Predicting Transport Coefficients of Liquids — A Unified Approach

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The fundamental similarity between mass heat and momentum transfer has been recognized for some time, yet available equations for predicting the transport coefficients for these processes differ widely. This is so partly because most predictive equations for transport coefficients are empirical and not based on any particular model of the liquid state. In this note, equations for self-diffusion and thermal conductivity based on molal expansion are presented. Hildebrand (1971) has already proposed a similar equation for viscosity. These three equations emphasize the basic similarity between these transport processes.

Hildebrand and co-workers (1977) extensively studied the viscosity of liquids and its dependence on molal expansion. The reciprocal of viscosity was shown to be directly related to molal expansion

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

V is the molal volume and V_0 is the intrinsic molal volume which is a corresponding states ratio of the critical volume. The intrinsic state is defined as the state (molal volume) where fluidity and diffusion coefficient are zero. B denotes the capacity of the molecules to absorb externally imposed momentum.

The above relationship was shown (Hildebrand 1977) to hold for liquids, liquid metals and compressed gases. Sridhar et al. (1978) extended this equation to non-Newtonian solutions, where B and V_0 now become shear rate dependent. The above equation is therefore extremely versatile.

SELF-DIFFUSION COEFFICIENTS

Hildebrand (1977) suggested that the coefficient of self-diffusion should also be related to molal expansion by an expression similar to Equation (1)

$$D = B_1\left(\frac{V - V_0}{V_0}\right) \tag{2}$$

Compared with the fluidity equation, the diffusion analog has not been widely tested. Ertl and Dullien (1973) tested Equation (2) for benzene and halogenated benzenes and found nonlinearity in each case, indicating failure of the equation. Thus, while the fluidity equation is valid above a reduced temperature of 0.46, the analogous diffusion equation departs from the predicted linear relationship for the entire temperature range. A modified form of Equation (2) was suggested by Ertl and Dullien (1973)

$$D = B_2\left(\frac{V - V_0}{V_0}\right)^m \tag{3}$$

where m is a constant greater than unity. This empirical modification was found to be reliable but is theoretically difficult to justify.

The failure of Equation (2) is unfortunate, for if it were valid, a unified theory for viscosity and diffusion based merely on molal expansion could be postulated. The fundamental similarity between viscosity and diffusion has been recognized for a long time. Hence one would expect that, considering the success of the fluidity equation, diffusion should be related to molal expansion. We examine this possibility.

Our approach to this problem begins with Lamm's (1952) theory. Dullien (1963) used this theory to establish a new relationship between viscosity and diffusion coefficients

$$\delta = \left|\frac{2DV\mu}{RT}\right|^{0.5} \tag{4}$$

δ is the mean momentum transfer distance between molecules. Equation (4) is especially useful, since it is not based on any particular model of the liquid state. Assumption of a particular model yields a relationship between δ and the apparent molecular diameter. Such a procedure was used by Dullien (1972) to yield a useful predictive equation for self diffusion coefficient. But if we incorporate the fluidity model into Equation (4) we obtain

$$D = \chi\frac{T}{V}\left(\frac{V - V_0}{V_0}\right) \tag{5}$$

The similarity between the above equation and Equation (1) is obvious. The physical significance of χ is obtained from

$$\chi = \frac{R\delta^2 B}{2} \tag{6}$$

χ therefore represents not only the capacity of the molecule to absorb momentum but also depends on the square of the momentum transfer distance. χ is a characteristic parameter of the liquid, but is probably slightly dependent on temperature. For most practical purposes, it can be assumed to be temperature independent.

Equation (5) also shows the dependence of diffusion coefficient on molal expansion. Equation (5) was tested for a few liquids. Figure 1 shows the results where the good fit is obvious. There is divergence below a reduced temperature of 0.46. A possible explanation and an empirical correction for this divergence is based on increases in molecular diameter (Sridhar and Potter 1978).

