Measurement of diffusion coefficients of thallium ion in H_2O and D_2O systems at different concentrations

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Abstract. Sliding cell method, developed in our laboratory, has been used to measure the inter diffusion coefficient of thallium ion in thallous sulphate solution over a wide concentration range using both water and heavy water as solvent at 35°C. The results have been analysed from the point of view of both ion–ion and ion–solvent interactions. The comparison of the diffusivities of the same ion in D_2O and H_2O electrolyte solutions at the same temperature indicate that the addition of salt affects the two solvents differently.

1. Introduction

The interest in diffusion phenomena arises from both fundamental and applied points of view and the correlation of macroscopic parameter like diffusion coefficient with local density fluctuations is an important problem. In recent years there have been many developments in the study of diffusion phenomena both theoretically and experimentally. The difficulty in the study of liquids lies in the fact that kinetic energy and potential energy of the constituent particles in a liquid are comparable and both must be taken into account to calculate any property which is to be compared with observed results. In general by employing techniques which increase the thermal motion of constituent particles or by varying the composition of the binary or ternary systems much information can be gathered about liquids and in this respect diffusion study in liquids is an important tool.

In the case of experiments with electrolytic solutions the composition can be varied by changing the concentration of the solution. Electrolytes when dissolved in aqueous systems dissociate into ions. In most cases, the analysis of the experimental findings centred practically on ion–ion interactions with almost no emphasis on ion–solvent interactions [Harned and Owen 1954; Bennetto and Spitzer 1976; Passiniemi 1983]. This picture is almost true in case of infinite dilute region but in practice, as soon as concentration increases, the dipole orientation of the solvent molecules to an ion changes and consequently the ion–solvent interaction becomes important to influence the mobility of ions. Here we are trying to see both ion–ion and ion–solvent effects by measuring the diffusion coefficient of one ion in both water and heavy water systems over a wide concentration range.

All the tracer methods used for the study of diffusion utilize two properties of the radioactive isotopes: 1. they emit radiations which can be easily detected and 2. for most purposes they can be treated equivalent to their nonradioactive counterparts. In our technique we measure the time dependence of what is an effectively weighted spatial average of radioactivity in the liquid systems. This very consistent and accurate method enabled us to measure the concentration dependence of isotopic diffusion in various liquid systems within $\pm 1\%$ accuracy.

2. Experimental

A radioactive tracer technique was developed in our laboratory for the study of diffusion in liquids [Changdar 1973]. The technique is based on sliding cell mechanism and the experimental geometry consists of radioactive and nonradioactive columns of equal lengths with radioactive detector placed vertically over the diffusion column. The fundamental differential equation of diffusion in an isotropic medium is given by,

$$\frac{\delta c(x,t)}{\delta t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right)$$

where c is the concentration of the diffusing substance and D is the diffusion coefficient. We consider only the one-dimensional flow in the x direction and our boundary conditions are,

$$\text{at } t = 0, \ c = c_0 \qquad x = 0 \text{ to } x = l$$
$$c = 0 \qquad x \geqslant l \text{ to } x = 2l$$
$$\left.\frac{\delta c}{\delta x}\right|_{x=0} = \left.\frac{\delta c}{\delta x}\right|_{x=2l} = 0$$
$$\text{at } t \rightarrow \alpha, \ C = C_0\frac{l}{2l} = \frac{C_0}{2}.$$

The solution of Fick's law under these boundary conditions gives the distribution of radioisotopes in the liquid system at any time and the integrated weighted average of $c(x,t)$ can be converted to the number of counts detected by the radioactive detector at any time interval. This in turn gives the working formula which is utilized for the present measurement [Chakraborti and Changdar 1991; Das and Changdar 1991] as

$$N_0 - N_t = B\exp(-kt)$$

where N_0 is the total saturation count taken over time τ, N_t is the total count taken at time t over the same interval τ and noting the saturation count when the liquid column is completely mixed up mechanically, the diffusion coefficient D can be evaluated directly from the value of k.

For the present set of measurements [204]Tl is the tracer and the solutions of thallous sulphate in water and heavy water are the liquid systems. Thallous sulphate solution has been used over a wide range of concentration (1 mg/cc $-$ 40 mg/cc) and the temperature kept fixed at $35 \pm 0.1°C$.

At first the aqueous solution of the experimental electrolyte is prepared for any

Table 1. Values of diffusion coefficients of thallium ion in thallous sulphate solution using H_2O and D_2O as solvents.

