Prediction of Liquid Viscosities

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INTRODUCTION

Progress on the development of a general predictive theory for the viscosity of liquids has not been rapid despite years of concentrated effort aimed at understanding the mechanism of momentum transfer in liquids. The liquid state has been analyzed by models that emphasize its similarity either to gases or solids. Unfortunately, neither the quasi-gas models (including radial distribution theories) nor the quasi-solid models (including lattice theories) have had much success in yielding equations for predicting the viscosity of liquids. Most of the success in this area has been through empirical equations, the earliest of these being the work of Andrade, which formed the basis of many empirical equations that followed. Efforts have also been made to extend Eyring's reaction rate theory to explain the phenomenon of viscosity. The results are still not satisfactory for engineering estimates of viscosities. The literature has been reviewed by Reid et al. (1977) and Sridhar (1983).

Currently, the most popular methods of predicting viscosity are through group contribution techniques. Thomas (1946) has suggested the following equation for predicting liquid viscosities:

$$\log\left(8.569\,\frac{\eta_L}{\rho_l^{1/2}}\right) = \left(\theta\left(\frac{1}{T_r} - 1\right)\right) \tag{1}$$

The parameter θ is a constant that depends on the structure of the liquid and is obtained by adding the contributions of individual atoms in the liquid molecule. This method is not suitable for alcohols, acids, heterocyclics, amines, or aldehydes.

Morris (see Reid et al., 1977) presented another group contribution equation:

$$\log\left(\frac{\eta_L}{\eta_L^+}\right) = J\left(\frac{1}{T_r} - 1\right) \tag{2}$$

where η_L^+, is the pseudocritical viscosity and is a constant for each class of liquids, J is calculated from group contributions.

The more recent work of Van Velzen et al. (1972) is based on an extensive study of the effects of molecular structure on viscosity and uses a modification of the Andrade equation:

$$\log \eta_L = A\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{3}$$

B and T_0 are related to liquid structure. The method is rather complicated to use.

Reid et al. (1977) conclude that the above equations are the best available for predicting viscosity. In any case, the errors are larger than 15%. These methods are difficult to use, and there is the problem of using these methods for compounds possessing rare structural groups. Errors are large for the first members of a homologous series. The methods are valid up to a reduced temperature of 0.75.

It is evident that there is a need for a simple equation to predict viscosities based on a sound model of the liquid state. In this paper use is made of Hildebrand's (1971) modification of the Batschinski equation for deriving an equation for liquid viscosities. It will be shown that it is possible to relate the parameters of the Hildebrand equation to liquid properties.

DEVELOPMENT OF CORRELATION

Hildebrand (1971) showed that the fluidity of nonassociating liquids is proportional to the fractional excess of its molal volume, over the molal volume V_0, at which the molecules are so close that viscous flow stops.

$$\frac{1}{\eta_L} = B\left(\frac{V - V_0}{V_0}\right) \tag{4}$$

The parameter B denotes the capacity of molecules to absorb momentum due to molecular mass, flexibility, or rotation. This model of the liquid state has had much success in modeling transport properties of liquids. It has been shown to be valid for liquids and compressed gases (Hildebrand, 1977), and it has been extended to polymer solutions (Sridhar et al. 1978), binary liquids (Cullinan and Kosanovich, 1975; Kosanovich and Cullinan, 1976), diffusion of free radicals in solution (Sridhar and Potter, 1977), thermal conductivity of liquids (Chhabra et al. 1980), fluidity of molten salts (Chhabra and Hunter, 1981), and diffusion in liquid metals (Chhabra and Sridhar, 1982). Efforts to predict the parameters of this equation have not been successful and is the subject of this investigation.

The data base used in this work is similar to the one used by Reid et al. (1977). The 27 compounds chosen for this study are listed in Table 1. The viscosity data for each compound were taken from the Landolt-Bornstein tables or from the API compilation. The temperature range for each compound is also listed in Table 1. The values of the parameters B and V_0 were obtained by linear regression and are listed in Table 1. Also given are the correlation coefficient indicating that Eq. 4 fits the data extremely well.

