

16. W. Baumjohann *et al.*, *J. Geophys. Res.* **85**, 1963 (1980).
17. J. C. Foster, *Geophys. Res. Lett.* **14**, 160 (1987).
18. J. C. Foster *et al.*, *ibid.* **13**, 656 (1986).
19. Y. Kamide and J. F. Vickrey, *J. Geophys. Res.* **88**, 7989 (1983).
20. S.-I. Akasofu, *Space Sci. Rev.* **28**, 121 (1981).
21. The author thanks W. Baumjohann and J. C. Foster for their useful comments on an early version of the

manuscript. A special note of thanks is extended to B.-H. Ahn, S.-I. Akasofu, J. D. Craven, D. J. Gorney, H. W. Kroehl, Y. Ishihara, and A. D. Richmond for their collaboration. The work reported in this paper was supported in part by a grant-in-aid from the Ministry of Education, Science, and Culture in Japan.

29 March 1988; accepted 19 May 1988

Diffusion of Small Solutes in Polymer-Containing Solutions

KIT L. YAM, DONALD K. ANDERSON, ROBERT E. BUXBAUM*

Diffusion processes involving polymers are common in scientific and engineering separations and are a major component of biological functions. Analyses of these systems are usually based on versions of the Stokes-Einstein equation, although order of magnitude deviations have been observed. Presented here is a theoretical correction to the Stokes-Einstein equation containing a "local viscosity" function that combines diffusional hydrodynamics with Maxwell's treatment of electrical resistance in inhomogeneous regions. The resulting equation accurately predicts experimental diffusion data within tight bounds for polymer concentrations from 0 to 9 percent. It requires knowledge only of thermodynamics and of pure solvent and solution viscosities.

FOR THREE-COMPONENT DIFFUSION where one component is a dilute polymer, Stokes-Einstein type equations (for example, Eqs. 1 and 2) produce errors as large as 10,000 times (1-8). Notwithstanding, Eq. 1 is used as the basis for most correlations of protein sedimentation (6), polymerization (4), gel chromatography (5), and systems of biological interest (8), despite the presence of dilute polymers.

Several sound theoretical approaches can be used to derive Stokes-Einstein type equations (9-13); however, all of them contain a difficult assumption, that the mechanisms of molecular drag are identical with those of global viscosity. Thus, for ideal solutions at infinite dilution, the binary-liquid diffusion coefficient, D_{AB} , is predicted to be inversely proportional to viscosity (1-13):

$$D_{AB} = \frac{kT}{6\pi\eta r_A} \quad (1)$$

where η is the solution (global) viscosity, k is the Boltzmann constant, T is temperature, and r_A is the hydrodynamic radius of the dilute diffusing species. From nonequilibrium thermodynamics (14), Eq. 1 becomes, for nonideal solutions,

$$D_{AB} = \frac{kT}{6\pi\eta r_A} \left(1 + \frac{d \ln \gamma_A}{d \ln x_A} \right) \quad (2)$$

where γ_A and x_A are, respectively, the activi-

ty coefficient and mole fraction of species A, and r is the hydrodynamic radius of the diffusing species. Various statistical and hydrodynamic treatments have related r to molar volume; we have found those of Hartley and Crank (15), Protopapas *et al.* (16), and Perrin (17) particularly noteworthy (18-20); the fit is excellent in many systems. For engineering purposes, the effect of solvent association on r is typically dealt with by the correlation of Wilke and Chang (21) or through cluster diffusion correlations (22, 23).

