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Isotope effect in liquids as shown by tracer diffusion at 25 °C of several labeled benzenes in benzene, chlorobenzene, *n*-octane, and cyclohexane, and the relationship to the isotope effect in solids

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Mutual and tracer diffusion coefficients at 25 °C are reported for the liquid systems perdeuterobenzene(C_6D_6)-chlorobenzene, benzene(C_6H_6)-chlorobenzene, C_6D_6-*n*-octane, C_6H_6-*n*-octane, C_6D_6-cyclohexane, and C_6H_6-cyclohexane. These data are compared with similar data previously obtained in this laboratory. All the data indicate a very *slight* isotope effect for tracer diffusion of benzene in benzene, in chlorobenzene, in *n*-octane, and in cyclohexane. Application to the above data of the equation usually used to describe the "isotope effect" in solids, indicates that diffusion in these systems may be governed to a large extent by the viscosity of the solvent.

In two previous papers[1,2] we have reported tracer diffusion coefficients[3] D_T for ^{14}C-substituted benzenes diffusing in benzene, *n*-heptane, *n*-octane, and cyclohexane. The data indicated that these coefficients were *very slight* linear functions of the molecular weight of the tracer species and not, as has sometimes been suggested for liquid systems,[4] inversely proportional to the square root of the molecular weight of the tracer or to the square root of the reduced mass of the system. The purpose of this paper is (a) to report binary diffusion coefficients[3] D for the liquid systems C_6D_6-chlorobenzene, C_6D_6-*n*-octane, C_6D_6-cyclohexane, C_6H_6-chlorobenzene, C_6H_6-*n*-octane, and C_6H_6-cyclohexane which may be extrapolated to yield limiting tracer and mutual diffusion coefficients, (b) to report tracer diffusion coefficients D_T for ^{14}C-substituted benzenes diffusing in chlorobenzene, (c) to compare all these coefficients with similar values recently obtained in this laboratory with ^{14}C-substituted benzenes of varying molecular weight,[2] and (d) to indicate an interesting conclusion concerning transport in liquids that follows from the application to the above data of an equation usually used to describe the isotope effect in solids.[5,6]

The labeled and unlabeled compounds used in this study were chosen for the following reasons: (a) because all the species are essentially unassociated in the liquid state and therefore any isotope effects are unlikely to be masked, (b) because the diffusion data could be obtained by both optical and radio-isotope techniques, (c) because of the six carbon atoms in benzene it was quite easy to vary its molecular weight over a large range, and (d) because of the extremely long half-life of ^{14}C.

EXPERIMENTAL

The mutual diffusion coefficients for the six systems were measured with a Gouy diffusiometer[7] and a special diffusion cell both of which have been previously described,[8,9] as have also the experimental techniques and computations which were used to obtain the results. The cell was constructed with a Tiselius-type design, but did not have moving surfaces which required lubrication. It is believed that the data are accurate to (0.1–0.2)%. Using ^{14}C-substituted benzenes of varying molecular weight, tracer-diffusion coefficients were measured for the system C_6H_6-chlorobenzene by means of a diaphragm-cell which has been previously described.[1,2,10] Both sets of data are summarized in Table I. All solvents were analyzed by gas phase chromatography and, except for C_6D_6, were found to contain less than 0.01% impurity; the latter solvent was found to contain less than 0.4% impurity.

The mutual data for the systems C_6D_6-chlorobenzene and C_6H_6-chlorobenzene are shown in Fig. 1 as function of the mole fraction x_2 of the heavy component. In the absence of an "isotope effect," the two sets of data should extrapolate to give the same intercept at $x_2 = 1$. In Fig. 2 are plotted as a function of molecular weight all the tracer diffusion coefficients measured in this study, together with those measured previously.[2,11] The limiting values D^0 were obtained by extrapolating to $x_2 = 1$ mutual coefficients measured with the Gouy diffusiometer (see Table II). These values differ slightly from those previously reported,[2,10] but are more reliable because of the improved performance of the diffusion cell used in this work. The *tracer* diffusion coefficients for the perdeuterobenzene were obtained by extrapolating the mutual data. Inspection of Fig. 2 indicates that there is a *very slight* isotope effect and that, within an assumed *average* error for all experiments of ±0.2%, the tracer diffusion coefficients are a linear function of molecular weight (see Discussion). It is pleasing to note that the tracer coefficients obtained with C_6D_6 and with ^{14}C-substituted benzenes are perfectly consistent.

