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Viscosity Prediction of Nonpolar, Polar, and Associating Fluids over a Wide *PρT* Range from a Modified Square Well Intermolecular Potential Model

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A theoretically based predictive model for calculating both liquid and gas phase viscosities has been developed by modifying a statistical mechanics viscosity model based on the square well intermolecular potential. The original theory was corrected to account for the assumptions of only two-body interactions and molecular chaos for velocities and the inadequacy of the square well potential. In addition, the modified model approaches a consistent low-density limit with improved dilute gas temperature dependence. The model parameters are obtained from gas and liquid viscosity data and generalized with corresponding states expressions and group contributions. Gas and liquid viscosities for a wide variety of 174 nonpolar, polar, and hydrogen-bonding compounds are correlated with average deviations of 0.5% and 1.8% and predicted with average deviations of 2.2% and 6.1%, respectively.

Introduction

In the chemical and process industries, viscosity is an important property in hydraulics, heat- and mass-transfer calculations for surface-processing facilities, pipeline systems, and porous media. An extensive review of viscosity prediction and correlation methods was completed by Monnery et al. (1995), which discussed the abundance of literature and summarized many viscosity models. Among the predictive methods, most have only been fitted and/or are restricted to a narrow range of compounds or mixtures. Conversely, only a few empirical models have been widely generalized. Also, typically, most methods are applicable over limited ranges of temperature and pressure and relatively few are applicable continuously from dilute gas to liquid phase. Simple semitheoretical methods based in statistical mechanics (such as corresponding states, hard sphere, and square well theories) appear to be the most promising for engineering use. Their theoretical basis gives the correct qualitative trends with temperature and density, resulting in more confident extrapolation. Moreover, the parameters typically have some physical significance. However, more work is needed to apply these models to a wide variety of compounds and mixtures over wide ranges of temperature and pressure, generalizing parameters in order to keep the models predictive. This is especially true for polar and hydrogen bonding or associating fluids. For example, the modified hard sphere model of Chung et al. (1984, 1988) has been generalized and applied to a variety of compounds and mixtures, although for associating fluids it requires a parameter which has been determined and generalized for relatively few compounds (e.g., water, 1-alkanols). The extended corresponding states method is also predictive but does not give particularly good

results for fluids significantly different in structure from the reference fluid(s) and has not been extended and generalized for polar and associating fluids. As such, there is a need for a reliable and analytical predictive model for viscosity calculations. Also, like some pressure−volume−temperature data, viscosity data provide a macroscopic physical link to the intermolecular pair potential. In addition, Monnery et al. (1995) showed a need for a pure component model since the best mixture viscosity models are functions of the pure component viscosities.

Recently, we presented a modified square well model and applied it to a wide variety of nonpolar fluids (Monnery et al., 1996) and polar fluids (Monnery et al., 1997). The nonpolar results were excellent for gas and liquid viscosities of 65 components correlated with average deviations of 0.7% and 1.3% and predicted with average deviations of 2.2% and 4.7%, respectively. The polar results were also excellent with gas and liquid viscosities for over 100 components correlated with average deviations of 0.4% and 2.1% and predicted with average deviations of 2.1% and 6.8%, respectively. In this work, we combine all the results and make extensive comparisons to the best recommended models determined from our recent review (Monnery et al., 1995) and our own comparison to the database we used. In addition, we show how the model extrapolates into the compressed liquid and dense phase regions.

Modified Square Well Viscosity Model

The square well intermolecular potential is the simplest potential model which accounts for both repulsion and attraction, albeit crudely. However, as stated in Reed and Gubbins (1973), the resulting viscosity model is an excellent compromise between realism and ease of calculation. As discussed in Monnery et al. (1996, 1997), Davis et al. (1961, 1965) derived the following model:

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$$\frac{\eta}{\eta_0} = \frac{[1 + 0.4b\rho(g(\sigma_1) + R^3 g(R\sigma_1)\psi_1)]^2}{g(\sigma_1) + R^2 g(R\sigma_1)\left[\psi^2 + \frac{1}{6}\left(\frac{\epsilon}{kT}\right)^2\right]} +$$
$$\frac{48}{25\pi}(b\rho)^2[g(\sigma_1) + R^4 g(R\sigma_1)\psi_2] \quad (1)$$

For a given component at a given density and temperature, this model requires five parameters, namely σ_1 (or b), ϵ (or ϵ/k), R, $g(\sigma_1)$, and $g(R\sigma_1)$, as well as values of the parameters ψ_1 and ψ_2.

