ELSEVIER

Journal of Molecular Liquids 122 (2005) 28–31

journal of MOLECULAR LIQUIDS

www.elsevier.com/locate/molliq

Influence of alcohols on Ca^{2+} hydration

Katarzyna Pałka, Ewa Hawlicka*

Institute of Applied Radiation Chemistry, Department of Chemistry, Technical University, Zeromskiego 116, 90-924 Lodz, Poland

Received 29 October 2004; accepted 20 January 2005
Available online 12 April 2005

Abstract

Self-diffusion coefficients of Ca^{2+} and Cl^- were measured at 298 K in aqueous solutions of methanol, *n*-propanol and *tert*-butanol. An influence of alcohol concentration on Ca^{2+} and Cl^- radii was investigated. Ca^{2+} radius in aqueous solution coincides with the size of the first coordination shell. Cl^- radius is smaller than the size of the first coordination shell. Alcohols destabilize the hydration shell of Cl^- and its radius is like that in crystal. Hydration of Ca^{2+} depends on the solvent structure. Small amounts of methanol and *tert*-butanol, but not of *n*-propanol, destroy slightly the first shell of Ca^{2+}, whereas in 'mixed state region' of *n*-propanol and *tert*-butanol aqueous solutions the shells of Ca^{2+} are like those in water, because cations are embedded in water domains.

Keywords: Ion hydration; Ion self-diffusion

1. Introduction

Much attention has been devoted to study a hydration of Ca^{2+}. This ion has many important biochemical functions, e.g. in the control of metabolism, muscle contraction, blood clotting and hormonal activities [1]. Some of the biochemical properties, as for example a binding of Ca^{2+} by polyelectrolytes, are believed to depend on the ion hydration [2,3]. X-ray and neutron diffraction techniques, particularly neutron diffraction with isotope substitution (NDIS), are a powerful tool to investigate the coordination shells of the ions. All these methods require, however, high electrolyte concentration, where ion association may occur and, in consequence, experimental results might be not clear. X-ray diffraction of aqueous solutions of calcium chloride [4,5] and bromide [6] yields coordination number, which varies between 6 and 10. Neutron diffraction of $CaCl_2$ and $Ca(NO_3)_2$ solutions in D_2O [7] has shown a decrease of Ca^{2+} hydration number from 10 to 6, when the salt concentration increases from 1 to 4.5 M.

Contact $Ca^{2+}\cdot\cdot Cl^-$ pairs have been detected, via X-ray diffraction, in $CaCl_2\cdot 6H_2O$ melt [8] and 3 M $Ca(NO_3)_2$ solution [9]. These pairs yield a peak of a distribution function, at 0.275 nm, very close to the Ca^{2+}–O peak, found [4–12] between 0.24 and 0.25 nm. This affects the calcium weighted distribution function calculated from NDIS experiments and leads to unapt assignment for the Ca^{2+} coordination number [12].

The hydration of Ca^{2+} in diluted solutions, below 1 M, cannot be investigated using the scattering methods. Therefore, information about the coordination shell of Ca^{2+} must be deduced from other properties of the solutions, for example from transport properties. The simplest transport property is the self-diffusion coefficient, which depends on the size of a solute molecule and its coordination shell [13].

The purpose of this work was to investigate Ca^{2+} hydration in dilute, below 1 M, aqueous solution, when the scattering techniques are useless, basing on self-diffusion experiments. Previous studies [13,14] showed that small amount of methanol, *n*-propanol, *iso*-propanol and *tert*-butanol demolished partially the Na^+ hydration shell. The distortion of the Na^+ shell was observed in highly associated solvents [13–15]. This has led to the conclusion that a tendency to preserve a H-bonded network competes

---

* Corresponding author. Tel.: +48 42 6313097; fax: +48 42 6365008.
E-mail address: hawlicka@p.lodz.pl (E. Hawlicka).

0167-7322/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molliq.2005.01.007

with strong interactions between Na^+ and solvent molecules. Thus, the question appears whether this tendency may affect the hydration shell of the divalent Ca^{2+} ion.

2. Experimental

Methanol (spectroscopy grade, POCh), *n*-propanol (pro analysis, Merck), *tert*-butanol (pro analysis, Merck) and $CaCl_2$ (pro analysis, POCh) were used as received. Water was deionized, double distilled and degassed. All solutions were prepared by weight.

Self-diffusion coefficients were measured by the open-end capillary method [16], using $^{45}Ca^{2+}$ and $^{35}Cl^-$ as radioactive tracers. Radioactivity of the samples was determined in Ultima Gold XR (Packard) liquid scintillation cocktail by the liquid scintillation counter RackBeta (LKB). Self-diffusion coefficients were measured for different duration of the experiments. D-coefficients, presented here, were calculated as the mean value from no less than 9 independent experimental results. Their experimental errors were computed at 0.95 confidence level. An Ubbelohde type viscosimeter AVS-100 (Schott-Geräte) was used to measure the viscosity. All experiments were carried out at 298 K. Concentration of $CaCl_2$ was $5 \cdot 10^{-3}$ M and the alcohol mole fraction, x_{ROH}, did not exceed 0.3.

