The Effect of Isotopic Substitution on Diffusion in Liquids

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1 Introduction

During the past decade a considerable body of experimental data has been accumulated which describes the dependence of diffusion coefficients in liquid media upon the isotopic substitution of the diffusing species. There have also been recent theoretical developments which treat the same topic in some detail. There have been no previous reviews on this topic and therefore it seems timely to assess the trends shown by the data, to compare the experimental and theoretical approaches, and to consider the best avenues for future work.

At first sight the topic of this review might seem a very specialized and narrow one. We alter only the isotopic composition of a diffusing molecule and then measure the change in its mobility due to this substitution. The interest in this type of study lies in the fact that we are able to isolate the effect of mass on the diffusion rate. Diffusion rates are generally considered to depend on such factors as mass, shape, and interaction potentials, but when the diffusing species differ chemically the latter two factors are usually much larger than the mass factor and so obscure it. In the systems considered here these 'chemical' factors are virtually eliminated, so allowing concentration on mass effects alone.

The reasons for studying the effect of mass in this way are several. Any theory of liquids which attempts to calculate liquid diffusion coefficients *a priori* must be able to incorporate the effect of mass. This review shows also that in certain isotopically related systems, some information on rotational–translational coupling can be obtained, so giving insight into a very relevant topic, that of microscopic motions within liquids. Further the comparative measurement of the diffusion rates of isotopic ions allows an assessment of the practicability of using diffusion in liquid media for the purpose of isotopic enrichment. Studies of this type are reported in the electrolyte section below.

Differences in the diffusion rates of molecules having different isotopic compositions have been well studied for gaseous and solid systems. Studies of mass effects in gaseous diffusion extend at least as far back as 1833, when Graham enunciated his inverse square-root law. For a dilute gas at constant temperature and number density, the Chapman–Enskog theory predicts that the diffusion coefficient D is inversely proportional to the square root of the reduced mass of the components. The separation of the hexafluorides of uranium is probably the best known example of the practical application of these laws. In solids, appreciable differences in the diffusion rates of isotopic species in a host crystal are observed and these have been attributed to the effect of mass on the jump frequency. Comparison of experimental data with calculations from theoretical models is used to determine the possible mechanisms of diffusion. By contrast, there has been little progress in the theoretical study of isotope effects in liquid diffusion (or indeed for other transport properties) and, until recently, few meaningful experimental results to show whether or not they exist. It now appears that such effects are present in some cases, but are usually small, and may therefore only be measured by precise and accurate techniques.

Before reviewing the theoretical and experimental evidence for isotope effects in diffusion, it is important to define the types of diffusion to be considered and the nomenclature appropriate to them. The nature of the problem essentially restricts consideration to two types only, self-diffusion and tracer diffusion, which are defined below.

A. Self-diffusion.*—The self-diffusion coefficient, D_S, of a pure liquid where all particles are of the *same* isotopic mass is related to the distance travelled by specified particles from an arbitrary origin in a given time. The mechanism of diffusion is by a Brownian movement process at the molecular level. Following Einstein[1] it may be expressed in terms of the velocity auto-correlation function

$$D_S = \tfrac{1}{3}\int_0^\infty \langle \mathbf{v}(0)\,.\,\mathbf{v}(t)\rangle\,\mathrm{d}t \qquad (1)$$

It is through this formalism that D_S is computed in a molecular dynamics experiment. An n.m.r. spin–echo experiment yields a very close approximation to D_S, subject to the conditions that D_S does not depend on the energy difference of the nuclear spin states of the particle observed nor on the magnetic field strength. Commonly D_S is approximated by tracer diffusion measurements where it is assumed either that isotopic effects are negligible or that an extrapolation can be made to the isotopic mass of the bulk liquid. It is important to realize that here tracer diffusion is only being used as a means to an end, *i.e.* to obtain self-diffusion coefficients.

In this review we shall be comparing under the heading 'self-diffusion' the self-diffusion coefficients of pure liquids which are themselves isotopically substituted in some manner, *e.g.* D_S of H_2O with D_S of D_2O. The situation is illustrated in Figure 1(a), where the asterisk denotes some form of labelling (for measurement purposes) which does not sensibly affect the given mass. The mass numbers given in Figure 1(a) indicate that here we are comparing self-diffusion in normal benzene with that in fully deuteriated benzene.

B. Tracer Diffusion.—The comparison in this case is between the diffusion

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* It should be noted that a survey of the literature shows that there are two schools of thought with regard to the use of the term 'Self-diffusion'. One set of workers prefers to restrict the term to molecular motion in one-component systems, and this is the approach followed in this review. Others use it more generally to describe the thermal motion of a specified component in both single and multicomponent systems.

[1] A. Einstein, *Ann. Physik*, 1905, **17**, 549; 1906, **19**, 289, 371.

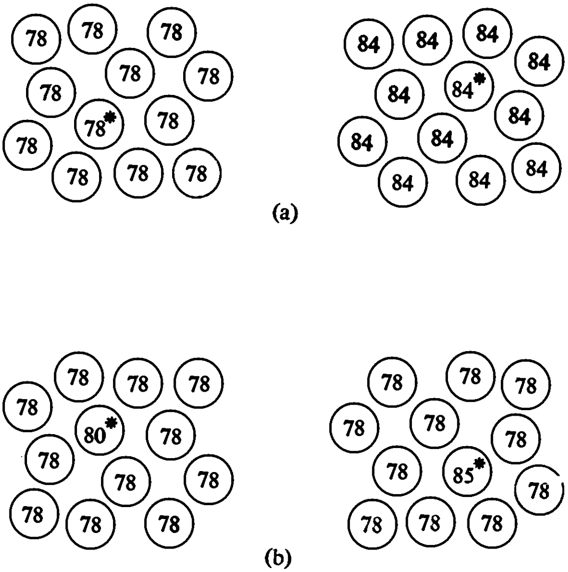

Figure 1 (a) *Diagrammatic representation of self diffusion in two pure isotopically related liquids, one of mass* 78 *and the other of mass* 84
(b) *Tracer or solute diffusion of two trace species of mass* 80 *and mass* 85 *diffusing in a common solvent of mass* 78

coefficients (D_T) of trace amounts of different species of one component having different isotopic substitution in a common solvent or solution, *e.g.* HTO and HDO in H_2O or $^{12}C_6H_5T$, $^{12}C_6D_5T$, and $^{12}C_5\,^{14}CH_6$ in $^{12}C_6H_6$ (D = deuterium, T = tritium). In such systems the only concentration gradient is that of the trace species itself. The situation is illustrated in Figure 1(b), in which trace species of mass 80 and 85 are compared in a medium of mass 78. It should be noted that the bulk medium need not be a pure fluid but may consist of several components (as is the case with the electrolyte solutions discussed later), the essential requirement being that the addition of the isotopically substituted species does not alter the bulk properties of the medium. It will be appreciated that whereas in the self-diffusion case tracer diffusion was merely a means to an end, in the present context it is an end in itself.

