

t_f = final temperature of calorimeter, °C
 t_h = reference temperature to which combustion reaction is referred (25 °C)
 Δt_{corr} = rise in temperature of calorimeter because of thermal leakage of outer jacket
 $\Delta t_c = t_f - t_i + \Delta t_{\text{corr}}$
 $\xi(\text{calor})$ = energy equivalent of calorimeter, cal/deg
 $\xi(\text{cont})$ = energy equivalent of contents, cal/deg ($\xi^i(\text{cont})(t_i - 25) + \xi^f(\text{cont})(25 - t_f + \Delta t_{\text{corr}})$ where $\xi^i(\text{cont})$ and $\xi^f(\text{cont})$ are energy equivalents of contents before and after combustion, respectively)
 ΔE_{ign} = energy released because of ignition, cal
 E_c°/M = standard energy of idealized combustion reaction, cal/g
 ΔE_{corr} = energy reduction to standard states, cal (10, 13)
 $\Delta E_{\text{dec}}(\text{HNO}_3)$ = energy released from formation of nitric acid, cal
 ΔE_c° = standard energy of idealized combustion reaction, cal/mol
 ΔH_c° = standard heat of combustion of compound at constant pressure, kcal
 ΔH_f° = enthalpy of formation of TPTA, kcal/mol

Literature Cited

- (1) Baroody, E. E., Carpenter, G. A., Robb, R. A., Zimmer, M. F., *J. Chem. Eng. Data*, **13** (2), 215 (1968).
- (2) Baroody, E. E., Wynne, J., Zimmer, M. F., U.S. Naval Propellant Plant, Naval Weapons Rep. 8686, Tech. Rep. 154 (1964).
- (3) Cameron, A. E., Wichers, E., *J. Am. Chem. Soc.*, **84**, 4175 (1962).
- (4) Cohen, E. R., DuMond, J. W. M., *Rev. Mod. Phys.*, **37**, 537 (1965).
- (5) Dornalski, E. S., National Bureau of Standards, Gaithersburg, Md., private communication, Jan 1970.
- (6) Good, W. D., Scott, E. W., Waddington, G., *J. Phys. Chem.*, **63**, 1080 (1959).
- (7) Hall, P. N., Naval Surface Weapons Center, White Oak, Md., private communication, Nov 1974.
- (8) "Handbook of Chemistry and Physics", 43d ed, Chemical Rubber Co., Cleveland, Ohio, 1961-1962, p 1165.
- (9) Hubbard, W. N., Scott, D. W., Waddington, G., in "Experimental Thermochemistry", F.D. Rossini, Ed., Interscience, New York, N.Y., 1956, Chapter 5, pp 75, 128.
- (10) Rossini, F. D., ref 9, Vol. I, 1962, pp 90, 107.
- (11) Rossini, F. D., ref 9, p 81.
- (12) Rossini, F. D., ref 9, p 93.
- (13) Skinner, H. A., ref 9, Vol. II, pp 25-28.
- (14) Wagman, D. D., Kilpatrick, J. E., Taylor, W. J., Pitzer, S. P., Rossini, F. D., *J. Res. Natl. Bur. Stand.*, **34**, 143 (1945).
- (15) Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., *Natl. Bur. Stand. (U.S.), Tech. Note* 270-3, 22 (1968).
- (16) Zimmer, M. F., Baroody, E. E., Schwartz, M., McAllister, M. P., *J. Chem. Eng. Data*, **9**, 527 (1964).

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Liquid Diffusivities in Normal Paraffin Solutions

Walter Hayduk* and Sotirios Ioakimidis

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

An apparatus was constructed for measuring diffusivities in miscible liquid solutions which has all the essential features of a diaphragm cell but with two additional features. The diaphragm is composed of uniform stainless steel precision capillaries imbedded in a Teflon plug. As a result, the physical system for the diffusion process is clearly defined and can be mathematically described so that the diffusion cell requires no prior calibration. The diffusion cell was also designed for operation in the transient mode when the transfer rates are much higher than those obtained at steady state. As a result diffusivities can be measured in relatively short times. Diffusivities of tetracosane and dotriacontane (C₂₄ and C₃₂) at low concentrations were measured in hexane and octane at 25 °C. Diffusivities were also measured at 25 °C for dilute solutions of cyclohexane in carbon tetrachloride and dodecane in hexane. Data from the literature, along with those reported here, were used to construct a viscosity-diffusivity map for normal paraffin solutes of carbon content from 1 (methane) to 32 (dotriacontane).