3. Results and discussion

Self-diffusion coefficient of the calcium ion, D_{Ca}, was determined in aqueous solution and in aqueous solutions of methanol, *n*-propanol and *tert*-butanol. The self-diffusion coefficient of the chloride ion, D_{Cl}, was measured in aqueous solutions of methanol and *tert*-butanol. The results of D_{ion} coefficients and of viscosities of all solutions are summarized in Table 1.

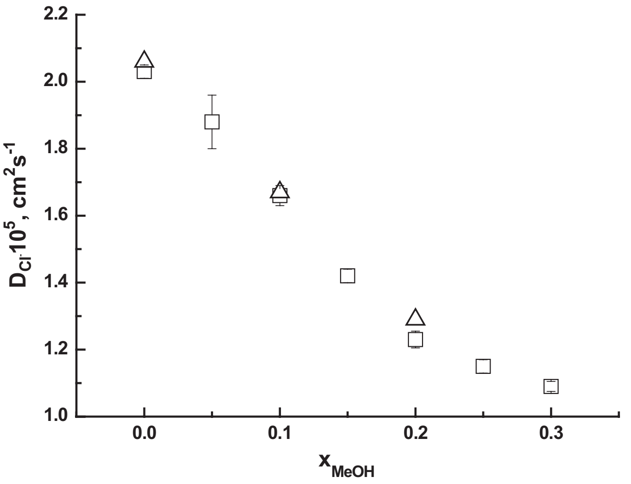

Fig. 1. Dependence of self-diffusion coefficient of chloride ions on methanol mole fraction x_{MeOH} in $5 \cdot 10^{-3}$ M $CaCl_2$ (□) and infinite diluted NaCl (△) solution [14] at 298 K.

D_{Cl} coefficients, measured in $5 \cdot 10^{-3}$ M $CaCl_2$ solutions, are compared in Fig. 1 with the D_{Cl}^{∞} results, which have been obtained from the dependence of D_{Cl} on NaCl molarity [14]. The latter values represent translations of free Cl^- ions in infinitely diluted solution. As it can be seen from Fig. 1, the D_{Cl} coefficients, measured in $5 \cdot 10^{-3}$ M $CaCl_2$ solution, are equal, within the experimental error, to the D_{Cl}^{∞} values. Thus, D_{Cl} coefficients measured in $5 \cdot 10^{-3}$ M $CaCl_2$ solution represent translations of free chloride ions. This means that a pairing of Cl^- and Ca^{2+} ions is negligible and the D_{Ca} coefficients, measured in $5 \cdot 10^{-3}$ M $CaCl_2$ solution, represent motions of free Ca^{2+} ions.

A hydrodynamic radius, calculated from the Stokes–Einstein relation, is frequently considered as a size of a diffusing unit, i.e. ion and its coordination shell. However, for motions of the ion, dielectric frictions cannot be neglected. In such case, the radius of the ion and its coordination shell, r_{ion}, are represented by a sum [17] of the

Table 1
Self-diffusion coefficients of methanol and ions, Ca^{2+} and Cl^- and viscosity for $5 \cdot 10^{-3}$ M $CaCl_2$ solutions in mixtures of water with methanol, *n*-propanol and *tert*-butanol at 298 K

Alcohol mole fraction x_{ROH}	Self-diffusion coefficient, $D \cdot 10^9$ (m^2 s^{-1})					Viscosity, $\eta \cdot 10^3$ (N s m^2)		
	Ca^{2+}			Cl^-		Methanol	*n*-Propanol	*tert*-Butanol
	Methanol	*n*-Propanol	*tert*-Butanol	Methanol	*tert*-Butanol			
0.00	0.89 ± 0.06	0.89 ± 0.06	0.89 ± 0.06	1.99 ± 0.08		0.8975	0.8975	0.8975
0.025			0.58 ± 0.02		1.55 ± 0.20			1.4469
0.05	0.74 ± 0.04	0.46 ± 0.02	0.44 ± 0.03	2.18 ± 0.25	1.34 ± 0.22	1.1305	1.5857	2.1154
0.06			0.32 ± 0.02					2.2976
0.075			0.27 ± 0.04		1.01 ± 0.14			2.6719
0.08			0.24 ± 0.02					2.7730
0.10	0.69 ± 0.02	0.37 ± 0.03	0.35 ± 0.03	1.66 ± 0.18	0.85 ± 0.09	1.3645	2.0166	3.2393
0.15	0.56 ± 0.03	0.30 ± 0.03	0.22 ± 0.03	1.42 ± 0.08	0.79 ± 0.08	1.4934	2.3710	3.8573
0.20	0.46 ± 0.02	0.27 ± 0.03	0.20 ± 0.02	1.23 ± 0.08	0.77 ± 0.09	1.5505	2.5815	4.3426
0.25	0.42 ± 0.03	0.30 ± 0.03	0.14 ± 0.02	1.15 ± 0.05	0.72 ± 0.07	1.5813	2.5957	4.6150
0.30	0.39 ± 0.03	0.30 ± 0.02		1.09 ± 0.12		1.5929	2.6052	4.7475