Equations (1) and (5) represent the fundamental relationship between viscosity, diffusion and molal expansion. Most of the available correlations for diffusion coefficient can be derived from Equation (5) by postulating different dependences of the parameter χ on liquid phase properties. For example, if δ is

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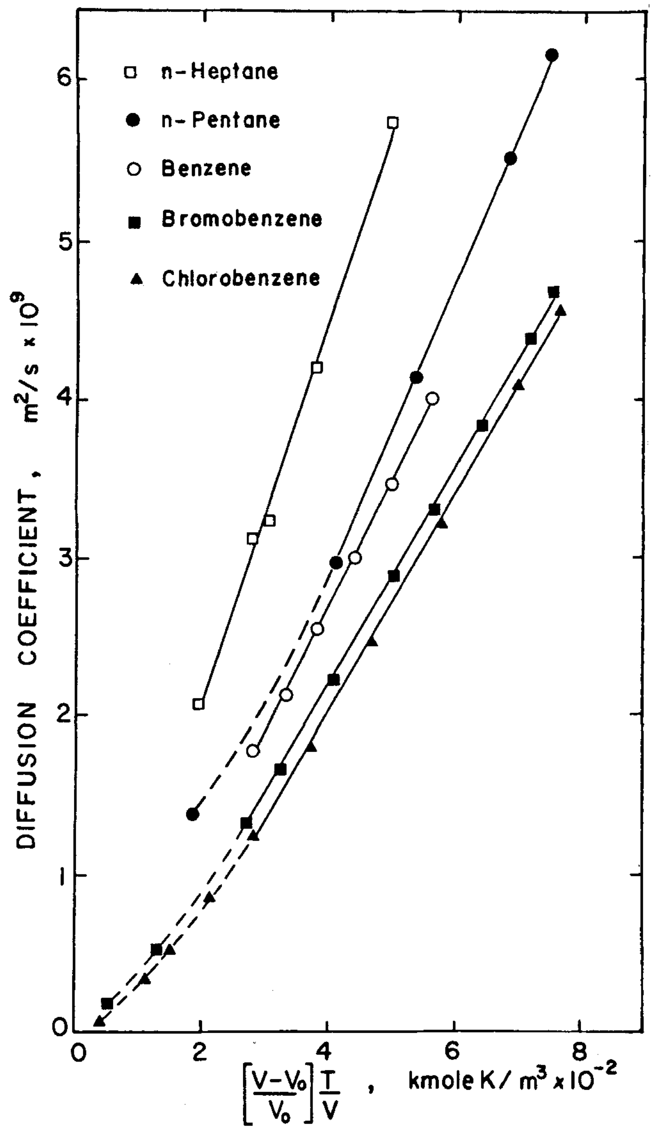

Figure 1. Dependence of self-diffusion coefficient on molal expansion. Experimental data taken from Dullien (1972), Ertl and Dullien, (1973).

given by

$$\delta = \left[\frac{2V}{3\pi N d}\right]^{0.5} \tag{7}$$

then (5) reduces to

$$D = \frac{kT}{3\pi\mu d} \tag{8}$$

which is the Stokes-Einstein equation.

The central problem in understanding the liquid state is the a priori prediction of the parameters χ and B. Molecular mobility is the best tool for extracting such information (Hildebrand and Lamoreaux 1972). Independent data are not available to quantify molecular flexibility, inertia of rotation and their effects on molecular mobility.

THERMAL CONDUCTIVITY

Thermal conductivity is an important physical property in heat transfer applications and design. The laboratory measurement of thermal conductivity is comparatively difficult. The usefulness of a predictive equation for thermal conductivity is obvious. Procedures for estimating thermal conductivity of liquids have been reviewed by McLaughlin (1964) and Reid and Sherwood (1966). The success of the fluidity approach in relating viscosity and self diffusion coefficients to molal expansion suggests that a similar relationship should hold for thermal conductivity.