In the absence of strong molecular interactions, diffusivities of a substance dissolved in a number of different solvents tend to diminish with increasing solvent viscosity. This relation may usually be represented by a straight line on a log-log plot of diffusivity vs. solvent viscosity as expressed by Hayduk and Cheng (11) in the form:

$$D = A\mu^{-B} \quad (1)$$

The slope, B , of the log D -log μ relation usually increases for diffusing substances of larger molecular size. Similarly, diffusivities of a number of substances in the same solvent tend

to decrease with increasing solute molecular size or molar volume. Both of the above relations can be observed for solutions of normal paraffins. It is possible to summarize the above generalizations for normal paraffins by way of a diffusivity-viscosity map. While experimental data, as reported in the literature for all the possible solute-solvent combinations, are far from complete, enough data are available to construct the viscosity-diffusivity relationship by interpolation. While at least one attempt has been made to quantitatively describe the diffusivity behavior in liquid n -paraffins, Shieh and Lyons (22), it appears of questionable value for application to gaseous or solid solutes using parameters such as liquid density and liquid viscosity. The diffusivity-viscosity map can be used directly, however, to estimate most probable diffusivities at 25 °C in any dilute normal paraffin solution.

A diaphragm cell consisting of uniform capillaries was first reported by Ross and Hildebrand (20) for use at steady state in measuring diffusivities of gases dissolved in carbon tetrachloride. The capillaries consisted of holes drilled 1 mm in diameter in a 0.9 cm thick plate. A subsequent variation of the diaphragm, as reported by Nakanishi et al. (19), consisted of a bundle of hypodermic tubes held together in a close-packed formation by a solder plug. In both cases, diffusion occurred from a gas-saturated liquid layer above the plate to a reservoir of initially deaerated liquid below the plate, while the rate of diffusion was measured volumetrically by observing the change in the enclosed volume of gas held at constant pressure above the liquid. Malik and Hayduk (16) described a steady-state volumetric method for measuring diffusivities of gases in liquids utilizing a column of liquid solvent confined in a single glass capillary.

The steady-state diaphragm cell method was adapted for elevated temperatures by Sanni and Hutchison (21). The cells were actually used in the temperature range from 25 to 60 °C. Provision was made for preheating fresh solvent, replacing the

contents of one chamber of the cell, and for allowing for a volume change of the solution during the measurement. These cells were used in the quasi-steady-state mode and were calibrated with aqueous KCl. Continuous analysis of the concentration within the top chamber was accomplished by means of a calibrated capacitance probe. Diffusivities for various organic acids utilizing a continuous analytical method consisting of a pH probe and caustic titrimeter were reported by Albery et al. (7). The use of a continuous analyzer in conjunction with a diaphragm cell would appear to greatly simplify diffusivity measurements. Unfortunately, many solutions in which diffusivities are required cannot be quantitatively analyzed by means of a probe. In those cases samples must be withdrawn for external analysis.

Transient diffusion rates at open-ended capillaries were first measured by Anderson and Saddington (3) utilizing radioactive tracers. The method was subsequently used by Wang (24) and Eriksen (9) and modified by Witherspoon and Saraf (25) for use with gas-liquid systems. A relatively long period of time for transient effusion was required since, from a certain initial concentration of solute, the residual solute confined within the capillary was finally analyzed. Effusion times corresponding to $Dt/l^2 > 0.23$ were used by Witherspoon and Saraf. It is noteworthy that much higher effusion rates may be obtained for shorter times corresponding to $Dt/l^2 < 0.1$.

A technique for measuring liquid-phase diffusivities utilizing a porous procelain frit in the transient mode has been reported by Mitchell et al. (17) and by Moore and Weltek (18). The method involves initially saturating a flat porous frit with a solution containing carbon-14 tagged solute to a uniform concentration, and subsequently immersing the frit into a known volume of pure solvent. Analyses were made by samples of solution withdrawn at suitable time intervals. The glass frit required calibration with a solute of known diffusivity because the effective exposed area and diffusion path length were not directly measurable. In addition, the solute content of the liquid initially adhering to the surface of the frit had to be corrected for. Diffusivities were deduced by means of the mathematical equation describing the transient solution to the corresponding semiinfinite diffusion problem. The method is comparable to membrane sorption or desorption experiments as discussed by Crank (7). Some question remains as to the true effects of the nonuniformity in area as well as inequality in length of the frit pores, however. This observation is made with particular reference to the reported deviations in results when compared with measurements made using other methods.

Further modifications to the diaphragm cell technique are reported here in the interest of obtaining rapid, but accurate, diffusivities over a wide temperature range.

