Self-Diffusion of Sodium, Chloride and Iodide Ions in Methanol-Water Mixture

E. Hawlicka *

Institute of Applied Radiation Chemistry, Technical University, Wroblewskiego 15,
93-590, Lodz, Poland

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The self-diffusion coefficients of Na^+, Cl^- and I^- in methanol-water solutions at 35 ± 0.01 °C have been measured in their dependence on the salt molarity in the range $1 \cdot 10^{-4} - 1 \cdot 10^{-2}$ mol dm^{-3}. The ionic self-diffusion coefficients in infinitely diluted solutions have been computed. The influence of the solvent composition on the solvation of the ions is discussed. A preferential hydration of Na^+, Cl^- and I^- ions in water-methanol mixtures has been found.

In spite of the great interest in the porperties of water-organic solvent electrolyte solutions, data on the ionic mobilities in such systems are scarce. Usually the ionic mobility is calculated from the equivalent conductance and the transference number. Ionic transference numbers have been reported for water and 17 organic solvents [1], but only for a few water-organic solvents mixtures.

Similar information can be obtained from the ionic self-diffusion coefficients, which have been reported for a few water-organic solvent systems [2–5].

The aim of the present work was to determine the self-diffusion coefficients of sodium, chloride and iodide ions in water-methanol mixtures and to study the ion-solvent interactions.

Experimental

Methanol (spectroscopy grade, Merck), NaI (suprapur, Merck), NaCl (suprapur, Merck) and double distilled, degassed water were used to prepare the solutions. ^{22}Na, and Na^{36} from the USSR, and ^{24}Na, Na^{125} and ^{131}I from Poland were used as radioactive tracers. The radioactivities of ^{24}Na, ^{36}Cl and ^{125}I were measured in toluene-ethanol solutions of 2,5-diphenyloxazole (PPO) with a liquid scintillation counter, whereas the radioacitivites of ^{22}Na and ^{131}I were determined in aqueous solution with a NaI(Tl) scintillation crystal of the well-type (2 × 2″).

For the self-diffusion measurements the open-end capillary method was used. The details of the experimental procedure have been described in [6].

The labelling of the sodium ions with ^{22}Na or ^{24}Na and the iodide ions with ^{125}I or ^{131}I, respectively, did not make any difference in the results.

Results

All self-diffusion experiments have been carried out at 25.0 ± 0.05 °C. The measurements have covered the whole composition range of the solvent mixtures. The molarity of the salts was varied between $1.0 \cdot 10^{-4}$ and $1.0 \cdot 10^{-2}$.

Some concentration dependences of the ionic self-diffusion coefficients are presented in Figure 1. All values have been calculated from 9 independent experiments obtained for 3 different diffusion times ranging from 10 to 72 hrs. The statistical error of the D-values is less than 1%.

The D-values have been used to compute the limiting self-diffusion coefficients D^∞, i.e. the coefficients in the infinitely diluted solutions.

Taking into account the relaxation effect in the self-diffusion process of ions, Robinson and Stokes [8] proposed the following equation, which describes the influence of the salt molarity m on the ionic self-diffusion coefficient D_i of an ion i for a 1:1 electrolyte:

$$D_\mathrm{i} = D_\mathrm{i}^\infty \left[1 - \frac{2.801 \cdot 10^3}{(\varepsilon_0 T)^{1.5}} \left(1 - \sqrt{\mathrm{d}(\mu_\mathrm{i})}\right) \sqrt{m} \right], \qquad (1)$$

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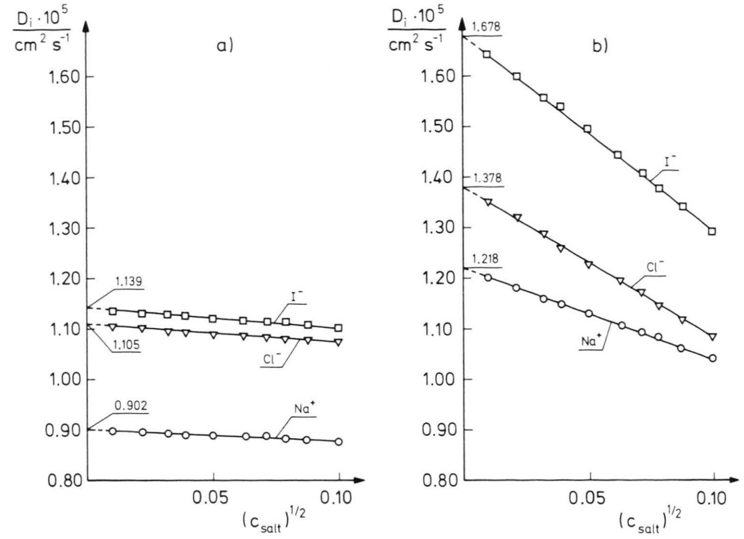