In Sections 2 and 3 we discuss the effect of isotopic substitution in self-diffusion and tracer diffusion respectively.

2 Self-diffusion

A. Theoretical Approaches.—For self-diffusion in pure one-component liquids Longuet-Higgins and Pople[2] and Brown and March[3] have derived equations

[2] H. C. Longuet-Higgins and J. A. Pople, *J. Chem. Phys.*, 1956, **25**, 884.
[3] R. C. Brown and N. H. March, *Phys. and Chem. Liquids*, 1969, **1**, 141.

which show the effect of mass explicitly. These approaches both predict an inverse square-root mass dependence. The starting point for the derivations is the auto-correlation function description of self-diffusion [equation (1)], and to obtain a simplified picture it is usually assumed either that the molecules are hard spheres or that molecular interactions between species of different mass are the same. Friedman[4] has recently made an extensive study of isotopic mass dependence in self-diffusion within the more general framework of classical linear response theory. Assuming that the intermolecular forces are unchanged by the isotopic substitution, he finds that for homoatomic molecules (*e.g.* $^{16}O_2$ and $^{17}O_2$), where the mass is the only variable in the equations, D_S is proportional to $m^{-\frac{1}{2}}$. However, for heteroatomic molecules (*e.g.* C_6H_6 and C_6D_6) or homoatomic molecules with incomplete substitution (*e.g.* $^{16}O_2$ and $^{16}O^{17}O$) the substitution changes more than the single mass variable, and the rotational (and perhaps vibrational) degrees of freedom must be taken into account. We note that Rowlinson,[5] using dimensional analysis, has also derived a simple square-root mass relationship for the viscosity of isotopically related fluids, and McLaughlin[6] has extended this analysis to self-diffusion. Pople[7] has discussed deviations from the simple law for viscosity (such as evidenced by H_2O and D_2O) in terms of moment of inertia effects. (All of the above theoretical treatments are derived for classical systems, and quantum effects are neglected.)

In summary, these theoretical approaches predict that the simple mass law for isotopically substituted molecules can only be expected as a first approximation. More sophisticated theories must eventually be developed to explain deviations from it in terms of such factors as correlated motions, ordering due to molecular interactions, coupling between rotational and translational motions, and quantum effects.

B. Experimental Studies.—Data for self-diffusion in isotopically related pure liquids are not plentiful but some results are available from n.m.r. and tracer techniques.

The pulsed n.m.r. spin–echo method has been used to measure self-diffusion in molten lithium isotopes by both Murday and Cotts[8] and Kruger, Müller-Warmuth, and Klemm.[9] The motivation for these studies stemmed from the work of Ban, Randall, and Montgomery,[10] who measured the viscosities of pure ^6Li and ^7Li isotopes and found a large deviation from the $m^{\frac{1}{2}}$ relation appropriate to that property. The experimental difficulties in using n.m.r. for the diffusion studies were severe, and suspensions of the liquid metal were necessary to allow

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[4] H. L. Friedman, 'Isotope Effects upon Motions in Liquids in the Classical Limit', in 'Molecular Motions in Liquids', ed. J. Lascombe, D. Reidel, Dordrecht, Holland, 1974, p. 87.

[5] J. S. Rowlinson, *Physica*, 1953, **19**, 303.

[6] E. McLaughlin, *Physica*, 1960, **26**, 650.

[7] J. A. Pople, *Physica*, 1953, **19**, 668.

[8] J. S. Murday and R. M. Cotts, *Z. Naturforsch.*, 1971, **26a**, 85.

[9] G. J. Kruger, W. Müller-Warmuth, and A. Klemm, *Z. Naturforsch.*, 1971, **26a**, 94.

[10] N. T. Ban, C. M. Randall, and D. J. Montgomery, *Phys. Rev.*, 1962, **128**, 6.

penetration by the r.f. fields. Corrections for restricted diffusion had therefore to be applied. When these uncertainties are coupled with the other errors inherent in the n.m.r. method it is evident that the overall errors are rather large. Murday and Cotts have reported a self-diffusion ratio for $D(^6Li)/D(^7Li)$ of 1.18 ± 0.07 (180.5—260 °C) and Kruger *et al.* reported the value 1.09 ± 0.06 (189 °C), whereas the theoretical inverse square-root mass ratio is 1.081 and the viscosity ratio is 1.44 ± 0.02. In view of the large errors associated with each set of measurements, all that can be deduced is that the anomalous viscosity behaviour is not reproduced by the diffusion results, and that the latter also tend to favour the theoretical mass law.

N.m.r. self-diffusion measurements have also been made for H_2O and D_2O by Murday and Cotts,[11] but again the errors of about 5% associated with each set of measurements allow no real test of theory. In fact there seems little point in using n.m.r. techniques for isotopic mass measurements of this kind until the precision of the method is of order ±0.5%.

Isotopic self-diffusion measurements using the diaphragm-cell method and radiotracer techniques have recently been made by Mills[12] for the H_2O–D_2O and C_6H_6–C_6D_6 pairs. These data, with their high precision (±0.3%), provide the first significant test for the theoretical mass law. These results and other relevant data are shown in Table 1.

