Self-Diffusion and Viscosity of Some Liquids as a Function of Temperature

Self-diffusion coefficients of 15 liquids have been measured as a function of temperature between their melting and boiling points. The systems investigated were the benzenes, C_6H_5X where $X = H$, F, Cl, Br, and I, *n*-paraffins, C_nH_{n+2} where $n = 7, 9, 10, 12, 14, 16$, and 18, acetone, acetic acid and water. The pulsed nmr technique was employed for the diffusion measurements. In addition, the viscosities of the halogenated benzenes have been measured between 20°C and their melting points.

The diffusion results obtained in this study have been found in excellent agreement with the best values available for benzene (Collings and Mills, 1970) and water (Longworth, 1960). The relation between the apparent molecular diameter d $(d = 2.24(\eta VD/RT)^{1/2})$ and the critical volume as suggested by Dullien (1972) has been extended to include the temperature dependence of d. It is also shown that the temperature dependence of d is similar for all liquids studied here with respect to the reduced temperature. The increase of d for $T_r < 0.46$ shows the invalidity of the Stokes-Einstein relation for this temperature range $(T_r = T/T_c)$.

A normalized plot of d has been found very useful in checking the consistency of viscosity and self-diffusion data. The relations proposed in this work can be used to predict self-diffusion coefficients and viscosities over the normal liquid range.

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SCOPE

In chemical engineering calculations it is often necessary to estimate liquid properties. Amongst the transport properties the significance of viscosity is well appreciated. The temperature dependence of viscosity of some liquids has been studied here in conjunction with the self-diffusion coefficient. The study of self-diffusion serves principally two purposes. On the one hand, there is theoretical interest in the mechanism of the diffusion process in liquids and, on the other hand, there is a theoretical possibility of predicting mutual diffusivities from the diffusivities of the pure components. A number of predictive equations exist for viscosity and diffusivity. However, these equations are usually restricted to certain classes of liquids and narrow temperature ranges. This work gives a more general predictive equation.

Part of the work deals with the question of validity of the Stokes-Einstein relation. Since this relation is in widespread use, the lack of validity pointed out here is of practical importance.

The objective of this work was to accurately determine self-diffusion coefficients as function of temperature between the melting point and the normal boiling point and to establish the temperature dependence of apparent molecular diameters. The normal paraffins were selected for study since the apparent molecular diameter of some of them exhibited abnormal behavior when calculated from literature self-diffusion data. Since the calculations for chlorobenzene also deviated from the general trend, the system of halogenated benzenes was also included in the study.

CONCLUSIONS AND SIGNIFICANCE

Calculation of the apparent molecular diameter d for a large number of liquids has shown a similar dependence on the reduced temperature T_r. The curves all have broad minima of the reduced apparent molecular diameter d_r in the range $0.45 < T_r < 0.5$. The temperature dependence has been described for all the liquids studied by

$$d_r = \frac{d}{d_{\min}} = \frac{2.55 \times 10^{-3}}{T_r^4} + 0.179 + 0.35\ T_r$$

with an average error of 1.1%.

The increase of the apparent molecular diameter for reduced temperatures <0.45 has revealed that the self-diffusion coefficient is not proportional to 1/viscosity as assumed in most diffusion theories. Thus the Stokes-Einstein relation does not apply for the liquid range $T_r < 0.45$. The increase of d can be explained on the basis of coordinated movement of groups of molecules in the liquid as the freezing point is approached. Whenever the viscosity shows an anomalous behavior the apparent molecular diameter does likewise. The anomalies of both properties begin at about the same temperature.

The usefulness of the above equation in checking the consistency of viscosity and self-diffusivity data has been demonstrated.

The following relation has been found

$$\left(\frac{\eta VD}{RT}\right)_{\min} = -1.42 + 0.152\ V_c^{2/3}$$

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to correlate the data of 21 liquids with an average error of about 4%. This equation together with the equation giving the temperature dependence of d_r can be used to predict self-diffusion coefficients or viscosities of liquids in the temperature range between the melting point and the normal boiling point.

PREVIOUS WORK

Dullien (1972) derived the following relationship between d, called the apparent molecular diameter, and physical properties of liquids:

$$d = 2.24 \sqrt{\frac{\eta V D}{RT}} \qquad (1)$$

The liquid model used for the derivation assumes the liquid to consist of rigid molecules. In nonexpanded states of the liquids, translational motion of the molecules is not considered to contribute to diffusion but the main mechanism is rather the cooperative movement of all molecules. The molecules are considered to be in close proximity of their immediate neighbors most of the time and to exchange momentum with them continually as they keep colliding at a high frequency. For simple molecules (spherical shape and n-paraffins) d was also calculated from molecular dimensions as the momentum transfer distance of a pair of colliding molecules averaged over all possible mutual orientations. Equation (1) was tested for a large number of liquids and the calculated diameters were plausible values without exception. They also showed consistency when compared for the various liquids. The calculations showed a constancy of d over a temperature range followed by an increase at higher temperatures. This dependence was explained (Dullien, 1972) as the apparent result of two opposing effects which offset each other initially. d will tend to increase with temperature because of the increased probability for momentum transfer by translational mechanism (causing a gradual breakdown of the model), whereas the molecular diameter can be expected to decrease.

Except for two liquids, water and benzene, Equation (1) had not been tested for temperatures approaching the freezing point because of lack of data. The melting point of benzene, however, is not contained in the interesting temperature region, that is, $T_r < 0.45$, for which the apparent molecular diameter increases with decreasing temperature. For water the measured self-diffusion coefficients disagree widely.

Using the reported temperature dependence of D for the n-paraffins by Douglass and McCall (1958) the apparent molecular diameter d had been calculated over a wide temperature range before starting this work. The results, shown in Figure 1, indicate an erratic dependence which is unexpected for an homologous series.