Experimental Section

The capillary tube diaphragm cell was constructed from two stainless steel end pieces forming two chambers having unequal volumes, separated by the diaphragm. The volumes for the top, and bottom, chambers were respectively 25 and 205 ml, while only the top chamber was equipped with a stirring device. The shaft for the stirrer was a hollow syringe needle which permitted the withdrawal of solution from the top compartment by syringe when required. When in operation, the stirrer was driven by a synchronous motor supplied by the Harvard Apparatus Company, at the relatively low speed of 0.5 rpm. Details of the diffusion cell are shown in Figure 1. The diaphragm consisted of a Teflon cylindrical disk containing 252 drilled holes each fitted with a precision stainless steel capillary 2.0 cm long and 1 mm i.d. giving a combined internal cross-sectional area for the diaphragm of 1.98 cm². Prior to the installation of the tubes the surface of the Teflon disk was machined concave so that liquid would tend to flow to the center. Similarly the upper surface of the stainless steel covering cap was machined with a conical surface to ensure complete liquid filling of the top compartment.

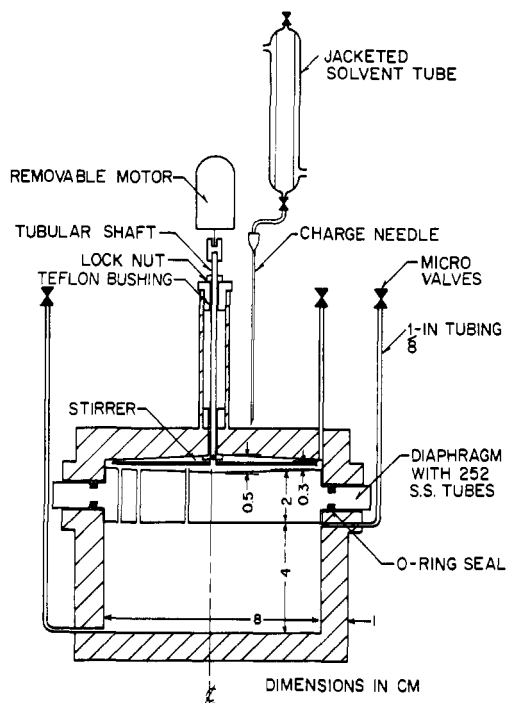


Figure 1. Sectional diagram of capillary diaphragm cell.

A small hole in the stirring shaft located at the bearing permitted gas to escape up the shaft. The stirring bar was silver soldered to the shaft so that it swept across the ends of the capillaries with a clearance of about 1 mm. The two end pieces of the cell were clamped over the diaphragm which was equipped with O-rings to assure a leak-proof seal. The cell was filled by means of 1/8 in. stainless steel tubing equipped with miniature needle valves. The diffusion cell was mounted in a brass cradle in a manner ensuring a horizontal position of the diaphragm and complete rigidity of the whole unit. The cell was maintained at constant temperature by submerging in a bath of ethylene glycol-water solution and controlled to ± 0.02 °C.

Prior to filling, the diffusion cell was purged with helium and the solution was bubbled with the same gas as a substitute for actual complete deaeration. This procedure was adopted because of the very low solubility of helium, and the difficulty of filling the diffusion cell under vacuum. It is noted that the solubility of helium actually increases in most solvents as the temperature increases; hence no bubbles of gas would form on heating a helium-saturated solution. The lower compartment of the cell was filled with solution of higher solute concentration and density, in all experiments. Helium-saturated solution from a solution preparation vessel was permitted to enter the lower chamber and then to fill the whole cell. The inlet and outlet valves for the lower compartment were then closed. The cell was then immersed in the bath for temperature equilibration.

For both the steady-state and transient experiments the solution in the top chamber of the cell had to be replaced with solvent. For this purpose a jacketed tube was filled with approximately 150 ml of solvent and deaerated with helium while bath liquid was circulated through the jacket. A valve and syringe needle arrangement at the lower end of the tube was available for inserting into the cell purge tube. A separate syringe, fitted with a long square-ground needle, was used to withdraw all the solution from the top compartment after which fresh solvent was charged. The operation was made three times in rapid succession, a sequence that was found necessary to completely flush out the top compartment. The wash solution was accumulated for analysis. Particularly for transient experiments, the flushing

time had to be accurately accounted for, so it was timed with a stopwatch and kept to a period of time not exceeding 2 min. For the transient experiments the initial time was considered to be the beginning of the first solvent charging operation, while solute accumulation was considered to commence at the completion of the third charging operation. Transient experiments were from 4 to 8 h in duration after flushing, while steady-state experiments required a preliminary period for establishing the steady-state concentration profile of up to 12 h added to the diffusion period lasting from 1 to 5 days. Experiments were performed with two similar diffusion cells to reduce the total time for the experimental work.