Model Parameters. Parameters ψ_1 and ψ_2 have been approximated by the following algebraic equations which reproduce the theoretical values of ψ_1 and ψ_2 within 0.8% for $0 \le \epsilon/kT \le 4$ and extrapolate smoothly:

$$I(\psi_1) = 1.0/\{[2.2519 + 0.46614(\epsilon/kT) +$$
$$1.4843(\epsilon/kT)^2 - 0.44117(\epsilon/kT)^3 + 0.18849(\epsilon/kT)^4]\}$$

$$\psi_1 = 1 - \exp(\epsilon/kT) +$$
$$(\epsilon/2kT)[1 + (4/\sqrt{\pi})\exp(\epsilon/kT)I(\psi_1)] \quad (2)$$

$$I(\psi_2) = \frac{[0.50419 + 0.28304(\epsilon/kT)]}{[1.0 + 0.15360(\epsilon/kT)]}$$
$$\psi_2 = \exp(\epsilon/kT) - \epsilon/2kT - 2I(\psi_2) \quad (3)$$

The well width parameter, R, was set to 1.5 which is a typical value shown to provide a good compromise between fitting second virial coefficient data and critical temperature and volume for real fluids (Collings and McLaughlin, 1980). Furthermore, with a constant value of $R = 1.5$, calculation of radial distribution functions is considerably simpler, ultimately resulting in a more practical model.

The radial distribution function values are determined by the "exp" approximation of the WCA perturbation theory (Weeks et al., 1971; Andersen et al., 1976), as proposed by Vimalchand et al. (1992):

$$g(\sigma_1) = g_{HS}(\sigma_1)\exp[\alpha(\sigma_1)\epsilon/kT] \quad (4)$$

$$g(R\sigma_1) = g_{HS}(R\sigma_1)\exp[\alpha(R\sigma_1)\epsilon/kT] \quad (5)$$

where $g_{HS}(\sigma_1)$ = the hard sphere value of the radial distribution function at σ_1, determined from the Carnahan–Starling (1969) equation and $g_{HS}(R\sigma_1)$ = the hard sphere value of the radial distribution function at $R\sigma_1$, determined from a correlation fitted to the Monte Carlo simulation results of Barker and Henderson (1971):

$$g_{HS}(\sigma_1) = [1.0 - 0.5(b\rho/4)]/[1.0 - (b\rho/4)]^3 \quad (6)$$

$$g_{HS}(R\sigma_1) = 0.99948 + 0.20601b\rho - 0.21686(b\rho)^2 \quad (7)$$

Equation 7 matches the results of Barker and Henderson (1971) with an overall AAD of 0.35% over a reduced density range of $0.2 \le \rho\sigma^3 \le 0.9$ ($0.419 \le b\rho \le 1.885$).

The values of $\alpha(\sigma_1)$ and $\alpha(R\sigma_1)$ were determined to be -0.2 and -0.5, respectively, by minimizing the deviations between the predicted values from eqs 4–7 and the Monte Carlo simulation values of Henderson et al. (1976), matching these values within 5% (Monnery, 1996).

With the well width parameter set and the radial distribution function values determined, the square well model is reduced to two parameters, b and ϵ/k.

Model Modifications and Corrections. In the ideal gas limit, the square well model reduces to $\eta = \eta_0/D(\epsilon/kT)$ where

$$D(\epsilon/kT) = g(\sigma_1;\rho \to 0) + R^2 g(R\sigma_1;\rho \to 0) \, f(\epsilon/kT) \quad (8)$$

$$f(\epsilon/kT) = \psi_2 + (1/6)(\epsilon/kT)^2 \quad (9)$$

As discussed in Monnery et al. (1996), the dilute gas limit of the square well model does not match the Chapman–Enskog theory. To ensure the proper ideal gas limit is reached with the radial distribution function values determined from the perturbation theory, $f(\epsilon/kT)$ has been modified and is determined from the following expression (Monnery et al., 1996):

$$f(\epsilon/kT) = -0.811 + 0.788\exp(\epsilon/2.055kT) \quad (10)$$

As previously stated, the assumptions made in the derivation of the square well model are essentially the same as those made in the derivation of the dense hard sphere model of Enskog. As such, it likely suffers from the same shortcomings. For dense hard spheres, by comparing the results of the Enskog model to the results of molecular dynamics simulations, Alder et al. (1970) showed that the assumption of molecular chaos breaks down at sufficiently high densities, resulting in significant underprediction of viscosity and they provided approximate corrections for this. Analogously, Michels and Trappeniers (1980) have compared viscosity results of the square well model to molecular dynamics simulation results which show significant underprediction of the model at high densities and low temperatures. On the basis of these results, a multiplicative correction term was formulated as a function of reduced density, $b\rho$, such that the model matched the simulation results at higher densities and tended to unity in the ideal gas limit, where no correction is required:

$$\eta = \eta_{SW}(1.0 + k_5(b\rho)^{k_4}) \quad (11)$$

where η_{SW} is the original square well model from Davis et al. (1961, 1965). Parameter k_5 was found to be a function of ϵ/kT and expressed as

