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Diffusion of aromatic compounds: An investigation on the effects of molecular shape, mass, and dipole moment

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TABLE I. Summary of calculated energies and bond lengths.[a]

	Calculations	Energy (hartree)	Bond length (bohr)
Li_2:	[5s]	− 14.6545	5.630
	[5s3p]	− 14.6406	6.390
	[5s3p2d]	− 14.6347	6.753
	[5s3p1d][b]	− 14.6304	6.788
	[5s3p1d][b]	− 14.8710	5.250
N_2:	[8s6p]	− 105.7239	2.060
	[8s6p1d]	− 105.7567	2.069
	3-21G	− 105.6721	1.965
	3-21G	− 108.3037	2.065
CH_4:	[8s4p/3s]	− 37.4151	1.725
	3-21G	− 37.7601	1.692
	3-21G	− 39.9989	2.150

[a] The last line for each molecule is the normal SCF result, all other lines being the scaled estimates.
[b] M. M. Heaton, Ref. 6.

the Ar nucleus. Doubling the size of this wave function then puts all ten electrons of HF on the fluorine atom to the detriment of the approximation in Eq. (1). For hydrocarbons the effect is still worse: all four hydrogen electrons are shifted onto the carbon in methane in the scaled $MgHe_4^{+}$ [10] system. Notice from the figure that at shorter bond distances, the approximation does become better, as expected, since this unphysical electron shifting becomes less important.

Because the scaled system represents a dramatic shrinking of the unscaled one, a direct scaling of an approximate contracted Gaussian basis set from the unscaled system leaves some questions about the accuracy of the representation of Eq. (1). Accordingly, we have examined a few cases using extended atomic basis functions chosen directly for the scaled systems. We did this for Li_2, where the bond length of

one previous calculation by Heaton[6] is much worse than any of the present results; for N_2 with increasingly elaborate bases; and for CH_4. Extended Gaussian basis sets appropriate to the scaled atoms were chosen,[9,10] and used for uncontracted SCF atomic calculations on the appropriate scaled ions (e.g., C^{+3} is the scaled system for Li). For molecular use, the atomic ionic bases were contracted in a well-known manner, and for Li_2 and N_2 additional polarization basis functions were added.[9] The contracted atomic basis sets were as good as near Hartree–Fock values[11] for the ions, suggesting that the molecular results summarized in Table I are close to representing the limit of the approximation of Eq. (1). These extended basis results are very similar to the previous ones, confirming that analysis and indicating the demise of this approximation for estimating useful molecular properties.

[1] B. H. Robinson and L. J. Schaad, J. Chem. Phys. 59, 6189 (1973).
[2] L. J. Schaad, B. H. Robinson, and B. A. Hess, Jr., J. Chem. Phys. 67, 4616 (1977).
[3] C. V. R. Rao and K. D. Sen, J. Chem. Phys. 70, 586 (1979).
[4] A. François and L. Pujol, J. Chem. Phys. 71, 1066 (1979).
[5] L. Pujol and A. François, J. Chem. Phys. 73, 6263 (1980).
[6] M. M. Heaton, J. Chem. Phys. 70, 4434 (1979).
[7] B. G. Niyogi, B. R. De, and A. B. Sannigrahi, Indian J. Pure Appl. Phys. 17, 13 (1978).
[8] J. S. Brinkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc. 102, 939 (1980).
[9] T. H. Dunning, Jr. and P. J. Hay, in Modern Theoretical Chemistry 3: Methods of Electronic Structure Theory, edited by H. F. Schaefer III, (Plenum, New York, 1977).
[10] A. Veillard, Theor. Chim. Acta (Berlin) 12, 405 (1968).
[11] E. Clementi and C. Roetti, Atomic Data Nucl. Data Tables 14, 177 (1974).