Concentration in mg/cc	Concentration in mol/l(C)	$\frac{\sqrt{C}}{\text{in}}$ $\sqrt{\text{mol/l}}$	$D \times 10^5$ in cm^2s^{-1}	
			D_{H_2O}	D_{D_2O}
40	0·079	0·282	1·37 ± 0·004	1·11
30	0·059	0·244	1·40	1·15
20	0·040	0·199	1·44	1·19
15	0·030	0·172	1·51	1·21
10	0·020	0·141	1·55	1·25
5	0·010	0·100	1·60	1·39
4	0·008	0·089	1·67	1·43
2	0·004	0·063	1·73	1·51
1	0·002	0·044	1·81	1·61

chosen concentration by the weighing method. The radioactive part is prepared by introducing [204]Tl within it. The diffusion experiment is performed by superposing the upper column of H_2O and D_2O system over the radioactive part. To get the consistent values of D, each experiment is repeated for each particular concentration at least thrice with different diffusion column length and diameters. The diffusion coefficients are given in table 1.

3. Results

Experimental investigation clearly shows a decrease of diffusion coefficient with increasing concentration both in D_2O and H_2O. The resulting $D - \sqrt[3]{C}$ curves are shown in figure 1. The diffusion coefficient of the same ion at same temperature is higher in H_2O medium compared to the D_2O medium and this trend is seen throughout the concentration range (about 16% at 5 mg/cc and about 22% at 40 mg/cc).

4. Discussion

The diffusion process at lower concentrations obey Nernst's limiting law but at higher concentration it can be explained only by Onsager's phenomenological theory. The calculation of Nernst's limiting value of diffusion coefficient of thallium ion in thallous sulphate solution using H_2O as the solvent gives,

$$D^0(H_2O) = \frac{2RT}{F^2}\left(\frac{u_1 u_2}{u_1 + u_2}\right) = 2·05 \times 10^{-5} cm^2 s^{-1}$$

where u_1, u_2 give the mobility of ionic species at infinite dilution. In the case of Tl_2SO_4 solution in D_2O, due to the inadequacy of the mobility data of ionic species at infinite dilution, we can calculate Nernst's limiting value approximately by multiplying $D^0(H_2O)$ by $\sqrt{M_{H_2O}/M_{D_2O}}$ where M_{H_2O} is the molecular weight of water and M_{D_2O} that of D_2O. Calculation shows that $D^0(D_2O) = 1·945 \times 10^{-5} cm^2 s^{-1}$.
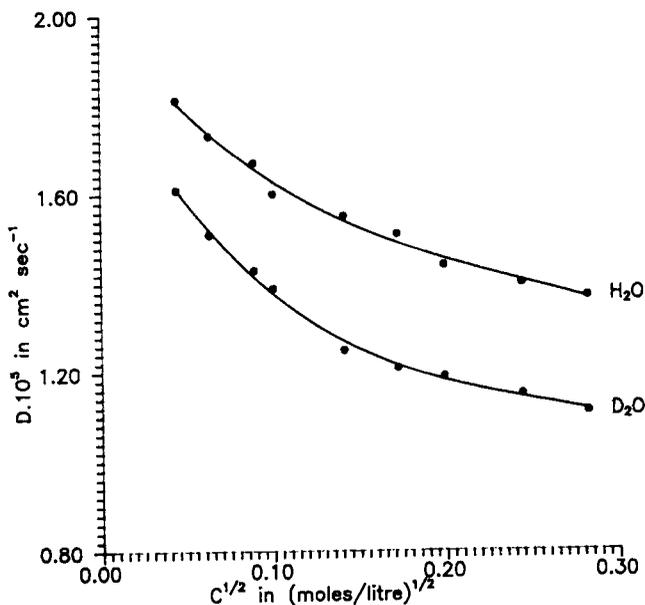
Figure 1. D versus $\sqrt{C}$ curve for thallium ion in thallous sulphate solution using H_2O and D_2O as solvents.

Extrapolating our experimental curves, the obtained values of diffusion coefficients at zero concentration are,

$$D^0_{H_2O}(\text{Expt}) = 2.003 \times 10^{-5} \text{cm}^2\text{s}^{-1} \text{ and}$$
$$D^0_{D_2O}(\text{Expt}) = 1.886 \times 10^{-5} \text{cm}^2\text{s}^{-1}$$

which are surprisingly close to Nernst's limiting value for both D_2O and H_2O systems. The difference in diffusion coefficient in H_2O and D_2O systems may be due to the difference in mass of two solvent systems, but only mass difference cannot account for the variation of D in the two systems as shown in figure 1. The work of Ostroff *et al* (1969) indicated fundamental changes in the structure of the solvents upon the dissolution of a salt which was evident from their viscosity measurements. Comparison of the diffusion coefficients obtained in our laboratory also show the same fact. The diffusion data at various concentrations of the solute indicate that the molecular displacements are greater in H_2O system in comparison with D_2O system. These findings are again consistent with the larger viscosity and longer relaxation time of D_2O [Woessner *et al* 1968]. Thus we may conclude that over the wide concentration range both ion–ion and ion–solvent interactions play a fundamental role in deciding the mobility of the ions and hence the measured diffusion coefficients.

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