Measurement of Mutual Diffusion Coefficients and Thermal Diffusivities by Quasi-Elastic Light Scattering

Quasi-elastic light scattering techniques have been employed to measure the mutual diffusion coefficient D_{AB} as a function of concentration in eight binary mixtures and the thermal diffusivity χ in nine pure liquids and two binary mixtures. The mass diffusivities obtained are typically accurate to 3% while thermal diffusivities are known to be accurate to 5%; both types of values are in substantial agreement with the available bulk values. Under most circumstances light scattering is found to offer distinct advantages over the standard techniques for determining mass and thermal diffusivities.

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SCOPE

Because both the mutual diffusion coefficient D_{AB} and the thermal diffusivity χ appear in transport equations, a knowledge of their values is of particular importance in many chemical engineering applications. However, reliable values of mass and thermal diffusivities are relatively scarce. In recent years with the advances in laser technology, spectroscopic methods, and the theory of light scattering by fluids, quasi-elastic light scattering techniques have been successfully used to measure macromolecular diffusion coefficients and mass and thermal diffusivities for systems in the neighborhood of their critical point. In these cases light is scattered very strongly by the large temperature or concentration fluctuations. In contrast, normal mixtures and pure liquids scatter 10^4-10^5 times less—thus, there have been only a few attempts at determining D_{AB} and χ for these systems.

The objective of this study was to establish quasi-elastic light scattering as a convenient tool for the rapid and accurate determination of mass and thermal diffusivities. Mutual diffusion coefficients as a function of concentration are reported for eight systems. Extensive literature data exist for most of the mixtures studied. Thermal diffusivity measurements for nine pure liquids and two mixtures are also reported and compared to the values calculated from conventional measurements of density, heat capacity, and thermal conductivity.

CONCLUSIONS AND SIGNIFICANCE

Using quasi-elastic light scattering, the thermal diffusivity χ and the binary mutual diffusion coefficient D_{AB} have been measured for a variety of pure liquids and binary mixtures. The resulting values are in close agreement with the available bulk values and are accurate to about 3% for mass diffusivities and 5% for thermal diffusivities. Because neither type of measurement is dependent on the imposition of a macroscopic gradient, many of the problems associated with conventional bulk measurements are eliminated.

Determinations require less than 2 hours for thermal diffusivities and 30 minutes for mass diffusivities, juxtaposed to the more time consuming classical approaches. On the basis of these experimental results, light scattering techniques can be used effectively to determine χ and D_{AB} for most liquid systems.

For almost half a century it has been known that the frequency spectra of light scattered from liquids by entropy and concentration fluctuations contain transport coefficient information (Landau and Placzek, 1934). To resolve the extremely narrow lines predicted from the theory of the distributed spectra, the resolving power (ω_0/ω) of the spectrometer must approach 10^{14}. The best conventional spectroscopic method, the spherical Fabry-Perot interferometer, has a limiting resolution of 1:10^8. Only with the advent of the laser as an intense, monochromatic light source and the development of optical homodyne and heterodyne spectroscopy has the study of the spectra from concentration and entropy fluctuations become possible. Cummins and Swinney (1970) and Chu (1970) have written extensive reviews of the optical-beating techniques.

The earliest quantitative spectral measurements were made on fluid systems near their critical point (Alpert, 1965; Ford and Benedek, 1965) and on macromolecular solutions (Dubin et al., 1967). In contrast to the now extensive use of quasi-elastic light scattering techniques to study critical phenomena and macromolecular dynamics, there have been only a few attempts to measure transport coefficients in systems removed from their critical point. These efforts by Lastovka and Benedek (1966), Aref'ev et al. (1967), Berge et al. (1969, 1970), Dubois et al. (1970), and Dubois and Berge (1971) demonstrated the feasibility of using light scattering techniques to determine transport coefficients. However, their limited results did not conclusively establish light scattering as a reliable and efficient method for obtaining liquid diffusivities for the following reasons. The systems chosen were selected for their high degree of scattering, thus facilitating signal detection. The possibility of extending diffusivity determinations to other systems remained unclear. In three of five cases where binary mutual diffusion coefficients were measured, no conventionally determined data existed for comparison. The thermal diffusivities measured were not in agreement with the bulk values which were calculated from literature data.

In an effort to expand previous research, we present data which indicate that light scattering provides an accurate and convenient method of determining mutul diffusion coefficients for a large class of binary mixtures and thermal diffusivities for most pure liquids.

THEORY

Light is scattered by optical inhomogeneities. The physical reason for optical inhomogeneities in pure fluids is density fluctuations, which concomitantly produce fluctuations in the dielectric constant. In solutions, concentration fluctuations are an additional cause of fluctuations in the dielectric constant. These sources of time-dependent optical inhomogeneities modulate the scattered light and produce the altered time dependence of the scattered electric field that contains information about the modes of fluctuation dissipation and hence the transport properties of the scattering medium.

Beginning with the expression from classical scattering theory for the scattered electric field (Landau and Lifshitz, 1960)

$$E_s(\mathbf{R}, t) \sim e^{-i\omega_0 t} \int_v \alpha(\mathbf{r}, t) \exp[i(\mathbf{k}_0 - \mathbf{k}_s) \cdot \mathbf{r}]\, d\mathbf{r} \tag{1}$$

and performing a Fourier decomposition on fluctuations in the polarizability α, it is evident that only the Fourier component

$$\mathbf{K} = \mathbf{k}_s - \mathbf{k}_0 \tag{2}$$

of the fluctuation is responsible for the scattering seen at **R**. The scattering wave vector is

$$K = 2 \left(\frac{2\pi n}{\lambda_0}\right) \sin\left(\frac{\theta}{2}\right) \tag{3}$$

With recognition that the polarizability is proportional to the dielectric constant ϵ, description of the scattered field reduces to the derivation of an expression for fluctuations in the dielectric constant $\delta\epsilon(\mathbf{K}, t)$.

Landau and Placzek (1934) used thermodynamic fluctuation theory in conjunction with the macroscopic equations of heat conduction and mass diffusion to describe the time decay of fluctuations in the dielectric constant and the shape of the resulting distributed spectra. They reasoned that fluctuations in density can be expressed in terms of the independent thermodynamic variables, pressure and entropy, that is, adiabatic and isobaric fluctuations. Modulation of light by adiabatic fluctuations of density physically represent local compressions and rarefactions of the fluid. Due to the elastic nature of the fluid, these fluctuations propagate throughout the sample and can be visualized as thermal elastic waves diffracted according to the Bragg condition. These waves result in the Brillouin peaks, which are not of further interest in this work.

