $\phi_r = \phi/\phi^0$, (ϕ^0, the fluidity of pure solvent) is shown in Fig. 2. A comparison of Figs. 1 and 2 shows that the concentration dependence of tracer diffusion coefficients of Cl^- is very similar to that of fluidity of the solution, which gives us an indication that there seems to be some empirical correlation between relative tracer-diffusion coefficient of chloride ions and the relative fluidity of the solution.

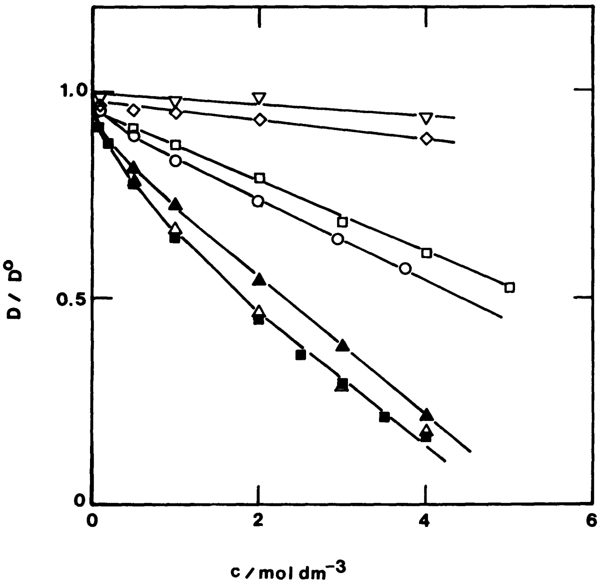

Fig. 1. Concentration dependence of the relative diffusion coefficients of Cl^- in aqueous solutions of LiCl (○), NaCl(□), KCl(◇), CsCl(▽), $\mathrm{MgCl_2}$(△), $\mathrm{CaCl_2}$ (▲) and $\mathrm{NiCl_2}$(■) at 25 °C.

In Fig. 3, the relative tracer diffusion coefficients of chloride ion are plotted against the relative fluidity of the solutions, where the diagonal line represents the relation,

$$D(\mathrm{Cl}^-)/D^0(\mathrm{Cl}^-) = \phi/\phi^0. \tag{1}$$

A striking feature of this plot is that the experimental points for concentrated solutions ($\geq 2\ \mathrm{mol\ kg^{-1}}$) of LiCl, NaCl, $\mathrm{MgCl_2}$, $\mathrm{CaCl_2}$, and $\mathrm{NiCl_2}$ (hereafter, these electrolytes will be called the LiCl-type for the sake of simplicity) are on or very close to the diagonal line, while those points for medium and low concentrations (0.5—2.0 $\mathrm{mol\ kg^{-1}}$) lie slightly below the line.

The present empirical finding suggests that in concentrated solutions, the LiCl-type electrolytes affect the chloride ion diffusion and the fluidity of the solutions in a similar manner, which may be interpreted in terms of the structural aspect of chloride ions in the solution. In this respect, it seems worthwhile to note the neutron diffraction studies by Enderby's group which show that the geometric arrangement of water molecules around chloride ions is independent of concentration and also counter cations for a wide variety of electrolytes.[31]

Let us now examine the D_r vs. ϕ_r plot for the tracer-diffusion of cations and water (Figs. 4 and 5, respectively) in aqueous solutions of the LiCl-type electrolytes. As can be seen from Fig. 4, the experimental points for the cations at lower concentrations are close to the diagonal line, whereas most of the points at higher concentrations lie above the line, suggesting that the retardation of the diffusion rates of these cations is less than that expected from the decrease in fluidity of the solution.

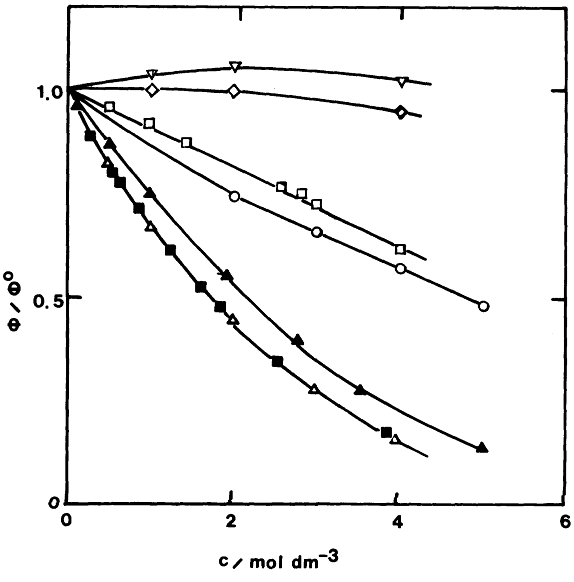

Fig. 2. Concentration dependence of relative fluidities of the aqueous electrolyte solutions (25 °C) given in Fig. 1; symbols are the same as those used in Fig. 1.