Empirical corrections of Eq. 1 suggest that diffusivity is inversely proportional to a variable power of solvent viscosity (1-6), proportional to viscosity raised to the power of a function of molar volume (24, 25), or proportional to a variable power of the solvent molecular weight (21). Although these corrections allow successful matching of experimental data (2-4, 21), the fundamental justification is unclear. From statistical mechanics also come several attractive modifications generally having the form (26, 27)

$$D = D_0 \exp(-\alpha c^\nu) \quad (3)$$

where D_0 is the diffusivity in the absence of polymer, c is polymer concentration, and α and ν are constants. With appropriate constants for α and ν , Eq. 3 can be made to fit a given set of data excellently; however, most theories predict that α should be approximately proportional to r (1) and ν should be a universal constant based on hydrodynamic screening lengths [which Ogston *et al.* (26)

and Alterberger and Tirrell (28) predict to be 1/2 (from quite different approaches), and others predict to be 2/3 or more (29, 30)]. The problem with Eq. 3 is that experimental measurements do not support any general correlation for α and ν , so that an *a priori* analytical treatment seems distant at present: α varies much more slowly than r ; and ν , instead of being a universal constant, appears to vary between 0.38 and 2.21 even for very dilute polymer solutions (31). In our opinion, these problems stem from the difficulty in treating the microscopic equivalent of hydrodynamic "wall drag" and "tortuosity" through statistical mechanics. We present here a theoretical analysis that leads to a useful local viscosity relation for describing experimental data for diffusion processes. Predictions of this equation should be useful in analyzing sedimentation, polymerization, gel chromatography, and systems of biological and physiological interest.

We measured the viscosities and mutual diffusion coefficients of benzene-cyclohexane-dilute polymer solutions with techniques described elsewhere (32, 33). Polymer concentration and molecular weight strongly affect global viscosity (Fig. 1) so that for a polymer concentration of 2 g/dl and a molecular weight of 1.8×10^6 , the viscosity of this three-component solution is almost 40 times that of cyclohexane-benzene without polymer. Although Eqs. 1 and 2 predict sharp decreases in diffusion coefficient with increased molecular weight or polymer concentration because of increases in viscosity, as does Eq. 3 for theoretical

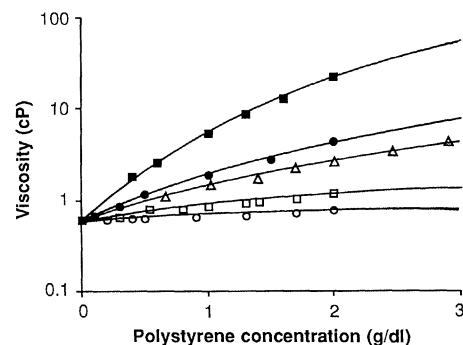


Fig. 1. Global viscosity of polystyrene-benzene-cyclohexane versus polystyrene concentration. Viscosities were measured with a Cannon-Ubbelohde viscometer; values for benzene and cyclohexane were compared with those in the literature (41), and the agreement was within 1%. Densities were measured with a pycnometer. Monodisperse polystyrene [$MW_n = 4 \times 10^3$ (○), 5×10^4 (□), 6×10^5 (●), 1.8×10^6 (■); $MW_w/MW_n < 1.1$, where MW_n is the number-average molecular weight] was purchased from Alfa Products, and polydisperse polystyrene [$MW_w = 3.21 \times 10^5$ (▲), $MW_w/MW_n = 3.8$, where MW_w is the weight-average molecular weight] was purchased from Aldrich. All measurements were made at 25°C.

Department of Chemical Engineering, Michigan State University, East Lansing, MI 48824.

*To whom correspondence should be addressed.

values of ν , the experimental diffusion coefficient is barely affected (Fig. 2A). For all molecular weights used, the diffusion coefficient shows no perceptible decrease at polymer concentrations below 2 g/dl even when the viscosity is more than 40 times that of cyclohexane-benzene. The correction factor of Hiss and Cussler (2) (viscosity to the $-2/3$ power) also predicts large decreases in diffusion with increased viscosity, far in excess of experimental observations (Fig. 2B). The Wilke-Chang equation (21) predicts diffusivities almost identical to those of Eq. 2.