$$k_5 = k_1 + k_2(\epsilon/kT)^{k_3} \quad (12)$$

With the values of k_1-k_4 set to match the square well model viscosity results to the molecular dynamics results of Michels and Trappeniers (1980), values of b and ϵ/k were regressed in an attempt to simultaneously match liquid and gas phase viscosity data for real fluids. The model could not match gas viscosities better than 10%, and liquid viscosities were only matched for a few hydrocarbon families. Although both gas and liquid phase data were used simultaneously, a sensitivity analysis of the regressions showed that liquid viscosity tended to control the optimum values of b and that with these resulting values, optimum ϵ/k values could not match gas viscosity well. This is the well-known problem of parameters regressed from a gas phase property giving poor results in the liquid phase and vice versa, which indicates inadequacy of the intermolecular potential and resulting model (Mazo, 1967; Chapman and Cowling, 1970). In addition, the square well model

does not represent the temperature dependence of dilute gas viscosity as well as the Lennard–Jones 6-12 potential. On the basis of these facts, the dilute gas part of the correction was modified by multiplying by a power function which approximated the ratio of the reduced collision integrals of the square well and Lennard–Jones potentials such that the dilute gas square well model has similar temperature dependence to a Lennard–Jones model. This ultimately resulted in the correction being expressed as

$$C = k_0(kT/\epsilon)^{0.28} + [k_1 + k_2(\epsilon/kT)^{k_3}](b\rho)^{k_4} \quad (13)$$

Physically, this correction accounts for the breakdown of the model assumptions at high densities and low temperatures and the inadequacy of the square well potential. The correction is perturbative with the first term accounting for the inadequacy of the square well potential where k_0 is a structural correction and $(kT/\epsilon)^{0.28}$ corrects the temperature dependence. This term dominates at low densities and is negligible at high densities. The second or perturbation term accounts for three-body or higher interactions and correlations of velocities between successive collisions. This term dominates at high densities but is negligible at low densities.

Parameters k_0–k_4 were also made adjustable to observe the optimum values and trends, resulting in seven adjustable parameters in the model, and as expected, the model now matched both gas and liquid viscosities very well ($\leq 1\%$ error). An analysis of regressed values of the parameters indicated definite trends for k_1, k_2, and k_4 and relatively low sensitivity of calculated viscosities to these parameters. In order to minimize adjustable parameters, these were generalized as functions of molar mass and acentric factor, reducing to their square well values as the acentric factor approaches zero:

$$k_1 = 0.03072 + 0.00128M\omega^{1/4} \quad (14)$$

$$k_2 = 0.6270 \exp(-0.00242M\omega^{1/2}) \quad (15)$$

$$k_4 = 1.0 + \exp(-0.03895M\omega^{1/2}) \quad (16)$$

Further analysis indicated that typically, $0.6 \leq \epsilon/kT_c \leq 0.7$ and could be generalized with critical temperature,

$$\epsilon/k = 0.65\,T_c \quad (17)$$

leaving three adjustable parameters, k_0, k_3, and b, which were then regressed again.

Database

The density and viscosity data used to regress the parameters and test the model were obtained from the DIPPR database (Daubert et al., 1994). The compounds were selected to represent a variety of organic families and are summarized in Table 1. The temperature range of the gas and liquid viscosity and density data was typically from a reduced temperature between 0.48 and 0.70–0.80. Ultimately, however, upper and lower bounds were set in accordance with the recommended temperature ranges for the data as stated in the database along with judgement based on consistency checks.

Table 1. Database Compounds

family	no. of compounds	family	no. of compounds
alkanes	31	esters	16
alkenes	12	alcohols	14
dienes	2	phenols	4
alkynes	3	diols	3
naphthenes	12	acids	9
aromatics	13	amines	17
ethers	15	nitriles	5
ketones	12	water	1
aldehydes	5	total	174

Table 2. Results of Square Well Viscosity Model Correlation and Prediction

	correlation		prediction	
family	% AADL	% AADG	% AADL	% AADG
alkanes	1.19	0.96	5.14	2.42
alkenes	1.03	0.47	4.27	2.93
dienes	0.86	0.26	7.76	4.42
alkynes	1.64	0.46	3.44	1.94
naphthenes	1.60	0.70	4.52	1.18
aromatics	2.05	0.51	4.24	1.82
ethers	0.70	0.60	7.34	3.50
ketones	1.13	0.34	4.16	1.39
aldehydes	0.88	0.43	5.37	1.46
esters	1.16	0.48	4.05	2.98
alcohols	3.47	0.59	7.49	1.79
phenols	3.97	0.17	7.35	1.44
diols	6.29	0.33	11.85	3.11
acids	0.54	0.11	9.21	1.81
amines	1.26	0.41	5.24	2.18
nitriles	1.84	0.36	5.70	1.20
overall	1.85	0.45	6.07	2.22
water	3.46	3.10		

