

Self-diffusion Coefficients of Na^+ in Water-methanol Mixtures

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Uma versão modificada do método do capilar aberto de Anderson e Saddington foi empregada na determinação do coeficiente de autodifusão do íon de Na^+ em solvente misto água-metanol. O $^{22}\text{Na}^+$ foi utilizado como radiotraçador e a técnica foi testada com uma solução aquosa de NaCl. Foram determinados coeficientes de autodifusão do Na^+ para diversas proporções de metanol em água e os resultados são interpretados em termos de viscosidade do meio e efeito de solvatação. A técnica proposta usa atividades mais baixas de radiotraçador de que aquelas empregadas por métodos análogos fornecendo resultados confiáveis, dentro da precisão esperada.

A modified version of Anderson and Saddington's open-ended capillary method has been employed for the determination of the self-diffusion coefficient of Na^+ in water-methanol NaCl solution. The $^{22}\text{Na}^+$ has been used as a radiotracer and the technique tested with an aqueous solution of NaCl. Self-diffusion coefficients of Na^+ at varying proportions of methanol in water have been measured and the behaviour is discussed in terms of viscosity of the medium and solvation effect. The proposed technique uses lower activities of radiotracer than those usually employed by analogous methods and yields results which are reliable within the precision expected from the method.

Key words: *sodium self-diffusion coefficient; open-ended capillary method; tracer diffusion.*

Introduction

Intradiffusion^{1,2} is defined as the mutual diffusion between two components chemically equivalent. Self-diffusion is a particular case of intradiffusion in a system which contains two distinguishable forms of the same chemical species. From the physical point of view self-diffusion is a statistical consequence of the brownian motion of species since the individual particles have randomic movement even in the absence of macroscopic gradients. Therefore, in a typical self-diffusion experiment there is no concentration gradient involved.

The Anderson and Saddington open-ended capillary method³ is a classical technique of determination of self-diffusion coefficients. In principle this method consists of a capillary tube with uniform section and length precisely known, filled with a solution of a radioactive isotope, which is immersed in a large volume of solution of the same solute. Both solutions are identical with respect to all physical and chemical properties except that the solution inside the capil-

lary tube is labelled with a radioactive isotope. After a period of time the activity of the solution inside the capillary tube is determined and compared with the initial activity. This simple idea has been the base for a number of methods which involve some more sophisticated experimental arrangements such as automatic data acquisition.

Self-diffusion coefficients of ions in aqueous solutions have been studied by a variety of techniques including the open-ended capillary method either in the discontinuous⁴⁻⁶ or continuous version⁷. The open-ended capillary method can be used to study binary as well as multicomponent systems^{8,9} employing γ or β -emitter radiotracers¹⁰ in electrolytic or non-electrolytic solutions^{11,12}. The method allows the study of electrolytes in aqueous and non-aqueous solutions¹³ as well as mixed solvents^{14,15}. A large range of concentrations can be studied by the open-ended capillary method including very dilute solutions where the behaviour is near-ideal¹⁵⁻¹⁸. This method is also an absolute method¹⁹ which requires no previous calibration. However, the main source of systematic error of all versions of the open-ended capillary methods is

the Δl effect²⁰. Experiments have been designed⁴ in order to minimise the Δl effect which is a consequence of inefficient flow control at the open end of the capillary. The boundary conditions of the diffusion problem require that the concentration of the radiotracer at the open end be equal to zero for any diffusion time. If the radiotracer is not continuously removed from the top of the capillary, its physical size l is added of a quantity Δl due to the presence of radiotracer outside the capillary. Similarly, the removal of radiotracer from inside of the capillary due to turbulent flows yields a negative Δl effect. Although the flow control can be critical, there is evidence in the literature²¹ that adequate flow may be chosen from a reasonably broad range without significant effect on the diffusion coefficient.

In the present work a modification to the original technique has been employed for the determination of self-diffusion coefficients of Na⁺ in water-methanol mixtures using ²²Na⁺ as a radiotracer²². By measuring the activity directly in the capillary tube, instead of doing it in the flowing solution²³, the required activity of the radioisotope can be lower than those usually employed in this method. This alternative technique, however, requires a good control of the background activity and the determination of a crystal efficiency function for the detection system. The additional difficulty of measuring the background with the proposed geometry was satisfactorily overcome and the introduction of a geometry dependent function allows for differences in the crystal efficiency.