Table 1 *Self-diffusion coefficient and viscosity ratios for* H_2O *and* D_2O *and for* C_6H_6 *and* C_6D_6

$T/°C$	$[m(D_2O)/m(H_2O)]^{\frac{1}{2}}$	$D_S(H_2O)/D_S(D_2O)$	$\eta(D_2O)/\eta(H_2O)$	$\eta(H_2{}^{18}O)/\eta(H_2{}^{16}O)$
5	1.054	1.294	1.313	—
25	1.054	1.228	1.232	1.054[a]
45	1.054	1.200	1.196	—
	$[m(C_6D_6)/m(C_6H_6)]^{\frac{1}{2}}$	$D_S(C_6H_6)/D_S(C_6D_6)$	$\eta(C_6D_6)/\eta(C_6H_6)$	
25	1.038	1.057	1.063[b,c]	

[a] A. I. Kudish, D. Wolf, and F. Steckel, *J.C.S.*, *Faraday I*, 1972, **68**, 2041. [b] J. A. Dixon and W. Schiessler, *J. Phys. Chem.*, 1954, **58**, 430. [c] I. R. Shankland and P. J. Dunlop, *J. Phys. Chem.*, 1975, **79**, 1319.

In contrast to the molten lithium case described above, the self-diffusion and viscosity ratios are practically identical for both the water pairs and the benzene pairs. The water ratios (for both self-diffusion and viscosity) are, however, much higher than the square-root mass ratios. In the viscosity case Pople[7] has pointed out that whereas in the pair H_2O–D_2O isotopic substitution alters the mass by a ratio 20:18, the moments of inertia are altered by a ratio close to 2:1. If rotational motion contributes to momentum transfer then this moment of

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[11] J. S. Murday and R. M. Cotts, *J. Chem. Phys.*, 1973, **50**, 4724.
[12] R. Mills, *J. Phys. Chem.*, 1973, **77**, 685; *ibid.*, 1976, in press.

inertia ratio, of which the square-root values range from 1.340 to 1.414, could account for the observed viscosity values. For the self-diffusion case no net momentum transfer occurs during the transport process. However, when inelastic collisions occur in H_2O and D_2O, a greater fraction of the total energy will be abstracted as rotational energy by those between D_2O molecules with their larger moments of inertia. This reduces the translational energy of the D_2O molecules, leading to the observed self-diffusion coefficients which are lower than those expected for a hard-sphere model but by a different amount to those of H_2O: hence the $m^{-\frac{1}{2}}$ relationship of the model does not fit the data. In Table 1 we have also included the viscosity ratio for the pair $H_2{}^{18}O/H_2{}^{16}O$ at 25 °C. Since the centre of mass of the water molecule is only slightly displaced from the oxygen atom, the moments of inertia for this pair will change very little upon isotopic substitution. It will be noted that now exact agreement with the square-root mass law is obtained. For benzene it will be seen from Table 1 that the D_S and η ratios are only about 2% greater than the simple mass ratio. This difference, though small, is considerably greater than the errors inherent in the measurements and must be a real one. Friedman,[4] for the case of systems such as C_6H_6–C_6D_6, noted that moment of inertia effects might have to be taken into account. However, the value of $[I(C_6D_6)/I(C_6H_6)]^{\frac{1}{2}}$ is calculated to be only 1.02, and in this case the higher transport ratios cannot easily be explained by a coupling between translational and rotational motions, as was invoked in the water case. An alternative explanation for the deviation of the benzene results from the simple mass law is available which does not involve moment of inertia changes. The theoretical treatments outlined in Section 2A all assume that the intermolecular potential is unchanged by isotopic substitution. Using the theorem of corresponding states, Steele[13] has been able to correlate the differences between molar volumes, viscosities, and vapour pressures of benzene and perdeuteriobenzene on the basis of quite small differences in the (two parameter) intermolecular potentials. In the limit where the differences are zero, the expressions reduce to the simple $m^{\frac{1}{2}}$ laws. We have applied Steele's equation for diffusion using his parameters ($\delta\epsilon = 0.4\%$, $\delta\sigma = -0.13\%$) and values of $(\partial \ln D/\partial p)_T$ and $(\partial \ln D/\partial T)_p$ calculated from the data of McCool, Collings, and Woolf.[14] Whilst the theory is only rigorously correct for monatomic fluids, as translational–rotational coupling is neglected, the diffusion coefficient ratio calculated is 1.057, in excellent agreement with the experimental value. We note that this correlation is not successful for water.

3 Tracer Diffusion

A. Theoretical.—Friedman,[4] in addition to the self-diffusion derivations mentioned in Section 2A, has also used linear response theory to consider the diffusion of single solute molecules of variable mass in a medium of identical solvent molecules [see Figure 1(b)]. Again as in Section 2A, he has used a purely classical approach,

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[13] W. A. Steele, *J. Chem. Phys.*, 1960, **33**, 1619.

[14] M. A. McCool, A. F. Collings, and L. A. Woolf, *J.C.S. Faraday I*, 1972, **68**, 1489.

quantum effects being neglected. The molecules are assumed to be spherical, and the effect of change of mass is assumed not to alter the intermolecular force between the solute particle and the solvent. It will be seen that these conditions closely represent an idealized tracer diffusion experiment where solute and solvent are the same chemical species. In this review, we extend the comparison to tracer species of varying mass in solvents which may have several components. Electrolyte solutions fall into the latter category. It is plausible to consider that trace species of the same chemical composition but differing mass will react similarly with the mean force field surrounding them if their environments are identical.

For the 'solute' or tracer diffusion case Friedman[4] has derived expressions which relate D_T, the solute diffusion coefficient, to solvent variables and the solute mass. These equations are rather complex, and the interested reader is referred to Section 6 of his paper, in which they are derived. It is, however, worth observing here that as $[m_0/m_i]^{\frac{1}{2}} \rightarrow 0$ (m_i = mass of solute i, m_0 = mass of solvent) D_T becomes independent of the solute mass. It will be realized that the best-known equation in the field of solute diffusion, the Stokes–Einstein equation, also expresses this independence of the solute mass. The conditions under which the latter equation was derived were for large spherical molecules in a continuous medium of small molecules, and here one would expect the condition $[m_0/m_i]^{\frac{1}{2}} \rightarrow 0$ to be fulfilled. It is also evident from the experimental data in Section C that the same independence exists when $[m_0/m_i]^{\frac{1}{2}} \approx 1$.

