

Strong evidence of an isotope effect in the diffusion of a NaCl and CsCl solution

Haimanti Chakrabarti

Solid State and Molecular Physics Division, Saha Institute of Nuclear Physics, 1/AF Bidhan nagar, Calcutta 700 064, India
(Received 16 September 1994; revised manuscript received 28 November 1994)

The existence of isotope effect in liquid diffusion is thoroughly investigated in aqueous solutions of NaCl and CsCl. The tracer diffusion coefficients with different isotopes of the same species are measured by the sliding-cell technique. The experimental data show strong evidence of the existence of an isotope effect in the diffusion of a NaCl and CsCl solution.

The phenomenon of diffusion, a fundamental rate process occurring in every physicochemical reaction, is a subject of great topical interest. There is a well-known controversy about the existence of the isotope effect in liquid diffusion¹ and still today it is not known whether this effect can be neglected or not. Many experimental investigations were carried out in this field, but none of them could provide conclusive evidence in favor of the isotope effect. The radioactive tracer technique is one of the sensitive tools which involves the use of isotopically labeled radioactive species for the measurement of the diffusion coefficients in liquids. If the isotope effect has any contribution, the mass change due to the labeling of the molecules with suitable radioactive isotopes will cause the measured tracer diffusion coefficient to differ from the true self-diffusion coefficient. This aspect needs a thorough investigation with different liquid systems. We chose the aqueous solution of the two most interesting binary electrolytes, NaCl and CsCl, in one of which the cations (Na) has a structure-forming capacity and other (Cs) has a structure-breaking capacity. This enables us to study the isotope effect in binary electrolytes of opposite cationic properties. An appreciable difference in the tracer diffusion coefficients of different isotopes for the same system at the same concentration is found which provides strong evidence for the existence of the isotope effect in the diffusion of aqueous NaCl and CsCl.

A critical survey through the literature about previous studies on the isotope effect reveals that Miller's work² of isotopic separation of lithium isotopes by diffusion in an aqueous solution leads to the conclusion that the lighter isotope (⁶Li) diffuses more rapidly than the heavier isotope (⁷Li). The observation is congruent with the findings of some other groups³⁻⁶ from their work on liquid ⁶Li and ⁷Li. The ratios of the self-diffusivities of ⁶Li and ⁷Li are found to be significantly greater than the square root of the inverse mass ratio. Feinauer *et al.* have parametrized the isotope effect from diffusivity studies on ⁶Li and ⁷Li.⁶ Their values are compatible with the ratio of self-diffusivities of ⁶Li and ⁷Li as obtained from a quantum mechanical calculation by Omini⁷ based on the pseudopotential method. Pikal⁸ studied the diffusion coefficient ratio of the ions ²²Na and ²⁴Na in a 0.1M NaCl solution and found that the lighter isotope diffused slightly more rapidly than the heavier one, the ratio of the diffusion coefficient of ²²Na to ²⁴Na being 1.002. He also found that the ratio to be 1.004 for sodium diffusion in 10M LiBr solution. These works show ($D_l - D_h$)

is greater, though not by much, than the experimental error. (D_l and D_h are the diffusion coefficients of light and heavy isotopes.) This led Pikal to conclude that the isotope effect is real. There is a report of a slightly higher value of the ratio of the diffusion coefficients for sodium isotopes by Barr and Elmessierey⁹ in 0.034M NaCl, done by a gel sectioning technique. Mills reported¹⁰ the diffusion of ¹³⁷Cs and ¹³⁴Cs in an aqueous solution of potassium chloride at 0.5M concentration to be 1.935×10^{-9} and $1.930 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, and concluded against the existence of the isotope effect.