Scattering from isobaric fluctuations in density is associated with temperature or entropy fluctuations. The dissipation of these fluctuations obeys the Fourier heat equation and is controlled by the thermal diffusivity. The component responsible for scattering is then

$$\delta T(\mathbf{K}, t) = \delta T(\mathbf{K}, 0) \exp[-\chi K^2 t] \tag{4}$$

Thus, fluctuations in temperature or entropy are exponentially decaying functions localized in space. An analogous situation exists for the dissipation of concentration fluctuations in binary mixtures. The diffusion equation is obeyed, and its solution yields

$$\delta C(\mathbf{K}, t) = \delta C(\mathbf{K}, 0) \exp[-D_{AB} K^2 t] \tag{5}$$

Mountain (1966), Mountain and Deutch (1969), and Kadanoff and Martin (1963) have presented a more rigorous development in which the linearized equations of hydrodynamics—the continuity equation, the Navier-Stokes equation, the diffusion equation, and the energy transport equation—were used to solve for the time dependence of concentration and density fluctuations. The results derived for a pure liquid are identical to those obtained from classical thermodynamic fluctuation theory; for binary mixtures, Mountain and Deutch observed a term resulting from the dynamics, which does not appear from the thermodynamic theory (Miller, 1967). This additional term is a result of the coupling of temperature and concentration dissipation, that is, the Dufour and Soret effects. Under the condition $\chi >> D_{AB}$, which obtains for the systems studied here, the formulae reduce to those developed from thermodynamic fluctuation theory, and the experimental separation of the contributions from entropy and concentration fluctuations is possible.

The quantities of direct interest in quasi-elastic light scattering are the density-density correlation function $F(\mathbf{K}, t)$ and its Fourier transform, the dynamic structure factor $S(\mathbf{K}, \omega)$, which is the spectrum of the electric field. For a pure fluid (Mountain, 1966)

$$F(\mathbf{K}, t) = <\rho(-\mathbf{K})\, \rho(\mathbf{K}, t)> \sim <|\delta\rho(\mathbf{K})|^2> \left\{ \frac{C_p - C_v}{C_p} \exp[-\chi K^2 t] \right\} \tag{6}$$

and

$$S(\mathbf{K}, \omega) \sim <|\delta\rho(\mathbf{K})|^2> \left(\frac{C_p - C_v}{C_p}\right) \left(\frac{2\chi K^2}{(\chi K^2)^2 + \omega^2}\right) \tag{7}$$

For a binary mixture (Mountain and Deutch, 1969)

$$F(\mathbf{K}, t) \sim \left(\frac{\partial\epsilon}{\partial C}\right)^2_{P,T} <|\delta C(\mathbf{K})|^2> \exp[-D_{AB} K^2 t] + \left(\frac{\delta\epsilon}{\delta T}\right)^2_{P,C} <|\delta T(\mathbf{K})|^2> \exp[-\chi K^2 t] \tag{8}$$

and

$$S(\mathbf{K}, \omega) \sim \left(\frac{\delta\epsilon}{\delta C}\right)^2_{P,T} <|\delta C(K)|^2> \left\{\frac{2 D_{AB} K^2}{(D_{AB} K^2)^2 + \omega^2}\right\} + \left(\frac{\delta\epsilon}{\delta T}\right)^2_{P,C} <|\delta T(K)|^2> \left\{\frac{2\chi K^2}{(\chi K^2)^2 + \omega^2}\right\} \tag{9}$$

subject to the condition $\chi >> D_{AB}$.

Equation (6) expresses the density correlation function in the real time domain as a decaying exponential with a decay time (the time required for the exponential to decay to e^{-1} of its initial value) of $(\chi K^2)^{-1}$. The corresponding spectrum in the frequency domain [Equation (7)] represents a Lorentzian with a half-width at half-height of $\chi K^2/2\pi$ Hz. Hence the thermal diffusion process may be characterized by either an exponential decay time

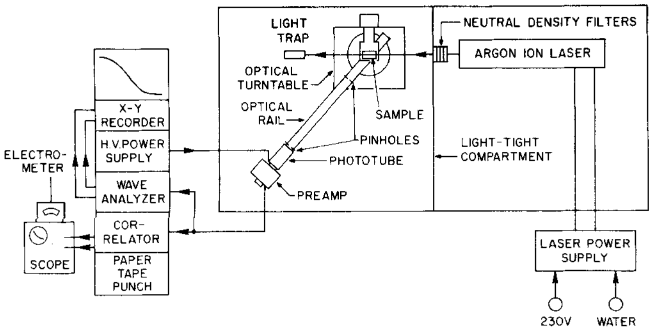


Fig. 1. A schematic drawing of the light scattering spectrometer used in this study.

or its conjugate half-width. Similarly, for a binary mixture with concentration fluctuations as the dominant source of scattering, the concentration correlation function [Equation (8)] is described by the decay time $(D_{AB}K^2)^{-1}$ or the corresponding half-width of Equation (9), $D_{AB}K^2/2\pi$. If temperature fluctuations should dominate, the characterization parameters are identical to those for a pure fluid.

The amplitude of the mass diffusivity term in Equation (9) is a function of the factors $(\delta\epsilon/\delta C)_{P,T}$ and $<|\delta C|^2>$. The first term is dependent upon the difference between mass reduced polarizabilities of solute and solvent, as is evident from the Lorentz-Lorenz formula

$$\frac{\epsilon-1}{\epsilon+2}=\frac{4\pi}{3}\rho'\left[C\frac{\alpha_1}{m_1}+(1-C)\frac{\alpha_2}{m_2}\right] \qquad (10)$$

and its derivative

$$\left(\frac{\delta\epsilon}{\delta C}\right)_{P,T}=\frac{4\pi}{3}\,\frac{(\epsilon+2)^2}{3}\,\rho'\left[\frac{\alpha_1}{m_1}-\frac{\alpha_2}{m_2}-\frac{3}{4\pi}\,\frac{\epsilon-1}{\epsilon+2}\left(\frac{1}{\rho_1'}-\frac{1}{\rho_2'}\right)\right] \qquad (11)$$

where $\rho' = [C/\rho_1' + (1-C)/\rho_2']^{-1}$ is the density of the mixture, α_i is the molecular polarizability, and m_i is the molecular mass; these equations are rigorously correct only for ideal solutions. It is evident that the amplitude of the concentration term in Equation (9) for a fixed composition is proportional to the difference between refractive indices of the two components. Experimentally one should expect reduced scattered intensities for solutions with comparable solute-solvent refractive indices and a corresponding reduction in accuracy of the experimental results.