One further remark in relation to solute or tracer diffusion is that from kinetic theory one would not expect the simple $(m_1/m_2)^{\frac{1}{2}}$ law (where 1 and 2 are isotopic species diffusing in the same medium) to apply. The net diffusional movement of one solute species must (in a fixed-volume system) result in the net movement of one of the solvent species. Therefore the appropriate relation involves the reduced mass:

$$\frac{D_{T1}}{D_{T2}} = \left(\frac{\mu_2}{\mu_1}\right)^{\frac{1}{2}} \text{ where } \mu_i = \frac{m_i m_0}{(m_i + m_0)}$$

In this section we include also a further formulation for tracer diffusion, which can be applied to isotopically-substituted systems, given by Bearman.[15] His derivation stems from the Kirkwood statistical mechanical approach to the description of transport processes. Specifically for tracer-diffusion in a regular binary solution he finds that

$$D_{T1}/D_{T2} = V_2/V_1 \tag{2}$$

where V_i is the molar volume of component i.

Although Bearman's equation is not restricted to isotopically substituted binary mixtures, it ought to be especially applicable to such mixtures, as they would be expected to be regular ones. Regular solutions can be briefly defined as those in which the two components have similar size, shape, and intermolecular potentials. It will be noted that there is no explicit dependence on

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[15] R. J. Bearman, *J. Phys. Chem.*, 1961, **65**, 1961.

mass in equation (2), and to this extent the approach agrees with that of Friedman.[4]

B. Experiments on Model Systems.—In this section we consider molecular dynamics 'experiments' which can test the theoretical predictions outlined above. These computer simulation experiments are used to calculate diffusion coefficients (and other properties) from correlation functions by solution of the Newtonian equations of motion for small numbers of particles at the appropriate density and temperature and having model potentials. The method simulates macroscopic systems by the use of periodic boundary conditions. (No molecular dynamics data were included in Section 2 since for self-diffusion the $m^{-\frac{1}{2}}$ law is implicit in the equations of motion.)

The most relevant of these is the molecular dynamics study of Ebbsjo, Schofield, Sköld, and Waller,[16] who performed molecular dynamics calculations of the intradiffusion[17] coefficients of Lennard-Jones particles having the potential parameters of argon. Mixtures of ^{40}Ar with the fictitious isotopes of masses 32, 80, and 200 were considered. Despite the large errors inherent in the calculation ($\geqslant 5\%$) they concluded that the intradiffusion coefficients of both components are essentially equal at any concentration, *i.e.* the isotope effect, if present, is quite small, even for such large mass differences.

A series of molecular dynamics studies by Herman and Alder[18] and by Alder, Alley, and Dymond[19] also have a bearing on the binary tracer diffusion case. Herman and Alder studied hard-sphere systems in which the solute and solvent are of the same size but in which the mass of the solute is varied. Friedman[20] has recast their results in a graphical form which clearly indicates that the ratios of the solute diffusion coefficients are much closer to unity than to the inverse square-root law.

Alder, Alley, and Dymond[19] have performed more extensive calculations for the tracer diffusion coefficient of a single hard sphere in a solvent of heavier and larger spheres (*i.e.* a 'dense Lorentz gas') in order to estimate the effect of correlated motions. They computed the ratio of D_T to that given by the Enskog theory for uncorrelated motions, and expressed the results in terms of tracer mass and size and solvent density. It was found that when the particles were of similar size there was no effect, in accord with the results of Ebbsjo *et al.* and the data of Herman and Alder, but that as the tracer was made smaller D_T increased and became mass dependent. The Enskog theory, which predicts that $D_T \propto \mu^{-\frac{1}{2}}$, has greater validity as the tracer becomes smaller in size and mass and the system density lower. Back-scattering becomes less important at the lower densities, and for smaller and more massive particles, and the persistence of velocities is greater.

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[16] I. Ebbsjo, P. Schofield, K. Sköld, and I. Waller, *J. Phys. (C)*, 1974, **7**, 3891.

[17] See J. G. Albright and R. Mills, *J. Phys. Chem.*, 1965, **69**, 3120, for a definition of 'intradiffusion'. In the present instance these coefficients can be regarded as equivalent to tracer diffusion ones.

[18] P. T. Herman and B. J. Alder, *J. Chem. Phys.*, 1972, **56**, 987.

[19] B. J. Alder, W. E. Alley, and J. H. Dymond, *J. Chem. Phys.*, 1974, **61**, 1415.

[20] H. L. Friedman, *Chem. in Britain*, 1973, **9**, 300.

Consequently one expects an isotope effect for small dense particles diffusing in a medium of larger and heavier ones, and a smaller effect as the tracer approaches the size of the solvent.

C. Experiments on Real Systems.—(i) *Atomic liquids*. Some experimental systems closely approximate the conditions used by Friedman[4] in his derivation. As an extension of their work on self-diffusion in molten lithium, both Murday and Cotts[8] and Kruger *et al.*[9] measured the concentration dependence of $D_T(^7Li)$ in ^6Li–^7Li mixtures. Murday and Cotts found no dependence and Kruger *et al.* obtained a result for $D_T(^6Li)/D_T(^7Li)$ of 1.03 ± 0.08 at $x(^6Li) = 0.2$ (where x is the mole fraction). On the other hand Löwenberg and Lodding,[21] using tracer techniques, found a large variation for $D_T(^7Li)$ at different ^6Li–^7Li compositions. One can therefore reach no firm conclusions for this system as regards solute diffusion.

For liquid noble-gas systems Cini-Castagloni and Ricci[22] (who, however, were not specifically investigating isotope effects) have reported values for tracer diffusion in argon in which both ^{37}Ar and ^{41}Ar have been used as tracers. No difference is evident although the errors of about 5% (which are necessarily associated with these difficult techniques) cloud the issue. N.m.r. and tracer data for xenon, where different isotopes have been used, are hardly worth consideration in view of the large errors involved in those particular measurements.