Experimental

The complete apparatus used for the self-diffusion measurements is shown in Figure 1. The diffusion cell is shown in some detail in Figure 2. The length of the glass capillaries employed in the experiments were 39.92 and 39.80 mm and the inner diameter 1.27 and 1.25 mm respectively. Both capillaries had their volume determined by mercury thread⁴ in order to verify the uniformity of the cylindrical geometry required²⁴. The lower end of each capillary was closed with a flat glass disc. The open end was connected to a 50 ml in

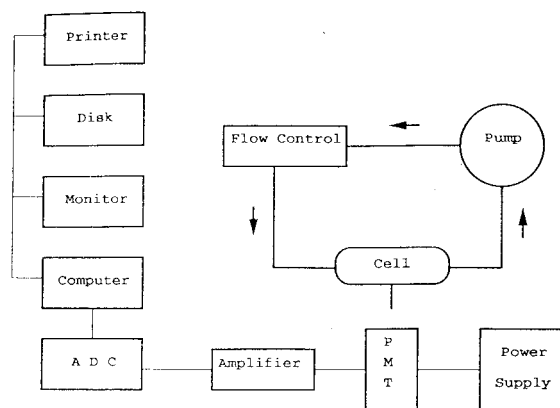


Figure 1. Block diagram of the experimental apparatus showing the proposed modification to the Anderson and Saddington's method. The activity is measured directly in the capillary tube.

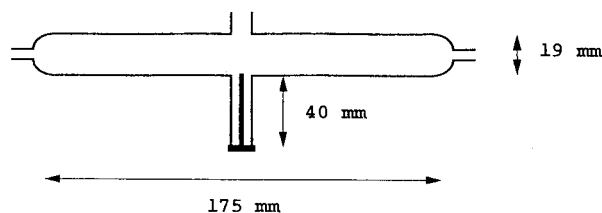


Figure 2. Diffusion cell used for the measurements of self-diffusion coefficients of Na⁺ in water and water-methanol mixtures.

volume glass tube which constitutes the body of the diffusion cell where a continuous flow was maintained during the experiments. The diffusion cell, used for independent measurements, was placed in front of the scintillation NaI-Tl crystal detector in a fixed position for which the crystal efficiency function, $h(x)$, had been previously determined.

The active NaCl 0.1 mol/dm³ solutions were prepared using a small amount of the ²²NaCl carrier-free aqueous solution²⁵ (ca. 30 μ l, 4 μ Ci) which was transferred to a conical-shape centrifuge tube and brought to dryness by careful heating. After checking the activity, a volume of inactive NaCl 0.1 mol/dm³ solution enough to fill the capillary tube was added. The inactive solution of NaCl 0.1 mol/dm³ was prepared by dissolving analytical grade NaCl in twice distilled water or in water-methanol mixtures depending on the experiment to be carried out. The water-methanol mixtures were prepared by mixing known volumes of water and methanol. The viscosity of the mixtures was determined with a Ostwald viscosymetre at 25.00 \pm 0.05 $^{\circ}$ C.

Using a glass syringe with a stainless-steel 95 mm needle the capillary was filled with the active NaCl solution and an additional drop was placed at its top to prevent evaporation while the cell was allowed to reach thermal equilibrium and to avoid the immersion effect^{20,26}.

The time zero of the diffusion corresponds to the first contact between the active and the inactive solutions. The flow of inactive solution through the body of the diffusion cell was kept in the range of 3.5 to 6.0 ml/min depending on the viscosity of the solution being studied. The flow was maintained constant by means of a peristaltic pump. The diffusion cell as well as all parts of apparatus which contained solution were kept at 25.00 \pm 0.05 $^{\circ}$ C by an appropriate thermostatic system.