The mean square concentration fluctuation term can be expressed by

$$<|\delta C|^2>_{P,T} = k_BT(\partial\mu|\partial C)_{P,T}{}^{-1} \qquad (12)$$

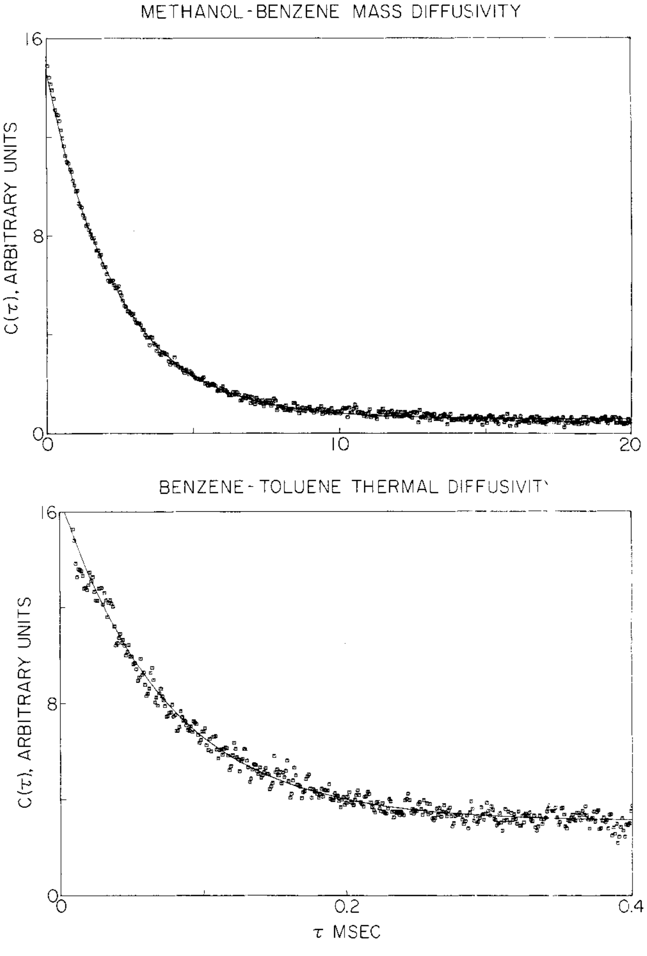
where μ is a suitably defined chemical potential of solution $\mu = \rho'(\mu_1 M_1{}^{-1} - \mu_2 M_2{}^{-1})$ (Dubois and Berge, 1971). $(\partial\mu|\partial C)_{P,T}$ is a complicated function of activities and molecular weights, but qualitatively, as solute and solvent approach equal concentrations, the term should increase in magnitude. Conversely, as the solution becomes more dilute in either component, the intensity of scattering should decrease and the accuracy of the associated data become poorer. Berge and Dubois (1971) have studied the functional dependence of the chemical potential derivative in detail.

APPARATUS AND EXPERIMENTAL METHODS

A schematic diagram of the light scattering spectrometer used in this study is given in Figure 1. The laser, detection optics, and sample were mounted on an NRC vibration isolation table to prevent extraneous vibrations from contributing to the time dependence of the scattered light. The incident light of approximately one watt was the 4880Å line of a Coherent Radiation 52A argon ion laser. Two pinholes with an angular acceptance of 0.2° defined the scattering volume, and the scattering angle was determined by triangulation to better than 0.06°. The sample volume was contained in a 10-cm path length cylindrical cell with optical quality flat windows. Stray light from imperfections and dust on the windows acted as a local oscillator source for the heterodyne spectroscopy. The detector, an EMI 9634QR phototube, carried the fluctuating photocurrent to a Saicor 43A correlator. The autocorrelation function was collected until the significant part of the function began to fill the memory—10 min. to 2 hrs. were required, depending upon the signal to noise ratio of the photocurrent. The 400-point autocorrelation function was then transferred in digital form from the correlator to paper tape for subsequent computer analysis. Typical correlograms appear in Figure 2.

Sample chemicals of reagent grade were used without further purification. The binary mixtures were prepared volumetrically with an estimated accuracy of 0.5%. All samples were multiply filtered through a fine fritted glass filter to remove dust. A Bausch and Lomb refractometer was used to measure refractive indices; values have been corrected to λ = 4880Å. The samples were maintained at room temperature, which did not drift more than 1°C during the course of an experiment. Because D_{AB} and χ exhibit a weak temperature dependence (typically less than 0.5%/°C), we estimate the maximum error due to temperature control to be less than 1%.

Current autocorrelation techniques were employed instead of swept filter spectrum analysis because correlation makes more efficient use of the signal and is able to perform signal averaging on the correlation function, thus improving the statistical accuracy of the data. In the case of heterodyne spectroscopy, the photocurrent autocorrelation function is an exact replica of


METHANOL-BENZENE MASS DIFFUSIVITY

BENZENE-TOLUENE THERMAL DIFFUSIVITY

Fig. 2. Typical correlograms for mass diffusion (acetone-carbon disulfide) and thermal diffusion in mixtures (benzene-toluene).

the density (electric field) autocorrelation function, hence

$$C_i(\tau) = \langle i(t)\, i(t+\tau)\rangle \sim F(\mathbf{K}, t) \qquad (13)$$

and the decay time of the current exponential contains the coefficient of interest. The points of the correlation function were fit to a single exponential using the Marquardt nonlinear least squares algorithm. The reciprocal decay time for a pure liquid

$$\tau^{-1} = \chi K^2 \qquad (14)$$

and the value of K^2 determine χ. Values of τ were collected over a range of scattering angles. For the binary mixtures two exponentials are observed. Because the magnitude of concentration fluctuations in binary mixtures is generally greater than the magnitude from temperature fluctuations, and because the decay time for thermal diffusivity is smaller than from mass diffusivity by approximately two orders of magnitude, the effect of thermal diffusion can be compressed into the initial part (approximately ten points) of the correlation function; these points are neglected in the fit to determine the mass diffusivity reciprocal decay time

$$\tau^{-1} = D_{AB} K^2 \qquad (15)$$

τ values for D_{AB} were collected as a function of concentration for a single scattering angle.

