

for the same system at similar conditions. High-quality data for mixtures with different size molecules at high pressures are limited. This in turn limits the ability to evaluate models for this case.

Discussion

Both the Lucas and Chung, et al. methods use the relations for the estimation of dense gas viscosity and apply a one-fluid approximation to relate the component parameters to composition. The TRAPP method uses the term $\Delta\eta^{\text{ENSKOG}}$ to improve the one-fluid approximation. In the Lucas method, the state variables are T , P , and composition, whereas in the TRAPP and Chung, et al. procedures, T , ρ , and composition are used.

The accuracy of the Lucas and Chung, et al. forms is somewhat less than when applied to pure, dense gases. Also, as noted at the end of Sec. 9-6, the accuracy is often poor when working in the critical region or at densities approaching those of a liquid at the same temperature. The TRAPP procedure can be extended into the liquid region. The paucity of accurate high-pressure gas mixture viscosity data has limited the testing that could be done, but Chung, et al. (1988) report absolute average deviations of 8 to 9% for both polar and nonpolar dense gas mixtures. A comparable error would be expected from the Lucas form. The TRAPP method gives similar deviations for nonpolar mixtures, but has not been tested for polar mixtures. Tilly, et al. (1994) recommended a variation of the TRAPP method to correlate viscosities of supercritical fluid mixtures in which various solutes were dissolved in supercritical carbon dioxide.

As a final comment to the first half of this chapter, it should be noted that, if one were planning a property estimation system for use on a computer, it is recommended that the Lucas, Chung, et al., or Brulé and Starling method be used in the dense gas mixture viscosity correlations. Then, at low pressures or for pure components, the relations simplify directly to those described in Secs. 9-4 to 9-6. In other words, it is not necessary, when using these particular methods, to program separate relations for low-pressure pure gases, low-pressure gas mixtures, and high-pressure pure gases. One program is sufficient to cover all those cases as well as high-pressure gas mixtures.

9-8 LIQUID VISCOSITY

Most gas and gas mixture estimation techniques for viscosity are modifications of theoretical expressions described briefly in Secs. 9-3 and 9-5. There is no comparable theoretical basis for the estimation of liquid viscosities. Thus, it is particularly desirable to determine liquid viscosities from experimental data when such data exist. Viswanath and Natarajan (1989) have published a compilation of liquid viscosity data for over 900 compounds and list constants that correlate these data. Liquid viscosity data can also be found in Gammon, et al. (1993–1998), Riddick, et al. (1986), Stephan and Lucas (1979), Stephen and Hildwein (1987), Stephan and Heckenberger (1988), Timmermans (1965), and Vargaftik, et al. (1996). Data for aqueous electrolyte solutions may be found in Kestin and Shankland (1981), Lobo (1990), and Zaytsev and Aseyev (1992). Tabulations of constants have been published in Daubert, et al. (1997), Duhne (1979), van Velzen et al. (1972), Yaws,

et al. (1976), and Yaws (1995, 1995a) that allow estimations of liquid viscosities. When these constants are derived from experimental data they can be used with confidence, but sometimes (Yaws, 1995, 1995a) they are based on estimated viscosities, and in such instances, they should be used only with caution. Liquid phase viscosity values can also be found in Dean (1999), Lide (1999), and Perry and Green (1997).

The viscosities of liquids are larger than those of gases at the same temperature. As an example, in Fig. 9-8, the viscosities of liquid and vapor benzene are plotted as functions of temperature. Near the normal boiling point (353.4 K), the liquid viscosity is about 36 times the vapor viscosity, and at lower temperatures, this ratio increases even further. Two vapor viscosities are shown in Fig. 9-8. The low-pressure gas line would correspond to vapor at about 1 bar. As noted earlier in Eq. (9-4.20), below T_c , low-pressure gas viscosities vary in a nearly linear manner with temperature. The curve noted as saturated vapor reflects the effect of the increase in vapor pressure at higher temperatures. The viscosity of the saturated vapor should equal that of the saturated liquid at the critical temperature (for benzene, $T_c = 562.0$ K).