Note that, in the database, inevitably there are some gaps in available experimental data which have been filled with predicted values. An attempt was made to minimize the use of predicted values, only using these where necessary to cover the desired range of compounds in a given family. On the basis of quality indicators that are stated in the database, for these compounds, predicted gas and and liquid viscosity data are typically considered to have an accuracy of 5%−10%. Overall, density data were considered accurate to ≤3% and the accuracy of the viscosity data were considered to be 5%−15%, based on database quality indicators and a comparison with DECHEMA (Stephan and Hildwein, 1987) and Thermodynamics Research Center (Marsh et al., 1985) data. The accuracy of data determined in this work appears to corroborate earlier estimations of overall data accuracy, such as data by Ely and Hanley (1981a).

Model Results and Comparison

Correlation of Viscosity Data. Adjustable parameters k_0, k_3, and b were regressed and the modified square well model simultaneously correlated gas and liquid viscosities excellently, as shown in Table 2. Except for alcohols, phenols, and glycols, the model can typically correlate liquid viscosities within about 2% and gas viscosities within about 1%, which is well within experimental error. The liquid viscosity data for these exceptions is experimental, but perhaps the data requires revalidation or should be remeasured and the model refitted. For example, the model fits the 1,2-propanediol data of van Velzen et al. (1972a) and the 1,3-propanediol data of Bleazard et al. (1996) considerably better. (AADs are 50% of the values given in Table 2.)
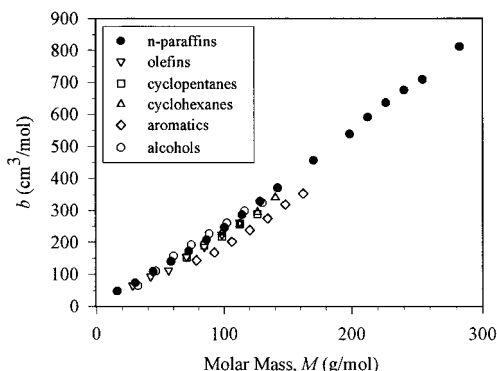
Figure 1. Parameter b vs molar mass, M.

Generalization Using Group Contribution Approach. Analysis of the regressed optimum values of k_0, k_3, and b showed that they could not be adequately generalized with corresponding states relationships, but showed trends within a given family of compounds, as shown in Figure 1. This suggested that these parameters were related to the structure of the molecule and could be generalized with a group contribution approach.

As pointed out by Constantinou and Gani (1994), the most common groups used for determining pure component properties are different from those used for determining mixture properties. For example, the groups used to determine critical properties of pure components given in Reid et al. (1987) are not the same as the groups used in the UNIFAC activity coefficient model, also given in Reid et al. In addition, there is no firm theoretical basis for most sets of groups (Reid et al., 1987).

In an attempt to provide some basis for group definitions, Wu and Sandler (1991) performed quantum mechanical calculations to determine the net charges of specific groups. Groups were established on the basis of having approximately the same charge to make the same contribution to a property, independent of the remainder of the molecule. A table of proposed groups was given which showed many groups which differed from the UNIFAC definitions.

In this work, for convenience and consistency, it was attempted to utilize existing groups and not develop new, customized ones, although initially it was not known which groups would work the best. It was found that, in most cases, the groups proposed by Wu and Sandler (1991) worked very well in correlating the model parameters along with the following additive equations:

$$b_i/100 = \sum_{j=1}^{g} n_{ij}\Delta b_j + 0.06617\left(\sum_{j=1}^{g} n_{ij}\Delta b_j\right)^2 \qquad (18)$$

$$k_{0,i} = \sum_{j=1}^{g} n_{ij}\Delta k_{0,j} \qquad (19)$$

$$k_{3,i} = 1.0 + \sum_{j=1}^{g} n_{ij}\Delta k_{3,j} \qquad (20)$$

The group contributions were obtained using one family at a time, starting with n-paraffins, to determine CH_3 and CH_2 groups and continuing in this manner to determine the remaining groups. The resulting groups

and contributions for all compounds are given in Table 3. As expected, first members of a homologous series (methanol, etc.) did not trend well with higher members, and to overcome this problem, each of these compounds is treated as its own group. In addition, water was considered as a unique component with the values of its parameters as $k_0 = 0.584$, $k_3 = 4.356$, and $b = 21.43$ cm^3/mol.

Some of the group contributions are corrected for the iso position, attached chain lengths, number of side chains, and occurrence number. These types of corrections are not unreasonable because, as pointed out by Makita (1984), liquid viscosity is remarkably sensitive to structure. For example, as a paraffinic side chain length increased, it was observed that ring structures tended to behave more paraffinic with the ring dominance decreasing. As such, chain length corrections have been expressed to model this behavior. The number of side chains on ring structures also appeared to have an effect.