Based on the calculations for methane, for which extensive experimental data are available, Dullien (1972) proposed a linear relation between d^2 and $V_c^{2/3}$, where V_c is the critical volume. A test showed that the relationship held for all the liquids where the necessary data was available then. However, only for a small number of liquids were the calculations carried out over a temperature range and none extended into the temperature region near the melting point. This relation

$$\eta VD/RT = 0.124 \; V_c^{2/3} \qquad (2)$$

therefore, did not take into account the temperature dependence of d. In this work it has been found that the suggested relationship still holds if the minimum values of d are employed. A prerequisite for the calculation of d is the availability of density, viscosity, and diffusivity data. Density data is, in general, more readily available than the other two properties. Even in the absence of density data extrapolations within the normal liquid range are not critical due to the weak temperature dependence. This does not apply for viscosity and diffusion coefficient because of their approximately exponential temperature dependence. Moreover, a change of the temperature dependence of viscosity is encountered near the melting point (Davies and Matheson, 1966) which, sometimes (for example, toluene) (Kruger and Weiss, 1970), is also observed for the diffusion coefficient. Experimental viscosity data can be found in literature but data become markedly scarce for temperatures below 0°C. Only recently have diffusivity data at high and low temperatures become available to any extent thanks mainly to the nmr technique. The accuracy of many of the reported measurements, however, leaves much to be desired.

EXPERIMENT

Diffusion

The measurement of the self-diffusion coefficients was carried out with a spin echo spectrometer of conventional design. The spectrometer was incoherent and operating at 19.45 MHz. A single coil was used for the resonant circuit. A 12-in. Varian magnet was used. The homogeneity could be improved by using shim plates at the pole faces. In the area of the sample the inhomogeneity was smaller than 0.005 gauss/cm which could be neglected.

The samples were contained in thin walled glass tubes with an I.D. of 6.5 mm. The filling height measured only about one-half of the coil length. The samples were frozen and the tubes sealed off under vacuum. Heating and cooling were accomplished by passing conditioned air or nitrogen gas through the Dewar flask containing the sample. The temperature was measured with a calibrated copper-constantan thermocouple which was placed close to the sample. The temperature was constant to better than ±0.2°C over the necessary time for a measurement, except at temperatures below −60°C where deviations of 0.5°C were possible.

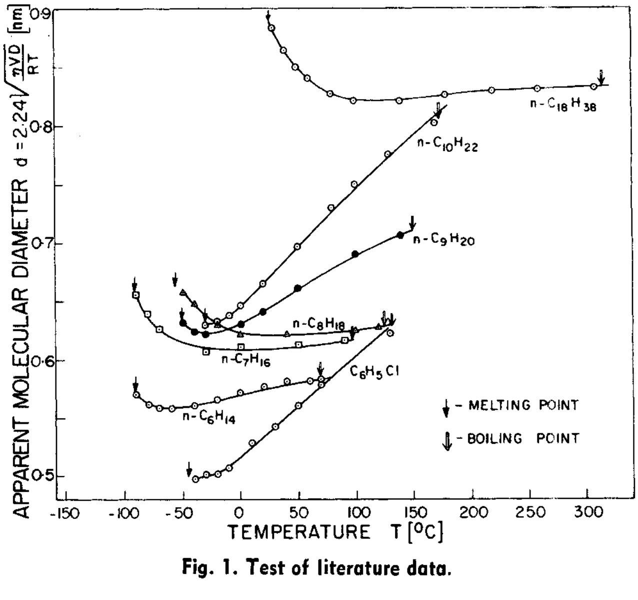

Fig. 1. Test of literature data.

Table 1. Comparison of D of Benzene of this Work with the Data by Collings and Mills (1970)

T °C	T °K	$D \times 10^9$ m²/s Collings and Mills	$D \times 10^9$ m²/s This work
15	288.2	1.86	1.85
25	298.2	2.207	2.21
35	308.2	2.605	2.61
45	318.2	3.01	3.05

The necessary field gradient G (Hahn 1950; Carr and Purcell, 1954) was applied with a pair of opposed Helmholtz coils. They consisted of 90 turns (each) of #30 copper wire, had a mean diameter of 41.6 mm, and a mean distance of 36 mm. The current was typically 50 mA producing a field gradient of about 1.35 gauss/cm. The condition $d \times G << H_1$ was well satisfied. For the two-pulse sequence employed for this work the ratio of the spin echo amplitudes without and with field gradient is given by (for example, Douglass and McCall, 1958)

$$\frac{A(t, G = 0)}{A(t, G)} = \exp\left(\frac{\gamma^2 G^2 D t^3}{12}\right) \tag{3}$$

where γ is the gyromagnetic ratio, D is the diffusion coefficient, and $t/2$ is the pulse separation time between 90° and 180° pulse. The constant field gradient-variable pulse separation time method gave results identical to the variable field gradient—constant separation time method, within experimental error. The field gradient was calibrated from the minima of the modulated spin echo (Carr and Parcell, 1954). Since the determination of the diffusion coefficient depends on the ratio of the amplitudes, careful steps were taken in the calibration of the receiver by means of a signal generator with an adjustable power output. The pulse separation time was measured with a Hewlett-Packard time counter, type 5326B.

Viscosity

A commercially available Cannon-Ubbelohde viscometer, supplied by Cannon Instrument Company, was used. The constant temperature bath was insulated by a 2-in. glass wool layer. The bath liquid was water for temperatures above 0°C and methanol for lower temperatures. Water was used as coolant for temperatures above 14°C and dry ice was used below 14°C. The experimental set-up could control the temperature to ±0.01°C between −2° and 60°C and ±0.05°C (accuracy of the thermometer) for temperatures to −50°C. Temperature was measured by standard thermometers supplied by the National Bureau of Standards. An electric stop watch was used for time measurements. The viscometer used was calibrated by means of two standard liquids supplied by the Cannon Instrument Company. Due to the particular design of the Cannon-Ubbelohde viscometer and because the efflux time was always greater than 200 seconds, the kinetic energy correction term B/t in the viscometer equation (for example, Swindells et al., 1954) was neglected:

$$\nu = \frac{\eta}{\rho} = At - B/t \tag{4}$$

where A is the calibration constant, B is the kinetic energy correction factor, and t is the efflux time. The constant A was independent of temperature and its average value was calculated to be 3.943×10^{-9} m²/s² with an estimated standard error (95% confidence interval) of 0.007×10^{-9} m²/s². The scatter of the measured efflux times was within 0.2% for the majority but never exceeded 0.4%.

