Self-Diffusion of Sodium, Chloride and Iodide Ions in Acetonitrile-Water Mixtures

E. Hawlicka

Institute of Applied Radiation Chemistry, Technical University, Łódź, Poland

The self-diffusion coefficient of sodium, chloride and iodide ions in acetonitrile-water mixtures at 25.0 ± 0.05 °C has been measured in dependence on the salt molarity in the range $1.0 \cdot 10^{-4}$ $1.0 \cdot 10^{-2}$ mol/dm³. 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. Preferential solvation of the ions by acetonitrile above 15 mol% of acetonitrile has been found. An effect of the sodium ions on the formation of acetonitrile globules is postulated.

The relation between the structure of a solvent and the solvation of solutes is a fundamental question in solution chemistry. A acetonitrile-water mixtures as solvents seem to be suitable systems to study that problem because they exhibit two structural discontinuities. From the viscosity and density investigations Moreau and Douhéret [1, 2] have postulated the existence of three fundamental structural regions: Up to 15 mol% of acetonitrile the water structure remains unchanged and the acetonitrile molecules occupy cavities in that structure. Above that concentration the water structure is disrupted and a segregation of water and acetonitrile molecules occurs, the mixture exhibiting phase segregation at a critical composition of about 38 mol% CH_3CN [3] and with an upper critical temperature of about 272 K [3 – 5]. In the acetonitrile rich solution (above 75 mol% CH_3CN) the water molecules accommodate in the structure of pure acetonitrile. Studies of the proton chemical shift [6] and self-diffusion [7, 8] have confirmed those structural regions.

The aim of the present work was to determine the self-diffusion coefficients of sodium, chlorine and iodine ions in acetonitrile-water mixture and to study the ion-solvent interactions.

Experimental

NaCl (suprapur, Merck), NaI (suprapur, Merck), acetonitrile (spectroscopy grade, Merck),

distilled over P_2O_5, and double distilled, degassed water were used to prepare the solutions. ^{22}Na, ^{36}Cl and ^{125}I were used as radioactive tracers. The radioactivities of the samples were measured in toluene-ethanol solution of 2,5-diphenyloxazole (PPO) with a liquid scintillation counter.

For the self-diffusion measurements the open-end capillary method was applied. The details of the experimental procedure have been described in [9].

Results

The self-diffusion experiments were carried out at 25.0 ± 0.01 °C. The measurements have covered the whole composition range of the solvent. The molarity of the salts was varied between $1.0 \cdot 10^{-4}$ and $1.0 \cdot 10^{-2}$. All D-values have been calculated from 9 independent experiments. The statistical error of the D-value is less than 1%.

As it was derived previously [10], the dependence of the ionic self-diffusion coefficient on the salt molarity m can be expressed in form:

$$D_i = D_i^\infty \left[1 - \frac{2.801 \cdot 10^6}{(\varepsilon_0 T)^{1.5}} \left(1 - \sqrt{\frac{B_i + 3}{4(B_i + 1)}} \right) m^{0.5} \right],$$

(1)

where T, ε_0 and D_i^∞ denote the temperature, the static dielectric constant of the solvent and the ionic self-diffusion coefficient in the infinitely diluted solution (limiting self-diffusion coefficient), respectively, and $B_i = D_i^\infty / D_j^\infty$, where D_i^∞ and D_j^∞ relate to the ion under study and the counterion, respectively.

Table 1. The limiting self-diffusion coefficients of sodium, chloride and iodide ions in acetonitrile-water mixtures. X_{AN} is the mole fraction of acetonitrile in the solvent. The static dielectric constants of the solvent were taken from [11].