To measure thermal diffusivities for binary mixtures, one must in general perform a two exponential fit to the data. Under the special circumstances of similar refractive indices for solute and solvent, density fluctuations become the predominant source of scattering and the data may be analyzed solely in terms of thermal diffusion. The two binary systems studied, toluene-benzene and toluene-bromobenzene, satisfy the criterion of matched refractive indices and hence have been analyzed in terms of Equations (6) and (14).

RESULTS AND DISCUSSION

In Figures 3 to 8, mutual diffusion coefficients from this study are plotted as a function of concentration with comparative literature data. Thermal diffusivity results are compared in Table 1 with the literature bulk values. Error bars in Figures 3 to 12 are based on two standard deviations of the single exponential fit plus an estimate of possi-

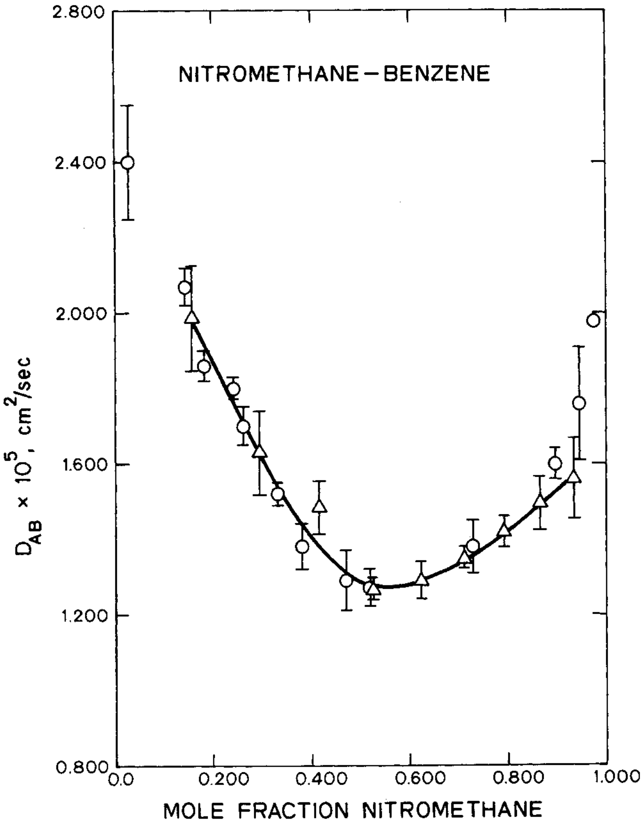


Fig. 3. Mutual diffusion data for the nitromethane-benzene system; △ this work, T = 20.0 ± .2°C; ○ Miller and Carman (1959), T = 20.0°C.

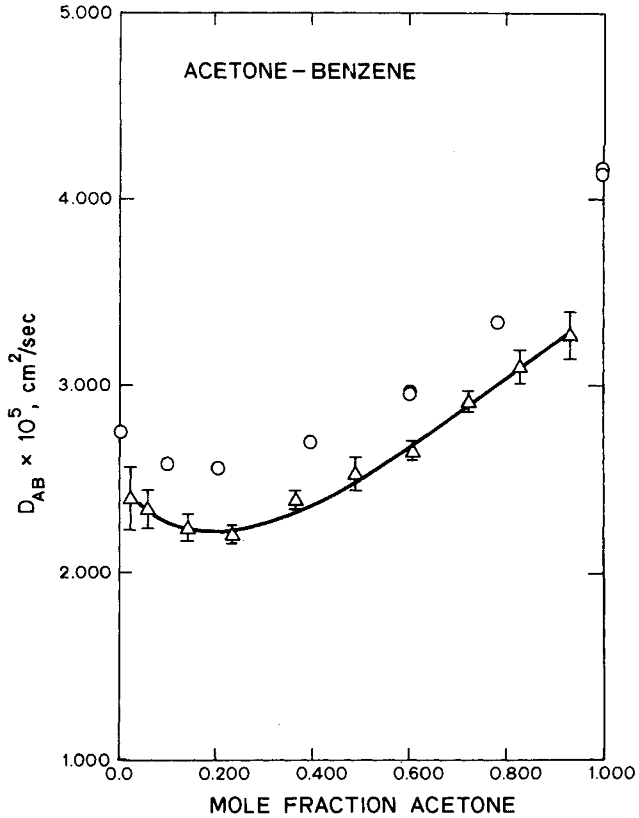


Fig. 4. Mutual diffusion data for the acetone-benzene system; △ this work, T = 19.9 ± .2°C; ○ Anderson et al. (1958), T = 25.15°C.

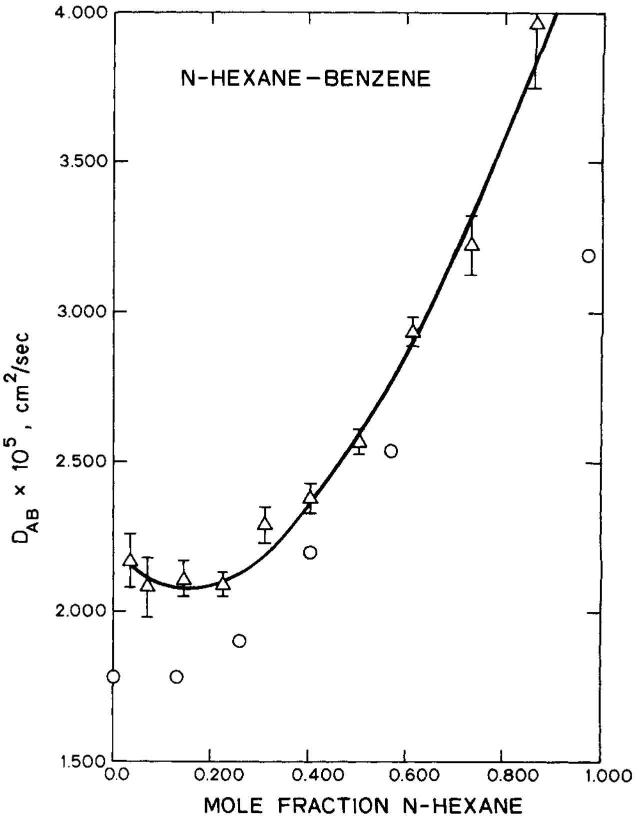


Fig. 5. Mutual diffusion data for the *n*-hexane-benzene system; △ this work, T = 19.9 ± .2°C; ○ Lemonde (1938), T = 5°C.

ble systematic errors. Errors appearing in Table 1 result from two standard deviations of the data to a best straight line plus possible systematic errors. Mass diffusivity values range in accuracy from 12% for dilute mixtures to better