Precautions had to be taken for measurements below 0°C. After filling, the viscometer limbs were connected to water aspirators via a calcium sulfate drying system in order to remove water vapor. Details of the experimental work have been described by Ertl (1973).

Liquids

The liquids were obtained from the following sources.

n-C_7H_{16}	Spectral quality	Matheson Coleman & Bell
n-$C_{10}H_{22}$	99% Olefin free	
n-$C_{12}H_{26}$		
n-$C_{14}H_{30}$		
n-$C_{16}H_{34}$		
n-$C_{18}H_{38}$		
n-C_9H_{20}	Baker grade	J. T. Baker Chemical Co.
C_6H_5F		
C_6H_5I		
C_6H_5Cl	Baker analyzed reagent	
C_6H_5Br		
C_6H_6	Spectroanalyzed	Fisher Scientific
Acetone		
Acetic Acid d_1 (CH_3COOD)	99% atom	International Chemical Nuclear Corp.
Water	doubly distilled	

The chemicals were used without further purification.

RESULTS AND DISCUSSION

Diffusion

Although diffusion measurements by the nmr technique are absolute in the sense that no calibration liquid is required, it is advisable to check measurements against systems with accurately known diffusion coefficients. Benzene was used for comparison because very accurate data (± 0.2%) are available from the measurements by Collings and Mills (1970) which were obtained by radio isotope technique using a diaphragm cell. The comparison is shown in Figure 2 and Table 1. The values of this work

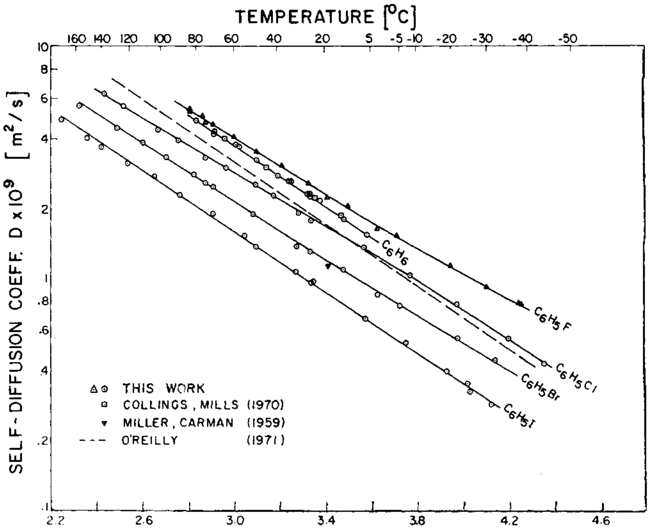

Fig. 2. Experimental diffusivities of benzenes.

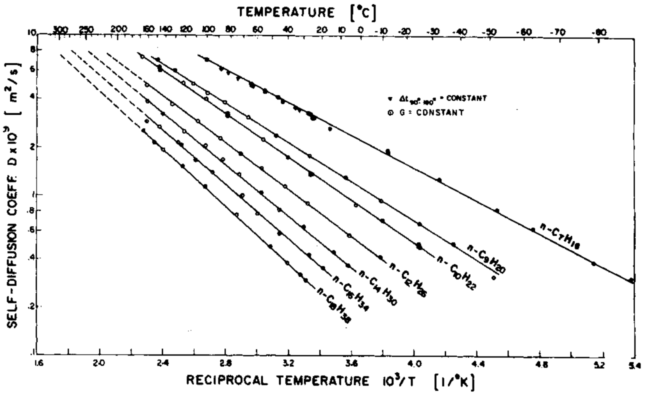

Fig. 3. Experimental diffusivities of n-paraffins.

TABLE 2. VALUES OF THE PARAMETERS D_0 AND E FOR THE LIQUIDS STUDIED

System	T_m °C	T_b °C	ΔT covered in experiment °C	$D_0 \times 10^7$ m²/s	E kJ/mole	ϵ %	n data
C_6H_6	5.5	80.1	5.9-79	3.72 ± 0.22	12.73 ± 0.38	1.40	19
C_6H_5F	−41.2	85.1	−38.2-83	2.49 ± 0.27	11.43 ± 0.29	2.35	18
C_6H_5Cl	−45.3	132.2	−43.6-137.3	1.75 ± 0.16	11.43 ± 0.29	1.93	15
C_6H_5Br	−30.7	156.2	−31.9-151.2	1.55 ± 0.13	11.85 ± 0.25	2.26	17
C_6H_5I	−31.3	188.6	−30.5-172.2	1.29 ± 0.10	12.14 ± 0.25	2.85	18
n-C_7H_{16}	−30.6	98.4	−87.6-100	1.55 ± 0.11	9.67 ± 0.21	1.79	27
n-C_9H_{20}	−51.0	150.8	−51.1-148.8	1.98 ± 0.19	11.76 ± 0.29	2.29	13
n-$C_{10}H_{22}$	−29.7	174.1	−25.3-167	2.39 ± 0.14	12.77 ± 0.21	1.61	19
n-$C_{12}H_{26}$	−9.6	216.3	−9.0-161.6	2.13 ± 0.17	13.65 ± 0.25	1.24	10
n-$C_{14}H_{30}$	5.9	253.7	6.2-163	2.45 ± 0.23	14.99 ± 0.33	2.04	11
n-$C_{16}H_{34}$	18.2	287.0	18.7-161.1	2.12 ± 0.63	15.41 ± 0.96	3.97	11
n-$C_{18}H_{38}$	28.2	316.1	28.7-165.6	2.59 ± 0.37	16.96 ± 0.50	1.41	10
Acetone	−95.4	56.2	−90.3-58	1.34 ± 0.14	8.33 ± 0.25	1.93	12
Acetic acid	16.6	117.9	17.1-116	2.96 ± 0.26	13.98 ± 0.25	1.0	8