(ii) *Non-electrolytes*. It is probably fair to say that the first real tests of Friedman's theoretical predictions have come from tracer diffusion measurements on organic liquids. The techniques used in the studies to be reported have a precision of a few tenths of a percent and so mass effects can be tested with some degree of certainty. Interest in isotope effects stemmed from the data published by Eppstein and Albright[23] for D_T of benzene at 25 °C using ^{14}C-labelled tracers with molecular weights corresponding to one and two heavy isotopes per molecule. Taken in conjunction with the mutual diffusion data of Birkett and Lyons[24] for benzene–perdeuteriobenzene at 25 °C, the data indicated D_T to depend on $m^{-\frac{1}{2}}$. This was at variance with the earlier work of Harris, Pua, and Dunlop,[25] who had found no such effect using similar techniques with ^{14}C tracers of several different molecular weights. Allen and Dunlop[26] consequently repeated the study, using the tracer samples of Eppstein and Albright, and in summary decided that D_T has the following very small mass dependence

$$D_T = 2.219 - 0.001_2(m_i - m_0) \qquad (3)$$

where m_i is the mass of the trace and m_0 that of the solvent benzene.

Because the ^{14}C tracer samples of benzene are actually mixtures of differently substituted molecules, there may be uncertainty in specifying the exact mass.

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[21] L. Löwenberg and A. Lodding, *Z. Naturforsch.*, 1965, **22a**, 2077.
[22] G. Cini-Castagnoli and F. P. Ricci, *Nuovo Cimento*, 1960, **15**, 795.
[23] L. B. Eppstein and J. G. Albright, *J. Phys. Chem.*, 1971, **75**, 1315.
[24] J. D. Birkett and P. A. Lyons, *J. Phys. Chem.*, 1965, **69**, 2782.
[25] K. R. Harris, C. K. N. Pua, and P. J. Dunlop, *J. Phys. Chem.*, 1970, **74**, 3518.
[26] G. G. Allen and P. J. Dunlop, *Phys. Rev. Letters*, 1973, **30**, 316.

Mills[27] therefore used tracers of benzene and perdeuteriobenzene substituted with one tritium atom per molecule. No mass dependence was observed with these tracers. The same result was observed for tritiated cyclohexane and perdeuteriocyclohexane tracers diffusing in cyclohexane, despite the quite large mass difference of 11 g mol^{-1}. Further, Shankland and Dunlop[28] have measured the mutual diffusion coefficients of benzene–perdeuteriobenzene as a function of concentration and shown that the data of Birkett and Lyons are consistent with the tracer results. Both sets of data are more in accord with Friedman's theoretical predictions than are the data of Eppstein and Albright, which would appear to be experimentally incorrect.

Another very interesting system in which the diffusion rate of tracers of different mass has been studied is a benzene–perdeuteriobenzene mixture. Mills[29] has recently measured tracer diffusion coefficients of C_6H_5T and C_6D_5T in 50 mole percent C_6H_6–C_6D_6 mixtures and found that the heavier tracer diffused about 0.5% faster than the lighter one. It can be seen from molar volume measurements that deuteriated compounds have a slightly smaller volume than the corresponding hydrogenated ones. Measurements of the two types of tracer species in both normal benzene and cyclohexane were made also, and he found in all these cases that the inverse ratio of the molecular volumes is approximately equal to the diffusion coefficient ratio. This is the dependence predicted by Bearman in equation (2) and its importance in the present context is that there is no explicit mass dependence.

In this tracer diffusion section we have so far been dealing with trace species diffusing in isotopically related solvents, and logically the diffusion of deuteriated and tritiated water in H_2O and D_2O comes within this category. However, owing to the large mass dependence found for this system, we propose to treat it as a special case at the end of the section.

Turning now to systems in which the tracer species are themselves isotopically related, but not to the solvent, we deal first with organic liquids. Several studies of the tracer diffusion of labelled benzenes in various solvents have been made by Dunlop and co-workers[25,26,30,31] and Albright and Aoyagi.[32,33] Again the diaphragm cell method was used with a precision of about ±0.3% for the ^{14}C tracer work, and Gouy and Rayleigh optical techniques of similar precision were used to obtain mutual diffusion coefficients. Data obtained by these methods could be extrapolated to zero concentration to give the tracer coefficients. The tracer data of Aoyagi and Albright differ systematically from those of Dunlop's group and those of Mills by about 0.5%, and have been corrected by this amount in the summary of all the data given in Figure 2.

Examination of the Figure shows that in each case an isotope effect appears

[27] R. Mills, *J. Phys. Chem.*, 1975, **79**, 852.
[28] I. R. Shankland and P. J. Dunlop, *J. Phys. Chem.*, 1975, **79**, 1319.
[29] R. Mills, *J. Phys. Chem.*, 1976, in press.
[30] S. J. Thornton and P. J. Dunlop, *J. Phys. Chem.*, 1974, **78**, 846.
[31] I. R. Shankland, P. J. Dunlop, and L. W. Barr, *Phys. Rev. (B)*, 1975, **12**, 2249.
[32] K. Aoyagi and J. G. Albright, *J. Phys. Chem.*, 1972, **76**, 2572.
[33] J. G. Albright and K. Aoyagi, personal communication.