To examine whether the above discrepancies could be caused by the thermodynamic effect of polymer addition, we estimated the activity term $[1 + (d\ln\gamma_i/d\ln x_i)]$ in Eq. 2 with the UNIFAC group-contribution method (13):

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^r \quad (4)$$

The combinatorial part (γ_i^c) is due to differences in size and shape of the molecules, and the residual part (γ_i^r) is due to group interactions (molecular association effects). The activity term for benzene and cyclohexane was calculated to be 0.78 ± 0.01 at all polymer concentrations. Thus, shifts in the activity term could not have caused the large discrepancies between the theory and experiment.

Fig. 2. (A) Experimental diffusion coefficient D of benzene-cyclohexane at 25°C versus polystyrene concentration (added to increase solution viscosity). Symbols are as in Fig. 1. The solid lines represent predictions from Eq. 2, which are almost identical with those of the Wilke-Chang equation (21). Although all theoretically consistent hydrodynamic treatments of diffusion predict strong dependences on polymer concentration or molecular weight, or both, experimental observation is contrary to these predictions. In these experiments we used a Mach-Zehnder interferometer; we checked the reliability by comparing measurements for several benzene:cyclohexane solutions with literature values (42); the agreement was within 1% for all cases. Each experiment involved layering two solutions atop one another in a window diffusion cell with a sharp boundary layer between. The first solution consisted of a small amount of polystyrene in 25 cm³ of benzene:cyclohexane (volume ratio 1:1.02), and the second consisted of an equal amount of polystyrene in another 25 cm³ of benzene:cyclohexane (volume ratio 1:0.98). Interference fringe patterns caused by diffusion were photographed at predetermined time intervals, and the diffusion coefficient of benzene:cyclohexane at the average volume ratio (1:1) was calculated. Details of this experimental method are described elsewhere (32, 33). Corrections arising from polymer diffusion are believed to be small because of the small activity gradient for polymer diffusion and the large hydrodynamic radii of the polymer molecules. **(B)** Comparison of predictions from Eq. 2, from the Hiss-Cussler equation (2), and from the local viscosity model (Eq. 12) with experimental data ($MW_n = 3.21 \times 10^5$). Each datum represents the mean of three or more measurements, and each error bar represents the interval between ± 2 SD from the mean.

As a possible model, let us treat dilute (and possibly concentrated) polymer solutions as inhomogeneous with respect to molecular drag. Thus polymer molecules affect diffusivity by effectively increasing the local viscosity in a set of irregularly distributed contiguous regions (34) near the polymer. As a first approximation for treating this, we used Maxwell's simple equation (35) for regular distributions of spherical regions (Fig. 3). The effective diffusivity is (36)

$$\frac{D_{\text{eff}}}{D_0} = \frac{\frac{2}{D_{\text{pr}}} + \frac{1}{D_0} - 2\phi_{\text{pr}}\left(\frac{1}{D_{\text{pr}}} - \frac{1}{D_0}\right)}{\frac{2}{D_{\text{pr}}} + \frac{1}{D_0} + \phi_{\text{pr}}\left(\frac{1}{D_{\text{pr}}} + \frac{1}{D_0}\right)} \quad (5)$$

where D_0 is the diffusivity in polymer-unaffected regions, and D_{pr} and ϕ_{pr} are, respectively, the diffusivity and volume fraction of the polymer-affected regions.

Application of the Stokes-Einstein equation in each region gives

$$D = \frac{kT}{6\pi\eta^*r} \left(1 + \frac{d\ln\gamma_A}{d\ln x_A}\right) \quad (6)$$

where η^* is the local viscosity in that region, and r in this case is the average benzene-cyclohexane radius. Obviously, the local viscosity of polymer-unaffected regions must be that of the solvent, η_0 , and the local