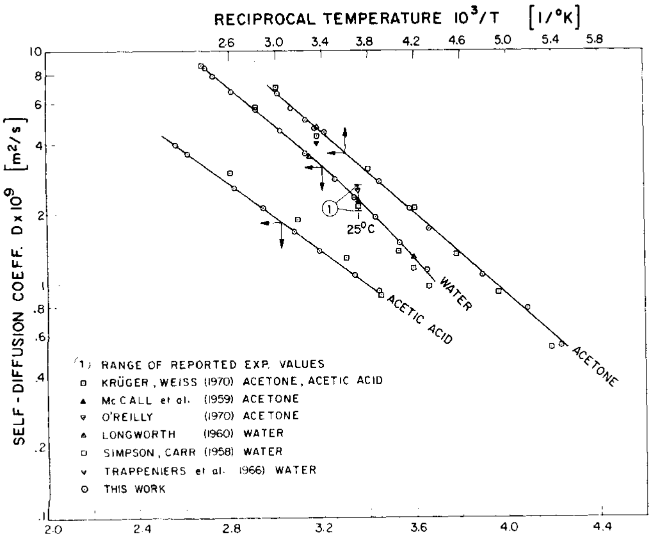

Fig. 4. Experimental diffusivities.

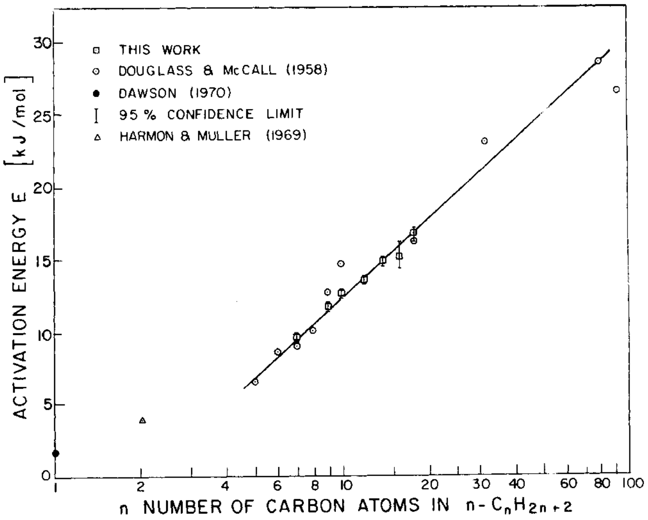

Fig. 5. Activation energy of *n*-paraffins.

were obtained from nonlinear least squares fit of the Arrhenius equation to 19 measurements between 5° and 80°C. As it is apparent the agreement is excellent.

The experimental results for the halogenated benzenes are also shown in Figure 2; other results have been plotted in Figures 3 and 4. A tabulation of the experimental data can be found in Ertl (1973). For analytical presentation, the diffusion coefficients were fitted to

$$D = D_0 \exp(-E/RT) \tag{5}$$

Use of this equation does not imply that the concept of an activation process for diffusive motion has been accepted in this work. The equation is merely used for the sake of convenience. Other forms of equations, for example, $D = D_0 \exp(V/V - V_0)$, are equally suited to describe the experimental data in most cases. Table 2 lists the parameters of Equation (5) for the liquids studied. Water is not included in the tabulation because Equation (5) is not suitable to describe the temperature dependence of D for water. The table also contains the estimated standard error of the parameters for a 95% confidence interval, the error ϵ about the regression line, the number of measurements n, the experimental temperature range, and the melting and normal boiling point temperatures. $\epsilon = \frac{100}{n} \sum_i |D_i - \hat{D}_i|/D_i$, where D_i and $\hat{D}_i$ are the experimental and best fit values for the diffusion coefficient, respectively.

Although ϵ of the halogenated benzenes is only slightly larger on the average than for the other systems, inspection of the residuals shows that their distribution along the regression line is nonrandom (Draper and Smith, 1966). In other words for this class of liquids the log D versus $1/T$ plots do not appear to be straight lines. Fits with the three parameter equation similar to Equation (10) did not significantly reduce ϵ. The tabulated values of ϵ may be regarded as fair estimates of the experimental errors.

The measurements for acetone are in good agreement with those of McCall et al. (1959) and Krüger and Weiss (1970). The former reported a value of 8.50 kJ/mole for E and the latter 8.79 kJ/mole. These values are compared with 8.33 ± 0.25 kJ/mole as obtained in this work. The measurements by O'Reilly and Peterson (1971) were not confirmed in this work. Water is remarkable in that respect that extensive measurements have been carried out for this liquid. Trappeniers et al. (1965), Mills (1971), and more recently Pruppacher (1972) gave tabulations of the experimental results. The values range from 2.04 $\times 10^{-9}$ m²/s to 2.66 $\times 10^{-9}$ m²/s at 25°C, see Figure 4. Measurements using the same experimental technique also show large discrepancies. Simpson and Carr (1958) employed the nmr technique. Their data agree well with the present measurements at high temperatures but diverge towards lower temperatures. Mills (1971) has pointed out that the measurements by Longworth (1960), using interferometry, can be considered the most accurate ones.

As is evident from Figure 4 the present measurements are in very good agreement with Longworth's data. This agreement together with that found for benzene is indication of the absence of a systematic error in the measurements of this work.

As a byproduct of this investigation a relationship between E [Equation (5)] and the number of carbon atoms n in n-paraffins was found (Figure 5). The figure also shows the 95% confidence interval as well as the values reported by Douglass et al. (1958). It can be noticed from the plot that the confidence intervals do not include their values for n-nonane and n-decane. The relation is

$$E = -6.11 + 8.04 \ln(n) \tag{6}$$

where the units of E are in kJ/mole. This equation applies for n between 5 and 20 and it becomes invalid for smaller n values. The equation can serve in interpolating missing values. The inadequacy of Equation (6) for small n values is possibly explained by the change of molecular shape. A decreasing influence of chain length on the diffusion process is also implied by this equation. This is plausible because the movements and orientations of parts of the molecule become increasingly independent for larger n-paraffins. It is not the molecule as a whole that undergoes a diffusive displacement but, due to the increasing flexibility, the contribution of segmental movements becomes more dominant. The flexibility is reflected by the degrees of freedom (d.f.) of a molecule. Bondi (1967) reported for n-C_6H_{14} d.f. = 6.84, n-C_9H_{20} d.f. = 8.1, and n-$C_{14}H_{30}$ d.f. = 10.2.