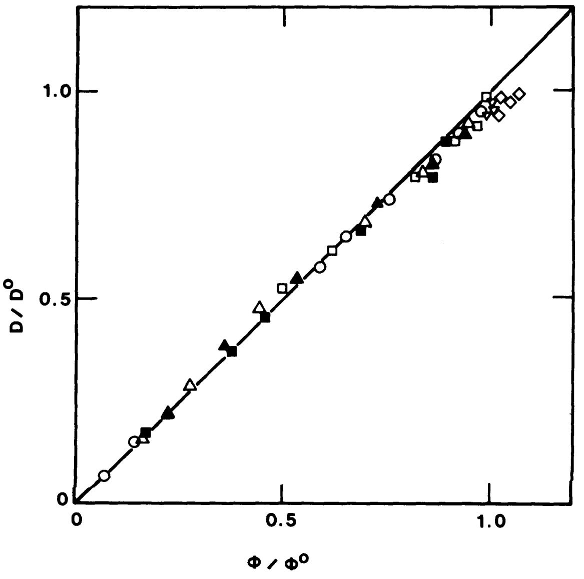

Fig. 3. D_r vs. ϕ_r plots for Cl^- in the solutions of LiCl (○), NaCl(□), KCl(▽), CsCl(◇), $\mathrm{MgCl_2}$(△), $\mathrm{CaCl_2}$ (▲) and $\mathrm{NiCl_2}$(■) at 25 °C.

It should be noticed that most of the experimental points are on the same curve irrespective of the kind of cations.

The tracer diffusion of water in aqueous solutions of the LiCl-type electrolytes behaves very similarly to that of the cations (compare Figs. 4 and 5). This result may give a qualitative explanation that the above-mentioned behavior is associated with the strong interaction of water molecules with the cations in solutions of the LiCl-type electrolytes.

Relative diffusion coefficient vs. relative fluidity relationships for aqueous solutions of KCl and CsCl are different from those observed with the LiCl-type electrolytes. In the case of KCl and CsCl solutions, the fluidity and diffusion coefficient do not change very much with concentration; fluidity first increases and then decreases slightly with increasing concentration (see Fig. 2) and the increase in fluidity is more pronounced for CsCl at lower temperatures. The experimental points for these electrolyte solutions are located in the region corresponding to $\phi_r=1$ and $D_r=1$ of the D_r vs. ϕ_r diagram (see Figs. 3, 4, and 5). The points for the cations and chloride ion are always below the diagonal line. The observed transport behaviour of KCl and CsCl solutions may be related to the fact that K^+ and Cs^+ ions have large crystallographic radii and low charge densities so that

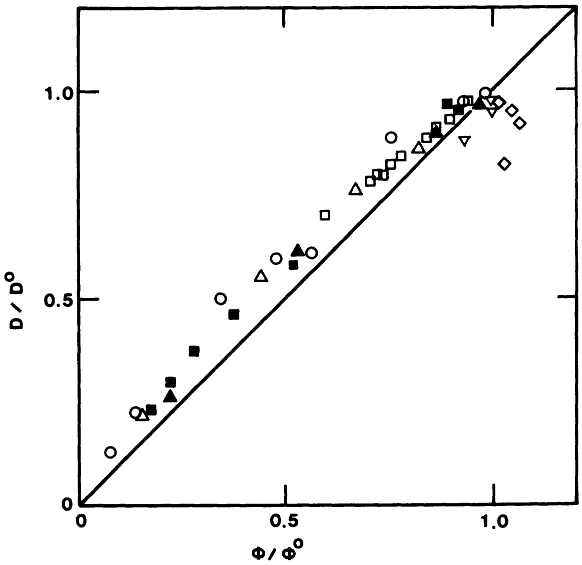

Fig. 4. D_r vs. ϕ_r plots for cations of the solutions given in Fig. 3.