An accurate method of analysis for low solute concentrations was essential for this work. A Brice-Phoenix differential refractometer was found quite suitable for the solutions utilized. A similar method of analysis has been used by Van Geet and Adamson (23) for solutions of octane in dodecane. Differences in refractive indices between solvent and solution were reproducible at 25 °C to 0.000 003 using a green light source (546 mμ). The differential refractometer was calibrated using aqueous KCl solutions of known concentrations. The calibration constant was obtained from a linear least-mean-squares fit of the readings obtained at several KCl concentrations:

$$\Delta n = K\Delta d \quad (2a)$$

$$\Delta d = (d_2 - d_1) - (d_2^1 - d_1^1) \quad (2b)$$

Readings were taken at the two refractometer positions for both solution and solvent for analysis. Subsequently solutions of known solute content were analyzed to construct calibration lines for the various solutions used in this work. Regardless of the experimental temperature, all analyses were performed at 25 ± 0.1 °C. Further analytical details are described by Ioakimidis (13).

The solvents hexane and octane were of the chromatography grade and cyclohexane and carbon tetrachloride of the spectroscopy grade, all having a minimum specified purity of 99% and purchased from Fisher Chemicals. The solid paraffins, dotriacontane and tetracosane, obtained in a fine flake form were of the highest purity grade and also purchased from Fisher Chemicals. All chemicals were used without further purification. Viscosities and densities were obtained for the pure solvents from the ASTM publication (2).

Mathematical Section

The relations describing the diffusion process in the diaphragm capillaries may be formulated from:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3)$$

$$\begin{array}{ll} \text{(a) } C(x,0) = C_0 & \text{(b) } C(x,0) = C_0 \\ C(0,t) = C_1 & C(0,t) = C_1 \\ C(\infty,t) = C_0 & C(l,t) = C_0 \end{array}$$

In the above expression, both D and C are considered constant along the diffusion path. At least three mathematical solutions to eq 3 are possible. The first solution applies during the initial diffusion period when each capillary may be considered to be effectively infinitely long. The solution for the concentration gradient is:

$$Y = \frac{C - C_1}{C_0 - C_1} = \text{erf} \frac{x}{2\sqrt{Dt}} \quad (4)$$

The time that the concentration remains essentially unchanged at $x = l$ may be estimated from:

$$\sqrt{\frac{Dt}{\rho}} \leq 3.6 \quad (5)$$

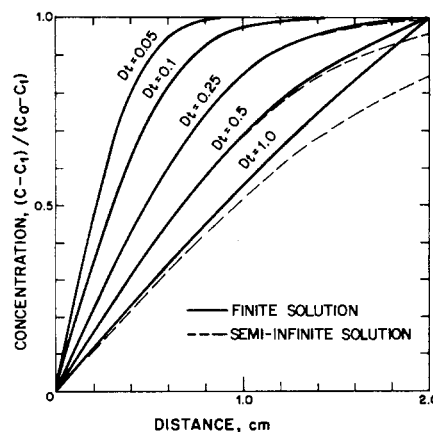


Figure 2. Transient concentration profiles for capillaries of finite and infinite length.

The amount of solute transferred up to time t is given by:

$$M_t = -D \int \frac{\partial C}{\partial x} \Big|_{x=0} dt \quad (6)$$

The solution in dimensionless form is:

$$\frac{M_t}{(C_0 - C_1)l} = 2 \sqrt{\frac{Dt}{\pi \rho}} \quad (7)$$

A second solution to eq 3 considers the capillary to be of finite length, hence the solution may be represented by a Fourier series:

$$Y = \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin(n\pi x/l) \exp(-n^2\pi^2 Dt/\rho) \quad (8)$$

Equation 8 differs slightly from the solutions for flow through a membrane as listed by Crank (7) or Jost (14), but in both cases, their solutions may be shown to be equivalent. Further, eq 8 is not suitable for evaluating the initial profiles without requiring an excessive number of terms. The amount of solute transferred up to time t is given by:

$$\frac{M_t}{(C_0 - C_1)l} = \frac{Dt}{\rho} + \frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2\pi^2 Dt/\rho) \quad (9)$$

The third solution for diffusion through a membrane is the steady-state solution:

$$Y = \frac{x}{l} \quad (10)$$

The corresponding amount transferred during any steady-state time period is given by:

$$\frac{M_t}{(C_0 - C_1)_{LM}l} = \frac{Dt}{\rho} \quad (11)$$

In Figure 2 the two transient concentration profiles, as calculated from eq 4 and 8, are compared for values of Dt ranging from 0.05 to 1.0. Only for times exceeding $Dt = 0.25$ are concentration profiles for the two solutions significantly different. It is noted, however, that for $Dt = 0.05$ up to nine terms of the series of eq 8 were required for convergence. Figure 3 shows a comparison of the dimensionless solute fluxes as determined from eq 7 and 9. These are essentially indistinguishable to a value of $Dt = 0.7$. Hence, the use of eq 4 and 7 in this work for the determination of diffusivities as measured in the initial transient period appears entirely justified.