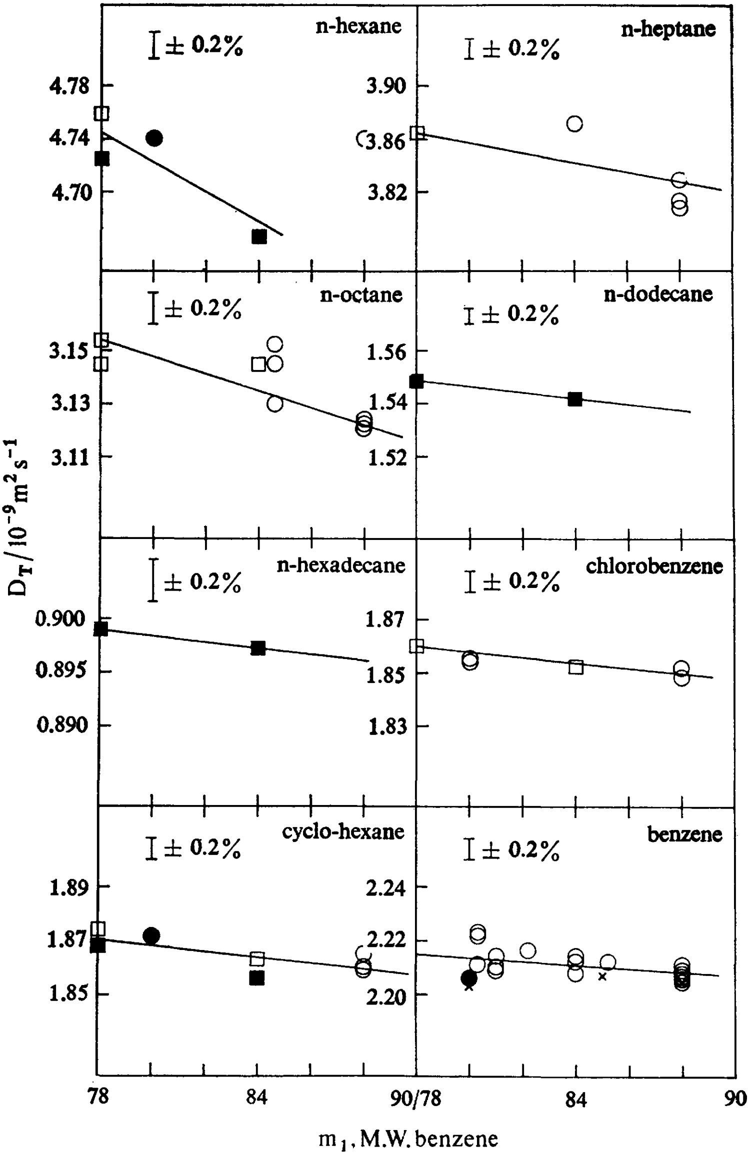

Figure 2 *Tracer diffusion coefficients of labelled benzenes* (1) *in various solvents* (0) *as a function of* m_1*:* D_T: ○, *Dunlop* et al.; ●, *Albright and Aoyagi* (+0.5%); ×, *Mills.* ${}^1D$ (*mutual*); □, *Dunlop* et al.; ■, *Albright and Aoyagi. Data from ref.* 25 *have been assigned the appropriate value of* m_1 (K. R. Harris, Ph.D. Thesis, University of Adelaide, 1970). *Data from* ref. 30 *have been corrected for a calibration error—see* ref. 28, *footnote* 11

to be present. For the n-alkane series the isotope effect on the tracer diffusion coefficient of benzene seems to increase as the solvent alkane becomes smaller and lighter. We note here that recent work by Harris and Mills[34] using tritiated benzene and perdeuteriobenzene as tracers in octamethylcyclotetrasiloxane has shown no isotope effect. These results seem to disagree with the molecular dynamics studies of Alder *et al.*[19] which showed that diffusion of a light, small molecule in a solvent of heavier and larger ones was strongly affected by back-scattering. It would therefore seem that smooth hard-sphere models are not applicable to these systems.

Other studies that fall within this general section are those of Hildebrand and co-workers,[35,36] who have measured the tracer diffusion coefficients of a number of gases in CCl_4 and $(C_4F_9)_3N$ at 25 °C. The ratio $D_T(H_2)/D_T(D_2)$ in these solvents was found to be 1.27 and 1.18 respectively. However, they suggested that quantum effects, rather than mass effects, were important, and correlated data for a range of solutions with the de Boer parameter of the solute gas.

(iii) *Electrolytes.* The other large class of systems in which the mass effects of solute species have been studied is aqueous electrolytes, and here we are concerned with the diffusion of ions of varying isotopic mass. The question of whether isotopic ions have differing mobilities has been of interest for a number of years. For instance, Chemla and co-workers have been active for over two decades in studying ionic isotopic effects in aqueous electrolytes and also molten salts. Most of these studies have been of the electromigration type, in which an electric field is used to accelerate the migrating ions, and therefore do not come within the scope of this review. However, one study by Apercé, Lantelme, and Chemla[37] does come in the pure diffusive category. These workers studied a molten salt system in which small amounts of $LiNO_3$ diffused in a solvent consisting of a mixture of KNO_3 and $NaNO_3$. A small separation of the lithium isotopes was observed. The conductivity studies of Kunze and Fuoss[38] with Li^+ isotopes in aqueous electrolytes indicate a definite mass effect, though much smaller than the inverse mass law would predict, and therefore, since the limiting mobilities of ions are linked through the Nernst–Einstein equation, a corresponding effect in the diffusion case might be expected, at least for light ions.

In 1957, Stokes, Woolf, and Mills[39] measured the tracer diffusion of iodide ion in a series of aqueous alkali chloride solutions. In this study ^{131}I was used as a radioactive tracer in one set of experiments and ^{127}I was the other tracer, which was analysed chemically. No difference in diffusion rate was observed within the $\pm 0.4\%$ precision of the data. More recently Pikal[40] has made a study of the diffusion of ^{22}Na and ^{24}Na in aqueous electrolytes and found a slight systematic difference of about $\pm 0.2\%$, which was roughly in agreement with the inverse

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[34] K. R. Harris and R. Mills, unpublished data.
[35] M. Ross and J. H. Hildebrand, *J. Chem. Phys.*, 1964, **40**, 2397.
[36] K Nakanishi, E.-M. Voigt, and J. H. Hildebrand, *J. Chem. Phys.*, 1965, **42**, 1860.
[37] J. P. Apercé, F. Lantelme, and M. Chemla, *Compt. rend.*, 1967, **264**, 461.
[38] R. K. Kunze and R. M. Fuoss, *J. Phys. Chem.*, 1962, 66, 930.
[39] R. H. Stokes, L. A. Woolf, and R. Mills, *J. Phys. Chem.*, 1957, **61**, 1634.
[40] M. J. Pikal, *J. Phys. Chem.*, 1972, 76, 3038.

square-root law for the reduced mass although his experimental error was of the same order. A complicating factor is the degree of hydration of the Na^+ ions which makes interpretation of the results difficult. In studies using diffusion cascades to separate isotopic ions, Miller[41,42] reported separation of lithium isotopes, with ^6Li diffusing faster than ^7Li. Later he obtained separation factors for uranyl diffusion[43] which indicated that there could be an appreciable difference in the diffusion rate of the two isotopes. His results were doubly interesting in that the heavier ion, $^{238}UO_2^{2+}$, appeared to diffuse faster than the lighter one, $^{235}UO_2^{2+}$. Miller attributed this reversal in diffusion rate to persistence of velocity and back-scattering effects and considered that such effects would be applicable to heavy ions generally.