Fig. 1. Dependence of the ionic self-diffusion coefficients on the square root of the salt molarity, c_{salt}, for two solvent compositions (x_{M} mole fraction of methanol): a) $x_{\mathrm{M}} = 0.31$; b) $x_{\mathrm{M}} = 1.00$.

where T, ε_0 and m denote the temperature, the static dielectric constant of the solvent and the molarity of the salt, respectively. $\mathrm{d}(\mu_i)$ is a function of the mobilities of both ions. This function has been defined as

$$\mathrm{d}(\mu_i) = \tfrac{1}{4}(1 + 2t_j^0), \tag{2}$$

where t_i^0 and $t_j^0 = 1 - t_i^0$ are the transport numbers of the ion under study and its counterion, respectively, at infinite dilution.

The t_j^0 value can be expressed by the limiting self-diffusion coefficients of the ions:

$$t_j^0 = \frac{D_j^\infty}{D_i^\infty + D_j^\infty}. \tag{3}$$

Introduction (3) into (2) yields

$$\mathrm{d}(\mu_i) = \frac{B_i + 3}{4(B_i + 1)} \tag{4}$$

with $B_i = D_i^\infty / D_j^\infty$, and from (4) and (1) follows

$$D_i = D_i^\infty \left[1 - \frac{2.80 \cdot 10^6}{(\varepsilon_0 T)^{1.5}} \left(1 - \sqrt{\frac{B_i + 3}{4(B_i + 1)}} \right) \sqrt{m} \right]. \tag{5}$$

To calculate the D_i^∞ and D_j^∞ values from (5), a computer program has been written to minimize simultaneously the two mean square deviations

$$\sigma_i = \sqrt{[D_i(\mathrm{cal}) - D_i(\mathrm{exp})]^2} \tag{6}$$

for i = cation and i = anion. The computed D^∞ values for the sodium, chloride and iodide ions are given in Table 1. As it was expected, the same limiting self-diffusion coefficients of the sodium ions resulted from the experiments with NaCl and NaI. The influence of the solvent composition on the D_i^∞ values is presented in Figure 2. As it can be

Table 1. The limiting self-diffusion coefficients of sodium, chloride and iodide ions in water-methanol mixtures. x_{M} is the mole fraction of methanol in the solvent.

x_{M}	$D_{\mathrm{Na^+}}^\infty \cdot 10^5$ / cm² s⁻¹		$D_{\mathrm{Cl^-}}^\infty \cdot 10^5$ / cm² s⁻¹	$D_{\mathrm{I^-}}^\infty \cdot 10^5$ / cm² s⁻¹
	NaCl	NaI		
0.000	1.328	1.325 [a]	2.064	2.094 [a]
0.100	1.178	1.180 [a]	1.672	1.741 [a]
0.229	1.021	1.025	1.271	1.303 [a]
0.310	0.902	0.902	1.105	1.139
0.400	0.814	0.814 [a]	1.062	1.101 [a]
0.471	0.810	0.809 [a]	1.079	1.140 [a]
0.551		0.810 [a]	1.111	1.237 [a]
0.641	0.925	0.927	1.178	1.315
0.690		0.973	1.201	1.378
0.817	1.097	1.099 [a]	1.286	1.501 [a]
0.900	1.156	1.152	1.329	1.582
1.000	1.222	1.218 [a]	1.378	1.678 [a]

[a] Recalculated results from Ref. [7].

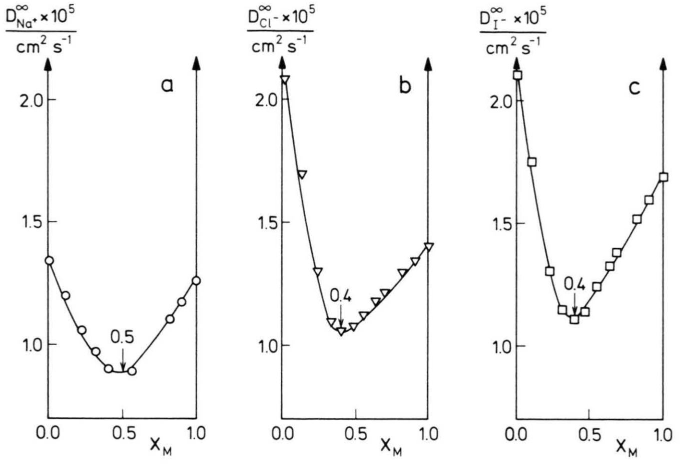

Fig. 2. The dependence of the limiting self-diffusion coefficients $D^{\infty}_{Na^+}$ (a), $D^{\infty}_{Cl^-}$ (b) and $D^{\infty}_{I^-}$ (c) on x_M.