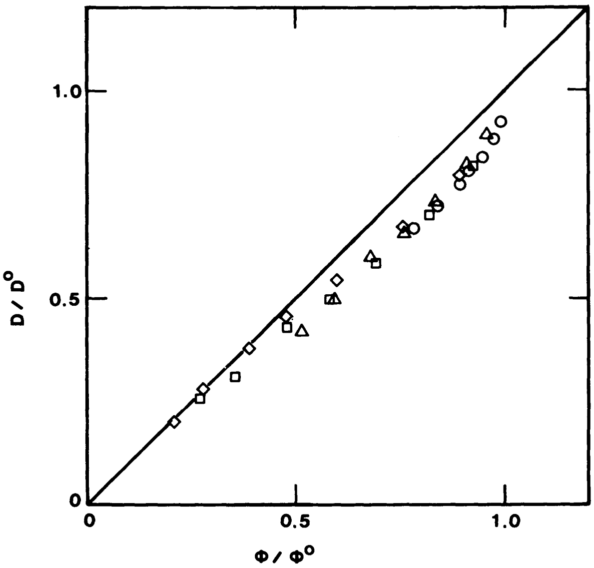

Fig. 6. D_r vs. ϕ_r plots for Br^- in aqueous solutions of Me_4NBr(○), Et_4NBr(△), n-Pr_4NBr(□) and n-Bu_4NBr (◇).

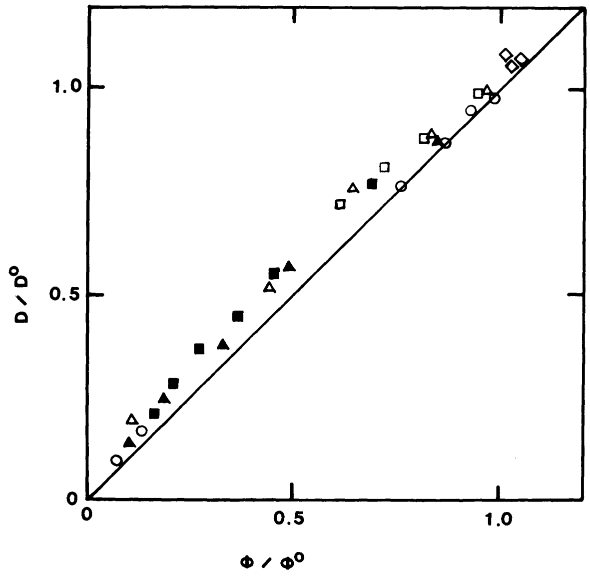

Fig. 5. D_r vs. ϕ_r plots for water of the solutions given in Fig. 3.

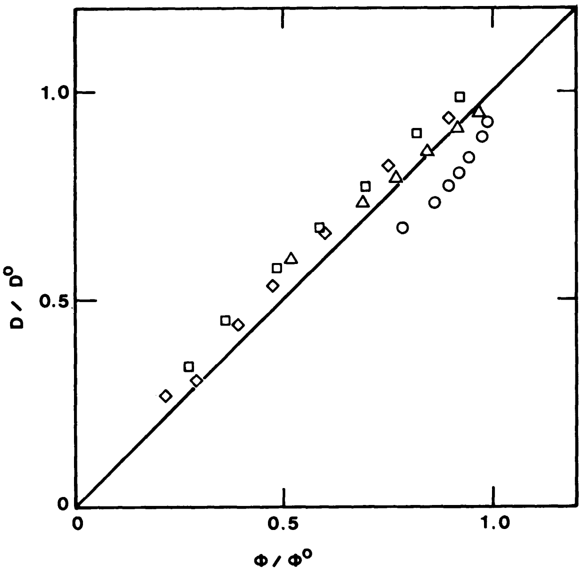

Fig. 7. D_r vs. ϕ_r plots for R_4N^+ of the solutions given in Fig. 6.

they cause weaker hydration.