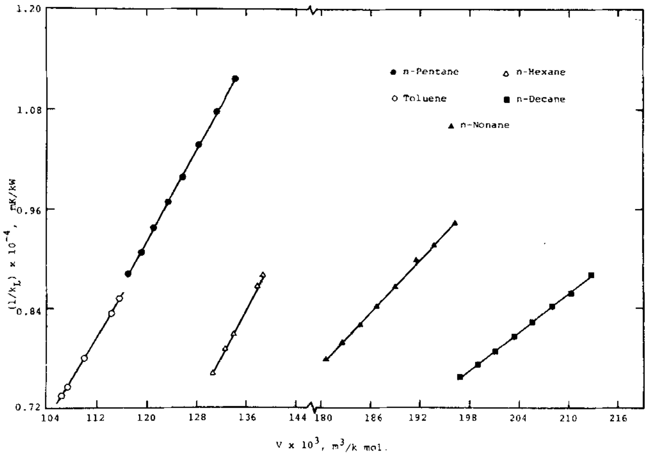

Figure 2. The reciprocal of thermal conductivities as a function of molal volume.

Figure 2 presents the relationship between the reciprocal of thermal conductivity and molal volume for a few normal alkanes. Density values were obtained from International Critical Tables (1926). The relationship is linear, as expected. As the temperature is reduced, liquid transport properties can be expected to approach the values for the solid state. In the case of fluidity and diffusion coefficient, this is effectively zero. But in the case of thermal conductivity, the value for the solid is the same order of magnitude as that for the liquid. Thus as the molal volume approaches V_0, k_L will be expected to approach k_o, the thermal conductivity of the solid.

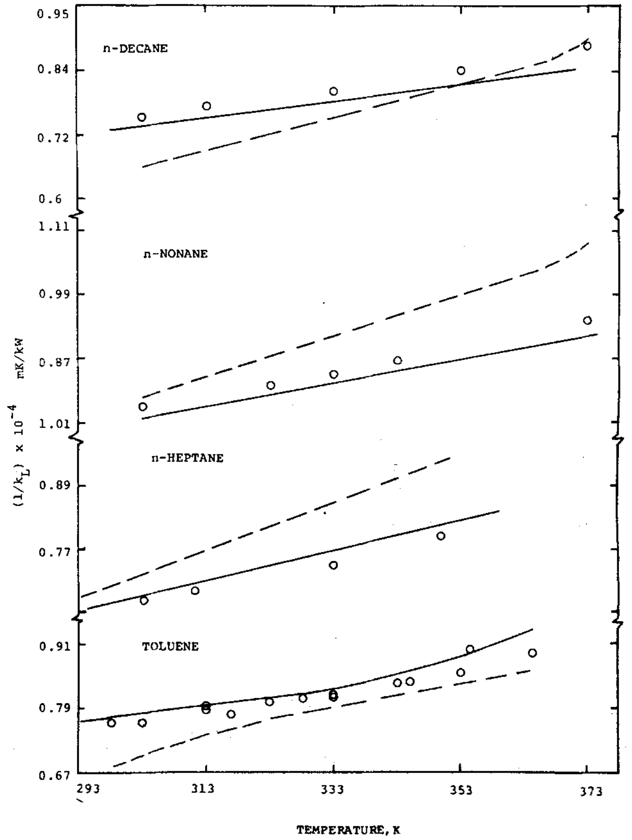

Figure 3. Temperature dependence of thermal conductivity. Data sources listed in Table 1. Broken line represents prediction by Robbins and Kingrea. Continuous line represents prediction by Equation (10).