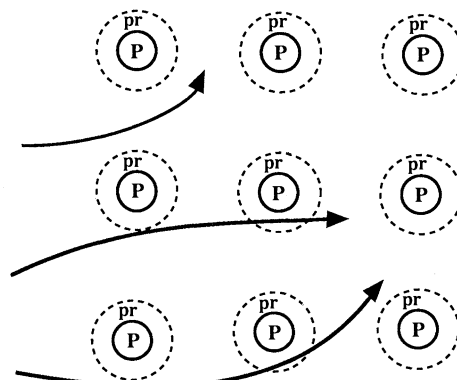


Fig. 3. Diffusion through regularly dispersed regions of different diffusivity. We treat the local diffusivity in the bulk as the same as that in the solvent; the local diffusivity in the polymer-affected regions (pr) is presumably lower. The polymer chain is indicated by the regions marked "P." The relative size of the polymer-affected regions is derived explicitly from our treatment of wall drag.

viscosity of polymer-affected regions, η_{pr}^* , must be the global viscosity (17) or higher: $\eta < \eta_{\text{pr}}^* < \infty$. The activity term $[1 + (d\ln\gamma_i/d\ln x_i)] = 0.78 \pm 0.01$ at all polystyrene concentrations of interest.

To estimate ϕ_{pr} we observe from theoretical and experimental evidence that wall drag (in the absence of strongly binding wall interactions) reduces the diffusivity in straight tubes according to the relation (37)

$$\frac{D}{D_0} = 1 + \frac{9}{8}\ln\lambda - 1.54\lambda + O(\lambda^2) \quad (7)$$

where $O(\lambda^2)$ refers to terms of order λ^2 , D/D_0 is the ratio of diffusivities caused by the wall effect, and $\lambda = 2r/d$ is the average diffusant diameter divided by the tube diameter. For diffusion in polymers, take d as the effective diameter between polymers, so that

$$\phi_{\text{pr}} = 1 - [1 + \frac{9}{8}\ln\lambda - 1.54\lambda + O(\lambda^2)](1 - \phi_p) + \phi_p \quad (8)$$

We now use the Ergun (38) equation's equivalent diameter

$$d = 4V/A \quad (9)$$

to solve for λ . Here $V = (1 - \phi_p)$ is the open volume per cubic centimeter of solution, and ϕ_p is the volume fraction of polymer; A is the polymer surface area per cubic centimeter of solution estimated by using the observation (39) that vinyl polymers, including polystyrene, approximate cylinders of length per repeated unit, $\ell_r = 2.5 \times 10^{-8}$ cm. Thus,

$$A = 2\left(\frac{\ell_r \pi c \phi_p N}{M_r}\right)^{1/2} \quad (10)$$

and

$$\lambda = \frac{2r}{d} = \frac{r}{1 - \phi_p} \left(\frac{\ell_r \pi c \phi_p N}{M_r}\right)^{1/2} \quad (11)$$

where c is the polymer concentration (in grams per cubic centimeter), M_r is the molecular weight of the repeated unit, N is the Avogadro number; r is the diffusant radius calculated preferably from Eq. 2 with experimental data in the absence of polymer. Calculating r (Stokes-Einstein radius) in this way avoids several problems arising from solvent association (21, 34) and size (18, 40) and guarantees a consistent solution at least at vanishing polymer concentrations. When no experimental data are available, we recommend the radius estimation techniques described in (15–17). From Eq. 8, ϕ_{pr} is always larger than ϕ_p , for example, ranging from 4.7 times ϕ_p at low polystyrene concentrations to 3.8 times ϕ_p at 9% polystyrene.

Combining Eqs. 4 and 5 produces the equation

$$D_{\text{eff}} = \frac{kT}{6\pi\eta_0 r} \times \left(1 + \frac{d\ln\gamma_A}{d\ln x_A} \right) \times \left[\frac{2\eta_{pr}^* + \eta_0 - 2\phi_{pr}(\eta_{pr}^* - \eta_0)}{2\eta_{pr}^* + \eta_0 + \phi_{pr}(\eta_{pr}^* - \eta_0)} \right] \quad (12)$$

where ϕ_{pr} is calculated from Eqs. 8 and 11; all of these terms are readily measured or estimated for most polymer solutions. Resulting values of D_{eff} , for $\eta_{pr}^* = \eta$ and $\eta_{pr}^* = \infty$, are plotted in Fig. 2B, where from solution density data

$$\phi_p = \frac{0.9975c}{0.818 + c} \quad (13)$$

The agreement with experiment is far better than predictions from Eq. 2 or the Hiss-Cussler equation (2), and the constants are all estimated a priori in a way that is not yet possible with the equations of Ogston *et al.* (26) and Cukier *et al.* (27); we take this as evidence for the efficacy of Eq. 12 and presume further that some local viscosity relation of this type controls most polymer solution diffusion.