Hildebrand (1971) modified Batschinski's (1913) equation to obtain

$$\frac{1}{\eta} = B\left(\frac{V - V_0}{V_0}\right) \tag{7}$$

and he suggested that such a relation should also apply for the diffusion coefficient if $1/\eta$ is replaced by D. According to this equation a linear relation between D and molar volume V is expected. The benzenes were checked and a curvature was found in every case, indicating failure of Equation (7). A modified form, however, was found to describe the experimental data satisfactorily over the normal liquid range

$$D = B\left(\frac{V - V_0}{V_0}\right)^m \tag{8}$$

where m is a constant greater than one. The parameters of Equation (8), obtained by nonlinear least squares method, are listed in Table 3. ϵ and n have the same meaning as in Table 2. Approximately the same goodness of fit was obtained as in the case of Equation (5). In favor of Equation (8), in spite of having three parameters, is its physical content, namely that the diffusion process depends on relative volume expansion. The implication of $m > 1$ is that diffusion depends on volume expansion more than viscous flow for which $m = 1$ was found (Hildebrand, 1971).

Viscosity

For comparison, the measurements were extended into the temperature region of literature viscosity data, and the results are plotted in Figure 6. For all the liquids the values measured in this work join smoothly the literature data (Landolt Bornstein, 1969). The numerical η data of this work are presented in Table 4. The table also contains the absolute viscosities. The necessary density data were calculated using the equation given in *International Critical Tables*, 1928.

To present the temperature dependence of viscosity in analytical form, the combined literature data and those obtained in this work were fitted by nonlinear regression technique to

$$\eta = A \exp(B/T) \tag{9}$$

and

$$\eta = A \exp(B/(T - C)) \tag{10}$$

These equations were found (Barlow et al., 1966) suitable to describe the temperature dependence of the great majority of liquids. According to these authors Equation (9) is usually better suited for higher temperatures and Equation (10) for lower ones. This is also found to be the case for the halogenated benzenes, Figure 6. Inspection of this figure reveals that if the high temperature η data are fitted with Equation (9) and the resulting relationship is extended into the region of $T_r < 0.46$, there is an increasing departure from the measured data. This also holds for a great number of other liquids (Ertl and Dullien, 1973). Tables 5 and 6 give the values of the parameters of Equations (9) and (10) and the tempera-

TABLE 3. VALUES OF THE PARAMETERS IN $D = B\left(\frac{V - V_0}{V_0}\right)^m$

Liquid	$B \times 10^8$ m²/s	$V_0 \times 10^6$ m³/mole	m	ϵ %	n data
C_6H_6	4.81	81.3	1.34	1.21	19
C_6H_5F	6.18	81.0	1.80	1.87	18
C_6H_5Cl	5.17	91.4	1.58	1.38	15
C_6H_5Br	4.71	96.7	1.49	4.19	17
C_6H_5I	4.04	103.8	1.46	3.27	18

TABLE 4. VISCOSITY MEASUREMENTS OF THE HALOGENATED BENZENES
1cS = 10^{-6} m²/s; 1cP = 10^{-3} Ns/m²

	C_6H_5F		C_6H_5Cl		C_6H_5Br		C_6H_5I	
T °C	$\nu \times 10^6$ m²/s	$\eta \times 10^3$ Ns/m²	$\nu \times 10^6$ m²/s	$\eta \times 10^3$ Ns/m²	$\nu \times 10^6$ m²/s	$\eta \times 10^3$ Ns/m²	$\nu \times 10^6$ m²/s	$\eta \times 10^3$ Ns/m²
−45			2.264	2.661				
−41	1.532	1.674	2.026	2.373				
−38	1.449	1.578	1.886	2.203				
−34	1.322	1.434	1.716	1.997				
−31							2.806	5.348
−30	1.199	1.295	1.580	1.832	1.821	2.847	2.721	5.182
−26	1.112	1.197	1.443	1.667	1.661	2.586	2.398	4.554
−20	0.986	1.055	1.270	1.460	1.474	2.284	2.036	3.849
−10	0.853	0.903	1.097	1.249	1.203	1.847	1.607	3.014
0	0.7386	0.773	0.943	1.063	1.017	1.548	1.305	2.429
20			0.729	0.807	0.764	1.143	0.930	1.702

ture ranges. The temperature range for Equation (9) corresponds to $T_r > 0.46$ because the log η vs. $1/T$ plot started to become nonlinear at about this point. Equation (10) was at first fitted to the data comprising the whole liquid range. The distribution of the residuals along the curves was found random, by inspection, for fluoro- and bromobenzene, thus indicating an adequate fit. For chloro- and iodobenzene, however, the residuals were distributed in groups, like $++++$ $-------$ $++++++$, where $+$ stands for a positive and $-$ for a negative deviation, respectively, from the experimental data. Therefore, for these two liquids Equation (10) was eventually fitted to the data for the range $T_r < 0.46$, resulting in adequate fits.

Equation (7) was found by Hildebrand to be obeyed by a number of liquids including benzene and n-C_7H_{16}. However, the applicable temperature range was not mentioned. Equation (7) was fitted to n-C_7H_{16}, benzene, and the halogenated benzenes over the whole normal liquid range employing the experimental data of this work and literature data (Landolt-Bornstein, 1969). Except for the case of benzene and fluorobenzene, these fits resulted in extremely nonrandom distribution of the residuals along the lines, indicating failure of Equation (7) to describe the data. Table 7 compares the η values of these fits with the experimental data for temperatures close to the freezing point. It can be noticed from this comparison that for T_m/T_c appreciably smaller than 0.46 the difference between experimental and calculated values becomes pronounced. The deviations would be even greater if Equation (7) were fitted only to the high temperature data and the results extrapolated to temperatures below $T_r < 0.46$. One can conclude that the validity of Equation (7) is also restricted to the high temperature region ($T_r > 0.46$). If only this range is considered, agreement with the values of the parameters quoted by Hildebrand (1971) is obtained (Ertl, 1973).