TABLE 1. PREDICTIONS OF EQUATIONS COMPARED

		THERMAL CONDUCTIVITY × 10⁴ kw/mK			
Compound	T(K)	Experimental	Eqn. (10)	Eqn. (12)	Data Source*
Propane	323	0.783	0.783	0.787	4
n-Butane	277	1.096	1.148	0.745	3
n-Pentane	303	1.135	1.181	1.320	1,4
	313	1.100,1.197	1.140	1.247	
	323	1.066	1.100	1.184	
n-Hexane	293	1.308	1.286	1.392	4
	303	1.267	1.247	1.321	
	311	1.234	1.216	1.176	
	333	1.134	1.132	1.133	
n-Heptane	303	1.255,1.280	1.234	1.268	1,4
n-Octane	293	1.323,1.363	1.410	1.994	1,5
	311	1.224,1.297	1.357	1.826	
	350	1.160	1.167	1.146	
n-Nonane	323	1.220	1.251	1.155	1
n-Decane	313	1.300	1.333	1.370	1
n-Tetradecane	316	1.370	1.264	1.330	3
n-Hexadecane	316	1.414	1.246	0.993	3
Toluene	293	1.289,1.360	1.294	1.410	2,4,7,8
Chloroform	293	1.030,1.190	0.977	1.178	2,4
2-Methyl Pentane	305	1.084	1.215	1.100	4
Cyclo Pentane	293	1.322	1.375	1.255	4
Cyclo Hexane	293	1.243	1.427	1.393	1
Carbon Tetra-Chloride	273	1.100	1.213	1.093	2
	293	0.951,1.033	1.184	1.086	2,6
	303	0.931,1.017	1.050	1.079	2,6
	308	0.983	1.034	1.075	4
Chloro Benzene	293	1.368	1.356	1.337	2
Bromo Benzene	293	1.117	1.268	1.096	2
Iodo Benzene	293	0.987,1.021	1.276	0.967	2,4
Benzene	293	1.359,1.477	1.342	1.543	4,6,8
	303	1.440	1.295	1.464	8
	313	1.352,1.400	1.252	1.418	6,8
	323	1.368	1.211	1.402	4
	343	1.31	1.137	1.292	8

*(1) Mallan et al. (1972)
(2) Pachaiyappan V. and Vaidyanathan, K.R. (1973)
(3) Mathur, V.K. et al. (1978)
(4) Reid and Sherwood (1966).
(5) Kandiyoti et al. (1972)
(6) Poltz, H. and Jugel, R. (1967)
(7) Ziebland (1961)
(8) Venart (1965).

On the basis of Figure 2, we postulated the thermal conductivity starts at $(1/k_o)$ and varies linearly with molal expansion

$$\frac{1}{k_L} = \frac{1}{k_o} + \gamma\left(\frac{V - V_0}{V_0}\right) \tag{9}$$

Plots of $(1/k_L)$ against molal expansion were linear. The constant γ will depend on specific heat, molecular weight and the Hildebrand parameter B. A simple dimensional analysis indicates that γ will be proportional to MB/C_p. McLaughlin (1964) showed that the dimensionless group $(Mk_L/C_p\mu)$ is a constant for a series of liquids. To evaluate $(1/k_o)$, the Sheffy and Johnson correlation (see Reid and Sherwood 1966) for predicting thermal conductivities at the melting point was used. k_o is not necessarily the thermal conductivity at the melting point, but at the intrinsic state which, in some cases, can be obtained only by supercooling the liquid. Hence k_o is given by the Sheffy and Johnson correlation but with different constants.

The relationship for thermal conductivity can be written as

$$\frac{1}{k_L} = 2.09\,\frac{MB}{C_p}\left(\frac{V - V_0}{V_0}\right) + \frac{1}{k_o} \tag{10}$$

where

$$\frac{1}{k_o} = 442.16\,T_m^{0.216}M^{0.3} \tag{11}$$

T_m = melting point, K, k_L = thermal conductivity, kW/m K; B = Hildebrand's parameter, $(N\ \mathrm{s/m^2})^{-1}$; C_p = specific heat kJ/kmol K; and M = molecular weight. The constants were determined by a least squares analysis.