REFERENCES AND NOTES

1. T. H. Lin and G. D. Phillies, *J. Colloid Sci.* **100**, 82 (1984).
2. T. G. Hiss and E. L. Cussler, *Am. Inst. Chem. Eng. J.* **19**, 698 (1973).
3. D. F. Evans, T. Tominaga, H. T. Davis, *J. Chem. Phys.* **74**, 1298 (1981).
4. M. Lohse, E. Alper, G. Quicker, W.-D. Deckwer, *Am. Inst. Chem. Eng. J.* **27**, 626 (1981).
5. C. J. O. R. Morris and P. Morris, *Biochem. J.* **124**, 517 (1971).
6. T. C. Laurent, I. Björk, A. Pietruszkiewicz, H. Persson, *Biochim. Biophys. Acta* **76**, 351 (1963).
7. R. S. Koene and M. Mandel, *Macromolecules* **16**, 973 (1983).
8. K. Luby-Phelps, D. L. Taylor, F. Lanni, *J. Cell Biol.* **102**, 2015 (1986).
9. J. Glasstone, K. J. Laidler, H. Eyring, *Theory of Rate Processes* (McGraw-Hill, New York, 1941).
10. G. K. Batchelor, *J. Fluid Mech.* **74**, 1 (1976).
11. A. Einstein, *Investigations on the Brownian Movement* (Dover, New York, 1956), p. 68.
12. E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems* (Cambridge Univ. Press, New York, 1984), p. 121.

13. R. C. Reid, J. M. Prausnitz, T. K. Sherwood, *The Properties of Gases and Liquids* (McGraw-Hill, New York, ed 3, 1977).
14. S. R. deGroot and P. Mazur, *Nonequilibrium Thermodynamics* (Dover, New York, 1983), pp. 250–257.
15. G. S. Hartley and F. Crank, *Trans. Faraday Soc.* **45**, 801 (1949).
16. P. Protapas, H. C. Anderson, N. A. D. Parlee, *J. Chem. Phys.* **59**, 15 (1973).
17. F. Perrin, *J. Phys. Radium* **7**, 1 (1936).
18. T. K. Kett and D. K. Anderson, *J. Phys. Chem.* **73**, 1262 (1969).
19. R. E. Buxbaum and E. F. Johnson, *Ind. Eng. Chem. Fundam.* **24**, 180 (1985).
20. L. B. Tentoni and R. E. Buxbaum, paper presented at 2nd International Conference on Fusion Reaction Materials, Chicago, IL, sponsored by Argonne National Laboratory, Argonne, IL, April 1986.
21. C. R. Wilke and P. Chang, *Am. Inst. Chem. Eng. J.* **1**, 264 (1955).
22. E. L. Cussler, *ibid.* **26**, 43 (1980).
23. H. T. Cullinan, Jr., *ibid.* **31**, 1740 (1985).
24. A. K. Shyu, D. H. Chen, C. L. Yaws, R. N. Maddox, *Comput. Aids Chem. Eng. Educ. News* **24**, 3 (1987).
25. W. Hayduk and B. S. Minhas, *Can. J. Chem. Eng.* **60**, 295 (1982).
26. A. G. Ogston, B. N. Preston, J. D. Wells, *Proc. R. Soc. London Ser. A* **333**, 297 (1973).
27. R. I. Cukier, *Macromolecules* **17**, 252 (1984).
28. A. R. Altenberger and M. Tirrell, *J. Chem. Phys.* **80**, 208 (1984).
29. D. Langevin and F. Rondelez, *Polymer* **14**, 875 (1978).
30. G. D. Phillies, *Biopolymers* **24**, 379 (1985).
31. ———, *Macromolecules* **19**, 2367 (1986).
32. P. V. S. R. Raju, thesis, Michigan State University, East Lansing (1978).
33. D. Beysens, *Rev. Sci. Instrum.* **50**, 509 (1979).
34. J. D. Benjamin, C. J. Adkins, J. E. VanCleve, *J. Phys. C* **17**, 559 (1984).
35. J. C. Maxwell, *A Treatise on Electricity and Magnetism* (Clarendon, Oxford, 1873), vol. 1, p. 365.
36. E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems* (Cambridge Univ. Press, Cambridge, 1984), chap. 7.
37. L. J. Gajdos and H. Brenner, *Sep. Sci. Technol.* **13**, 215 (1978).
38. S. Ergun, *Chem. Eng. Prog.* **48**, 89 (1952).
39. P. J. Flory and H. Höcker, *Trans. Faraday Soc.* **67**, 2258 (1972).
40. W. B. Russel, *Annu. Rev. Fluid Mech.* **13**, 425 (1981).
41. R. C. Weast, *Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 1983–1984), pp. F39–40.
42. S. A. Sanni, C. J. D. Fell, P. H. Hutchison, *J. Chem. Eng. Data* **16**, 424 (1971).
43. We thank S. R. Heidemann, A. Acrivos, C. Zucowski, H. Brenner, and G. D. Phillies for helpful discussions. Supported by NIH grant GM36894 and NSF grant BNS8401904 and by funds from the College of Engineering, Michigan State University.