The parameter B can be correlated by the following equation:

$$B = \frac{0.33\,V_c}{f_1} - 1.12 \tag{5}$$

where

$$f_1 = 4.27 + 0.032\,M_W - 0.077\,P_c + 0.014\,T_f - 3.82\,\frac{T_f}{T_c} \tag{6}$$

Equation 6 predicts B with an average error of 6.9%. The complexity of the correlation indicates that we do not have a parameter that properly quantifies molecular flexibility and their ability to absorb momentum.

Before proceeding to predict V_0, it is appropriate to mention that

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TABLE 1. DATA BASE

Name	V_0	B	Correlation Coefficient	Ref.*	Temp. Range	No. of Data Points	Avg. Error %
Acetone	62.398	17.097	0.997	a	233–333	9	6.6
Acetic acid	53.948	13.356	1.00	a	288–383	11	14.2
Aniline	90.14	14.13	0.996	a	323–393	7	11.1
Benzene	81.944	18.280	1.00	b	293–463	7	24.0
n-Butane	78.290	20.278	1.00	b	183–273	6	5.9
1-Butene	71.665	20.915	0.999	b	173–233	3	10.1
Carbon tetrachloride	88.423	11.330	0.999	a	273–373	5	2.5
Chlorobenzene	93.813	14.770	1.00	a	273–393	6	8.0
Chloroform	70.237	12.565	1.00	a	283–333	4	0.9
Cyclohexane	101.320	15.503	0.999	b	278–353	5	12.0
Ethane	44.622	25.746	1.00	b	103–183	5	4.4
Ethyl acetate	85.26	14.88	0.993	a	273–463	7	6.2
Ethyl benzene	112.950	17.769	1.00	b	253–413	5	6.9
Ethyl bromide	65.058	17.254	0.999	a	288–433	6	4.5
Ethylene	40.882	29.374	0.997	b	123–173	4	3.1
Ethyl ether	86.059	20.673	0.999	a	197–373	8	10.5
Ethyl formate	70.303	17.203	0.999	a	273–373	6	1.6
Heptane	128.310	17.049	0.999	b	213–373	7	10.6
Hexane	111.300	18.291	1.00	b	183–343	5	6.8
Isobutane	81.261	20.102	1.00	b	193–253	4	22.2
Methane	31.920	45.560	0.999	b	93–113	3	6.5
2-Methyl butane	97.812	23.605	0.998	b	223–303	5	10.9
Pentane	93.810	18.682	0.999	b	173–303	4	9.1
Propane	60.738	18.481	0.999	b	153–213	3	4.7
Toluene	99.297	18.204	1.00	b	283–383	5	5.5
o-Xylene	113.040	18.527	1.00	b	273–413	3	14.5
m-Xylene	113.480	19.567	1.00	b			

* a = Landolt-Bornstein tables (1955); b = API tables (1953).

Hildebrand (1971) pointed out the relationship between V_0 and the critical volume:

$$V_0 = 0.3\ V_c \tag{7}$$

However, the sensitivity of Eq. 4 to the values of V_0 requires V_0 to be predicted with an accuracy greater than given by Eq. 7. If Eq. 7 were used, the average error in predicting viscosity is about 60%. In order to obtain a better equation for predicting V_0, we recognize that V_0 is very close to the volume at the melting point and proceed to correlate V_0 with the volume at the melting point. In order to calculate the volume at the melting point, the Gunn-Yamada equation (Gunn and Yamada, 1971) is used:

$$V = f_2(T)V_{SC} \tag{8}$$

where

$$f_2(T) = V_r(1 - \omega\Gamma) \tag{9}$$

$$V_r = 0.33593 - .33953\ T_r + 1.51941\ T_r^2 - 2.02512\ T_r^3 + 1.11422\ T_r^4 \tag{10}$$

$$\Gamma = 0.29607 - 0.09045\ T_r - 0.04842\ T_r^2 \tag{11}$$

V_{SC} is a scaling parameter and is calculated from Eq. 8 if volume is known at any temperature. V_{SC} is, in most cases, very close to the critical volume. Equation 8 was used to calculate the molal volume at the freezing point and correlated with the parameter V_0 to give

$$V_0 = 0.0085\ T_c\omega - 2.02 + \frac{V_m}{.342\frac{T_f}{T_c} + .894} \tag{12}$$

This equation predicts V_0 with an average error of 0.96% and a maximum error of 3.2%. Comparison of Eqs. 12 and 7 is shown in Table 2.