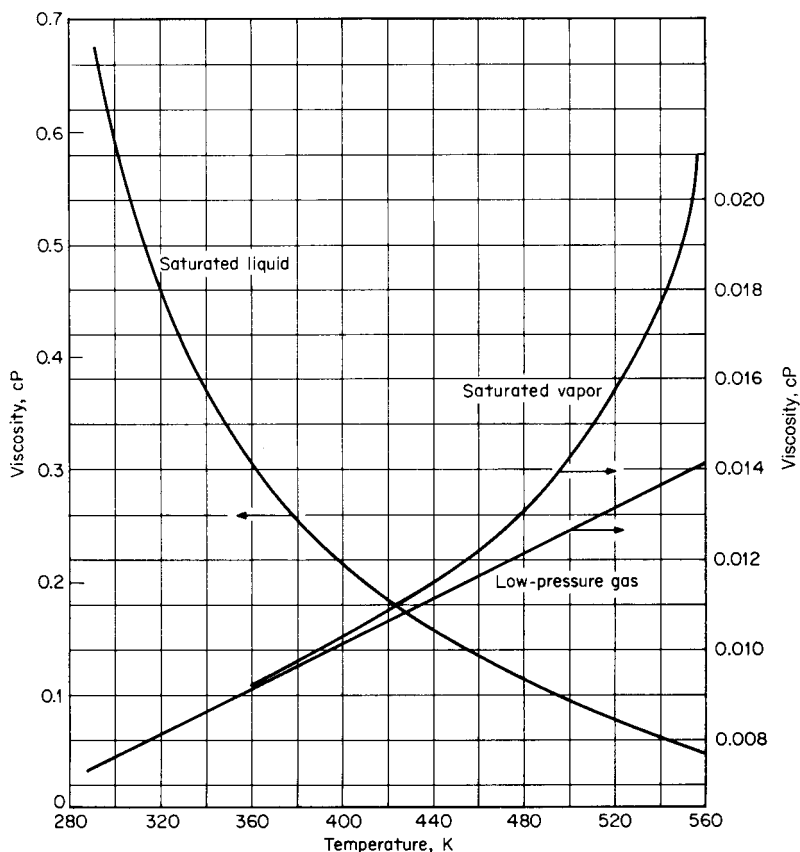


FIGURE 9-8 Viscosities of liquid and vapor benzene. ($T_b = 353.2$ K; $T_c = 562.0$ K).

Much of the curvature in the liquid viscosity-temperature curve may be eliminated if the logarithm of the viscosity is plotted as a function of reciprocal (absolute) temperature. This change is illustrated in Fig. 9-9 for four saturated liquids: ethanol, benzene, *n*-heptane, and nitrogen. (To allow for variations in the temperature range, the reciprocal of the reduced temperature is employed.) Typically, the normal boiling point would be at a value of $T_r^{-1} \approx 1.5$. For temperatures below the normal boiling point ($T_r^{-1} > 1.5$), the logarithm of the viscosity varies linearly with T_r^{-1} . Above the normal boiling point, this no longer holds. In the nonlinear region, several corresponding states estimation methods have been suggested, and they are covered in Sec. 9-12. In the linear region, most corresponding states methods have not been found to be accurate, and many estimation techniques employ a group contribution approach to emphasize the effects of the chemical structure on viscosity. The curves in Fig. 9-9 suggest that, at comparable reduced temperatures, viscosities of polar fluids are higher than those of nonpolar liquids such as hydrocarbons, which themselves are larger than those of simple molecules such as nitrogen. If one attempts to replot Fig. 9-9 by using a nondimensional viscosity such as $\eta\xi$ [see, for example, Eqs. (9-4.13) to (9-4.15)] as a function of T_r , the separation between curves diminishes, especially at $T_r > 0.7$. However, at lower values of T_r , there are still significant differences between the example compounds.

In the use of viscosity in engineering calculations, one is often interested not in the dynamic viscosity, but, rather, in the ratio of the dynamic viscosity to the density. This quantity, called the *kinematic viscosity*, would normally be expressed

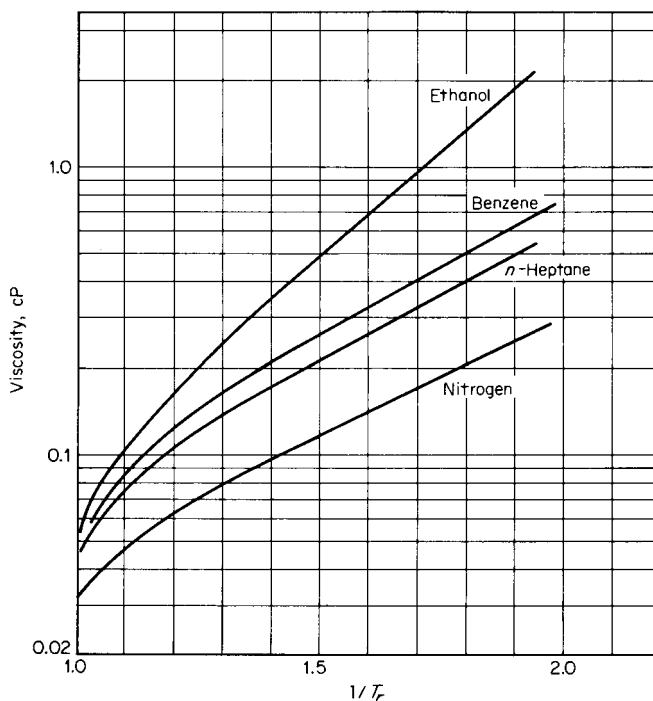


FIGURE 9-9 Viscosities of various liquids as functions of temperature. (Stephan and Lucas, 1979)