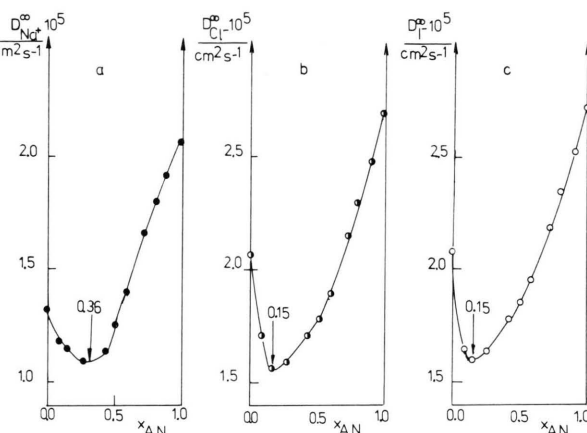| X_{AN}	$\dfrac{D_{Na^+}^{\infty} \cdot 10^5}{cm^2\,s^{-1}}$		$\dfrac{D_{Cl^-}^{\infty} \cdot 10^5}{cm^2\,s^{-1}}$	$\dfrac{D_{I^-}^{\infty} \cdot 10^5}{cm^2\,s^{-1}}$
	NaCl	NaI		
0.000	1.333	1.333	2.060	2.090
0.103	1.18	1.18	1.60	1.65
0.147	1.15	1.16	1.54	1.60
0.256	1.09	1.09	1.58	1.64
0.408	1.10	1.10	1.71	1.78
0.508	1.26	1.25	1.77	1.86
0.579	1.40	1.40	1.89	1.96
0.733	1.67	1.67	2.15	2.19
0.805	1.79	1.80	2.30	2.35
0.912	1.91	1.92	2.48	2.53
1.000	2.05	2.06	2.70	2.72

Fig. 1. The dependence of the limiting self-diffusion coefficients D_{Na^+} (a), D_{Cl^-} (b) and D_{I^-} (c) on X_{AN} at 25 °C.

To calculate D_i^{∞} and D_j^{∞} from (1) a computer program was written to minimize simultaneously the two mean square deviations

$$\sigma_i = \sqrt{\sum [D_i(cal) - D_i(exp)]^2} \qquad (2)$$

for i = cation and i = anion.

The computed D-values are summarized in Table 1. As it was expected, the same limiting self-diffusion coefficients of sodium ions resulted from the experiments with NaCl and NaI. The influence of the solvent composition on the limiting self-diffusion coefficients of the ions is presented in Figure 1. As it can be seen, all functions are similar and pass through a minimum. The smallest values of $D_{Cl^-}^{\infty}$ and $D_{I^-}^{\infty}$ are observed at $x_{AN} = 0.15$, and that of $D_{Na^+}^{\infty}$ at $x_{AN} = 0.36$.

Discussion

In order to investigate an influence of the solvent composition on ionic solvation one can compute ionic radii. As it has been shown previously [10], Gill's modification [12] of Stokes' law seems to be more accurate then the simple Einstein-Stokes approach to calculate ionic radii because both viscous and dielectric friction forces are taken into account. Gill's equation, applied to self-diffusion coefficients instead of the ionic conductance, can be rewritten as

$$r_i = \frac{k\,T}{4\,\pi\,\eta_0\,D_i^{\infty}} + 0.0103\,\varepsilon_0, \qquad (3)$$

where η_0 denotes the viscosity of the solvent.

As compared with Gill's original equation, in the first term of (3), resulting from the viscous friction forces, perfect slipping is assumed for the solvated ion-solvent boundary conditions [10, 13].

Based on the data given in Table 1 the ionic radii have been calculated from (3). The results are presented in Figure 2. For all studied ions the dependence of the r_i-values on x_{AN} is non-linear and exhibits a positive deviation from linearity, which might indicate a preferential solvation of ions by acetonitrile molecules. This conclusion disagrees with a weak preferential hydration of halide ions postulated from nmr studies [14] and with a preferential hydration of sodium ions concluded from upper critical temperature changes [3], free energy of transfer between water and water-acetonitrile
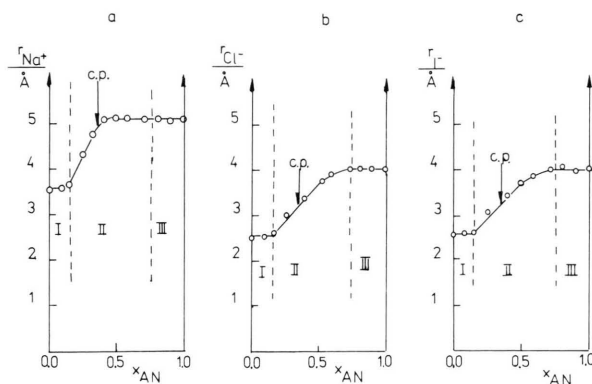

Fig. 2. Ionic radii calculated from (3). (The viscosity of the acetonitrile-water mixture was taken from [1]). The vertical lines mark the structural regions: I: water like structure, II: microphase coexistence, III: acetonitrile like structure.

mixture [15] and nmr studies [16]. Experimental B-viscosity coefficients of alkali metal halides in acetonitrile-water solutions [17] suggest, however, that preferential solvation by acetonitrile occurs.