Using the above values for B and V_0 the viscosity can be calculated. The average error for 146 data points is 8.7. The average errors for individual compounds are listed in Table 1. Comparison of the results of this work with the correlation available in literature is presented in Table 3. It is obvious that the Hildebrand equation using parameters estimated by the methods set out in this paper is a much better predictor and is far simpler to use.

TABLE 2. PREDICTION OF V_o

	This Work, Eq. 12	Hildebrand, Eq. 7
Average error, %	0.96	3.1
Maximum error, %	3.2	10.1
50% of compounds predicted with an error less than, %	0.8	2.2

TABLE 3. COMPARISON OF EQUATIONS

	Thomas, Eq. 1	Van Velzen, Eq. 3	Morris, Eq. 2	This Work, Eq. 4
Average error, %	21.2	16.1	14.2	8.7
Maximum error, %	90	165	94	40

The equation is based on a plausible model of the liquid state and hence permits use for compounds with uncommon structural groups. It allows the transport coefficients of liquids to be derived from a single model of the liquid state, thereby reaffirming the fundamental similarity of the mechanism of mass, heat and momentum transfer.

CONCLUSIONS

Using purely empirical means, the parameters involved in the Hildebrand equation are correlated with pure component properties. The resulting equation is more accurate than currently available means of predicting liquid viscosity.

ACKNOWLEDGMENT

This work was supported by the University Awards program of SUNY and the Research Corporation's Cottrell Research Grants.

NOTATION

A = constant, Eq. 3
B = constant, Eq. 4
J = constant, Eq. 2
M_W = molecular weight
P_C = critical pressure, atm
T = temperature, K
T_0 = constant, Eq. 3
T_f = freezing point temperature, K
T_c = critical temperature, K
T_r = reduced temperature, K
V_0 = intrinsic molal volume, $cm^3 \cdot mol^{-1}$
V_c = critical volume, $cm^3 \cdot mol^{-1}$
V_r = function defined by Eq. 10
V_{SC} = scaling parameter, Eq. 8

Greek Letters

Γ = function defined by Eq. 11
η_L = liquid viscosity, cP
η_L^+ = pseudocritical viscosity
θ = group contribution parameter, Eq. 1
ρ_L = liquid density
ω = acentric factor

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Manuscript received July 7, 1983; revision received, Oct. 5, and accepted Oct. 20.

The Adsorption of Dyestuffs from Aqueous Solutions Using Activated Carbon: An External Mass Transfer and Homogeneous Surface Diffusion Model

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Adsorption has been used extensively in industrial processes for the purposes of separation and purification. The removal of colored and colorless organics from water is an important application of adsorption. A study of agitated batch adsorbers yields important kinetic and design data useful in the prediction of batch adsorber performance. In the present work the adsorption of two dyestuffs, deorlene yellow (basic) and telon blue (acidic), in aqueous solution onto activated carbon has been studied using an agitated batch adsorber. The equilibrium isotherm for each single component system has been determined and a mass transfer model has been proposed to enable calculation of the time-dependent concentration decay curves.

In this paper the mass transport model is based on external mass transfer and homogeneous solid phase diffusion. In a previous model, based on film and solid phase diffusion, Matthews and Weber (1976) developed a mathematical technique for predicting concentration versus time decay curves. This initial procedure enabled the diffusion transport equation for batch adsorption to be evaluated using a numerical solution for both dimensionless time and dimensionless distance using the Crank-Nicholson method. The procedure developed in the present paper incorporates a time-dependent analytical solution for dimensionless distance and a numerical component for dimensionless time.

EXPERIMENT

The adsorption of two dyestuffs, telon blue (Acid Dye 25) and deorlene yellow (Basic Yellow 11), onto activated carbon (Filtrasorb 400 supplied by Chemviron, Ltd.) has been studied. The carbon was sieved before use