The decrease of the activity in the capillary was measured using an automatic data acquisition system. The activity was counted electronically during 600 s with time intervals of 7200 s between two consecutive countings. The 1.274 MeV γ ²²Na radiation peak²⁷ was monitored for a period of 5 days allowing 50 to 60 experimental points to be recorded. At the end of each experiment the flow was interrupted, the solution remaining of the body of the diffusion cell was

collected and the background radiation determined using a diffusion cell similar to the original one. The background counting was taken as the average of 10 measurements made in the same way as in the diffusion experiment. This procedure becomes necessary because during the diffusion time the originally inactive solution receives the $^{22}\text{Na}^+$ that leaves the capillary and is removed from its top.

Solution of the Diffusion Equation. Under constant temperature and pressure, Fick's second law may be written as

$$\frac{\partial C}{\partial t} = D \nabla^2 C - \lambda_r C \quad (1)$$

where λ_r is the decay constant of the radiotracer, D is the diffusion coefficient, t is the time and $C = C(\mathbf{r}, t)$ represents the concentration. The general boundary conditions for the diffusion of tracer species²⁸ across the section S are

$$\alpha C \Big|_S + \beta \frac{\partial C}{\partial n} \Big|_S = 0 \quad t > 0$$

where α and β are functions of the spatial coordinate \mathbf{r} and the differential is taken at normal direction to S .

Using the method of separation of variables, the general solution for equation (1) can be expressed as

$$C(\mathbf{r}, t) = b_0 \exp(-\lambda_r t) + \sum_{i=1}^{\infty} b_i R_i(\mathbf{r}) \exp[-(\lambda_i D + \lambda_r) t] \quad (2)$$

where λ_i are the eigenvalues associated with the eigenfunctions R_i . The coefficients b_i are determined from the initial condition and for the capillary method $b_0 = 0$.

Considering the symmetry of the present experiment the boundary problem consists of the unidimensional flow equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \lambda_r C \quad (3)$$

with boundary condition

$$\begin{aligned} C(x, t) &= 0 & x &= l \\ \partial C / \partial x &= 0 & x &= 0 \end{aligned}$$

and initial condition

$$C(x, 0) = C_0$$

where l is the capillary length and C_0 the initial concentration. The solution takes the form

$$\begin{aligned} C(x, t) = \sum_{n=0}^{\infty} (-1)^n \frac{4C_0}{(2n+1)\pi} \cos \left[\frac{(2n+1)\pi x}{2l} \right] \\ \times \exp \left\{ - \left[(2n+1)^2 \frac{\pi^2 D}{4l^2} + \lambda_r \right] t \right\} \quad (4) \end{aligned}$$

In the present work, ^{22}Na used as a radiotracer has a half-life of 2.6 years and a decay constant²⁷ of $8.4 \times 10^{-9} \text{ s}^{-1}$

and, when compared to a diffusion coefficient of the order of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, allows Equation 4 to be written as

$$C(x, y) = \frac{2C_0}{l} \sum_{n=0}^{\infty} \frac{(-1)^n}{\alpha_n} \cos(\alpha_n x) \exp(-\alpha_n^2 D t) \quad (5)$$

where $\alpha_n = (2n+1)\pi/2l$, $C_0 = C(x, 0)$, and D is the self-diffusion coefficient.

For a radioactive solution the number of counts is proportional to the radiotracer concentration, thus

$$A(t) = \int_0^l h(x) C(x, t) S dx \quad (6)$$

where $A(t)$ is the net activity in a capillary tube of uniform cross section S measured in a time t , $h(x)$ is the geometry dependent function experimentally determined. Eq. 6 is valid for all values of t , including $t = 0$. If A_0 is the activity for $t = 0$ then

$$\frac{A(t)}{A_0} = \frac{\int_0^l h(x) C(x, t) dx}{C_0 \int_0^l h(x) dx} = \frac{I_a}{C_0 I_b} \quad (7)$$