20 January 1988; accepted 18 May 1988

Design of a Monomeric Arsinogallane and Chemical Conversion to Gallium Arsenide

ERIN K. BYRNE, LASZLO PARKANYI,* KLAUS H. THEOPOLD†

A monomeric arsinogallane containing a covalent gallium–arsenic bond has been prepared, and its molecular structure has been determined by x-ray crystallography. The compound reacted with *tert*-butanol at ambient temperature to yield the III–V semiconductor gallium arsenide as a finely divided amorphous solid. During the initial stages of the reaction small clusters of gallium arsenide were apparently present in solution. The band gaps of these particles, as observed by their absorption spectra, were larger than that of the bulk material. This work is a step toward the development of new molecular precursors for technologically important materials and the study of quantum size effects in small semiconductor particles.

GALLIUM ARSENIIDE (GaAs) IS A III–V semiconductor, which compares favorably in certain respects (for example, carrier mobility and band gap) with silicon (1). Manufacture of devices based on this material depends on metal-organic chemical vapor deposition (MOCVD), a process involving reaction of trimethylgallium with an excess of the highly toxic gas arsine (AsH_3) at elevated temperatures (2). Many research groups are searching for alternative precursors and routes to GaAs. We report here the synthesis and characterization of the first monomeric

arsinogallane, its chemical conversion into GaAs, and some observations on quantum size effects exhibited by very small particles of this semiconductor.

Addition of 2.0 equivalents of $\text{Li}(\text{THF})_2\text{-As}(\text{SiMe}_3)_2$ (3) (THF = tetrahydrofuran, Me = methyl) to a pentane solution of $[(\text{C}_5\text{Me}_5)_2\text{GaCl}]_2$ (4) followed by filtration, evaporation of the solvent, and recrystallization of the product from pentane yielded yellow crystals of analytically pure arsinogallane $(\text{C}_5\text{Me}_5)_2\text{Ga-As}(\text{SiMe}_3)_2$ (1 in Fig. 1) in 63% isolated yield (Scheme I) (5). The compound was very soluble in standard organic solvents and decomposed slowly when heated above 60°C or exposed to air. Cryoscopic determination of the molecular weight of 1 in benzene at two different concentrations gave molecular weights of 457 (0.19m) and 528 (0.10m), respectively,

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853.

*On leave from the Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary.

†To whom correspondence should be sent.