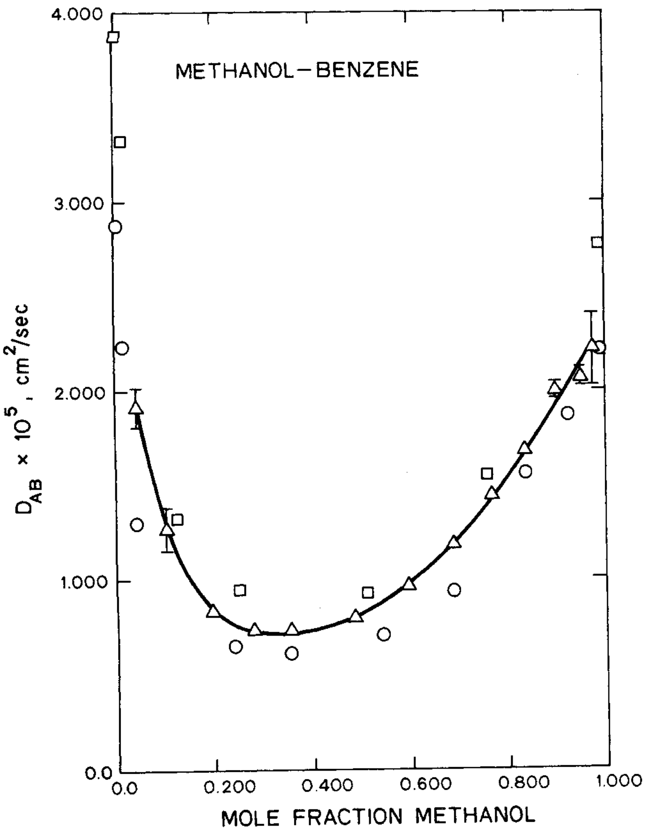


Fig. 6. Mutual diffusion data for the methanol-benzene system; △ *this work*, $T = 20.0 \pm .2$°C; □ Caldwell and Babb (1955), $T = 27.06$°C; ○ Lemonde (1938), $T = 11$°C.

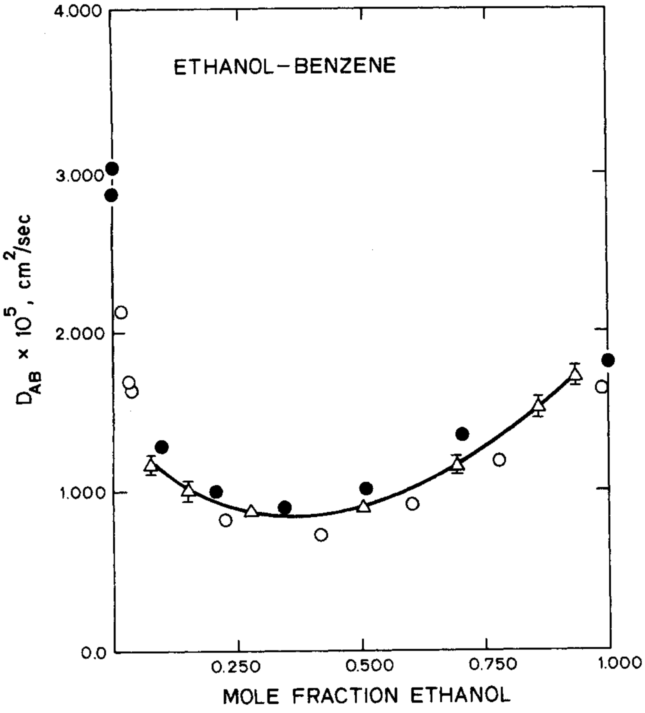


Fig. 7. Mutual diffusion data for the ethanol-benzene system: △ this work, $T = 18.6 \pm .2$°C; ● Anderson et al. (1958), $T = 25.15$°C; ○ Lemonde (1938), $T = 15$°C.

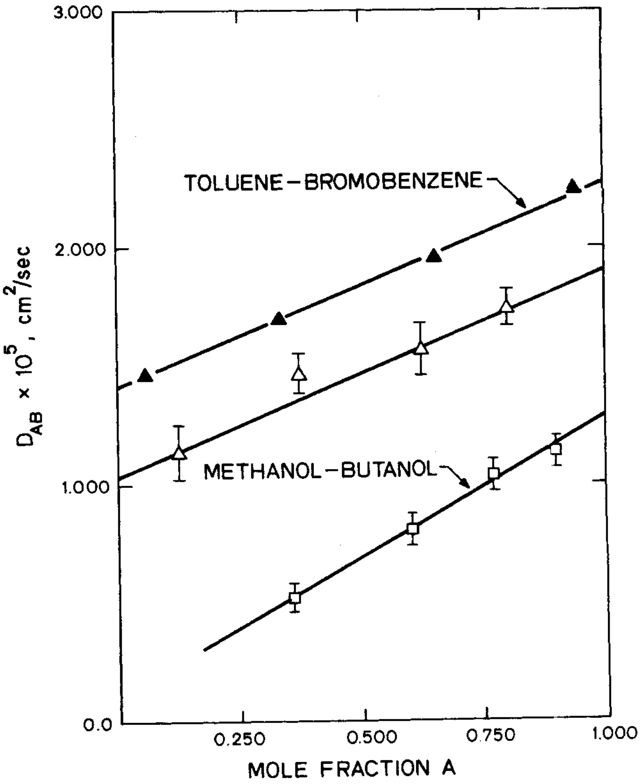


Fig. 8. Mutual diffusion data for the systems toluene-bromobenzene and methanol-butanol. Toluene-bromobenzene: △ this work, $T = 19.9 \pm .2$°C; ▲ Burchard and Toor (1962), $T = 29.6 \pm .03$°C. Methanol-butanol: □ this work, $T = 19.5 \pm .2$°C.