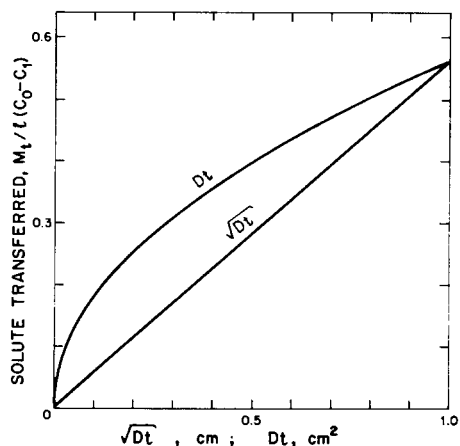


Figure 3. Amount of solute transferred from capillaries during transient effusion.

By application of eq 7 to the wash period as well as to the total transient diffusion period, the net amount of solute diffusing out of the capillaries becomes:

$$M_t = 2 \sqrt{\frac{D}{\pi}} [(C_0 - C_2)_{LM} \sqrt{t_2} - (C_0 - \bar{C}_1)_{LM} \sqrt{t_1}] \quad (12)$$

By means of a simple material balance, the net amount of solute transferred into the top chamber of the cell is:

$$M_t = \frac{VC_t}{A} \quad (13)$$

From a knowledge of the concentration of the wash solution, and final solution, it is possible to estimate the concentration that would have been obtained if the washing operation had not been performed:

$$C_2 = C_t + 3\bar{C}_1 \quad (14)$$

Diffusivities for the transient experiments were calculated by means of eq 12 and 13. The final concentration was less than 10% of the maximum concentration, which in turn was usually no greater than 2 mol %.

Results and Discussion

The results for the diffusivity measurements are listed in Table I according to the method of measurement employed. It appears significant that the diffusivities for dodecane dissolved in hexane, as well as for carbon tetrachloride dissolved in cyclohexane, as measured at steady state are very similar to those as measured in a transient mode both with only convective stirring. These diffusivities substantially corroborate those of Shieh and Lyons (22) for dodecane in hexane, and those of Sanni and Hutchison (21) for carbon tetrachloride in cyclohexane. It would, therefore, appear that convective mixing for the rates of transfer encountered from the capillaries was suitable for reliable diffusivities. On the other hand, counter to expectations, diffusivities obtained in the transient period with even a low rate of mechanical stirring in the top chamber, were significantly affected. Other transient experiments conducted under similar conditions also yielded results that were considered too high and were not tabulated. It may be concluded that with the stirring rod rotating at close proximity to the ends of the capillaries, some motion was induced within the capillaries by displacement to cause an enhancement in the diffusion rate. Some further modification to the capillary diaphragm cell would appear to be required if stirring is to be incorporated for the transient measurements. Such modifications may include locating the stirrer further from

Table I. Diffusivities Measured at 25 °C by Capillary Diaphragm Cell in Steady-State and Transient Modes

| Solvent: solute | \bar{x} | $10^5 D, \text{cm}^2/\text{s}$ | | | $\Delta, \%$ | Ref |
|----------------------------|----------------|--------------------------------|---------------------|-------------------|--------------|------|
| | | Steady state | Transient unstirred | Transient stirred | | |
| Hexane: C ₁₂ | 0.021 | 2.66 | 2.65 | 2.76 | +4 | (22) |
| | 0 ^a | 2.70 | 2.69 | 2.80 | | |
| | 0 | 2.715 | | | | |
| | 0 | 2.74 | | | | |
| C-hexane: CCl ₄ | 0.021 | 1.48 | 1.45 | — | (21) | |
| | 0 ^a | 1.481 | 1.45 | | | |
| | 0 | 1.49 | | | | |
| Hexane: C ₂₄ | 0.002 | 1.60 | 1.59 | — | | |
| Hexane: C ₃₂ | 0.002 | — | 1.36 | 1.63 | +20 | |
| Octane: C ₂₄ | 0.006 | — | 1.09 | 1.22 | +12 | |
| Octane: C ₃₂ | 0.002 | — | 0.916 | 0.970 | +6 | |
| Dodecane: C ₂₄ | 0.003 | 0.445 | — | — | | |

$\bar{\Delta} = 10\%$

^a Extrapolated to infinite dilution.

the capillary ends and reducing its size. It may also include a mechanical method of closing off entirely, by means of a movable piston, the anterior ends of the capillaries. A comparable approach has already been used successfully with a considerably smaller number of capillaries, for example, by Eriksen (9). It may be concluded that diffusivities measured in the transient mode with only convective mixing are reliable and accurate to within about 2%.

The application of the transient technique to diffusivity measurements in liquid solutions utilizing a capillary diaphragm appears at least partially successful. Most useful, perhaps, is that the transient experiments were of a few hours duration whereas the steady-state experiments were at least 2 days in duration. Neither experiment, however, required prior calibration. The easily measured parameters required in utilizing the capillary diaphragm cell, and the relative speed with which transient experiments are possible, should greatly increase its usefulness.