TABLE 5. VALUES OF THE PARAMETERS OF $\eta = A \exp(B/T)$
$1\text{cP} = 10^{-3}\ \text{Ns/m}^2$

Liquid	Temp. range, °C	$A \times 10^5$ Ns/m²	B °K	ϵ %	n data
C_6H_5F	0-81	1.974	993.2	0.54	12
C_6H_5Cl	20-132	2.40	1,028.5	0.40	22
C_6H_5Br	40-150	3.285	1,027.4	0.76	12
C_6H_5I	60-150	3.351	1,128.7	0.29	9

TABLE 6. VALUES OF THE PARAMETERS OF $\eta = A \exp[B/(T - T_0)]$
$1\text{cP} = 10^{-3}\ \text{Ns/m}^2$

Liquid	Temp. range, °C	$A \times 10^5$ Ns/m²	B °K	T_0 °K	ϵ %	n data
C_6H_5F	−41-81	5.262	479.2	93.9	0.80	20
C_6H_5Cl	−45-20	9.256	397.5	109.7	0.40	16
C_6H_5Br	−30-150	5.924	632.2	79.8	0.72	29
C_6H_5I	−31-60	11.187	464.5	122.0	0.47	13

TABLE 7. COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED VISCOSITY VALUES NEAR THE MELTING POINT

Equation for calculated viscosity: $1/\eta = B\left(\dfrac{V - V_0}{V_0}\right)$

$1\text{cP} = 10^{-3}\ \text{Ns/m}^2$

Liquid	T_m °C	T_m/T_c	$10^3 \times$ $\eta_{\exp}{}^{t\ °C}$ Ns/m²	$10^3 \times$ η_{calc} Ns/m²	ϵ %	n data
C_6H_6	5.5	0.496	0.826^{5}	0.841	0.76	9
C_6H_5F	−41.2	0.413	1.674^{-41}	1.668	0.87	20
C_6H_5Cl	−45.3	0.36	2.661^{-45}	3.028	1.82	37
C_6H_5Br	−30.7	0.362	2.845^{-30}	3.234	1.92	29
C_6H_5I	−31.3	0.335	5.348^{-31}	6.552	3.56	22
n-C_7H_{16}	−90.61	0.338	$3.90^{-90.3}$	7.96	14.44	26

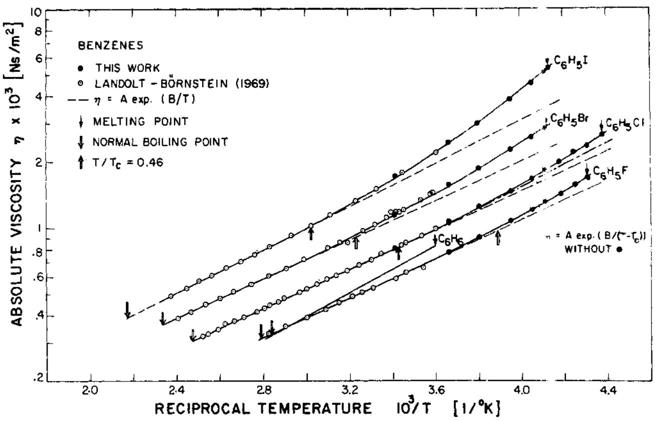

Fig. 6. Deviations from Arrhenius viscosity behavior.

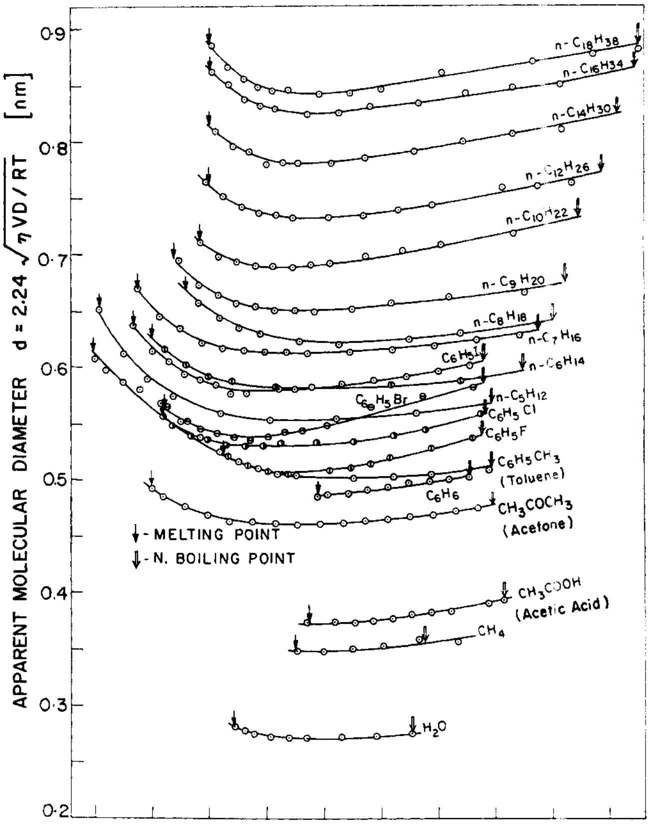

Fig. 7. Similarity of molecular diameter plots.

Apparent Molecular Diameter d

The results of the calculations for d [Equation (1)] are shown in Figure 7. d of several liquids calculated from literature data have also been included. The similarity of the temperature dependence of d of all liquids is apparent and also the increase for T_r values smaller than about 0.46. The liquids shown in Figure 7 comprise a diversity of molecular structures. The liquids are chemically very

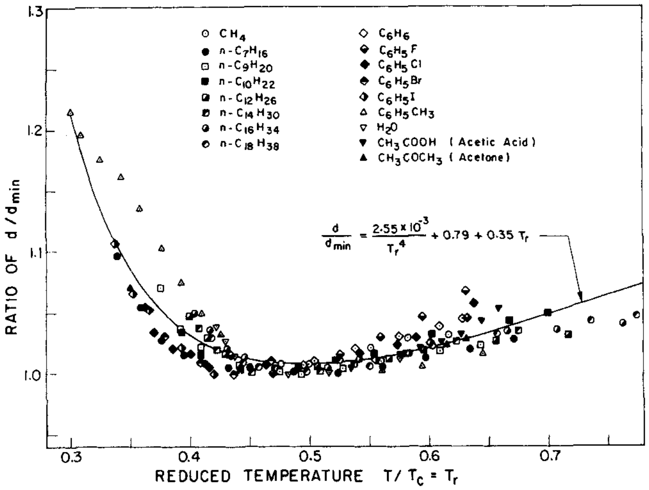

Fig. 8. Reduced molecular diameter.