As other examples, it is not expected that the contribution of CH_2 groups on different cyclic rings would be identical and it appeared that more than one occurrence of a group, as in dienes, has an effect. These effects have also been accounted for in the work of Constantinou and Gani (1994) as second-order corrections. However, as can be seen, in this model the corrections are very simple and do not complicate the calculation procedure.

Comparison with Other Methods. The modified square well viscosity model was compared to the best predictive methods for gases and liquids, which were determined by taking those that appeared to be the best in our recent review (Monnery et al., 1995) and comparing their predicted viscosities to the database values. The resulting methods for comparison were those of Reichenberg (1973, 1975, 1979) and Chung et al. (1984, 1988) for gases and those of van Velzen et al. (1972a,b) and Chung et al. for liquids. In addition, we also compared the results of the TRAPP program (Ely and Hanley, 1981b). These methods are all described in detail in Monnery et al. (1995).

The results of predicted viscosities using the group contributions are also shown in Table 2. For comparison, the viscosity prediction results of the other methods are shown in Table 4. Note that N/A (not applicable) in Table 4 means either a group contribution method did not have the required group or that the method had a numerical problem with the particular compounds. For the most part, these results are consistent with results reported in Reid et al. (1987). However, it should be noted that the method of Chung et al. (1984, 1988) performs much better when the association factor in the model is available and that the TRAPP method is not really intended for polar and associating compounds (although, overall, it does remarkably well).

The important point to be made is that the results in Tables 2 and 4 clearly show that the predictive modified square well method compares very favorably with the best available methods. Overall, the modified square well model both correlates and predicts viscosities very well within the range of reduced temperature studied in this work ($0.48 \leq T_r \leq 0.7-0.8$).

Extrapolation. To provide some insight of how well the model extrapolates, Figure 2 compares the calculated gas and liquid viscosities from the model to experimental data for propane, which has the lowest

Table 3. Parameter Group Contributions for Square Well Viscosity Model

group	Δb	Δk_0	Δk_3
		Alkanes	
CH_4	0.4663	0.7130	1.2610
CH_3e (end)	0.3586	0.3514	0.4661
CH_2	0.2899	−0.0041	0.2251
CH	0.3021	−0.3271	0.5021
C	0.3329	−0.6442	1.0379
CH_3b (branch)	$0.3586f_{CH_3b}$	0.3514	$0.4661f_{CH_3k_3}$
		Alkenes	
$CH_2{=}CH_2$	0.6356	0.6690	1.0850
$CH_2{=}CH$	0.5063	0.3216	0.6563
$CH{=}CH$	$0.4278f_{dio}$	−0.0278	$0.0705f_{dio}$
$CH_2{=}C$	$0.4834f_{dio}$	0.0152	$0.6174f_{dio}$
		Alkynes	
$CH{\equiv}CH$	0.5800	0.6830	0.0000
$CH{\equiv}C$	0.4540	0.3116	0.3168
		Naphthenes	
cyclic C_3 ring CH_2	0.2826	0.2340	0.2723
cyclic C_4 ring CH_2	0.2859	0.1910	0.3415
cyclic C_5 ring CH_2	0.2798	0.1524	$0.5270f_{CC_5}$
cyclic C_5 ring CH	0.1941	−0.2170	−0.0030
cyclic C_6 ring CH_2	0.3003	0.1328	$0.6360f_{CC_6}$
cyclic C_6 ring CH	0.1375	−0.2715	−1.0750
		Aromatics	
aCH	0.2212	0.1185	$0.5270f_{ben}$
aC1 (1 ring)	$0.0654f_{aC1b}$	−0.2490	$-0.6320f_{aC1k_3}$
aC2 (2 rings)	0.1593	−0.1180	−1.1438
		Alcohols	
CH_3OH	0.6285	0.7970	3.5090
CH_3CH_2OH	1.0371	0.5168	6.0770
CH_2OH	$0.7739f_{glyb}$	$0.5168f_{alck_0}f_{glyk_0}$	$6.4610f_{alck_3}f_{glyk_3}$
$CHOH$	$0.7919f_{glyb}$	$0.1697f_{alck_0}f_{glyk_0}$	$8.3901f_{glyk_3}$
COH	0.9105	−0.2351	14.9816
		Phenols	
aCOH	0.4110	0.1565	$2.8160f_{aCOH}$
		Ethers	
CH_3OCH_3	0.7260	0.6130	0.6710
CH_2OCH_2	0.6640	−0.0026	1.4871
CH_3OCH_2	0.6845	0.3256	1.3645
cCH_2OCH_2	0.6605	0.5070	$1.0260f_{ethc}$
$aCOaC$	0.4093	−0.4760	−2.0100
CH_3OaC	0.5655	0.0915	0.3230
CH_3OC	0.6471	−0.3071	1.2216
		Ketones	
CH_3COCH_3	1.0240	0.6470	1.9220
CH_2COCH_2	0.8124	−0.0408	1.6220
CH_3COCH_2	0.9363	0.3204	1.6838
CH_3COaC	0.7922	0.1268	−0.4560
		Aldehydes	
HCHO	0.4567	0.7250	2.2000
CH_3CHO	0.7213	0.6410	2.3770
CH_2CHO	0.6802	0.3287	1.6268
aCCHO	0.7288	0.1595	−1.5860
		Esters	
$HCOOCH_3$	0.8590	0.6890	2.4900
$HCOOCH_2$	0.8175	0.3716	2.0403
CH_3COOCH_3	1.1414	0.6580	2.1650
CH_2COOCH_2	0.9970	−0.0207	2.0739
CH_3COOCH_2	1.0776	0.3346	2.1724
CH_3COOaC	0.7289	0.0505	1.5935
		Acids	
HCOOH	0.6173	0.6870	4.7170
CH_3COOH	0.9445	0.7470	3.4540
CH_2COOH	0.9075	0.3746	$2.7872f_{aci}$
CHCOOH	0.8501	0.0523	2.7937
aCCOOH	0.0101	−0.0950	11.6910
		Amines	
CH_3NH_2	0.5951	0.6600	2.6270
CH_2NH_2	0.5432	0.3386	3.1088
$CHNH_2$	0.5801	0.0362	1.2230
$(CH_3)_2NH$	0.8831	0.7690	1.9091
$(CH_2)_2NH$	0.7495	0.0202	2.2677