It should be pointed out that in the use of a fritted glass diaphragm cell in the transient mode, some additional difficulties may be encountered. Some of these have been described by Moore and Wellek (18). In addition to the necessity for calibration to determine an effective frit capillary length and area, an initial curve-fitting parameter is required to account for erosion of solution at the frit entrance. Whether as a result of the calibration techniques or of the physical manipulation of the frit in the solvent, an apparent discrepancy can be found with some of the results obtained by those workers. For example, the diffusivity for decane in a dilute solution of hexane at 25 °C was reported as $4.63 \times 10^{-5} \text{cm}^2/\text{s}$, a value higher than the self-diffusivity of hexane as reported by other workers (please see Table II), a most unlikely result. Similarly, the decane self-diffusivity at 25 °C was significantly higher than that reported by Douglas and McCall (8), whose results have been found generally self-consistent and reliable by a number of workers. Other differences are discussed by Moore and Wellek. While the construction of a capillary diaphragm cell is undoubtedly somewhat more difficult than that of a fritted glass cell, its utilization would appear to be simpler and results more reliable.

It should be recognized that diffusion coefficients for straight-chained paraffins tend to be higher than those for essentially spherical molecules of the same molar volume. The difference is attributable to the shape of the diffusing molecules as discussed by Hayduk and Buckley (10). The aspect of shape factor as it affects molecular diffusion is illustrated in Figure 4.

Diffusivity data for liquid solutions from the literature and including those from this work have been utilized to construct a

Table II. Sources of Diffusivity Data at 25 °C in *n*-Paraffin Solutions

| Solute | 10 ⁵ D ⁰ , cm ² /s in solvents indicated | | | | | | Ref |
|-----------------|---|----------------|----------------|----------------------------------|-----------------|-----------------|------|
| | C ₆ | C ₇ | C ₈ | C ₉ , C ₁₀ | C ₁₂ | C ₁₆ | |
| C ₁ | 8.64 | 7.52 | 6.49 | | 3.94 | 2.66 | (10) |
| C ₂ | 5.79 | 5.44 | 4.57 | | 2.73 | 1.95 | (11) |
| C ₃ | 4.87 | 4.40 | 3.83 | | | 1.48 | (12) |
| C ₅ | 4.59 | | | | | | (6) |
| C ₆ | 4.13 | | | | 1.39 | | (22) |
| | 4.21 (8) | | | | 1.42 (4) | 0.85 (5) | |
| C ₇ | 3.78 (6) | 3.12 (8) | | | | 0.74 (4) | |
| C ₈ | 3.47 (6) | | 2.36 (23) | | 1.14 (23) | 0.67 (22) | |
| C ₉ | | | | 1.70 | | | (8) |
| C ₁₀ | 3.02 (6) | | | 1.31 (8) | | | |
| C ₁₂ | 2.74 (6) | | | | | 0.49 (15) | |
| | 2.71 | | | | 0.84 | 0.57 | (22) |
| | | | 1.72 | | 0.81 | | (23) |
| C ₁₆ | 2.21 (5) | 1.78 (4) | 1.43 (22) | | 0.67 (15) | | |
| C ₁₈ | 2.01 (6) | | 1.20 (23) | | 0.59 (23) | | |

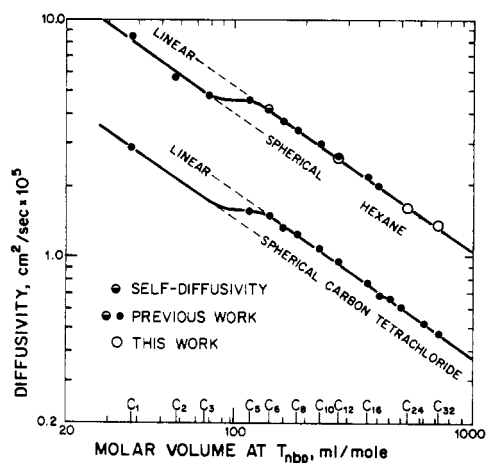


Figure 4. Diffusivities of *n*-paraffins in hexane and carbon tetrachloride at 25 °C.