Diffusion of aromatic compounds: An investigation on the effects of molecular shape, mass, and dipole moment

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Theories of diffusion in dense fluids are currently based on simplified models. Traditionally, diffusion in liquid state has been described with the hydrodynamic theory represented by the Stokes–Einstein equation. This equation predicts diffusion coefficients in terms of solute radius, solvent viscosity, temperature, and a hydrodynamic frictional coefficient. While the Stokes–Einstein equation accounts well for the diffusion of large spherical solutes, it fails completely for solute molecules small in size compared to the solvent molecules.[1–4] The validity and invalidity of the Stokes–Einstein equation have been discussed in detail.[1–3] Recently there has been a good deal of interest in the use of the rough-hard-

sphere (RHS) theory as a basis for the interpretation of diffusion data.[3–19] According to that theory, the transport coefficients are dependent on particle mass, temperature, fluid density, particle size, and a constant accounting for the translation-rotation coupling.[19,20] Unfortunately, the range of applicability of the theory has not been critically tested. It should be noted that in the above theories of diffusion all molecules are assumed to be spherical in shape. The theories are further based on the assumption that attractive forces are negligible in determining the molecular dynamics of liquids.

It appears that still little is known about the effects of molecular shape and dipole moment on diffusion. In view of

TABLE I. Limiting mutual diffusion coefficient $(D_{12} \times 10^9$ m^2 s$^{-1})$ at 298.15 K.

	van der Waals volume[a] (Å^3)	Dipole moment[c] (D)	Solvent		
			Acetone	Ethanol	n-Tetradecane
1,4 Me–C$_6$H$_4$–Me	114.2	0	3.52 ± 0.04	1.54 ± 0.02	1.02 ± 0.01
1,4 Me–C$_6$H$_4$–Cl	113.7	2.21	3.50 ± 0.03	1.54 ± 0.02	1.01 ± 0.01
1,4 Cl–C$_6$H$_4$–Cl	113.2	0	3.46 ± 0.04	1.54 ± 0.02	1.00 ± 0.01
1,3 Me–C$_6$H$_4$–Me	114.2	0.35[d]	3.42 ± 0.03	1.44 ± 0.02	0.943 ± 0.005
1,3 Cl–C$_6$H$_4$–Cl	113.2	1.72	3.38 ± 0.04	1.43 ± 0.01	0.936 ± 0.006
1,2 Me–C$_6$H$_4$–Me	114.2	0.62	3.39 ± 0.04	1.40 ± 0.01	0.892 ± 0.007
1,2 Cl–C$_6$H$_4$–Cl	113.2	2.50	3.35 ± 0.03	1.37 ± 0.01	0.888 ± 0.006
Me$_4$Sn	114.9[b]	0	3.38 ± 0.03[e]	1.25[e]	0.812 ± 0.007[f]

[a] The values are averages from Refs. 23–26.
[b] Sn contribution taken from Ref. 24.
[c] From Ref. 27 except where noted otherwise.
[d] T. Nagai, Y. Koya, H. Takahashi, and K. Higasi, Bull. Chem. Soc. Jpn. **47**, 1022 (1974).
[e] From Ref. 1.
[f] From Ref. 2.

the fact that most real molecules possess dipole moment and are nonspherical, the lack of experimental studies of these effects may hinder further development of the general theories of diffusion in liquids. For this reason, we have recently carried out a series of diffusion measurements designed to provide careful evaluation of the various molecular effects on diffusion. In a previous paper[5] we have already reported the effects of dipole moment on the diffusion of pseudospherical solutes in various solvents.

In this note we present the mutual diffusion coefficient of p-chlorotoluene, (o-, m-, and p-)dichlorobenzene, and (o-, m-, and p-)xylene at infinite dilution in acetone, ethanol, and n-tetradecane at 298.15 ± 0.02 K. The solvents are chosen to represent protic, aprotic, and hydrocarbon solvents. All disubstituted benzene molecules in this study are of the same molecular volume. More importantly, they are pseudoplanar molecules with a size similar to that of the previously studied tetramethyltin.[1,2] Thus direct comparisons between the diffusion coefficients for the pseudoplanar and the pseudospherical solutes are useful. In addition to being equal in size, the solutes p-dichlorobenzene and p-xylene are selected because they are of the same shape and without dipole moment. These data permit the effects of mass on diffusion to be critically examined. The molecule p-chlorotoluene differs from the above two solutes in dipole moment, the effects of which can be ascertained from the data. Moreover, the isomers of dichlorobenzene and xylene are designed to test the effects of molecular geometry on diffusion.