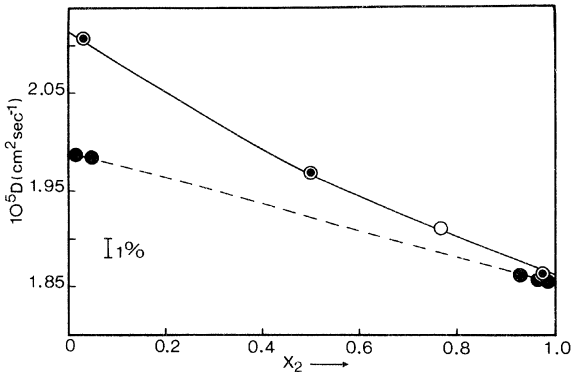

FIG. 1. Mutual diffusion coefficients at 25°: ○, benzene-chlorobenzene (◉, duplicate points); ●, perdeuterobenzene-chlorobenzene.

TABLE I. Mutual diffusion coefficients at 25 °C.

$\bar{x}_2$[a]	Δx_2[a]	J[b]	10^5D (cm^2sec^{-1})
	C_6H_6-chlorobenzene		
0.027 05	0.0541_0	88.98	2.108
0.035 24	0.0704_8	115.47	2.107
0.498_0	0.0629_8	91.26	1.967
0.501_5	0.0706_4	103.09	1.969
0.774_4	0.0645_6	88.56	1.910
0.973_3	0.0533_3	69.47	1.862
0.978_7	0.0425_3	55.21	1.864
	C_6D_6-chlorobenzene		
0.016 59	0.033 18	60.57	1.986
0.0439_5	0.0879_0	161.00	1.985
0.932_7	0.1346_0	193.98	1.861
0.969_5	0.0610_1	88.82	1.857
0.976_7	0.0465_3	66.18	1.855
	C_6H_6-cyclohexane[c]		
$0.008\,62_0$	0.017 24	116.08	2.104
0.0496_9	0.016 77	108.94	2.049
0.899_7	0.029 83	98.07	1.861
0.984_8	0.030 35	92.47	1.872
0.991_4	0.017 27	52.35	1.873
	C_6D_6-cyclohexane		
0.899_3	0.031 29	98.72	1.838
0.984_8	0.030 49	89.30	1.859
	C_6H_6-*n*-octane		
0.981_0	0.037 90	114.16	3.128
0.898_8	0.030 16	100.01	3.007
	C_6D_6-*n*-octane		
0.984_9	0.030 15	88.93	3.119
0.903_8	0.024 33	101.84	2.978

[a] $\bar{x}_2$ and Δx_2 are the mean mole fraction and the difference in mole fraction, respectively, used in each experiment.

[b] J is the total number of interference fringes obtained in each Gouy experiment.

[c] These points agree well with the data of L. Rodwin, J. A. Harpst, and P. A. Lyons, J. Phys. Chem. 69, 2783 (1965).

DISCUSSION

Like self-diffusion in liquid benzene[1] the tracer diffusion coefficients of ^{14}C-substituted and perdeuterated benzenes in chlorobenzene, *n*-octane, and cyclohexane may be represented by an equation of the form

$$D_T = D^0 - A(M_T - M_0), \tag{1}$$

where D^0 is the limiting tracer diffusion coefficient, M_T is the molecular weight of the tracer species, M_0 is the molecular weight of the solvent,

TABLE II. Values of *extrapolated* mutual diffusion coefficients, and *experimental* tracer diffusion coefficients D_T.