in m^2/s or in stokes. One stoke (St) is equivalent to $10^{-4} \text{ m}^2/\text{s}$. The kinematic viscosity ν , decreases with increasing temperature in a manner such that $\ln \nu$ is nearly linear in temperature for both the saturated liquid and vapor as illustrated in Fig. 9-10 for benzene. As with the dynamic viscosity, the kinematic viscosities of the saturated vapor and liquid become equal at the critical point.

The behavior of the kinematic viscosity with temperature has led to several correlation schemes to estimate ν rather than η . However, in most instances, $\ln \nu$ is related to T^{-1} rather than T . If Fig. 9-10 is replotted by using T^{-1} , again there is a nearly linear correlation with some curvature near the critical point (as there is in Fig. 9-9).

In summary, pure liquid viscosities at high reduced temperatures are usually correlated with some variation of the law of corresponding states (Sec. 9-12). At lower temperatures, most methods are empirical and involve a group contribution approach (Sec. 9-11). Current liquid *mixture* correlations are essentially mixing rules relating pure component viscosities to composition (Sec. 9-13). Little theory has been shown to be applicable to estimating liquid viscosities (Andrade, 1954; Brokaw, et al., 1965; Brush, 1962; Gemant, 1941; Hirschfelder, et al., 1954).

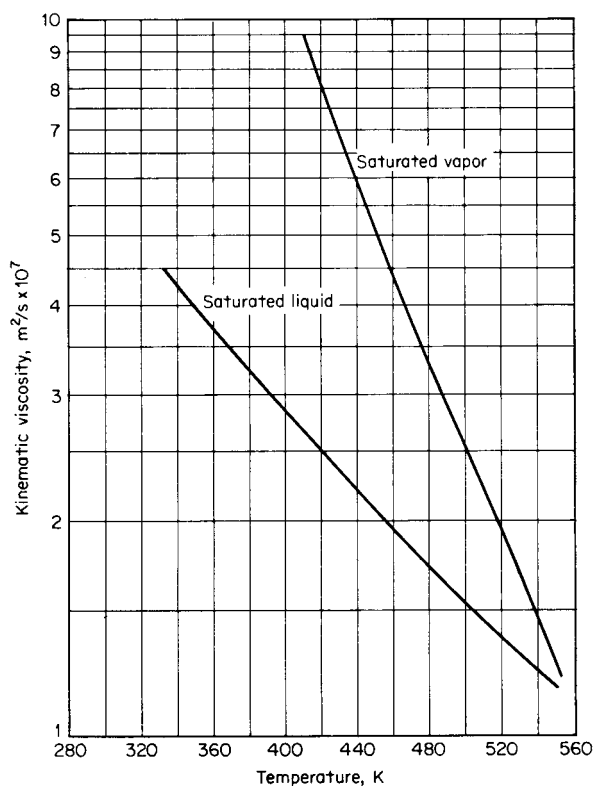


FIGURE 9-10 Kinematic viscosities of saturated liquid and vapor benzene ($T_b = 353.2 \text{ K}$; $T_c = 562.0 \text{ K}$).

9-9 EFFECT OF HIGH PRESSURE ON LIQUID VISCOSITY

Increasing the pressure over a liquid results in an increase in viscosity. Lucas (1981) has suggested that the change may be estimated from Eq. (9-9.1)

$$\frac{\eta}{\eta_{SL}} = \frac{1 + D(\Delta P_r/2.118)^A}{1 + C\omega\Delta P_r} \quad (9-9.1)$$

where η = viscosity of the liquid at pressure P

η_{SL} = viscosity of the saturated liquid at P_{vp}

$\Delta P_r = (P - P_{vp})/P_c$

ω = acentric factor

$A = 0.9991 - [4.674 \times 10^{-4}/(1.0523T_r^{-0.03877} - 1.0513)]$

$D = [0.3257/(1.0039 - T_r^{2.573})^{0.2906}] - 0.2086$

$C = -0.07921 + 2.1616T_r - 13.4040T_r^2 + 44.1706T_r^3 - 84.8291T_r^4 + 96.1209T_r^5 - 59.8127T_r^6 + 15.6719T_r^7$

In a test with 55 liquids, polar and nonpolar, Lucas found errors in the calculated viscosities of less than 10%. To illustrate the predicted values of Eq. (9-9.1), Figs. 9-11 and 9-12 were prepared. In both, η/η_{SL} was plotted as a function of ΔP_r for various reduced temperatures. In Fig. 9-11, $\omega = 0$, and in Fig. 9-12, $\omega = 0.2$. Except at high values of T_r , η/η_{SL} is approximately proportional to ΔP_r . The effect of pressure is more important at the high reduced temperatures. As the acentric factor increases, there is a somewhat smaller effect of pressure. The method is illustrated in Example 9-15.