The integral in the denominator is easily evaluated since $h(x)$ is a polynomial of the type

$$h(x) = \sum_{i=0}^6 a_i x^i \quad (8)$$

where the coefficients a_i are determined experimentally. Hence the integral I_b results in

$$I_b = l \sum_{i=0}^6 \frac{a_i l^i}{(i+1)} \quad (9)$$

On the other hand, the solution of the integral I_a which appears in Eq. 7 yields

$$\begin{aligned} I_a = \frac{2C_0}{l} \sum_{n=0}^{\infty} \frac{\exp(-\alpha_n^2 D t)}{\alpha_n^2} \left[\sum_{j=0}^2 \frac{(-1)^j}{\alpha_n^{2j}} \sum_{i=2j+i}^6 \frac{a_i l^{i-2j} i!}{(i-2j)!} \right. \\ \left. + \sum_{i=0}^3 \frac{(-1)^i (2i)! a_{2i}}{\alpha_n^{2i}} \right. \\ \left. + (-1)^n \sum_{i=0}^2 \frac{(-1)^{i+1} (2i+1)! a_{2i+1}}{\alpha_n^{2i+1}} \right] \quad (10) \end{aligned}$$

Substituting equations (9) and (10) into equation (7) gives

$$\frac{A(t)}{A_0} = U(l) \sum_{n=0}^{\infty} W(n, l) \exp(-\alpha_n^2 D t) \quad (11)$$

where

$$U(l) = l \sum_{i=0}^6 \frac{a_i l^i}{(i+1)} \quad (12)$$

and

$$W(n, l) = \frac{2}{\alpha_n^2} \left[\sum_{j=0}^2 \frac{(-1)^j}{\alpha_n^{2j}} \sum_{i=2j+1}^6 \frac{a_i l^{2j} i!}{(i-2j)!} + \sum_{i=0}^3 \frac{(-1)^i (2i)! a_{2i}}{\alpha_n^{2i}} + (-1)^n \sum_{i=0}^2 \frac{(-1)^{i+1} (2i+1)! a_{2i+1}}{\alpha_n^{2i+1}} \right] \quad (13)$$

The functions $U(l)$ and $W(n, l)$ can be evaluated for a given capillary length; the activity $A(t)$ has to be determined experimentally as a function of time and, if A_0 is known, the diffusion coefficient can be obtained from Equation 11.

The determination of A_0 is not a trivial problem since it represents the total activity inside the capillary tube at the beginning of the experiment. A drop of the labelled solution has to be placed on top of the capillary tube in order to avoid evaporation of the solution inside the capillary as well as the immersion effect^{20,26} which results from the undesirable removal of radioactive tracer when the labelled solution comes into contact with the inactive one. Several techniques have been proposed²⁹⁻³² to overcome the problem of calculating A_0 . In the present paper the least squares technique proposed by Gosman and Tluchoř³² was used in order to calculate the diffusion coefficient D .

According to Eq. 11, the function that gives the best fit to the experimental points can be obtained by

$$H = \sum_{k=1}^m \left[A_k - A_0 U(l) \sum_{n=0}^{\infty} W(n, l) \exp(-\alpha_n^2 D t_k) \right]^2 \quad (14)$$

where k represents a particular measurement from a total of m measurements. The function H should be minimised for both A_0 and D by making $(\partial H / \partial D) = 0$ and $(\partial H / \partial A_0) = 0$ resulting

$$S_1 - A_0 U(l) S_2 = 0 \quad (15)$$

and

$$S_3 - A_0 U(l) S_4 = 0 \quad (16)$$

where

$$S_1 = \sum_{k=1}^m A_k t_k \sum_{n=0}^{\infty} \alpha_n^2 W(n, l) \exp(-\alpha_n^2 D t_k) \quad (17)$$

$$S_2 = \sum_{k=1}^m \left[\sum_{n=0}^{\infty} W(n, l) \exp(-\alpha_n^2 D t_k) \sum_{n=0}^{\infty} W(n, l) \alpha_n^2 t_k \exp(-\alpha_n^2 D t_k) \right] \quad (18)$$

$$S_3 = \sum_{k=1}^m A_k \sum_{n=0}^{\infty} W(n, l) \exp(-\alpha_n^2 D t_k) \quad (19)$$

$$S_4 = \sum_{k=1}^m \left[\sum_{n=0}^{\infty} W(n, l) \exp(-\alpha_n^2 D t_k) \right]^2 \quad (20)$$