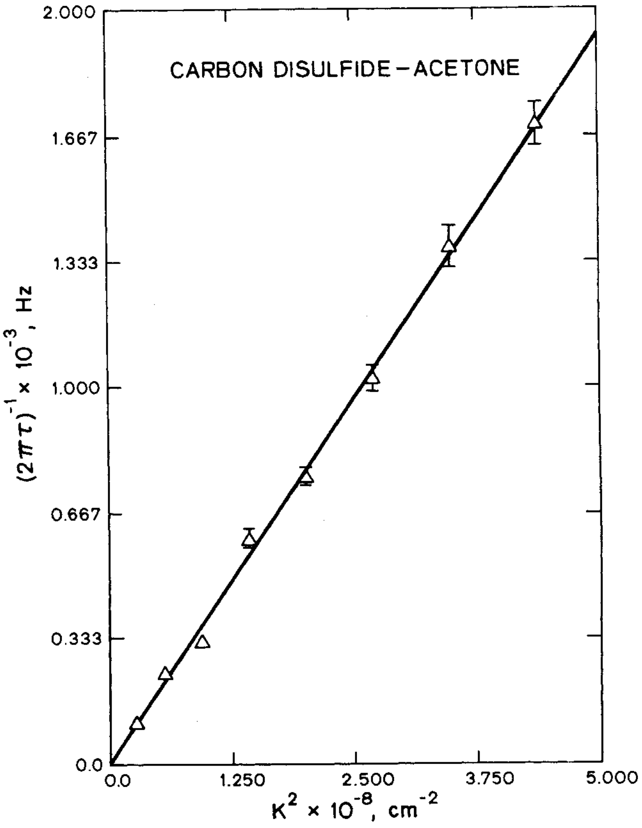


Fig. 9. The inverse decay time $(2\pi\tau)^{-1}$ vs. K^2 due to concentration fluctuations in a 10% (vol.) acetone-carbon disulfide mixture. $(2\pi\tau)^{-1}$ for the exponential correlation function corresponds to the Lorentzian halfwidth Γ (in Hz) of the spectrum.

Table 1. Thermal Diffusivities of Pure Liquids and Binary Mixtures
$\chi \times 10^3$ (cm^2/s)

System (pure liquids)	This study	T, °C	Bulk value, 20°C	Other light scattering determinations, 20°C unless otherwise specified
Acetone	0.881 ± 0.033	(18.2)	0.934 (Touloukian, vols. 3 & 6)	
Benzene	0.956 ± 0.040	(19.5)	0.963 (*ibid.*)	0.655 ± 0.070* (Berge and Dubois, 1969) 0.87 ± 0.1 (Berge, unpublished) 1.03 ± 0.05 (Oliver and Pike, 1970) 0.90 ± 0.02 (Searby, 1971) 0.94 ± 0.05 (Beysens, 1973)
Bromobenzene	0.518 ± 0.025	(20.0)	0.749 (Riedel, 1951; Shaw, 1969)	
Carbon disulfide	1.10 ± 0.04	(19.3)	1.29 (Bridgman, 1923; Shaw, 1969)	1.1* (Berge et al., 1970)
Carbon tetrachloride	0.719 ± 0.016	(20.0)	0.771 (Touloukian, vols. 3 & 6)	0.84 ± 0.05 (Oliver and Pike, 1970)
Ethanol†	0.839 ± 0.046	(19.8)	0.889 (*ibid.*)	
N-hexane	0.740 ± 0.033	(20.0)	0.837 (*ibid.*)	
Methanol†	1.16 ± 0.10	(18.2)	1.035 (*ibid.*)	
Toluene	0.849 ± 0.039	(19.0)	0.922 (*ibid.*)	0.879 ± 0.025 (Lastovka and Benedek, 1966) 0.98 ± 0.05 (Oliver and Pike, 1970)
(binary mixtures)				
Toluene-bromobenzene				
12.5% toluene	0.649 ± 0.025	(19.9)		
62.5%	0.688 ± 0.039	(19.9)		
Toluene-benzene				
30.0% toluene	0.869 ± 0.040	(20.0)		
50.0%	0.815 ± 0.035	(20.0)		
70.0%	0.772 ± 0.030	(20.0)		
90.0%	0.847 ± 0.035	(20.0)		

† Single data were collected for methanol and ethanol.
* Room temperature.

than 1% for more equimolar solutions. The accuracy of χ values in all cases is better than 10% and is typically 5%. Figures 9 to 12 exhibit values of the inverse decay time of the Rayleigh line as a function of the square of the scattering wave vector for light scattered from concentration fluctuations (Figure 9) and entropy fluctuations (Figures 10 to 12). Each datum represents a single correlation function. Half-widths are related to the exponential decay time τ by

$$\Gamma = (2\pi\tau)^{-1} \tag{16}$$

where Γ represents the conjugate Lorentzian half-width of the spectrum [Equations (7) and (9)], thus the vertical axis represents both the inverse decay time of the exponential correlation function and the half-width of the corresponding Lorentzian.

As seen from these plots, the linear dependence predicted from theory by Equations (14) and (15) is accurately obeyed. Least squares fitting with statistical weighting has been used to determine the best straight lines.

Figures 3 through 8 show that our mutual diffusion coefficients are in excellent agreement with the bulk values reported in the literature. Two other light scattering measurements of mass diffusivities are available for comparison—both are from the system carbon disulfide-acetone. Berge et al. (1970) reported $D_{AB} = 2.32 \times 10^{-5}$ cm^2/s at room temperature for a 10% by volume acetone mixture. Aref'ev et al. (1967) reported $D_{AB} = 0.30 \pm 0.04 \times 10^{-5}$ cm^2/s for a 10% by weight acetone mixture at room temperature. In comparison our values are 2.42 ± 0.04 × 10^{-5} at 20.0°C for a 10% by volume mixture and 2.23 ± 0.06 × 10^{-5} at 18.5°C for a 10% by weight acetone in carbon disulfide solution. It is concluded that Aref'ev's value is questionable.

The agreement between our values of thermal diffusivity and the values calculated from bulk measurements of λ, ρ, and C_p data is satisfactory as is evident from Table 1. Included in Table 1 are the only other light scattering determinations of thermal diffusivity. Our value of 1.10 ± 0.02 × 10^{-3} cm^2/s for pure carbon disulfide is the same as Berge's value of 1.1 × 10^{-3} cm^2/s (Berge et al., 1970). Berge and Dubois (1969) in the first experimental work on benzene reported $\chi = 0.655 \pm 0.070 \times 10^{-3}$ cm^2/s. These authors subsequently improved their techniques and found $\chi = 0.87 \pm 0.1 \times 10^3$ cm^2/s (unpublished work). Values obtained at higher angles by Fabry-Perot interferometry are $\chi = 1.03 \pm 0.05 \times 10^{-3}$ cm^2/s (Oliver and Pike, 1970), 0.90 ± 0.02 × 10^{-3} cm^2/s (Searby, 1971), and 0.94 ± 0.05 × 10^{-3} cm^2/s (Beysens, 1973). These are to be compared to our experimental value of $\chi = 0.940 \pm 0.050$ cm^2/s and the bulk value of $\chi = 0.963 \times 10^{-3}$ cm^2/s. Other Fabry-Perot values available are 0.84 ± 0.05 × 10^{-3} cm^2/s for carbon tetrachloride and 0.98 ± 0.05 × 10^{-3} cm^2/s for toluene (Oliver and Pike, 1970). Lastovka and Benedek (1966) reported $\chi = 0.879 \pm 0.025 \times 10^{-3}$ cm^2/s for toluene, which agrees with our value of 0.849 ± 0.038 × 10^{-3} cm^2/s.