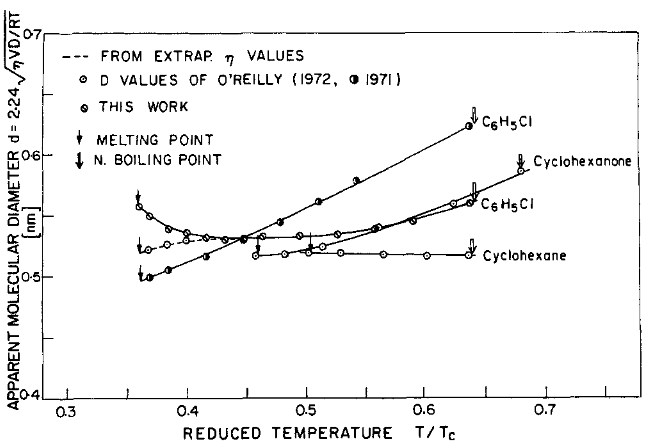

Fig. 9. Test of literature data.

distinct and there is also a considerable range in molecular size. It is remarkable that in spite of this variety the same trend is recognizable. This point is well illustrated in Figure 8 which is a normalized plot of Figure 7. The ratio of $d/d_{\min}$ has been plotted vs. T_r. The very small scatter in the neighborhood of $T_r = 0.46$ is a consequence of using $d/d_{\min}$. Although there is an increasing scatter towards the melting and boiling points, the characteristic behavior is easy to recognize. Part of the scatter is due to the sensitiveness of the $d/d_{\min}$ ratio to the values of viscosity and diffusivity. Close inspection of Figure 7 shows that d of benzene and the halogenated benzenes tend to increase faster to the right of the minimum than is the case for the other liquids. As the benzenes possess fewer degrees of freedom, this behavior could be an indication of a dependence of d on the number of degrees of freedom a molecule possesses.

An equation, analogous in form to the empirical relation found suitable to describe the excess heat capacity, was fitted to the $d/d_{\min}$ values. The solid line in Figure 8 is the best fit to

$$\frac{d}{d_{\min}} = \frac{A}{T_r^4} + B + CT_r \tag{11}$$

where the parameters have the values: $A = 2.55 \times 10^{-3}$, $B = 0.179$, and $C = 0.35$. Use of these parameters results in $\epsilon = 1.1\%$. The T_r range of Figure 8 covers the normal liquid range of the vast majority of liquids. Few liquids only extend into temperatures corresponding to $T_r < 0.3$. Unfortunately, none of these liquids could be included in the calculations due to the lack of necessary data.

The anomalous viscosity behavior has been interpreted by McLaughlin and Ubbelohde (1958) on the basis of cluster formation. As Ubbelohde and co-workers have shown clusters may result through the entanglement of molecules having a structure with branched or re-entrant portions. In the present work, however, the word *cluster* is applied in a more general sense whenever a substance freezes only under $T_r \approx 0.46$ (Ertl, 1973). It appears that restricted rotation of the molecules and cluster formation may be the result of one and the same cause, namely, the scarcity of free volume. According to this interpretation, clusters are short-lived dynamic arrangements of adjacent molecules having coordinated movements. If such an interpretation is also applied to the apparent molecular diameter d which is the average value of the center-to-center momentum transfer distance of a pair of colliding molecules, the increase of d for $T_r < 0.46$ is reconcilable.

The plots of Figures 7 and 8 have been found valuable in checking the consistency of viscosity and self-diffusion data. The following examples demonstrate the usefulness.

1. Chlorobenzene is an example for the case of viscosity. The decision to measure the viscosity of C_6H_5Cl (and those of the other halogenated benzenes) was prompted by the unexpected temperature dependence obtained for the apparent molecular diameter d dotted line in Figure 9. Contrary to the general trend, d decreased for $T_r < 0.46$. Similar abnormal behavior, although to a lesser extent, was also observed for the other halogenated benzenes if the viscosities used in this range were extrapolated values obtained by using the three parameter equation [Equation (10)], shown in Figure 6. The d values calculated from the measured viscosities bend upwards for $T_r < 0.46$ as for the other liquids as shown in Figure 9. The extrapolated value of viscosity is 2.36 cP at −45°C which is close to the melting point. The corresponding actual viscosity is 2.66 cP. It is evident that in the absence of comparison data the extrapolation would not have been suspect.

2. Chlorobenzene is also a suitable candidate to demonstrate the case of diffusivity data. The D measurements of O'Reilly and Peterson (1971) are shown in Figure 2 (dashed line) for comparison. When disagreement is found as is the case here, it is difficult to ascertain the correct data. If only the diffusivity data are analyzed alone there has to be something very conspicuously unusual about the trend of the measurements in order to arouse any suspicion. However, the form used in Figures 7 and 8 is helpful. The D values of O'Reilly et al. result in steep rise of d with T, Figure 9, leading to a value of 1.25 for $d/d_{\min}$ at the boiling point ($T_r = 0.641$) which, in the light of Figure 8, is improbable.

3. The problems encountered with the normal paraffins have already been mentioned. A completely different behavior of a property is unexpected for any member of an homologous series as it was the case for the apparent molecular diameter d of some of the n-paraffins (Figure 1) when the D values of Douglass et al. (1958) were employed. Over the normal liquid range (high density region) only a small rise of d with T is usually found on the right-hand side of the minimum; hence, doubt was cast on the behavior of those n-paraffins exhibiting a steep rise of d with T. The diffusivity data were selected as probable cause because of their commonly poorer reliability. Accurate re-determination of D resulted in conformity with Figures 7 and 8. Again, if the diffusion coefficients are looked at separately there is no obvious way to check their consistency.