	Mutual coefficients[a]		
	$10^5D°$	10^5 Error	
C_6H_6-chlorobenzene	1.860	±0.003	
C_6D_6-chlorobenzene	1.854	±0.003	
C_6H_6-*n*-octane	3.156	±0.004	
C_6D_6-*n*-octane	3.145	±0.004	
C_6H_6-cyclohexane	1.874	±0.003	
C_6D_6-cyclohexane	1.863	±0.003	
	Tracer coefficients		
	10^5D_T	10^5error	M. W.[b]
C_6H_6-chlorobenzene	1.855	±0.002	80
	1.854	±0.003	80
	1.853	±0.003	88
	1.848	±0.002	88

[a] For these systems the limiting *mutual* diffusion coefficients are also *tracer* coefficients.

[b] The molecular weights of the tracer species were calculated from details of the preparations supplied by the manufacturer.

and A is a constant.

In the Appendix it is shown that Schoen's equation,[12-15] originally introduced for diffusion in solids,

$$\left(\frac{D^\alpha}{D^\beta}-1\right)=f^\alpha\left(\frac{\omega^\alpha}{\omega^\beta}-1\right), \tag{2}$$

where D^α, D^β, ω^α, and ω^β are the diffusion coefficients and jump frequencies of the isotopes α and β, which can be written in the form

$$D_T=D^0-\frac{D^0 f_T \Delta K}{2M_0}(M_T-M_0). \tag{3}$$

In this equation f_T is the correlation factor and ΔK is the fraction of the total kinetic energy, associated with the decomposition of the saddle point configuration, which resides in the migrating, isotopically labeled species *when only one molecule is relocated.* For a detailed treatment see LeClaire.[5,6] Comparison of Eqs. (1) and (3) shows that

$$A=D^0 f_T \Delta K/2M_0. \tag{4}$$

In Table III values of $f_T\Delta K$, calculated from the experimental A values, are tabulated for the systems studied in this work, and also for the case of benzene.[1] The values of A were obtained by least squaring the data to fit Eq. (1). Since only the product $f_T\Delta K$ is obtained one of these factors must be assumed before the other can be calculated.

Now for self-diffusion, where f_T is a geometrical factor, a good approximation[6] for f_T is

$$f_T=1-2/Z\ , \tag{5}$$

where Z is the coordination number. In the case of the liquids studied here a value of $Z\sim 10$ is not an unreasonable assumption. Results obtained for ΔK by using the resultant value of $f_T=0.8$ are given in Table III. It should be noted, however, that for impurity diffusion f_T is *not* a geometrical factor since it is dependent of the relative jump rates of tracer and host.

Inspection of Table III indicates that the ΔK values are all much less than unity, so that a very small fraction of the kinetic energy associated with a jump remains with the migrating species. A small value of ΔK indicates that, during the transition of a molecule to a vacancy position, momentum is transferred to the other molecules in the *immediate* vicinity and, presumably at a slightly later time, this excess momentum is redistributed to the bulk of the fluid.

On this basis one would *not* expect to find, as has sometimes been suggested, that the tracer diffusion coefficients of a liquid or solid in a liquid would be inversely proportional to the square roots of the masses of the tracer species, but possibly *approximately* proportional to some power of the viscosity of the fluid. There are two limiting cases for $f_T\sim 1$; $f_T\Delta K\sim 1$ and $f_T\Delta K\sim 0$. In the first case tracer diffusion coefficients would be inversely proportional to the square roots of the masses of the migrating species [see Eq. (A1)], and in the latter case, because of the complete momentum transfer during the decomposition of the saddle-point configuration, proportional to some power of the viscosity of the solvent. For the present systems