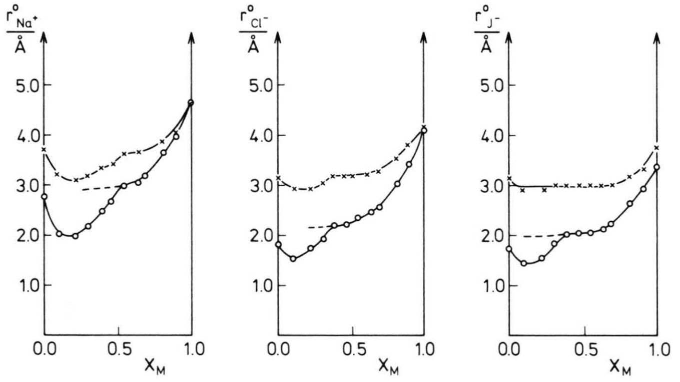

Fig. 3. Ionic radii calculated from Eq. (8) (○) and Eq. (9) (×). (The viscosity of methanol-water mixtures from [10, 11], the dielectric constants from [12].)

seen, all functions are similar and pass through a minimum. The smallest values of $D^{\infty}_{Cl^-}$ and $D^{\infty}_{I^-}$ are found at $x_M = 0.4$ and that of $D^{\infty}_{Na^+}$ at $x_M = 0.5$.

Discussion

In order to discus the solvation of ions one can compute hydrodynamic ionic radii. The simplest approach, frequently used for such calculations, is based on the Einstein-Stokes equation, which interrelates the self-diffusion coefficient with the solution viscosity. The applicability of this equation is, however, one of the most controversial questions in diffusion studies. These controversies result from the fact that this equation was derived for diffusing species large enough for a solvent to be treated as a continuum. It is obvious that such a condition is not fulfilled if the sizes of the diffusing particles and the solvent molecules are similar, as for example in self-diffusion of pure solvents. In our case of ionic self-diffusion one can assume, however, that the solvated ions are much greater than the water or methanol molecules. Then the hydrodynamic radius of the ion i, r_i, can be calculated from the equation

$$r_i = \frac{kT}{\pi \beta \eta_0 D_i^{\infty}}, \tag{7}$$

where η_0 is the viscosity of the solvent and β a parameter resulting from the solute-solvent boundary condition. For perfect sticking $\beta = 6$, whereas for perfect slipping $\beta = 4$. A detailed examination of solute-solvent boundary condition by Ravel et al. [9] indicated slipping to be more appropriate for ionic self-diffusion. Thus based on the data given in Table 1 the ionic radii shown in Fig. 3 have been computed from the equation

$$r_i = \frac{kT}{4 \pi \eta_0 D_i^{\infty}}. \tag{8}$$

Recently Gill [13], following Zwanzig's theoretical attempt [14], has proposed a modification of Stokes' law to calculate an ionic radius from an ionic conductance. Taking into account the relation between the ionic conductance and the ionic self-diffusion coefficient, Gill's equation can be rewritten as

$$r_i = \frac{kT}{6\pi\eta_0 D_i^\infty} + 0.0103\,\varepsilon_0 + r_y\,, \tag{9}$$

where r_y is a parameter dependent on the solvent properties, equal to 0.85 Å for nonassociated solvents and 1.13 Å for associated or hydrogen-bonded ones.

In (9) the first term results from viscous friction forces, assuming sticking, and the second from dielectric friction forces; the meaning of the third term r_y, however, is not so clear. To find a proper value of r_y, Gill [15] has examined the limiting conductance of tetra alkylammonium ions in several organic solvents and organic solvent mixtures. These ions have been assumed to be unsolvated, and the parameter r_y has been calculated as the difference between the crystallographic radii of these ions and the values resulting from the hydrodynamic and dielectric terms of (9).

Based on the data given in Table 1 and putting $r_y = 1.13$ Å (cf. [13]), the ionic radii have been calculated from (9). The results are pressented in Figure 3. As can be seen, the influence of the solvent composition on the ionic radii is similar, but the values calculated from (9) are greater than those from (8), and this difference becomes smaller with increasing methanol content. This discrepancy can result from the lack of a proper r_y value for aqueous solutions. In order to solve this problem we examined in a similar way as has been done by Gill [15] the conductances of tetraalkylammonium ions in aqueous and alcoholic solutions. The results are presented in Table 2. Unfortunately we did not find the proper value of r_y and we noticed that the value of r_y equal 1.13 Å does not fit the ionic radii in methanol and ethanol solutions. The discussion presented above leads to the conclusion that there does not exist a proper equation to calculate a real ionic radius.