We have measured the tracer diffusion coefficients in NaCl-H₂O (with tracer ²²Na) and CsCl-H₂O (with tracer ¹³⁷Cs) by a sliding cell technique at a temperature of 25 °C by varying the diffusing species in the course of the experiments. In short, the experimental geometry consists of two liquid columns, radioactive and nonradioactive, of equal length and equal cross section superposed over each other and the detector is placed vertically over it. The diffusion measurements of the two isotopes for any particular concentration were carried out in the electrolyte separately under the same physical conditions. The details of the experimental setup and derivation of the working formula are same as described in the Refs. 11 and 12 but the diffusing species are varied in the course of the experiments. Each datum reported in Tables I-III is the mean of at least three consecutive sets of experiments. Table I contains the diffusion coefficients of ²²Na in an aqueous solution of sodium chloride over the concentration range 0.0004M - 4.786M and the third column of Table III contains that of ¹³⁷Cs in an aqueous solution of cesium chloride over the concentration range 0.009M - 10.0M. In the literature there are separate sets of the ²²Na diffusion data in the aqueous solution of sodium chloride measured by the radioactive tracer techniques. We examine (Fig. 1) all these data thor-

TABLE I. Tracer diffusion coefficients of ²²Na in an aqueous sodium chloride solution.

Conc. (mol dm ⁻³)	Diff. coeff. (10 ⁻⁹ m ² s ⁻¹)	Conc. (mol dm ⁻³)	Diff. coeff. (10 ⁻⁹ m ² s ⁻¹)
0.0004	1.326	0.7749	1.199
0.0025	1.312	1.0680	1.125
0.0098	1.302	1.4242	1.046
0.0401	1.283	1.7091	1.009
0.0900	1.267	2.4444	0.953
0.2521	1.240	3.4190	0.910
0.4897	1.228	4.7863	0.804

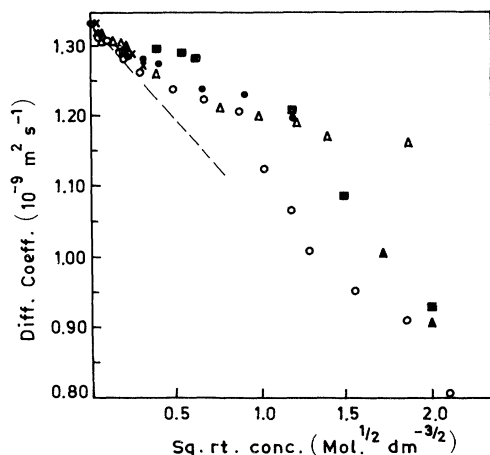


FIG. 1. Variation of the ^{22}Na tracer diffusion coefficient (in an aqueous sodium chloride solution) with the square root of concentration by different workers: \circ , author's data; \bullet , data of Passiniemi; \times , data of Mills and Godbole; \blacksquare , data of Mills and Adamson; \triangle , data of Nielsen *et al.*; \blacktriangle , data of Wang and Miller (Ref. 28).

oughly before coming to a conclusion about the isotope effect in the present investigation. It seems from Fig. 1 that all these sets of data are in excellent agreement in the dilute region (0.0–0.1M). In this range the most accurate set of data as judged by Mills and Lobo¹³ fits to a polynomial (in $c^{1/2}$), $10^9 D = 1.334 - 0.2706c^{1/2} + 0.4651c - 0.5003c^{3/2}$, and our data fit to the polynomial, $10^9 D = 1.334 - 0.2697c^{1/2} + 0.4417c - 0.5333c^{3/2}$. Both these polynomials are of the same nature, the coefficients differing by a very small fraction. These polynomials reduce to the limiting equations $10^9 D = 1.334 - 0.271c^{1/2}$ and $10^9 D = 1.334 - 0.270c^{1/2}$, respectively, which are in close agreement with Onsager's limiting equation $10^9 D = 1.334 - 0.268c^{1/2}$.