Table 3 (Continued)

group	Δb	Δk_0	Δk_3
		Amines	
$(CH)_2NH$	0.6313	−0.6715	1.0275
$(CH_3)_3N$	1.2119	0.6850	1.4880
$(CH_2)_3N$	0.8671	−0.3043	1.1770
$aCNH_2$	1.5230	0.7220	3.8910
		Nitriles	
CH_3CN	0.7725	0.6251	0.1940
CH_2CN	0.6730	0.2906	1.3692
$aCCN$	1.5975	0.6530	2.3060

Corrections

iso:
$f_{CH_3b} = \exp(-0.16n_{CH_2} - 0.06n_{CH} - 0.16n_{aCH} - 0.24n_{CH_3COCH_2} - 0.06n_{(CH_2)_2NH})$
$f_{CH_3k_3} = \exp(-0.10n_{CH_2}(n_{CH} + n_C) - 3.0(n_{CH_3b} - 1)(n_{CH_2COCH_2} + n_{(CH_2)_2NH}))$
diene:
if $(n_{CH_2=CH} + n_{CH=CH} + n_{CH_2=C}) > 1$
$f_{dio} = 0.8$
cyclic ring side chain length:
$f_{CC_5} = \exp(-0.20n_{CH_2})$
$f_{CC_6} = \exp(-0.15n_{CH_2})$
aromatic ring side chain length and number:
$f_{ben} = \exp(-0.11n_{CH_2})$
$f_{aC1b} = (0.613 + 0.387(n_{aC1} + n_{aCOH}))$
$f_{aC1k_3} = 1.0/(n_{aC1} + n_{aCOH})$
Alcohol Chain Length:
$f_{alck_0} = \exp(-0.03n_{CH_2})$
$f_{alck_3} = \exp(-0.00959(n_{CH_2} - 3)^2 + 0.28n_{CH})$
diol correction:
if $(n_{CH_2OH} + n_{CHOH}) > 1$
$f_{glyb} = 0.32n_{CH_2OH} + 0.52n_{CHOH} + 0.06n_{CH_2}$
$f_{glyk_0} = 0.40n_{CH_2OH} + 0.36n_{CHOH}$
$f_{glyk_3} = 0.27n_{CH_2OH} + 0.35n_{CHOH} + 0.09n_{CH_2}$
phenol side chain number:
$f_{aCOH} = n_{aCOH} + 0.33n_{aC1}$
cyclic ether:
$f_{ethc} = n_{cCH_2OCH_2}$
carboxylic acid chain length:
$f_{aci} = 1.0 + \ln(1.0 + 0.10n_{CH_2})$