4. The recent measurements (O'Reilly et al., 1972) of the self-diffusion coefficient of cyclohexanone, $C_6H_{10}O$ and

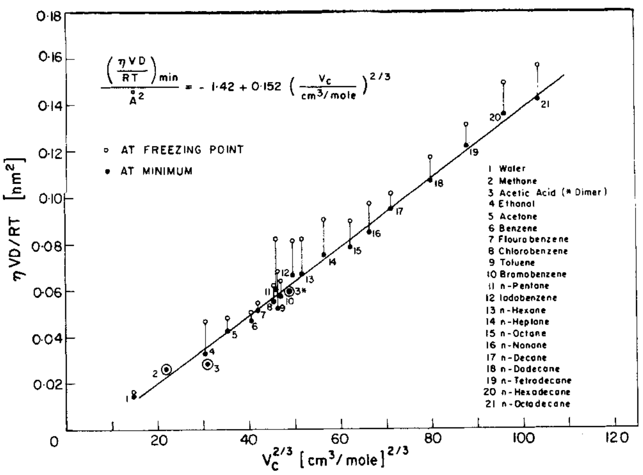

Fig. 10. Test of Dullien's correlation.

cyclohexane C_6H_{12} made it possible to calculate d for these liquids. d of cyclohexane turned out practically temperature independent whereas a steep increase has been found for cyclohexanone. The different behavior of these two liquids is difficult to explain on the basis of their structures, and in the light of Figures 7 and 8 neither can be anticipated to be correct. Whether these dependencies are due to incorrect viscosity of diffusivity data or both has yet to be checked.

Figure 10 is a plot of $\eta VD/RT$ $(= d^2/2.24^2)$ versus $V_c^{2/3}$ for all the liquids shown in Figure 7. The range between open and full circles corresponds to the value of d at the melting point and minimum, respectively. The plot shows that the relationship given by Equation (2) is not general, but it depends on the temperature. A new linear relation has been found to correlate the minimum values. The best fit has an average error of 4% and is given by

$$\left(\frac{\eta VD}{RT}\right)_{\min} = -1.42 + 0.152\ V_c^{2/3} \qquad (12)$$

where V_c is in cm^3/mole and the units of the left-hand side are Å^2.

The relation does not extrapolate through the origin. Equation (12) is valid for $V_c^{2/3} > 30$ (cm^3/mole)$^{2/3}$ with the stated error. It is known that acetic acid is likely to form a dimer. If this fact is taken into account, acetic acid is in better agreement with the correlation; see 3* of Figure 10.

In a recent paper, Vadovic and Colver (1972) have found that $V_c = 0.31\ V_m$. This relation has been applied to the liquids given in Figure 10 and resulted in a slightly larger average error. If this relation proves to be generally correct, then the use of V_m is advantageous because density data at the melting point are more readily obtained than at the critical point. The temperature dependence of the quantity on the left-hand side of Equation (12) can now be taken into account by the relationship given by Equation (11). The following equation is obtained

$$\frac{\eta VD}{RT} = \left(\frac{\eta VD}{RT}\right)_{\min}\left(\frac{d}{d_{\min}}\right)^2 \qquad (13)$$

where the first factor of this equation is given by Equation (12) and the second by Equation (11). Use of Equation (13) enables one to predict any one of η, V, or D as a function of temperature if the other quantities are known. It is particularly interesting that Equations (11) and (12) have been found to apply for a large variety of liquids and cover the normal liquid range. Using the calculations by Dullien (1972) for methane, Equation (13) is found to represent $d/d_{\min}$ correctly up to a reduced temperature of 0.85.

Almost all diffusion theories assume—directly or indirectly—the diffusion coefficient to be proportional to the reciprocal viscosity (= fluidity). The slight increase of the apparent molecular diameter d for $T_r > 0.46$ is reconcilable with this assumption but is contradicted for smaller reduced temperatures. This is mainly because for $T_r < 0.46$ the temperature dependence of viscosity changes to a higher than exponential order whereas the diffusion coefficient continues to decrease exponentially in most of the cases. Equations (11) and (13) should prove especially useful for the temperature range of $T_r < 0.46$.

ACKNOWLEDGMENT

The authors are grateful to Professor L. W. Reeves, Department of Chemistry, University of Waterloo, for permission to use his laboratories and part of the nmr equipment, and to the National Research Council of Canada for an operating grant.

NOTATION

A = amplitude of spin echo
A = constant
B = constant
C = constant
d = apparent molecular diameter
D = self-diffusion coefficient
D_0 = constant (frequency factor)
E = constant (activation energy)
G = field gradient
H = magnetic field
m = exponent
n = number of carbon atoms of n-paraffins
n = number of experimental points
R = gas constant
t = time
T = absolute temperature
$T_r = T/T_c$ = reduced temperature
V = molar volume
V_0 = constant (intrinsic volume)

Greek Letters

ϵ = average error about regression
η = absolute viscosity
μ = gyromagnetic ratio
ν = kinematic viscosity
ρ = density

Subscripts

c = critical
m = melting
r = reduced

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Manuscript received March 12, 1973; revision received July 10 and accepted July 11, 1973.

Liquid Phase Mass Transfer with Concurrent Flow Through Packed Towers

Liquid phase mass transfer coefficients were measured for the absorption of carbon dioxide into water in concurrent flow. Liquid flow rates ranged up to 300 kg-mol/min. m^2 or about 60,000 lb./hr. ft.^{2}. In comparison with countercurrent flow, the coefficients were lower by as much as a factor of 3 with a significant gas rate effect. Correlations for concurrent coefficients with liquid and gas flow rates were obtained in the form $k_x a = CL^r G^s$ for 19.0-mm Berl saddles and 6.35-mm and 12.7-mm Raschig rings.

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SCOPE

Recent interest and development in the field of gas-liquid reactions in packed beds stimulated this study. The literature contains much information about systems in which the gas and liquid streams flow countercurrently through the packed bed, but it contains relatively little about concurrent flow systems. The advantage of countercurrent operation in mass transfer is that it is more efficient in maintaining a relatively large concentration difference between the phases throughout the tower; however, countercurrent operation is limited by flooding, and greater pressure drops are required for given flow rates in countercurrent flow.

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