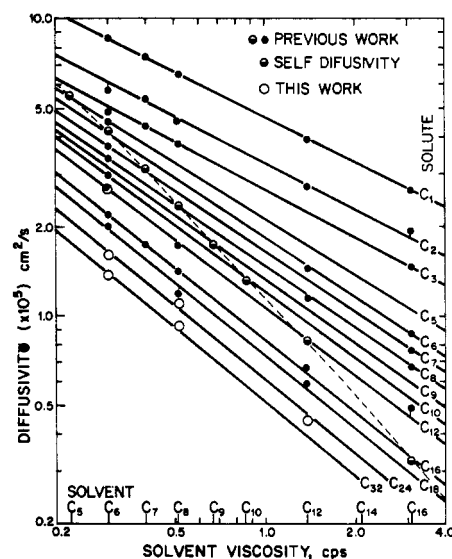


Figure 5. Diffusivity-viscosity map for *n*-paraffin solutions at 25 °C.

solute diffusivity-solvent viscosity map as shown in Figure 5. Sources of data are listed in Table II. While many different methods have been used for the diffusivity measurements, most of the data appear remarkably consistent. As expected, diffusivities of solutes of increasing molecular weight diminish regularly in any one solvent, while diffusivities of any solute diminish regularly in solvents of increasing viscosity. The relationship shown in Figure 5 appears most meaningful because it expresses diffusivities of dissolved gaseous paraffins as well as solid paraffins, and also of the self-diffusivities of the paraffin liquids all in a consistent fashion. Accurate interpolation should be readily possible. The observed behavior for normal paraffins may be used as a guide for the possible behavior of other hydrocarbon solutions. For example, any empirical correlation, which specifies the same effect of solvent viscosity for solutes of different molecular size, is likely of questionable accuracy.

Nomenclature

A = total cross-sectional area of capillaries, cm²
 A, B = constants in eq 1 for each different diffusing substance
 C = molar concentration, mol/l.
 C_0 = initial concentration in capillaries
 \bar{C}_1 = average concentration of wash solution

C_2 = concentration that would have been achieved if no solute had been removed by washing
 C_f = actual final solute concentration
 D = diffusion coefficient, cm²/s
 D_s = diffusivity obtained at steady state
 D_t = diffusivity obtained for transient conditions
 l = length of capillaries, cm
 M_t = amount of solute transferred during time interval t through area A , mol/cm²
 t = time, s
 t_1 = wash time, s
 t_2 = diffusion time including wash time, s
 V = volume of top chamber of cell, cm³
 x = distance from end of capillaries, cm
 $Y = (C - C_1)/(C_0 - C_1)$ = dimensionless concentration
 \bar{x} = average solute concentration, mole fraction
 μ = solvent viscosity, cP
 $\Delta = 100(D_t - D_s)/D_s$

Literature Cited

- (1) Albery, W. J., Greenwood, A. R., Kibble, R. F., *Trans. Faraday Soc.*, **63**, 360 (1967).
- (2) ASTM, *Data Ser.*, **DS 4A** (1971).
- (3) Anderson, J. S., Saddington, K., *J. Chem. Soc.*, **V**, S 381 (1949).

- (4) Bidlack, D. L., Anderson, D. K., *J. Phys. Chem.*, **68**, 3790 (1964).
 (5) Bidlack, D. L., Anderson, D. K., *J. Phys. Chem.*, **68**, 206 (1964).
 (6) Bidlack, D. L., Kett, T. K., Kelly, C. M., Anderson, K. K., *J. Chem. Eng. Data*, **14**, 342 (1969).
 (7) Crank, J., "The Mathematics of Diffusion", Oxford University Press, London, 1956, p 44.
 (8) Douglas, D. C., McCall, D. W., *J. Chem. Phys.*, **62**, 1102 (1958).
 (9) Eriksen, T., *Chem. Eng. Sci.*, **22**, 727 (1967).
 (10) Hayduk, W., Buckley, W. D., *Chem. Eng. Sci.*, **27**, 1967 (1972).
 (11) Hayduk, W., Cheng, S. C., *Chem. Eng. Sci.*, **26**, 635 (1971).
 (12) Hayduk, W., Castaneda, R., Bromfield, H., Ferras, R. R., *AIChE J.*, **19**, 859 (1973).
 (13) Ioakimidis, S., M.A.Sc. Thesis, Chemical Engineering Department, University of Ottawa, Ottawa, 1974.
 (14) Jost, W., "Diffusion in Solids, Liquids, Gases", Academic Press, London, 1960, p 42.
 (15) Kett, T. K., Ph.D. Dissertation, Michigan State University, 1968.
 (16) Malik, V. K., Hayduk, W., *Can. J. Chem. Eng.*, **46**, 462 (1968).
 (17) Mitchell, R. D., Moore, J. W., Wellek, R. M., *J. Chem. Eng. Data*, **16**, 57 (1971).
 (18) Moore, J. W., Wellek, R. M., *J. Chem. Eng. Data*, **19**, 136 (1974).
 (19) Nakanishi, K., Voigt, E. M., Hildebrand, J. H., *J. Chem. Phys.*, **42**, 1860 (1965).
 (20) Ross, M., Hildebrand, J. H., *J. Chem. Phys.*, **40**, 2397 (1964).
 (21) Sanni, S. A., Hutchinson, P., *J. Chem. Eng. Data*, **18**, 317 (1973).
 (22) Shieh, J. C., Lyons, P. A., *J. Phys. Chem.*, **73**, 3258 (1969).
 (23) Van Geet, A., Adamson, A. W., *J. Phys. Chem.*, **68**, 238 (1964).
 (24) Wang, J. H., *J. Am. Chem. Soc.*, **73**, 510 (1951).
 (25) Witherspoon, P. A., Saraf, D. N., *J. Phys. Chem.*, **69**, 3752 (1965).