As it can be seen from Fig. 2, in the regions I and III, i.e. below 15 mol% CH_3CN and above 75 mol% CH_3CN, the radii of the ions are the same as in the pure solvents. One can suppose that the presence of the cosolvent, acetonitrile and water, respectively, does not disturb the formation of the same solvation shell as in the pure solvent. This confirms also the previous conclusion [6, 7] that acetonitrile, while methanol [18 – 20] does, does not change the water structure.

In the region of microphase coexistence $(0.15 < x_{AN} < 0.75)$ the interactions between the solvent molecules and sodium ions differ from those the anions. In this range a linear increase of the radii of both anions is observed, whereas the radius of the sodium ions reaches its upper values, the same as in pure acetonitrile, already at $x_{AN} = 0.38$. The difference can be explained as follows: One can suppose that the critical composition (38 mol% CH_3CN) divides the microheterogenous region into two sections. Below that point the structure is formed by water globules and acetonitrile molecules and/or globules are distributed between them, whereas above that point the acetonitrile globules form the structure. Also in [6, 7] it was postulated that the structure of the water globules is more ordered than that of pure

water. If the disagreement between the spherical structure of the hydrated cation and the structure of the water globules is great, then sodium ions cannot from hydration shells and are removed from the water globules. The bare sodium ions cannot exist and are "forced" to create a solvation shell containing acetonitrile molecules. At the critical composition the concentration of acetonitrile is great enough to form the same solvation shell as in pure acetonitrile. In such a case one can suppose that the presence of the sodium ions induces the formation of the acetonitrile globules, because the cation-water interactions are weaker then water-water ones.

This "arranging effect" of sodium ions might explain the increase of the upper critical temperature observed in the presence of sodium nitrate [5]. The interactions of the anions with the solvent, both water and acetonitrile, are weaker them those of sodium ions. Therefore the anions do not induce the formation of acetonitrile globules, as can be seen from the linear dependence of the r_i-values on x_{AN} in the microheterogenous region.

It was found previously [21] that, if a preferential solvation occurs, the self-diffusion of the component forming the solvation shell is strongly affected by the presence of electrolyte. In order to confirm the concluded preferential solvation of ions by acetonitrile, studies of the self-diffusion of both components of the solvent in the presence of electrolytes are under way.

[1] C. Moreau and G. Douhéret, Thermochim. Acta 13, 385 (1975).
[2] C. Moreau and G. Douhéret, J. Chem. Thermodyn. 8, 403 (1976).
[3] G. Schneider, Z. physik. Chem. N.F. 41, 327 (1964).
[4] M. Ewert, Bull. Soc. Chim. Belgique 46, 327 (1937).
[5] M. Moolel and H. Schneider, Z. physik. Chem. N.F. 74, 327 (1971).
[6] A. J. Easteal, Aust. J. Chem. 32, 1379 (1979).
[7] A. J. Easteal, Aust. J. Chem. 33, 1667 (1980).
[8] H. G. Hertz and H. Leiter, Z. physik. Chem. N. F. 133, 45 (1983).
[9] E. Hawlicka, Ber. Bunsenges. Phys. Chem. 87, 425 (1983).
[10] E. Hawlicka, Z. Naturforsch. 41a, 939 (1986).
[11] A. D'Aprano and R. Fuoss, J. Phys. Chem. 73, 400 (1969).
[12] D. S. Gill, J. Chem. Soc. Faraday I 81, 687 (1985).
[13] A. A. Ravel and A. B. Porai-Kosic, Teor. Exp. Khim. 6, 311 (1970).
[14] T. R. Stengle, Y. C. E. Pan, and C. H. Langford, J. Amer. Chem. Soc. 94, 9037 (1972).
[15] B. G. Cox and R. Natarajan, J. Chem. Soc. Faraday I 75, 86 (1979).
[16] E. G. Bloor and R. G. Kidd, Can. J. Chem. 46, 3425 (1968).
[17] G. Kumar, N. C. Dey, B. K. Saikia, and I. Hagne, Bull. Chem. Soc. Japan 59, 1555 (1986).
[18] F. Franks and D. J. G. Ives, Quart. Rev. 20, 1 (1966).
[19] D. Feakins, D. J. Freemantle, and K. G. Lawrance, J. Chem. Soc. Chem. Commun. 1968, 970.
[20] D. Feakins, D. J. Freemantle, and K. G. Lawrance, J. Chem. Soc. Faraday I 70, 795 (1974).
[21] E. Hawlicka, Ber. Bunsenges. Phys. Chem. 87, 425 (1983).