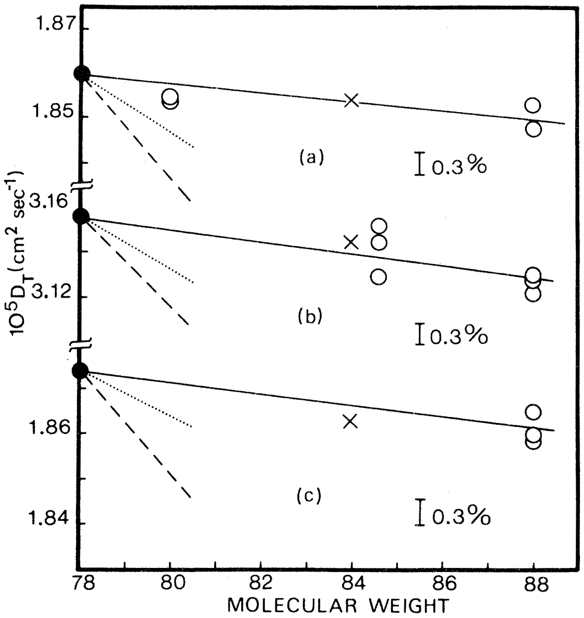

FIG. 2. Tracer diffusion coefficients for ^{14}C-substituted and perdeuterobenzene diffusing in (a) chlorobenzene (b) *n*-octane, and (c) cyclohexane: ○, experimental D_T points with ^{14}C isotopes; ×, experimental points with perdeuterobenzene; ●, limiting experimental mutual diffusion coefficients D^0. The dashed and dotted lines indicate the limiting mass dependences expected if the tracer diffusion coefficients of the labeled species are assumed to be *inversely* proportional to the square root of their mass and the reduced mass of the system, respectively.

TABLE III. Values of $f_T\Delta K$ and ΔK.

	$f_T\Delta K$	ΔK	% Error in ΔK [a]
C_6H_6 [b]	0.08_4	0.1_0	15
C_6H_6-chlorobenzene	0.07_1	0.09	47
C_6H_6-*n*-octane	0.20	0.2_7	49
C_6H_6-cyclohexane	0.12_0	0.1_6	32

[a] The errors in each ΔK have 95% fiducial limits.

[b] Data from Ref. 1 for ^{14}C-labeled benzenes diffusing in benzene.

$f_T \Delta K \leq 0.2$ indicates that the tracer coefficients are almost independent of mass, a prediction which is in reasonable agreement with fact. The values of $f_T \Delta K$ in Table III seem to indicate that the type of diffusion process reported in this work is governed to a large extent by the viscosity of the solvents (benzene, chlorobenzene, cyclohexane, and *n*-octane). It is interesting to note (see Fig. 1) that the ratio of the limiting diffusion coefficients of chlorobenzene in benzene and in perdeuterobenzene agrees to within 0.1% with the viscosity of C_6D_6 relative to C_6H_6,[15] a fact which suggests that the *tracer* diffusion coefficients are *inversely* proportional to the first power of the viscosity of the solvent.

LeClaire[6] has indicated that the discussion above, which assumes that only *one* molecule is relocated during decomposition at the saddle point, can be extended for the case when two or more molecules are relocated. When two molecules are relocated, as in the case for the interstitialcy mechanism for diffusion in solids, it would appear that the arguments in the above discussion still apply since the ΔK values, although increasing by 100%, still remain much smaller than unity.

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APPENDIX

Conventionally isotope effects in diffusion in solids have been studied by simultaneously diffusing two suitable isotopes, α and β, of the host and applying Schoen's equation[12]

$$\left(\frac{D^\alpha}{D^\beta} - 1\right) = f^\alpha\left(\frac{\omega^\alpha}{\omega^\beta} - 1\right) = f^\alpha \Delta K\left[\left(\frac{M^\beta}{M^\alpha}\right)^{1/2} - 1\right]. \tag{A1}$$

In this equation f^α is the correlation factor and ΔK is the fraction of the total kinetic energy, associated with the decomposition of the saddle point configuration, which resides on the migrating isotope. For self-diffusion in many solids, where *only one atom is relocated* $\Delta K \simeq 1$.

If Schoen's equation is written

$$\Delta D/D = f^\alpha(\Delta\omega/\omega), \tag{A2}$$

and, if ω is assumed proportional to $(M)^{-1/2}$, then

$$\Delta D/D = -(f^\alpha \Delta K/2M)\Delta M. \tag{A3}$$

Hence, using the notation D_T for the tracer diffusion coefficient, D^0 for the limiting tracer diffusion coefficient, and M_T and M_0 for the molecular weights of the tracer and solvent species, respectively,

$$\frac{D_T - D^0}{D^0} = -\frac{f_T \Delta K}{2M_0}(M_T - M_0) \tag{A4}$$

or

$$D_T = D^0 - \frac{D^0 f_T \Delta K}{2M_0}(M_T - M_0). \tag{A5}$$

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