It should be noted that where possible the quoted literature values for thermal diffusivity are taken from Touloukian, Volumes 3 and 6. These volumes contain a comprehensive study of all the available data on liquid thermal conductivity and heat capacity for selected substances; the recommended reference values cited for each liquid have been used in Table 1. The variation in experimentally determined thermal conductivities is of interest. Some results for the same system differ by as much as 50%, and variations of 25% are not uncommon, thus reflecting the difficulties associated with the conventional thermal conductivity measurements. The most significant problems are conduction corrections, convection currents, and radiation between the surfaces enclosing the liquid. In contrast, quasi-elastic light scattering does not require the imposition of macroscopic temperature gradients; thus convection is not a serious source of error. Spectrometers can easily be constructed which do not suffer from the problems of radiation and conduction associated with classical methods.

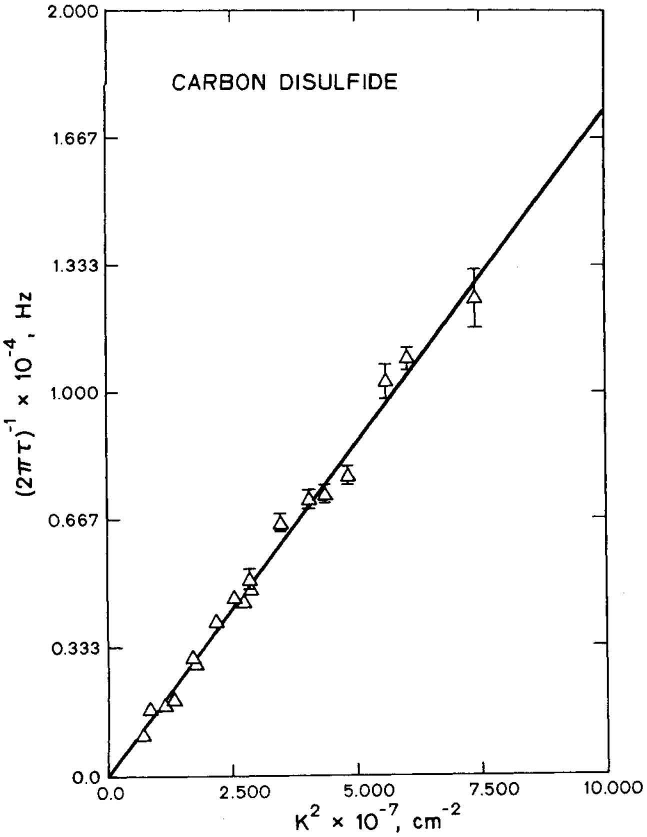


Fig. 10. Inverse decay time vs. K^2 for pure carbon disulfide.

The limitations inherent to classical diffusion measurements are not so serious, although large discrepancies exist between values obtained by different investigators on the same system. Johnson and Babb (1956) discuss the different conventional techniques for determining mass diffusivities as well as their limitations and the consistency of data taken by several investigators. The most important limitation of these techniques is the requirement of a macroscopic concentration gradient. As a result, one generally obtains an integral diffusion coefficient rather than the more meaningful differential coefficient. One of the more popular methods, the diaphragm cell technique, requires calibration and is subject to bulk flows (Board and Spalding, 1966); both can contribute to errors in the measurements of D_{AB}. Quasi-elastic light scattering needs no macroscopic concentration gradients and is not subject to calibration errors or bulk flow. Scattering arises from microscopic fluctuations in concentration, hence the mea-

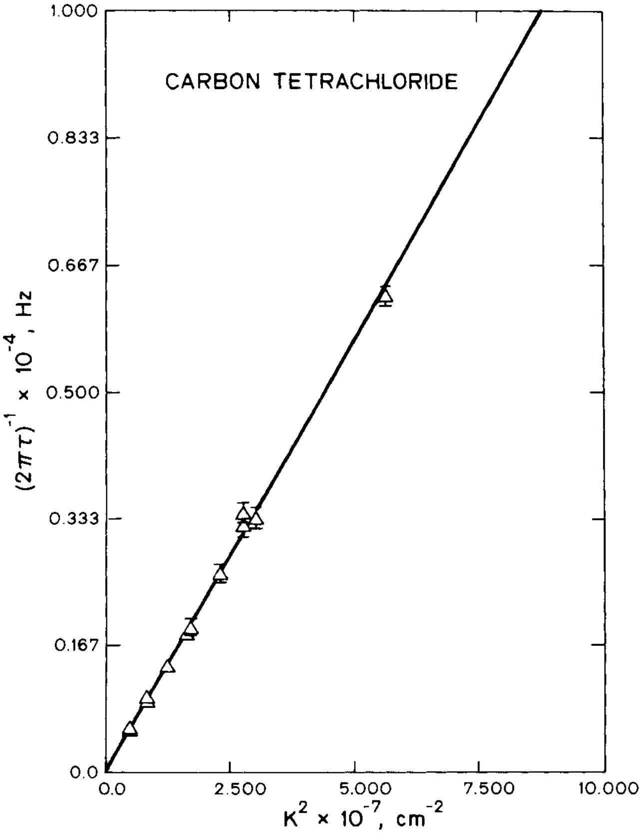


Fig. 11. Inverse decay time vs. K^2 for pure carbon tetrachloride.