In order to test this suggestion Mills[44] has recently studied the tracer diffusion of the heavy-ion pairs $^{125}I/^{131}I$ and $^{134}Cs/^{137}Cs$ under a wide variety of conditions. These ions were chosen because they are considered to be unhdyrated and the relative mass differences are large. The considerable amount of data from this study shows no isotopic effect within the average precision of ±0.2%. Subsequently Miller[45] reported that the high separation factors measured for uranyl ion isotopes were due to transient diffusion effects, *i.e.* sampling was carried out at the advancing diffusion front and not under steady-state conditions. Computer analysis of his data led him to estimate that the difference between the diffusional mobilities of the two uranium isotopes was about ±0.25%.

Summarizing the evidence for isotopic effects in ion diffusion in aqueous electrolytes, it would seem that small and opposite effects may be present at the two ends of the mass range. For very light ions there is some evidence from the work of Pikal[40] and of Miller[41,42] that isotopic diffusion rates tend towards the inverse square-root mass dependence. For heavy ions at the other end of the range there appears from Miller's[43] work to be an effect which causes the heavier isotopic ions to diffuse faster than the lighter ones. For moderately heavy ions Mills[44] has found that there is no detectable isotopic difference in diffusion rate (to ±0.1%).

(iv) *Special case of liquid water.* Finally we discuss the effect of isotopic substitution on tracer diffusion in both light (H_2O) and heavy (D_2O) water. Having already discussed self-diffusion in these two liquids earlier, here we are testing the theoretical derivations for tracer diffusion as given by Friedman.[4] This section has been left until the end because of the great importance of the properties of liquid water and because it is the only system in which a large isotope effect has been reported for this type of diffusion.

Measurements of self-diffusion in liquid water using isotopic tracers were reported by Wang[46] as early as 1950, and since then the subject has had a long and tortuous history, with at least three different forms of isotopic labelling being

[41] L. Miller, *J. S. African Chem. Inst.*, 1970, **23**, 121.

[42] L. Miller, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 206.

[43] L. Miller, *Nature*, 1973, **243**, 32.

[44] R. Mills, *Nature*, 1975, **256**, 638.

[45] L. Miller, *J. Phys. Chem.*, 1975, **79**, 1218.

[46] J. H. Wang, *J. Amer. Chem. Soc.*, 1951, **73**, 510; *ibid.*, 1951, **73**, 4181.

used. The large spread of coefficients obtained at 25 °C (±10%) did not, however, reflect isotopic effects but rather systematic errors in the experimental techniques. A recent paper by Mills[47] has surveyed the problem of experimental errors, so this aspect will not be discussed in this review.

In discussing isotopic effects for tracer diffusion in water we are assuming that two reliable sets of data exist. The first of these are mutual diffusion coefficient data for the system H_2O–D_2O over a range of compositions and temperatures which were measured by Longsworth.[48] The Raleigh interferometric method was used in this study, and in expert hands this has guaranteed accuracy and a precision of order ±0.1%. These data may be extrapolated to give the tracer diffusion coefficients of HDO in H_2O and HDO in D_2O. The second set of data are those reported by Mills[12] and are the tracer diffusion coefficients of HTO and DTO in H_2O and D_2O respectively over a range of temperatures. These data have a precision of ±0.3% and have been made with the well-tested diaphragm-cell method. Further confidence in their reliability is engendered by the very close parallelism of these results at all temperatures with those of Longsworth. The two sets of data are shown in Table 2.

Table 2 *Tracer diffusion of isotopic species in water*

T/°C	HTO *in* H_2O	HDO *in* H_2O	DTO *in* D_2O	HDO *in* D_2O	$\frac{[D_T(HDO) - D_T(HTO)] \times 10^2}{D_T(HDO)}$	$\frac{[D_T(HDO) - D_T(DTO)] \times 10^2}{D_T(HDO)}$
	$\underbrace{\qquad\qquad}_{D_T \times 10^9\ m^2\ s^{-1}}$				(H_2O)	(D_2O)
1	1.113	1.128				
4	1.236					
5	1.272	1.295	1.001	1.034	1.8%	3.2%
15	1.724					
25	2.236	2.272	1.849	1.902	1.6	2.8
35	2.838					
45	3.474	3.532	2.939	3.027	1.6	2.9

The differences between the two sets of data are noteworthy for the fact of their constancy and that they are roughly proportional to the mass difference in the tracers, *i.e.* it will be seen that the difference in diffusion mobility between HDO and DTO (mass difference 2) is roughly twice that between HDO and HTO (mass difference 1). This constant proportionality between diffusive mobility and mass was used to estimate the true self-diffusion coefficients of H_2O and D_2O which were given in Table 1. We have in this system the unambiguous example of an isotope effect for the solute or tracer diffusion case, and it is now of considerable interest to know the functional form of this isotopic dependence. There have been four approaches to this question which are detailed below.

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[47] R. Mills, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 195.

[48] L. G. Longsworth, *J. Phys. Chem.*, 1954, **58**, 770; *ibid.*, 1960, **64**, 1914

(*a*) *Gas kinetics model.* A simple relationship derived from the kinetic theory of gases[49] can as a first approximation be used to examine isotopic tracer behaviour in liquid water. The equation is

$$D_{\mathrm{T}1}/D_{\mathrm{T}2} = (m_2/m_1)^{\frac{1}{2}}\left(\frac{m_1 + m_0}{m_2 + m_0}\right)^{\frac{1}{2}} = (\mu_2/\mu_1)^{\frac{1}{2}} \qquad (4)$$

where m_1 and m_2 are the masses of the isotopic tracers, m_0 is the solvent mass, and μ is the reduced mass. The appropriate comparison is made in Table 3 below.