Limiting mutual diffusion coefficients were measured by using the chromatographic broadening method.[21] The apparatus and procedures used were the same as those reported elsewhere.[5] In this experiment, the solvents acetone (99.5% + BDH), ethanol (99.5% + Ajax), and n-tetradecane (99% + TCI) were used without further purification. The solute p-chlorotoluene (99% Merck) was purified by fractional distillation; o- and m-dichlorobenzene (both 99% + Merck), p-dichlorobenzene (99% + Koch–Light Laboratories), and the xylenes (all 99% + Carlo Erba) were used as received.

The measured diffusion coefficients are summarized in Table I. Each diffusivity reported is the mean value of at least three runs. The uncertainty listed is the average absolute error. The precision of our data is about ± 1%. To test our apparatus again, we have determined the limiting mutual diffusion coefficient of benzene (99% + BDH) in methanol (99.5% BDH) at 300.21 K. Our value of 2.74 (± 0.02) × 10^{-9} m^2 s^{-1} agrees with the literature value[22] of 2.76 (± 0.03) × 10^{-9} m^2 s^{-1}. This agreement with literature is consistent with those reported in our previous work.[5]

For comparisons, Table I includes previous data for tetramethyltin.[1,2] Also shown in the table are values of the dipole moment and van der Waals volume of the solute molecules. All solutes in this study are equal in size to within 1.5%. The close resemblance in size between a chloride group and a methyl group has already been discussed.[9] It should be pointed out that a 1% change in solute core diameter ($\simeq$3% change in van der Waals volume) produces typically a small 2% variation in the mutual diffusion coefficient.[4,11]

The major findings and conclusions which we wish to report are summarized as follows:

(i) The mutual diffusion coefficients are insensitive to the mass and dipole moment of the solute molecules studied. This can be seen by comparing the data in Table I for solutes with the same size and shape in each solvent. The present results are consistent with those for the pseudospherical solutes in our previous study.[5] The insensitivity of solute dipole moment on diffusion here further justifies the basic assumption[20] made in the RHS theory, i.e., attractive and other forces which vary slowly in space are unimportant as compared to the harsh repulsive parts of the intermolecular forces in affecting the molecular motions in liquids.

(ii) The data presented in Table I are slightly dependent on the geometry of the solute molecules. The diffusion coefficients are generally smaller for tetramethyltin than for the pseudoplanar solutes in any one solvent. Among the disubstituted benzenes, the diffusivity trends are $o < m < p$. Since the $para$-disubstituted benzene is more linear than the other

two isomers, the effects of solute shape on diffusion in this study appear to be such that the diffusivity increases in the order "spherical," "planar," and "linear." Further efforts with the goal of elucidating these effects are underway in our laboratory.

(iii) Another noteworthy feature of the data is that the effects of solute shape on diffusion are solvent dependent. The shape effects are rather insignificant in acetone,the largest effect being only 5% here. However, the effects are much greater in n-tetradecane and in ethanol, the maximum effects in this work being 26% and 23%, respectively. Since molecular shape effects are closely related to the degree of coupling[19] between the rotational and translational motions, the present experimental results suggest that in application of the RHS theory for real fluids it may be necessary to use a solvent and solute dependent translation-rotation coupling constant.

(iv) Precise measurements of diffusion coefficients for solutes with the same size can provide useful and straightforward information on the effects of mass, dipole moment, and shape of solute molecules on diffusion.

[1]D. F. Evans, T. C. Chan, and B. C. Lamartine, J. Am. Chem. Soc. 99, 6492 (1977).

[2]D. F. Evans, T. Tominaga, and T. C. Chan, J. Solution Chem. 8, 461 (1979).

[3]D. F. Evans, T. Tominaga, and H. T. Davis, J. Chem. Phys. 74, 1298 (1981).