For ^{22}Na diffusion in the low and moderate high concentration range, the experimental data obtained by Passiniemi¹⁴ are judged¹³ to be "the best" among all other sets which so far been reported. The data of Passiniemi¹⁴ and Nielsen *et al.*¹⁵ do not agree with the plateau of Mills and Adamson's data¹⁶ in the concentration range 0.16M–0.425M and suggests the latter are erroneously high. Our findings agree with the results of Passiniemi and Nielsen. In the concentration region from 0.1M to 0.9M our data agree with the values obtained by Passiniemi (within 7%) but not with the data of Mills and Adamson and of Mills and Godbole.¹⁷ The data of the last two groups in the region 0.1M–0.8M are higher. However, above the concentration 1.0M the trend of Passiniemi's data, measured only at 1.44M, significantly deviates from our findings. The data of Passiniemi at concentration 1.44M are in agreement with the data of Nielsen *et al.* and Mills and Adamson. Both these groups used the diaphragm cell technique, among which that used in the work of Mills and Adamson suffered from an error in the process of calibration and the data of Nielsen *et al.* are in severe disagreement with recent, more reliable measurements.¹³ In view of the unreliability of the data of Nielsen *et al.*, we carried out a thorough investigation in and above this region since no

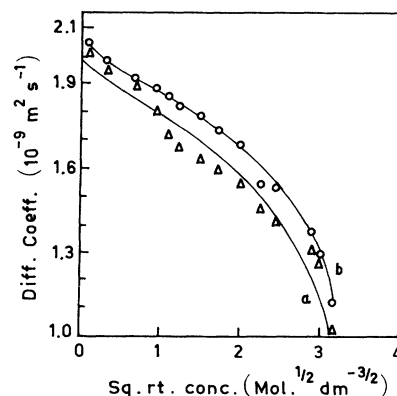


FIG. 2. Variation of the cesium tracer diffusion coefficients: (a) ^{137}Cs (triangles) and (b) ^{134}Cs (circles), with the square root of concentration.

conclusion can be drawn from the single measurement of Passiniemi at 1.44M. Figure 2(a) shows the concentration dependence of the ^{137}Cs diffusion coefficients over the concentration range 0–10.0M. Figure 2(b) represents the ^{134}Cs diffusion coefficients in the same system by the same technique at the same temperature (25°C). Both these curves represent the best-fitted polynomial to the respective experimental data. Until now no other workers have measured ^{137}Cs diffusion in an aqueous solution of cesium chloride. However, since the general trend of the diffusion pattern of ^{137}Cs in a CsCl aqueous solution is very much similar to that previously reported for ^{134}Cs ,¹² the structural explanation given in connection with those data is also valid for ^{137}Cs diffusion. A detailed analysis of the ^{134}Cs diffusion coefficients in an aqueous cesium chloride solution in comparison with four other sets of existing data has been given in an earlier work.¹²

By obtaining the positive results of reproducibility of the earlier data^{11,12} (in the same physical conditions) at several concentrations, the presently obtained diffusion data of ^{22}Na in aqueous solutions of NaCl and ^{137}Cs in aqueous solutions of CsCl are coupled with the diffusion data of ^{24}Na in NaCl solutions and ^{134}Cs in CsCl aqueous solutions in Tables II and III. From these tables it is seen that there is an appreciable difference between the tracer diffusion coefficients of different isotopes of the same species in the same system at the same concentration and at the same temperature. As we try to make a search for the possible sources for this difference, we find that these differences are above any sort of experimental error. The temperature is always kept at $(25 \pm 0.01)^\circ\text{C}$, and so these differences are not arising out of any tempo-

TABLE II. Tracer diffusion coefficients of isotopic heavy ions in an aqueous sodium chloride solution. Mass effect = square root of the ratio of the masses (heavy:light) = 1.0445.

Concentration (mol dm ⁻³)	Mean diff. coeff. (10 ⁻⁹ m ² s ⁻¹) for $^{22}\text{Na}(D_l)$	for $^{24}\text{Na}(D_h)$	D_l/D_h
1.068	1.125	0.990	1.130
1.424	1.046	0.935	1.119
1.709	1.009	0.908	1.111
2.444	0.953	0.871	1.094
3.419	0.910	0.846	1.075
4.786	0.804	0.760	1.058