Table 2. Results of examination of (9) for tetraalkylammonium ions (r_c = crystallographic radius, z = ionic charge, F = Faraday's constant, N = Avogadro's number, λ_i^0 = limiting conductance).

Solvent	r_c Å	$\frac{\lvert z\rvert F^2}{6\pi\eta_0 N\lambda_i^0} = a$ Å	$0.0103\,\varepsilon_0$	$r_y = r_c - (a + 0.0103\,\varepsilon_0)$
		Et_4N^+		
Water	4.00	2.82	0.81	+ 0.37
Methanol	4.00	2.49	0.34	+ 1.17
Ethanol	4.00	2.59	0.25	+ 1.16
		nPr_4N^+		
Water	4.60	3.93	0.81	− 0.14
Methanol	4.60	3.27	0.34	+ 0.99
Ethanol	4.60	3.29	0.25	+ 1.06
		nBu_4N^+		
Water	5.0	4.80	0.81	− 0.60
Methanol	5.0	3.86	0.34	+ 0.80
Ethanol	5.0	3.85	0.25	+ 0.90

(Ionic conductances in aqueous solution from [16].)

As can be seen from Fig. 3, the variations of the r_i values obtained from (8) and (9) with the variations of the composition of the solvent are similar. Thus one can suppose that the r_i value is proportional to the real value of the ionic radius and may reflect variations of the ionic solvation arising from changes of the solvent. The following discussion of the influence of the solvent composition on the ionic solvation is based on the r_i values calculated from (9), because this equation seems to be more accurate by its dielectric term.

For all studied ions the dependence of r_i on x_M is found to be non-linear; first the r_i values decrease from pure methanol to ca. 75 mol% of methanol, where they become constant for a certaint x_M range. This non-linearity might indicate that the competition the water and methanol molecules in the solvation shells of the ions plays an important role only if the concentration of water is too small to create a pure hydration shell. Thus one can assume a preferential hydration of Na^+, Cl^- and I^- in methanol-water solutions.

Additionally, in the case of sodium and chloride ions a minimum of r_i has been observed at x_M about 0.15. It is known [17] that the structure of aqueous solutions of methanol and other alcohols becomes more ordered at x_M about 0.12–0.15. One can suppose that the creation of a typical solvation shell of ions in a more ordered solvent is obstructed, which may result, as it has been suggested by Feakins [18], from a disagreement between the spherical structure of the hydrated ions and the structure of the solvent. Such a conclusion is confirmed by the fact that the minimum of r_i is deeper for sodium ions, because usually the hydration shell of Na^+ is assumed to be more pronouced [19] than that of Cl^-.

[1] B. S. Krumgalz, J. Chem. Soc. Faraday I **79,** 571 (1983).
[2] A. Lindheimer and B. Brune, J. Chim. Phys. **73,** 589 (1976).
[3] A. Lindheimer, J. Rouvier, F. Boyer, and B. Brune, J. Chim. Phys. **77,** 77 (1980).
[4] A. Lindheimer, J. Rouvier, and B. Brune, J. Chim. Phys. **78,** 51 (1981).
[5] A. Lindheimer, F. Boyer, and B. Brune, J. Chim. Phys. **78,** 441 (1981).
[6] W. Reimschüssel and E. Hawlicka, Ber. Bunsenges. Phys. Chem. **81,** 1221 (1977).
[7] E. Hawlicka, Ber. Bunsenges. Phys. Chem. **87,** 425 (1983).
[8] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2nd Ed., Butterworths Scientific Publications, London 1959.
[9] A. A. Ravel and A. B. Porai-Kosic, Teor. Exp. Khim. **6,** 311 (1970).
[10] S. Westmeier, Chem. Tech. Leipzig **28,** 350 (1976).
[11] S. Taniewska-Osinska and P. Chadzynski, Acta Univ. Lodz, Ser. II, **6,** 37 (1976).
[12] L. J. Gosting and P. S. Albright, J. Amer. Chem. Soc. **68,** 1061 (1946).
[13] D. S. Gill, J. Chem. Soc. Faraday I **81,** 687 (1985).
[14] R. Zwanzig, J. Chem. Phys. **52,** 3625 (1970).
[15] D. S. Gill, J. Chem. Soc. Faraday I **77,** 751 (1981).
[16] Handbook of Electrochemical Constants, Butterworths Scientific Publications, London 1959.
[17] F. Franks and D. J. G. Ives, Quart. Rev. **20,** 1 (1966).
[18] D. Feakins, D. J. Freemantle, and K. G. Lawrance, J. Chem. Soc. Faraday I **70,** 795 (1974).
[19] G. Jancsó, P. Bopp, and K. Heinzinger, Ionic Hydration of Alkali Halides Solutions, Hungerian Academy of Sciences, Central Institute of Physics, Budapest 1977.