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Dipole Moments of Some 2H-Cyclopenta[*d*]pyridazines

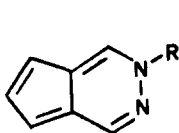
Arthur G. Anderson, Jr.,* and Lucinda W. Hickernell

Department of Chemistry, University of Washington, Seattle, Washington 98195

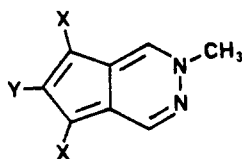
The magnitudes of the dipole moments of 2-methyl-2H-cyclopenta[*d*]pyridazine, 2-phenyl-2H-cyclopenta[*d*]pyridazine, and of 5,7-dichloro-, 5,6,7-trichloro-, 5,7-dibromo-, 5,6,7-tribromo-, and 5,7-bis(trifluoroacetyl)-2-methyl-2H-cyclopenta[*d*]pyridazine have been measured in benzene at 20° and found to be 2.83 ± 0.04, 2.88 ± 0.04, 3.80 ± 0.06, 5.02 ± 0.08, 4.32 ± 0.07, 5.25 ± 0.08, and 6.71 ± 0.07, respectively. In all cases the ring heteroatoms are at the positive end of the dipole.

The dipole moment of azulene has been determined by solution methods (4, 14, 16) and more exactly (0.796 ± 0.014 D) from microwave spectral data (15). The orientation of the dipole along the long axis of the molecule with the positive end in the seven-membered ring was shown by the measurement of the dipole moments of appropriate azulene derivatives (4, 9).

The present study (8) was undertaken to determine the effect on the dipole moment of the modification of the azulene structure into a π -excessive heteroanalogue containing a π -equivalent nitrogen adjacent to the π -excessive one, and was made possible by the recent availability (2, 3) of sufficient quantities of molecules of this type (I and II). For the determination of the direction of the dipole moments, several derivatives (III-VII) having electron attracting substituents on the five-membered ring were used. The low solubility of the parent molecule (I, R = H) precluded its inclusion in the series.



I, R = CH₃
 II, R = C₆H₅



III, X = Cl; Y = H
 IV, X = Y = Cl
 V, X = Br; Y = H
 VI, X = Y = Br
 VII, X = COCF₃; Y = H

A combination of the methods of Hedestrand (7) and Guggenheim (6, 11, 13) was used to calculate the dipole moments from the solution data obtained. A discussion of this, including a direct consideration of the instrument (Dipolemeter Type DM 01) used in this study, may be found in the literature (12). The method has the important advantage of not requiring the determination of the densities of the solutions. With benzene as the solvent, the expression for the dipole moment simplifies to eq 1 which involves the accurate measurement of only the dielectric constant and the refractive index. The sodium D line was used for the latter since this has been shown to give good results and the compounds did not absorb in this region.

$$\mu^2 = (0.895 \times 10^{-38})(\epsilon - a_n)M_2 \text{ dyne cm}^4 \quad (1)$$

where

$$a_\epsilon = \frac{\sum \epsilon_{12}\omega_2 - \sum \epsilon_1\omega_2}{\sum \omega_2^2}$$

and

$$a_n = \frac{\sum n_{12}^2\omega_2 - \sum n_1^2\omega_2}{\sum \omega_2^2}$$

M is the molecular weight, ϵ is the dielectric constant, *n* is the refractive index, and ω is the weight fraction of the solvent (1), solute (2), or solution (12). The primary data are given in Table I and the molecular weights and calculated values in Table II.

The results with I and II show a dipole moment some three times larger than that of azulene. The increase in the size of the moment in III-VII reveals the orientation of the dipoles in these compounds and in I and II have the positive end in the six-membered ring. Thus the direction as in azulene is preserved, and the electron donation by the π excessive nitrogen more than compensates for the inductive effects of the two nitrogens and the presence of the unshared pair on the π equivalent one.

This interpretation is consistent with the analogous benzenoid heterocyclic compounds wherein the substitution of an adjacent π equivalent nitrogen for a ring carbon in pyrrole ($\mu = 1.8$ D) results in a decrease in the moment for pyrazole ($\mu = 1.5$ D). The latter has the same dipole orientation as pyrrole and I (1). The dipole moment for the corresponding compound, 2-methyl-2-pyridine, related to I has not been measured, but Berson and