ral effect. Precautions were taken while using the tracers ^{134}Cs and ^{137}Cs so that no systematic error can creep into the process due to the difference in their characteristic radiations. In experiments using ^{24}Na tracer, the count rate obtained is corrected for a short half-life. Particular care is also taken about the purity of the radioactive sample to ensure the absence of any systematic error. The initial tracer concentration is kept (practically) same for each set of experiments. The random error due to statistical fluctuations in the counting data is found to be less than $\pm 0.2\%$ on an average. So these departures are attributed only to the difference in diffusing species which are the isotopes. It is also seen from the tables that the ratio of the diffusion coefficients is not equal to the mass effect. Thus the data present strong evidence for the isotope effect in the diffusion of NaCl and CsCl. The effect is more pronounced in the sodium chloride system than in the CsCl system. In the case of the NaCl system the maximum difference is 7.78% whereas in the case of CsCl it is 4.4%. This indicates that the effect is dependent directly on the charge density and inversely on the size of the diffusing ion. However, the higher value for the NaCl system may arise due to the hydration effect. Actually for both systems there is a different but appreciable isotope effect above certain concentrations and this effect is certainly greater than the mass effect. These concentrations are much above the dilute range of concentration and therefore fall in the domain where the Debye-Hückel picture is unable to give a realistic analysis and back scattering becomes important. The diffusion of the ion in the solutions at concentrations much above the D - H range can be pictured as the motion of an aggregate (composed of the ion and water, whose size fluctuates with time¹⁸) i.e., polyatomic molecules, the diffusion of which must involve translation-rotation coupling.

As mentioned earlier, Pikal carried out diffusion experiments with the tracers ^{22}Na and ^{24}Na in aqueous solutions of sodium chloride at 0.1M concentration (where the size of the isotope effect will plausibly be very low) simultaneously in a diaphragm cell and evaluated directly the ratio of the diffusion coefficients but the absolute value of the diffusion coefficients of ^{22}Na and ^{24}Na was

TABLE III. Tracer diffusion coefficients of isotopic heavy ions in an aqueous cesium chloride solution. Mass effect = square root of the ratio of the masses (heavy:light) = 1.011.

Concentration (mol dm ⁻³)	Mean diff. coeff. (10 ⁻⁹ m ² s ⁻¹) for $^{134}\text{Cs}(D_l)$	for $^{137}\text{Cs}(D_h)$	D_l/D_h
0.009	2.045	2.024	1.010
0.100	1.981	1.952	1.012
0.426	1.919	1.890	1.015
0.903	1.879	1.798	1.045
1.200	1.849	1.716	1.077
1.500	1.817	1.672	1.087
2.267	1.784	1.632	1.093
3.000	1.738	1.592	1.091
4.000	1.683	1.546	1.089
5.000	1.546	1.466	1.088
6.002	1.531	1.421	1.077
8.410	1.381	1.309	1.055
9.000	1.301	1.259	1.033
10.00	1.118	1.097	1.019

not determined. Thus we cannot crosscheck the diffusion data for ^{22}Na in 0.1M NaCl. As we have no data for ^{24}Na in a 0.01M NaCl aqueous solution we had no opportunity to clarify whether the ratio D_l/D_h has the same value as in our case or not. Actually there is no other set of ^{24}Na diffusion data. It seems necessary to mention that in a former work¹¹ ^{24}Na diffusion data were compared with that of ^{22}Na , because, until then the author had no direct experience of the existence of the isotope effect, but on the basis of the data of Pikal and the work of Liukkonen,¹⁹ the aqueous solution of sodium chloride had been treated as a ternary system (NaCl-H₂O- Na*Cl) while Onsager's transport coefficients were calculated.

There has been no report of ^{137}Cs diffusion in aqueous solutions of cesium chloride until now. Mill's data¹⁰ regarding diffusion of cesium should not be compared with ours because the environment is different in this case and such a change leads to an appreciable difference in the diffusion coefficients.²⁰ Furthermore, from simple kinematics it is inferred that for a potassium ion having mass 39, it is difficult (practically impossible) to make a distinction between cesium ions of masses 134 and 137. So the tracer diffusion coefficients measured by ^{134}Cs and ^{137}Cs in aqueous solutions of potassium chloride solution are almost the same. However, for a cesium ion of mass 133 it is easier to differentiate between the impacts with ions of masses 134 and 137, which is reflected in the diffusion data measured by ^{134}Cs and ^{137}Cs in aqueous solutions of cesium chloride. We obtained the diffusion coefficient of ^{134}Cs in a 0.5M KCl aqueous solution to be $1.962 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, while studying the effect of the environment on the transport of charge in ionic liquids (Fig. 3). As the experiment was repeated with ^{137}Cs , the diffusion coefficient came to be $1.957 \times 10^{-9} \text{ m}^2\text{s}^{-1}$. Thus the differences in these two sets of data for the two tracers are, respectively, $0.005 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ (Mill's work) and $0.007 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ (author's work); i.e., they are in good agreement. Although the two sets of measurements were carried out by two different techniques the results agree within 1.5%.