It is interesting to compare the predictions of Equation (10) with some other available correlations. Reid and Sherwood (1966) recommend the correlation of Robbins and Kingrea, which is given below

$$k_{RK} = \left[(88 - 4.94\,H)\,(10^{-3})/\Delta S^* \right] \left(\frac{0.55}{T_r} \right)^G C_p \rho^{4/3} \qquad (12)$$

where

$$\Delta S^* = (\Delta H_v/T_b) + R \ln (273/T_b)$$

The parameter H is obtained by adding various group contributions. G takes the value of zero or one depending on the value of the liquid density. Other properties necessary are the normal boiling point and the molal heat of vaporization. Clearly, the above equation is cumbersome to use.

Table 1 compares the predictions of Equation (10) with those from the Robbins and Kingrea correlation. Experimental values and their source are also listed. Values of the Hildebrand parameter were obtained from Hildebrand (1977). Equation (10) is as good a predictor as the Robbins and Kingrea correlation, and in many cases, it leads to a better prediction. We hesitate to use statistical methods for rigorous comparison because of the uncertainty of experimental error.

It would also be interesting to see how well Equation (10) predicts the temperature dependence of thermal conductivity. The results are presented in Figure 3. We draw special attention to the comparison with the data on toluene, which has been recommended as a standard by many authors (McLaughlin, 1964). Figure 3 shows that for the liquids tested, Equation (10) is a better predictor of temperature dependence than the Robbins and Kingrea equation.

The equation presented in this work has the advantage of being simpler. More importantly, it relates the reciprocal of thermal conductivity to molal expansion. The only unknown is B, which also occurs in the viscosity and diffusion equations. Since, in most cases, accurate experimental viscosities are available, B can be calculated. Equation (10) predicts thermal conductivities with an error of about 10%. The errors are largely due to errors in specific heat values. Thermal conductivity data also carry considerable error and data from different investigators do not always agree with each other (Reid and Sherwood 1966).

CONCLUSIONS

Molal expansion is a key parameter in understanding transport properties in liquids. The three transport properties of viscosity, diffusivity and thermal conductivity and their temperature dependence can be predicted, for liquids, from measurements of density as a function of temperature. V_0 can be obtained as a ratio of the critical volume. Estimating the other unknown, B, requires at least one experimental value, preferably viscosity. Equations (1), (5) and (10) emphasize the basic similarity in transport processes with the same parameter appearing in all of them. They provide a framework for the development of a unified theory for the prediction of transport processes.

NOTATION

B = parameter in Hildebrand's fluidity equation, $N^{-1}\,m^2\,s^{-1}$
B_1, B_2 = constants, $m^2\,s^{-1}$
C_p = heat capacity, kJ kmole^{-1} K^{-1}
d = molecular diameter, m
D = self-diffusion coefficient, $m^2\,s^{-1}$
G = parameter in Equation (12)
H = parameter in Equation (12)
k = Boltzmann constant in Equation (8), kJK^{-1}
k_L = thermal conductivity, kW m^{-1} K^{-1}
k_o = thermal conductivity at the intrinsic state, kW m^{-1} K^{-1}
k_{RK} = thermal conductivity from Equation (12), kW m^{-1} K^{-1}
m = exponent in Equation (3)
M = molecular weight
N = Avogadro number kmole^{-1}
R = gas constant, kJ kmole^{-1} K^{-1}
T = absolute temperature, K
T_b = normal boiling point, K
T_m = melting point, K
T_r = reduced temperature
V = molal volume, m^3 kmole^{-1}
V_0 = intrinsic molal volume, m^3 kmole^{-1}

Greek Symbols

γ = defined by Equation (9)
χ = defined by Equation (6)
δ = mean momentum transfer distance, m
μ = viscosity, N m^{-2} s
ρ = density, gmole cm^{-3}
Δs^* = modified Everett entropy of vaporization, cal gmole^{-1} K^{-1}
ΔH_V = molal heat of vaporization at normal boiling point, cal gmole^{-1}

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