Examples of the D_r vs. ϕ_r plots for aqueous solutions of tetraalkylammonium bromides which cause the so-called hydrophobic hydration, are given in Figs. 6, 7, and 8. For bromide ions all the experimental points lie on the same curve regardless of their counter tetraalkylammonium cations (Fig. 6); the correlation is similar to that observed for chloride ions in solutions of the LiCl-type electrolytes, although the linear relationship represented by Eq. 1 is satisfied at rather smaller relative fluidities ($\phi_r<0.5$) than in the case of the chloride ions of small electrolytes. Among the points for tetraalkylammonium cations, those for tetramethylammonium cation fall below the diagonal line, whereas those points for the other tetraalkylammonium cations are on or above the line (Fig. 7). The water diffusion in these solutions exhibits more complicated behavior (Fig. 8), and will not be discussed in detail until more experimental data have been available.

The D_r vs. ϕ_r relationships for aqueous solutions of cadmium chloride and iodides (Fig. 9) are examples where cations and anions have strong specific interactions such as complex formation. The most characteristic behavior of such systems can be seen on the correlation for the anions; all the points are far below the diagonal line, indicating that the anions in these solutions diffuse much slower than would be expected from the fluidity by Eq. 1. This transport behavior may be mainly ascribed to the specific ion–ion interaction, as a result of which the chloride and iodide ions are travelling together with cadmium ions whose diffusion coefficients are about one-third of the anions.

In this paper, we have demonstrated that different types of solute–solvent interactions exhibit different diffusion vs. fluidity correlations. The D_r vs. ϕ_r plots may not be adequate to study of validity of the Stokes–Einstein equation, and the correlations we found are entirely empirical. We believe, however, that the correlations will provide some fundamental information on the nature of ion–solvent interactions and structural properties of ions in concentrated electrolyte solutions. It is hoped that the empirical correlations presented in this paper could be explained by the future development of theories and models of concentrated electrolyte solutions.

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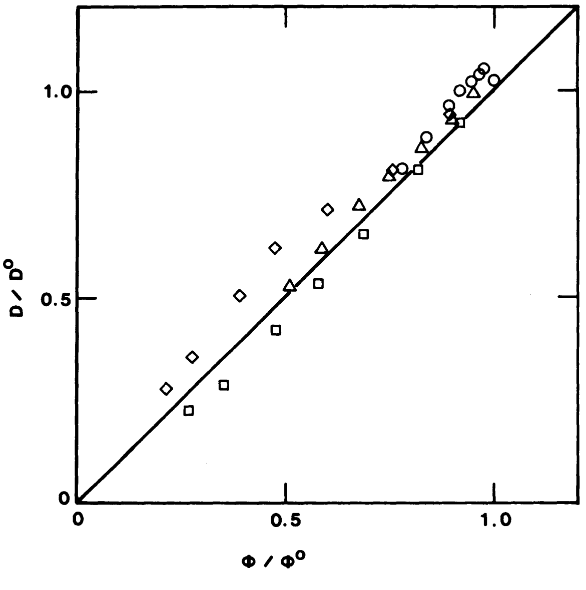

Fig. 8. D_r vs. ϕ_r plots for water of the solutions given in Fig. 6.

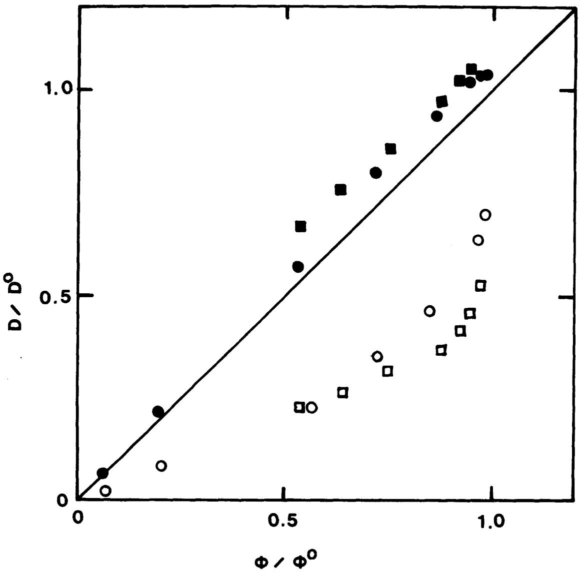

Fig. 9. D_r vs. ϕ_r plots for aqueous solutions of $CdCl_2$ and CdI_2 at 25 °C; Cd^{2+}(●) and Cl^-(○) in $CdCl_2$, and Cd^{2+}(■) and I^-(□) in CdI_2.

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