From (15) and (16) is possible to write

$$S_1 S_4 - S_2 S_3 = 0 \quad (21)$$

Equation 21 can be solved by an iterative procedure such as the Newton-Raphson method leading to the diffusion coefficient. In order to solve (21) it is necessary to truncate the infinite series which is part of the equation. When $(D t_k / \alpha_n^2) > 0.25$ the series converges rapidly²¹ and only the first term needs to be considered. For the present experiment that condition is achieved after 35 hours of diffusion. Alternatively, by using the first five terms of the summation it is possible to start the measurements 8 hours after the diffusion begins since after this time perturbations due to any initial turbulence have already ceased and a steady state for the background in the diffusion cell has been achieved

Results and Discussion

The efficiency of the proposed technique has been tested with the system ²²NaCl-NaCl-water for which reliable results obtained by different methods are available in the literature. The self-diffusion coefficient of Na⁺ in NaCl aqueous solution, 0.1 mol/dm³ at 25.00 ± 0.05 °C, was determined and the result is presented in Table 1.

The results obtained for the system ²²NaCl-NaCl-water show that the proposed modification to the open-ended capillary method is satisfactory. The method was employed for the study of the system ²²NaCl-NaCl-water-methanol in order to verify the diffusive behaviour of ²²NaCl in mixed solvents. The viscosity of water-methanol mixtures is a function of composition and shows a maximum at 38.61% in weight of methanol (11.4 mol/dm³). Although the system NaCl-water-methanol is a ternary system with four diffusion coefficients D_{11} , D_{22} , D_{12} and D_{21} according to Onsager's theory³⁵, Woolf *et al.*⁵ employing an analogous system showed that they have a *pseudo-binary* behaviour since D_{12} and D_{21} are small when compared with D_{11} and D_{22} . Thus, the hypothesis of pseudo-

Table 1. Self-diffusion coefficients of Na^+ in aqueous NaCl 0.1 mol/dm^3 , 25°C

$D \times 10^{-9} \text{ m}^2/\text{s}$	Reference
1.278 ± 0.005	a
1.284 ± 0.006	b
1.278 ± 0.002	c

a - This work, average (error = σ)

b - Reference 33, closed capillary method

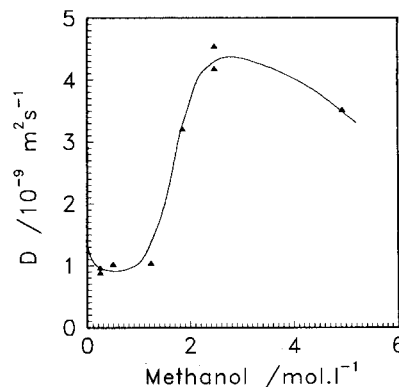
c - Reference 34, open-ended capillary method

binary behaviour for 1:1 electrolytes at low concentration in mixed solvents can also be applied to the present work.

The results for the diffusion coefficients of $^{22}\text{NaCl}$ in water-methanol mixtures are presented in Table 2. In the present work a peculiar behaviour of the diffusion coefficient of Na^+ in mixtures water-methanol has been found. In the range of methanol concentrations employed the plot D versus concentration of methanol, Figure 3, shows a minimum near 0.3 mol/dm^3 of methanol and a maximum near 2.5 mol/dm^3 . However, in the range of composition of the mixtures water-methanol employed, between 0.8 and 34.6 % in weight of methanol, the solvent viscosity increases as the weight fraction of methanol increases. It would be expected that for any mixture water-methanol in this range the self-diffusion coefficient were progressively smaller than $1.278 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Such behaviour was already described in the literature. Steel *et al.*³⁶ studied the mobility of individual ions in mixtures of water and non-electrolytic solvents at 25°C such as water-glycerol, water-manitol and water-sucrose in weight proportion of 10 % and 20 % of non-electrolyte. They verified that the individual mobility of ions decreases with the addition of non-electrolytic substances and the magnitude of the effect depends on the quantity added. They also concluded that the bigger the ion the more important the decrease of the mobility. Using the conductimetric method Kulkarni and Lyons³⁷ observed that the diffusion coefficient of KCl decreased with

Table 2. Self-diffusion coefficients of Na^+ in water-methanol NaCl 0.1 mol/dm^3 , 25°C .