Several possible explanations of this departure have already been suggested. Friedman,²¹ Pople,²² and McLaughlin²³ carried out theoretical studies in the framework of a linear response to explain the experimental data. But the failure of linear response theory beyond the concentration range of 0.1M demands the introduction of the concept of a nonlinear response to avoid the

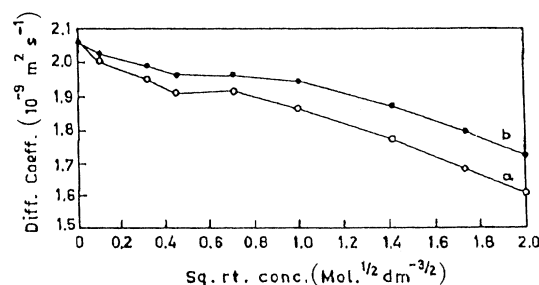


FIG. 3. Tracer diffusion coefficient of ^{134}Cs in different environments: in (a) an aqueous solution of cesium chloride (solid circles) and (b) in an aqueous solution of potassium chloride (open circles).

“great simplification of the collision kernel by assuming their eigenvalues are all degenerate except the zero eigenvalue.” An analysis arising from the correct choice of factors, (i) the nature of the intermolecular potential and (ii) the mode of energy transfer, can give the exact cause of the difference in the diffusion coefficients due to the isotopic mass difference.

Among the aforesaid two factors, the correct choice of the first one is very delicate because it requires a complex theoretical basis, which is not yet available. As far as the choice of mode of energy transfer is concerned, a positive improvement can be achieved with the introduction of the concept of an inelastic collision. The self-diffusion coefficients (or their practical alternatives, tracer diffusion coefficients) actually mean the translational diffusion coefficients in a system consisting of physically and chemically indistinguishable molecules, though for the sake of simplicity in the description of diffusion, only the translational motions (elastic collision) are considered, but in practical cases there is every possibility of rotational motions of the ions (electrolytes) or molecules (molecular liquids). This rotational motion (whatever may be the degree) will have a definite contribution towards the translational motion. So the coupling of rotational and translational motion will play an important role in a more realistic analysis of the diffusive motion. The unusual large isotope effect in the self-diffusion of hydrochloric acid²⁴ is evidence towards the existence of such translation-rotational coupling. Such coupling is also strongly supported by the molecular dynamic simulations of Evans *et al.*²⁵ The existence of a strong coupling between the translational and rotational motions means a change of moment of inertia (I) which would result in a change of the translational motion and hence a change in the diffusion coefficient. So Pople and McLaughlin correctly

suggested that the transport coefficients are dependent of the square root of the moment of inertia ($I^{1/2}$) instead of $m^{1/2}$, if I_h and I_l are the moment of inertia of the aggregate around the heavy and light isotopes. The relationship $(I_h/I_l)^{1/2} = D_l/D_h$ successfully explains the remarkable difference in the diffusion coefficients of water and D₂O. The relation is also found to be justified in the isotopic diffusion of molecular liquids.²⁶ Lowering of the isotope effect with increase of concentration (evidenced from the data of both the tables) can also be explained from the moment of inertia concept. With an increase of concentration the hydrogen bond lengths are shortened under the influence of Coulombic fields of cations.²⁷ This results in a smaller difference in the moment of inertia of the aggregates surrounding the two isotopes.