Table 4. Recommended Viscosity Prediction Methods Results

family	% AADG			% AADL		
	Reich.[a]	Chung[b]	TRAPP	Velzen[c]	Chung	TRAPP
alkanes	4.40	3.31	10.11	6.13	14.37	10.61
alkenes	1.50	2.45	7.87	8.07	18.40	15.04
dienes	0.30	5.16	9.27	2.75	47.61	16.63
alkynes	3.42	1.74	3.78	N/A	15.19	13.34
naphthenes	5.09	3.05	9.32	11.55	22.75	22.09
aromatics	1.24	3.32	12.12	8.28	23.56	13.89
ethers	1.91	5.38	14.27	15.54	18.28	22.93
ketones	1.66	3.33	13.49	3.39	30.17	14.51
aldehydes	1.06	6.01	18.50	3.47	N/A	18.78
esters	4.08	5.29	16.04	6.81	19.20	13.11
alcohols	2.31	2.93	22.53	12.87	39.36	40.67
phenols	0.71	14.69	13.64	31.24	43.88	19.42
diols	2.61	4.83	24.08	10.78	74.37	47.71
acids	1.12	10.22	31.81	16.30	37.91	25.35
amines	0.97	8.79	13.62	36.25	29.58	20.43
nitriles	4.43	24.09	23.92	N/A	N/A	7.79
overall	2.30	6.54	15.27	12.80	29.06	20.14

[a] Reich. = Reichenberg (1973, 1975, 1979). [b] Chung = Chung et al. (1984, 1988). [c] Velzen = van Velzen et al. (1972a,b).

reduced triple point of the *n*-alkanes. Experimental data were obtained from the DIPPR database (Daubert et al., 1994) and verified with the data of Diller (1982) and the National Institute of Standards and Technology (NIST) Database 12 Version 3 (1992) computer program.

As shown, at higher reduced temperatures, the model extrapolates well up to near the critical point for both gas and liquid. For liquid phase viscosities at lower reduced temperatures, the model extrapolates reasonably well (AAD ≤ 15%) to about halfway between $T_r =$ 0.5 and the reduced triple point, $T_r = 0.23$, below which it underpredicts. Similar analysis of a few other non-

polar compounds confirmed this behavior. However, for alcohols the model tends to overpredict liquid viscosity as temperature approaches the triple point. Low-temperature gas phase viscosities were predicted within 5%.

Predictions of compressed liquid viscosity were compared against two methane experimental data points ($T = 100$ K, $P = 5$ and 10 MPa) and five propane experimental data points ($P = 5$ MPa, $T = 100$, 140, 200, 300, and 340 K). The viscosity data were taken from Stephan and Lucas (1979) and Diller (1982) for methane and propane, respectively, while the density data were again from the NIST Database (1992). The
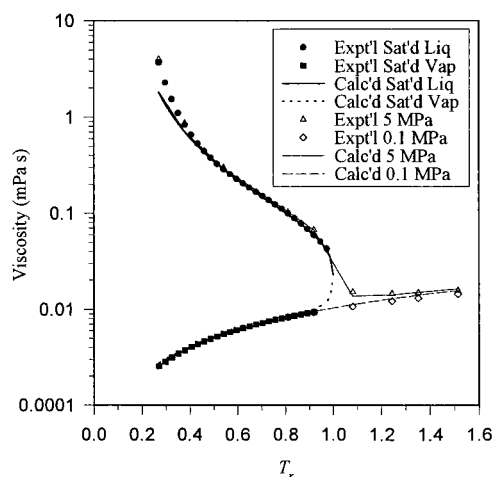
Figure 2. Modified square well viscosity model vs experimental data for propane.

Table 5. Dense Phase Predictions of Modified Square Well Viscosity Model

fluid	SW[a] % AAD	Chung[b] % AAD
methane	6.42	2.21
n-butane	2.50	4.63

[a] SW = Square well model. [b] Chung = Chung et al. (1984, 1988).

average deviation for the two methane points was −6.2%. For propane, the AAD for the points above 100 K was 4.9%, while at 100 K, the model underpredicted by 54%. Overall, for liquid phase viscosities, it appears that the model can be considered to be accurate within 15% from a minimum temperature of $0.26 + T_{tpr}/2$ up to about $T_r = 0.90-0.95$.

Dense Phase Viscosity Predictions. Since the modified square well viscosity model was fitted with gas and liquid phase viscosities below the critical point, dense phase viscosity predictions were tested. Although there are relatively few fluids for which a wide range of reliable viscosity data exist, reliable dense phase data for several fluids have been published in Stephan and Lucas (1979). Unfortunately, the correponding density data were not included, and these must be obtained elsewhere. This reduces the number of fluids which can be tested to those for which density can be accurately determined, since the model can be sensitive to the input density. The model was tested with only methane and n-butane as it was assumed that results would be similar for other light hydrocarbons and simple inorganics (for which reliable data are also available). The viscosity data were obtained from Stephan and Lucas (1979) and the density data were determined from the NIST Database (1992). The methane data were verified with Friend et al. (1989). The viscosity data are considered to be accurate to 3%−5% while the density data are accurate to within 1%. The methane data consisted of 12 points at temperatures of 200, 250, 300, and 400 K, each at pressures of 50, 100, and 200 bar. The n-butane data consisted of 6 points at temperatures 450 and 500 K, each at pressures of 50, 100, and 200 bar. The results are summarized in Table 5.