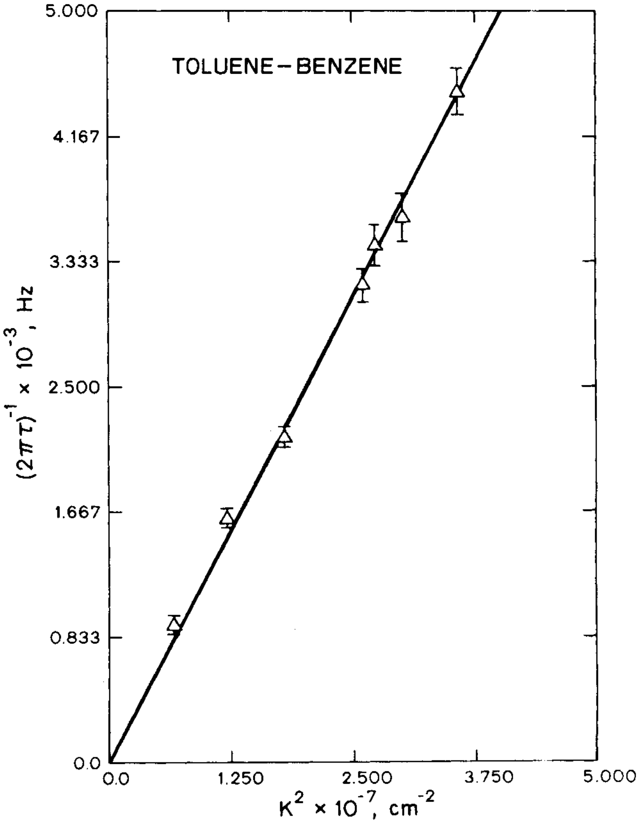


Fig. 12. Inverse decay time vs K^2 from entropy fluctuations in a toluene-benzene mixture

sured diffusion coefficient is of a differential form. Some techniques, such as the diaphragm cell, may require days of operation for a single point, while light scattering determinations take less than an hour. The most precise conventional techniques employ interferometric methods (Dunlop et al., 1972) for continuously analyzing the changes of concentration with distance and time in a cell. Analysis of the data requires involved mathematical analysis. These measurements are limited in the same way as light scattering—they require a difference in refractive index between sample and solvent. This is the most serious limitation of the light scattering technique. Determinations of D_{AB} improve in accuracy and precision with (1) increasing refractive index differences between the binary components, as is evident from the $(\partial\epsilon/\partial C)_{P,T}$ factor of Equation (8), and (2) the approach to equal concentrations, which is expressed in the $<|\delta C|>^2$ factor of the same equation.

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NOTATION

C = concentration, g/g of solution
C_p = specific heat at constant pressure, erg/°K-molecule
C_v = specific heat at constant volume, erg/°K-molecule
D_{AB} = binary diffusivity, cm^2/s
$\mathbf{E}_s$ = scattered electromagnetic field, statvolts/cm
$F(\mathbf{K}, t)$ = density-density autocorrelation function, dimensionless
$i(t)$ = photocurrent, esu/s
$\mathbf{K}$ = scattering wave vector, cm^{-1}
k_B = Boltzmann's constant, 1.38 10^{-16} erg/deg.
$\mathbf{k}_0$ = incident wave vector, cm^{-1}
$\mathbf{k}_s$ = wave vector in direction of scattering, cm^{-1}
M_i = molecular weight of ith species, g/mole
m_i = mass of ith molecular species, g
n = refractive index
$\mathbf{R}$ = observation vector, cm
$\mathbf{r}$ = position vector, cm
$S(\mathbf{K}, \omega)$ = dynamic structure factor, dimensionless
T = temperature, °K
t = time, sec

Greek Letters

α = polarizability, cm^3
Γ = half-width of Rayleigh line, Hz
δ = fluctuation above the mean of a physical quantity
ϵ = dielectric constant
θ = scattering angle, degrees
λ = thermal conductivity, erg/cm-°K-s
λ_0 = wavelength of light in vacuo, Å
μ = chemical potential, erg/mole
ν = frequency, Hz
ρ = pure fluid density, molecules/cm^3
ρ' = fluid density, molecules/gm of solution
τ = exponential decay time, s
χ = thermal diffusivity, cm^2/s
ω = difference between incident and scattered frequency, rad/s
ω_0 = incident frequency of laser light, rad/s

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Reaction Path Synthesis Strategies

A system is offered for the mathematical representation of the functional and structural features of organic molecules and their reactions. Two basic synthesis strategies, an antithetic method and a synthetic method, are defined and compared. The use of heuristic information in guiding synthesis is evaluated. A synthetic method which uses dynamic programming is presented and applied to the synthesis of bihelical DNA. Possible extensions to other classes of compounds are presented.

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SCOPE

The ability to invent chemical reactions which have desired properties is central to the practice of chemical engineering. Reactions are used to transform raw materials into desired products, to solve separation problems, and to heat and cool process streams. At present there exists very little in the way of systematic techniques to synthesize reaction paths which solve chemical processing problems. In this paper we review the current status of research in reaction path synthesis and present a new representation and search strategy for organic chemical reaction paths. Several of these techniques have been programmed for digital computers and allow the rapid search for optimal reaction paths.

CONCLUSIONS AND SIGNIFICANCE

It is possible, using a state-space representation, to generate systematically all possible reaction paths leading to a desired molecule. If evaluation data are available for the reactions involved, a dynamic programming search strategy can be used to select the optimum reaction path. This approach gives a much more systematic means for generating, evaluating, and selecting reaction paths. It also indicates that there now exists a straightforward way of teaching reaction path synthesis.

The invention of reaction paths with desired properties is central to the synthesis of chemical processing systems. Chemical reactions are used to transform raw materials into desired products, separate mixtures, and heat and cool process streams (Rudd, 1973; Powers, 1973; Lauer, 1952).

In order to put chemical synthesis into a more systematic format it is necessary to collect and classify the vast number of organic structures, functionalities, and reactions into a more useful system. It is also necessary to develop more formal methods for generating, evaluating, and selecting chemical reaction paths.

Such a system must be built around an operational definition of organic synthesis. Organic synthesis is concerned with the structure of molecules and the net transformations in structure which occur during chemical reaction. The current organization of knowledge about reactions is based on mechanism and is not particularly well suited for use in synthesis. (This classification, based on mechanism, undoubtedly contributes greatly to the confusion that engulfs students in introductory organic chemistry courses. They are taught mechanism and then asked to do synthesis.) The system selected for representing the states and operators which define chemical synthesis must be general so that new structures and reactions can be rapidly and easily included. Furthermore, the system should be defined so that all possible reaction paths, even those not presently known, could be generated.

Since synthesis is a goal-oriented activity, the system must include information on the context of the synthesis, that is, the target molecules and possible starting materials.

A system aimed at meeting these criteria is developed here and its application to the synthesis of bihelical DNA illustrated. A computer program, DINASYN, which is based on these concepts, is briefly described. It is hoped that this approach will have value in the area of industrial reactions. However, the detail of information required to evaluate industrial reaction paths is great, and this approach would therefore be best suited, initially, for small

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