Methanol (mol/dm^3)	Methanol (%)	$D \times 10^{-9} \text{ m}^2/\text{s}$
0.247	0.8	0.885
0.247	0.8	0.964
0.494	1.6	1.023
1.235	4.0	1.041
1.852	6.0	3.208
2.470	8.1	4.546
2.470	8.1	4.178
4.940	16.5	3.514

**Figure 3.** Variation of the self-diffusion coefficients of Na^+ in water-methanol NaCl (0.1 mol/dm^3) mixtures as a function of the methanol concentration at temperature of 25°C .

the increase of weight fraction of methanol in the mixtures 10%, 20% and 38,61% at 25°C . Leist and Lyons³⁸ extended the work of Kulkarni and Lyons for different systems such as KCl -water-methanol (40%), HCl -water-methanol (10%, 20%, 40%) and KCl -water-*t*-butanol (9.54%, 17.80%). In all systems they found that the diffusion coefficient decreases with the increase of alcohol concentration in the system. The diffusion of non-electrolytic substances were also studied using different methods and solvents^{2,14,15} and it was observed that the maximum viscosity of the system corresponds to a minimum diffusion coefficient.

A qualitative model can be formulated to explain the behaviour of the self-diffusion coefficient as a function of the methanol concentration in the mixed solvent based on two distinctive and opposite effects: the viscosity of the solvent and the hydration effect. When excessive distortion in the structure of the solvent is not present, the limiting mobility $\omega_i^o = D_i^o/kT$ of a particle i is expressed as

$$\omega_i^o = \frac{A_i}{\eta_o}$$

where η_o is the viscosity of the pure solvent, A_i is a constant characteristic of the diffusing species and $A_i = 1/6\pi r_i$ for a spherical particle according to Stokes-Einstein relationship $D_i = kT/6\pi\eta_o r_i$. Independently of the shape of the particle its mobility depends on $1/\eta_o$. Therefore, the decrease of the self-diffusion coefficient between 0 and 0.3 mol/dm^3 of methanol is associated with the increase of the solvent viscosity. In this range of concentration the fully hydrated Na^+ is present in the solution. Since the methanol concentration increases there is a variation in the structure of the diffusion species, i.e. the Na^+ loses hydration water. Wang³⁹ defined the hydration number, also called simply hydration, as the statistically averaged number of water molecule carried by the ion when the latter diffuses through solution. For each ionic strength this hydration number is constant and the size of the hydrated ion can also be considered as a constant. Although the increasing of the viscosity of the solvent would decrease the diffusion coefficient, in the range 0.3 to 2.5 mol/dm^3 of methanol the self-diffusion coefficient increases as a consequence of the change in the hydration of the cation.

In other words, the size of the species varies from fully hydrated to non-hydrated. The diffusion coefficient depends on the volume of the molecule^{11,40,41}. Methanol is a highly hygroscopic solvent and is reasonable to consider that the hydration of cations in methanol solutions depends on the methanol concentration. The greater the concentration of methanol, the smaller the volume of the hydrated ion and the greater its mobility. The cations Li⁺ and Cs⁺ in aqueous solution are extreme examples. The small anhydrous Li⁺ is highly hydrated and its radius is greater than the Cs⁺ weakly hydrated. The distortion in the local structure of the water caused by hydrated Li⁺ should be smaller than that corresponding to the hydrated Cs⁺. This excessive distortion in the structure of the water surrounding Cs⁺ appears as a decreasing of local viscosity and hence increasing of the mobility of Cs⁺. In the range of 0.3 to 2.5 mol/dm³ the effect of decreasing the hydration of the Na⁺ is greater than the increasing of the viscosity of the medium itself.

For concentrations bigger than 2.5 mol/dm³ of methanol the self-diffusion coefficient decreases as a consequence of the increasing of the viscosity of the solution and Na⁺ non-hydrated is present for any proportion of water-methanol.

Thus, the diffusive behaviour of the ion Na⁺ in mixed solvent water-methanol can be explained taking into account not only the solvent viscosity but also the hydration number of the diffusing species.

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