In light of the above observations and analyses we come to the conclusion that there is strong evidence of the isotope effect in the diffusion of aqueous solutions of NaCl and CsCl when the concentration is much above the $D-H$ range. In this context it is therefore essential to make a search for a complex theoretical basis acting as an alternative for the electrolyte solutions. Such a basis should take account of the nonlinear response, structuredness (affinity to have or form structure), especially the quasi-lattice in very concentrated electrolyte solutions, strong coupling between the translational and rotational motion of the particles, a realistic mode of energy transfer and inelastic collision, and preferential solvation of the system. A correct choice and a detailed analysis will throw new light on the isotope effect and thereby on the structure and dynamics of aqueous electrolytes.

The author gratefully acknowledges C.S.I.R. (India) for funding the work.

-
- ¹ H.J.V. Tyrrell and K.R. Harris, *Diffusion in Liquids: A Theoretical and Experimental Study* (Butterworths, London, 1984), p. 311.
- ² L.J. Miller, Ber. Bunsenges. Phys. Chem. **75**, 206 (1971).
- ³ N.T. Ban, C.M. Randall, and D.J. Montgomery, Phys. Rev. **128**, 6 (1962).
- ⁴ L. Löwenberg and A. Lodding, Z. Naturforsch. A **22**, 2077 (1967).
- ⁵ J.S. Murdy and R. Cotts, Z. Naturforsch. A **26**, 85 (1971).
- ⁶ A. Feinauer, G. Majer, and A. Seeger, J. Phys. Condens. Matter **6**, 355 (1994).
- ⁷ M. Omini, Philos. Mag. A **54**, 561 (1986).
- ⁸ M.J. Pikal, J. Phys. Chem. **76**, 3038 (1972).
- ⁹ L.W. Barr and M.A.M.I. Elmessiry, Nature **281**, 553 (1979).
- ¹⁰ R. Mills, Nature **256**, 638 (1975).
- ¹¹ H. Chakrabarti and S.N. Changdar, Appl. Radiat. Isot. **43**, 405 (1992).
- ¹² H. Chakrabarti, Appl. Radiat. Isot. **45**, 171 (1994).
- ¹³ R. Mills and V.M.M. Lobo, *Self Diffusion Data in Electrolyte Solutions* (Elsevier, Amsterdam, 1989).
- ¹⁴ P. Passiniemi, J. Soln. Chem. **12**, 801 (1983).
- ¹⁵ J.M. Nielsen, A.W. Adamson, and J.W. Cobble, J. Am. Chem. Soc. **74**, 446 (1952).
- ¹⁶ R. Mills and A.W. Adamson, J. Amer. Chem. Soc. **77**, 3454 (1955).
- ¹⁷ R. Mills and E.W. Godbole, J. Amer. Chem. Soc. **82**, 2395 (1960).
- ¹⁸ H.G. Hertz, M. Holz, and R. Mills, J. Chim. Phys. (France) **71**, 1355 (1974).
- ¹⁹ S. Liukkonen, Acta Polytechn. Scand. Chem. Incl. Metall. Ser. **113**, 36 (1973).
- ²⁰ H. Chakrabarti (unpublished).
- ²¹ H.L. Friedman, in *Molecular Motions in Liquids*, edited by J. Lascombe (Reidel, Dordrecht, 1974).
- ²² J.A. Pople, Physica **19**, 668 (1953).
- ²³ E.C. McLaughlin, Physica **26**, 650 (1960).
- ²⁴ K. Krynicki, S.N. Changdar, and J.G. Powles, Mol. Phys. **39**, 773 (1980).
- ²⁵ M.W. Evans, G.C. Lie, and E. Clementi, Phys. Rev. A **37**, 2548 (1988).
- ²⁶ M. Holz, H. Weingartner, and A. Sacco, Ber. Bunsenges. Phys. Chem. **94**, 332 (1990).
- ²⁷ I. Mayer, I. Lukovits, and T. Radnai, Chem. Phys. Lett. **188**, 595 (1992).
- ²⁸ J.H. Wang and S. Miller, J. Am. Chem. Soc. **77**, 3454 (1955).