As shown in Table 5, results are very good, with AADs of 6.4% and 2.5% for methane and n-butane, respectively. In comparison, the method of Chung et al. (1984, 1988) predicted dense phase viscosities with AADs of 2.2% and 4.6% for methane and n-butane, respectively.

Furthermore, the dense phase data for propane in Figure 2 were also predicted within a maximum of 10%. These results indicate that the model can be extrapolated with confidence into the dense phase, although more testing with other types of compounds would make the results more definitive. It should be emphasized that these results are completely predictive in that no dense phase data were used in fitting and generalizing the model.

It should be noted that like the other methods which depend on density, the predicted liquid phase viscosities are relatively sensitive to the density value input. For the modified square well viscosity model, liquid phase viscosities are predicted within about 10% if densities are within 3% of experimental.

Conclusions

A theoretically based viscosity model that is suitable for engineering calculations and can be applied to a wide variety of 174 nonpolar, polar, and associating compounds has been presented. It typically correlates gas and liquid viscosity data within 0.5% and 1.8%, respectively. The model has been generalized and typically predicts gas and liquid viscosities with average deviations of 2.2% and 6.1%, respectively, which compares very favorably with other recommended methods for calculating gas and liquid viscosities. Furthermore, the model extrapolates relatively well, predicting low-temperature liquid viscosities within 15% down to a reduced temperature of $0.26 + T_{tpr}/2$ and predicting dense phase viscosities within about 10%.

An example to illustrate the viscosity calculation procedure is given in the Appendix.

Nomenclature

a = aromatic (Table 3)
b = covolume = $(2/3)\pi N_A\sigma_1^3$, cm^3/mol
C = correction factor
$g(\sigma_1)$ = radial distribution function at repulsion diameter
$g(R\sigma_1)$ = radial distribution function at attraction diameter
k = Boltzmann constant
$k_0 ... k_4$ = parameters in correction term
m = particle mass, g
M = molar mass, g/mol
N_A = Avogadro's Number
n_{ij} = number of jth groups in compound i
R = well width parameter
T = temperature, K
T_c = critical temperature, K
T_r = reduced temperature
T_{tpr} = reduced triple point temperature

Greek Letters

α = empirical coefficient in radial distribution function perturbation theory
ΔP_j = group contribution of jth group for parameter P where P = b, k_0, or k_3
ϵ = energy well depth
η = viscosity, mPa·s
η_0 = hard sphere dilute gas viscosity = $(5/16\pi^{1/2})(mkT)^{1/2}/$
$\sigma_1^2 = 3.11630 \times 10^{-3}(MT)^{1/2}/b^{2/3}$, mPa·s
ρ = density, mol/cm^3
σ_1 = repulsion diameter ($R\sigma_1$ = attraction diameter)
ω = acentric factor
$\Omega^{(2,2)*}$ = reduced collision integral

Acronyms

AADL = average absolute deviation (liquid)

AADG = average absolute deviation (gas)
WCA = Weeks Chandler Andersen

Appendix

Estimate the saturated liquid viscosity of ethyl acetate at 350 K. Data: $M = 88.11$ g/mol, $T_c = 523.30$ K, $\omega = 0.3664$. Liquid molar volume at 350 K = 106.28 cm^3/mol.

Groups: $1 \times CH_3COOCH_2$ and $1 \times CH_3$. From eqs 18−20: $k_1 = 0.118$, $k_2 = 0.551$, and $k_4 = 1.125$.

From eqs 22−24, Table 2: $k_0 = 0.686$, $k_3 = 3.638$, and $b = 157.27$ cm^3/mol. From eq 21: $\epsilon/k = 340.14$ K; $\epsilon/kT = 0.972$. From eqs 2−5: $\psi_1 = -0.4080$, $\psi_2 = 0.8008$.

From the definition of the hard sphere dilute gas viscosity (in practical units): $\eta_0 = 3.1163 \times 10^{-3} (MT)^{1/2}/b^{2/3} = 0.01878$ mPa·s. From eqs 6 and 8 ($\alpha = -0.5$): $g(\sigma_1) = 2.6830$. From eqs 7 and 9 ($\alpha = -0.2$): $g(R\sigma_1) = 0.5102$. From eq 17: $C = 1.6476$. From eq 1 with $f(\epsilon/kT)$ from eq 13: $\eta_{pred} = 0.242$ mPa·s. Experimental $\eta_{exp} = 0.249$ mPa·s, error = −2.9%.

Overall error for ethyl acetate AADL = 2.3%.

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