[4]S. H. Chen, H. T. Davis, and D. F. Evans, J. Chem. Phys. 75, 1422 (1981); 77, 2540 (1982).

[5]T. C. Chan, J. Chem. Phys. 79, 3591 (1983).

[6]J. Jonas, D. Hasha, and S. G. Huang, J. Chem. Phys. 71, 3996 (1979); J. Phys. Chem. 84, 109 (1980).

[7]J. Jonas and J. A. Akai, J. Chem. Phys. 66, 4946 (1977).

[8]H. J. Parkhurst, Jr. and J. Jonas, J. Chem. Phys.63, 2698, 2705 (1975).

[9]S. J. Bertucci and W. H. Flygare, J. Chem. Phys. 63, 1 (1975).

[10]J. J. Van Loef, Physica B 95, 34 (1978).

[11]J. H. Dymond, J. Phys. Chem. 85, 3291 (1981); J. Chem. Soc. Faraday Trans. 1 78, 991 (1982).

[12]K. J. Czworniak, H. C. Andersen, and R. Pecora, Chem. Phys. 11, 451 (1975).

[13]M. Fury, G. Munie, and J. Jonas, J. Chem. Phys. 70, 1260 (1979).

[14]R. J. Finney, M. Fury, and J. Jonas, J. Chem. Phys. 66, 760 (1977).

[15]J. DeZwaan and J. Jonas, J. Chem. Phys. 63, 4606 (1975).

[16]K. R. Harris and W. J. Trappeniers, Physica A 104, 262 (1980).

[17]K. R. Harris, Physica A 93, 593 (1978).

[18]L. A. Woolf and K. R.Harris, Chem. Phys. 32, 349 (1978).

[19]D. Chandler, J. Chem. Phys. 62, 1358 (1975).

[20]D. Chandler, J. Chem. Phys. 60, 3500, 3508 (1974).

[21]E. Grushka and E. J. Kikta, Jr., J. Phys. Chem. 78, 2297 (1974).

[22]P. A. Johnson and A. L. Babb, Chem. Rev. 56, 387 (1956).

[23]A. Bondi, J. Phys. Chem. 68, 441 (1964).

[24]J. T. Edward, Chem. Ind. (London), 1956, 774.

[25]A. I. Kitaigorodskii, Organic Chemical Crystallography (Consultants Bureau, New York, 1961).

[26]A. E. Luzkii, Dokl. Akad. Nauk SSSR 44, 513 (1954); Russ. J. Phys. Chem. 28, 204 (1954).

[27]Handbook of Chemistry and Physics, edited by R. C. Weast, 62nd ed. (Chemical Rubber, Boca Raton, Florida, 1981).

Rational fraction analytic continuation method for complex resonance energies in multidimensional systems

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It has recently been demonstrated that complex resonance energies

$$\epsilon = E_{\text{res}} - i\Gamma/2 \tag{1}$$

are obtainable from stabilization calculations with real basis functions, without imposing scattering boundary conditions.[1–3] This is accomplished by analytic continuation of the energy of one or more eigenvalues as a function of a scale parameter. The procedures that have been used differ in detail. So far only the simplest procedure, based on a polynomial (cubic) fit to a single eigenvalue, has been applied to resonances in chemical reactions.[2] It is well known though that rational fractions are better suited than polynomials for analytic continuation.[4] In the present note, we apply rational fraction fits to stabilization eigenvalues for the same two-

dimensional examples treated previously, to learn if the accuracy is improved, and to some additional examples, to test the generality of resonance width calculations based on a single eigenvalue as a function of a scale parameter. Although the present note is explicitly concerned with collinear reactions that, after removal of the motion of the center of mass, involve two mathematical dimensions, the method presented is more general and is applicable to arbitrary multidimensional systems.

We consider collinear reactive scattering with two coordinates q_1 and q_2 and basis functions consisting of multinomials times $\exp[-\alpha^2(\beta_1^2 q_1^2 + \beta_2^2 q_2^2)]$, where α is the scale parameter.[5,6] The resonant eigenvalue is identified by its relative insensitivity to α and is denoted $E_k(\alpha)$. This eigen-