(*b*) *Solid-state model.* Dunlop[50] has recently applied the results of Mills and Longsworth to a general equation for isotope effects in solids which may be written

$$\frac{D_{\mathrm{T}}}{D_0} - 1 = f_{\mathrm{T}}\Delta K\left[\left(\frac{nm_0}{[m_i + (n-1)\,m_0]}\right)^{\frac{1}{2}} - 1\right] \qquad (5)$$

where D_{T} is the isotopic tracer diffusion coefficient, D_0 is the limiting tracer diffusion coefficient (in this case the self-diffusion coefficient), f_{T} is a correlation factor, ΔK is a constant for the system, m_0 and m_i are the molecular masses of the solvent and isotopic tracer, respectively, and n is the number of molecules relocated during the molecular transfer process. Using as a basis the molecular dynamics study of Rahman and Stillinger[51] on water, he assumes that $f_{\mathrm{T}} \approx 1$ and $\Delta K = \sim 0.5$, and when these are inserted in equation (5) he finds that consistent results are obtained for both H_2O and D_2O over a temperature range.

(*c*) *Rotational inertia effects.* A third explanation for the isotopic effect in liquid water was first suggested by Friedman.[4] The moments of inertia of the normal water molecule and those singly substituted with deuterium or tritium atoms are appreciably different, and one might therefore expect that these differences could affect the diffusion rate. Rotational effects could be particularly operative in water owing to the hydrogen-bonding network normally assumed to be present, and in fact it is generally thought that a rotational bond-breaking step is necessary before translational diffusion can take place. Calculations have therefore been made of the inverse square-root ratios of the reduced moments of inertia, and these are also shown in Table 3 below, together with the reduced-mass relation from (*a*).

(*d*) *Quantum effects.* Recently Friedman[52] has also suggested a further possible contribution to these isotopic effects which is the quantization of the librations (hindered rotations) in liquid water.

[49] S. Chapman and J. G. Cowling, 'The Mathematical Theory of Nonuniform Gases', University Press, Cambridge, 1960.

[50] P. J Dunlop, *Phys. Rev. Letters*, 1975, **35**, 292.

[51] A. Rahman and F. H. Stillinger, *J. Chem Phys.*, 1971, **55**, 3336.

[52] H. L. Friedman, personal communication.

Table 3 *Comparison of D_T ratios for* H_2O *and* D_2O *with reduced masses and moments of inertia*

T/ °C	*Tracer species*	*Solvent*	D_{T1}/D_{T2}	$[\mu(m_2)/\mu(m_1)]^{\frac{1}{2}}$	$[\mu(I_2)/\mu(I_1)]^{\frac{1}{2}}$ (*mean value over three axes*)
5	HDO(1)/HTO(2)	H_2O	1.013	1.013	1.047
25	HDO(1)/HTO(2)	H_2O	1.016	1.013	1.047
45	HDO(1)/HTO(2)	H_2O	1.017	1.013	1.047
5	HDO(1)/DTO(2)	D_2O	1.033	1.024	1.133
25	HDO(1)/DTO(2)	D_2O	1.029	1.024	1.133
45	HDO(1)/DTO(2)	D_2O	1.030	1.024	1.133

It is difficult to choose which mechanism is most appropriate to explain the isotopic effect in liquid water. The gas kinetics approach gives the closest agreement with experiment, but in view of the fact that no other purely translational isotopic mass effect has been found in solute diffusion it seems unlikely to be operative here. In the case of the solid-state model all that can be said is that the data can be made to fit with reasonable parameters. At this stage it would seem that either the relatively large rotational inertia difference between the two tracers or quantum effects are the most likely cause of the isotopic effect in liquid water.

4 Summary

Consideration of the self-diffusion data presented in this review leads one to believe that D_S for monatomic fluids behaves as is predicted by classical theories. The available data for monatomic fluids are not precise enough to verify the $m^{-\frac{1}{2}}$ dependence but self-diffusion results for more complex liquids provide good evidence for this belief. Thus the data for benzene and perdeuteriobenzene can be explained by the $m^{-\frac{1}{2}}$ law with an allowance for small differences in the intermolecular potentials. This result even seems to hold in the comparison of the viscosities of $H_2{}^{16}O$ and $H_2{}^{18}O$, which have almost the same moments of inertia, but not in the case of the transport properties of $H_2{}^{16}O$ and $D_2{}^{16}O$, where the different moments of inertia suggest different amounts of translational–rotational coupling. Although an alternative explanation such as the difference in energy between a hydrogen and a deuterium bond may be offered, the former explanation seems the more likely. More experimental self-diffusion measurements for $H_2{}^{18}O$ and $D_2{}^{18}O$ and intradiffusion in mixtures of H_2O and D_2O are also needed. N.m.r. techniques of precision ±1% or better would be needed for such studies. Another approach to studying rotational effects would involve the selective deuteriation of organic molecules to obtain a graded series of liquids with differing moments of inertia. Their self-diffusion coefficients might best be determined by labelling with tritium and using radiotracer techniques. In this way some guide to the extent that translational and rotational motions couple, a subject of considerable current interest, might be obtained. Complementary theoretical work is also needed on these problems to provide a quantitative analysis of the coupling process.

In the tracer or 'solute' diffusion case, what comes through the data very clearly is that diffusion rates of tracers are determined primarily by bulk solvent properties and not by changes in tracer mass. This is generally in accord with Friedman's predictions based on linear response theory and gives confidence in this approach, which to the best of the authors' knowledge has had as yet little contact with experiment. Molecular dynamics studies for hard-sphere diffusion complement the experimental work and show expected trends from changes in the mass ratio of solute and solvent ratios. It is now of interest to vary solute/solvent mass ratios to discover where the theoretical predictions break down, in particular by making the mass of the tracer very small. It would seem to be very difficult to do this experimentally (generally isotopically substituted molecules do not differ greatly in mass) and molecular dynamics studies could be extended in this direction.

Finally, looking at the more specific effects that are described in this review, it would appear from the data for diffusion of isotopic ions that liquid diffusion processes are not a practicable way of separating the isotopes of heavy ions. One must also comment on the tracer diffusion data for liquid water, where there is a large isotopic effect, for which a number of explanations are offered. As any new information on the properties of water is of prime importance, the interpretation of this phenomenon at this stage might profitably be attacked by the theoretical chemist.