Example 9-15 Estimate the viscosity of liquid methylcyclohexane at 300 K and 500 bar. The viscosity of the saturated liquid at 300 K is 0.68 cP, and the vapor pressure is less than 1 bar.

solution From Appendix A, $T_c = 572.19$ K, $P_c = 34.71$ bar, and $\omega = 0.235$. Thus $T_r = 300/572.19 = 0.524$ and $\Delta P_r = 500/34.71 = 14.4$. (P_{vp} was neglected.) Then

$$A = 0.9991 - \frac{4.674 \times 10^{-4}}{(1.0523)(0.524)^{-0.03877} - 1.0513} = 0.9822$$

$$D = \frac{0.3257}{[1.0039 - (0.524)^{2.573}]^{0.2906}} - 0.2086 = 0.1371$$

$$\begin{aligned} C &= -0.07921 + (2.1616)(0.524) - (13.4040)(0.524)^2 + (44.1706)(0.524)^3 \\ &\quad - (84.8291)(0.524)^4 + (96.1209)(0.524)^5 - (59.8127)(0.524)^6 \\ &\quad + (15.6719)(0.524)^7 = 0.0619 \end{aligned}$$

With Eq. (9-9.1),

$$\frac{\eta}{\eta_{SL}} = \frac{1 + (0.137)(14.4/2.118)^{0.9822}}{1 + (0.235)(14.4)(0.0619)} = 1.57$$

$$\eta = (1.57)(0.68) = 1.07 \text{ cP}$$

The experimental value of η at 300 K and 500 bar is 1.09 cP (Titani, 1929).

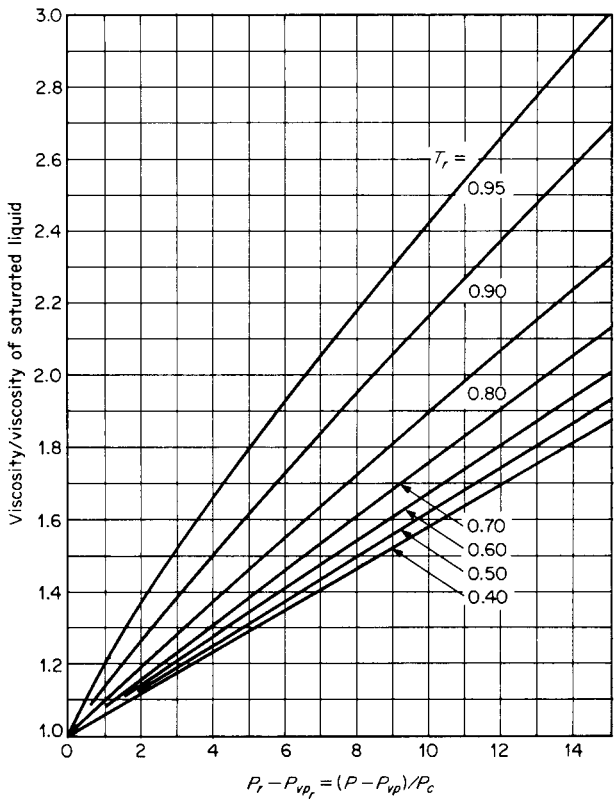


FIGURE 9-11 Effect of pressure on the viscosity of liquids $\omega = 0$.

$$\text{Error} = \frac{1.07 - 1.09}{1.09} \times 100 = -1.8\%$$

Whereas the correlation by Lucas would encompass most pressure ranges, at pressures over several thousand bar the data of Bridgman suggest that the logarithm of the viscosity is proportional to pressure and that the structural complexity of the molecule becomes important. Those who are interested in such high-pressure regions should consult the original publications of Bridgman (1926) or the work of Dymond and Assael (See Sec. 9.6, Assael, et al., 1996, or Dymond and Assael, 1996).

9-10 EFFECT OF TEMPERATURE ON LIQUID VISCOSITY

The viscosities of liquids decrease with increasing temperature either under isobaric conditions or as saturated liquids. This behavior can be seen in Fig. 9-9, where, for

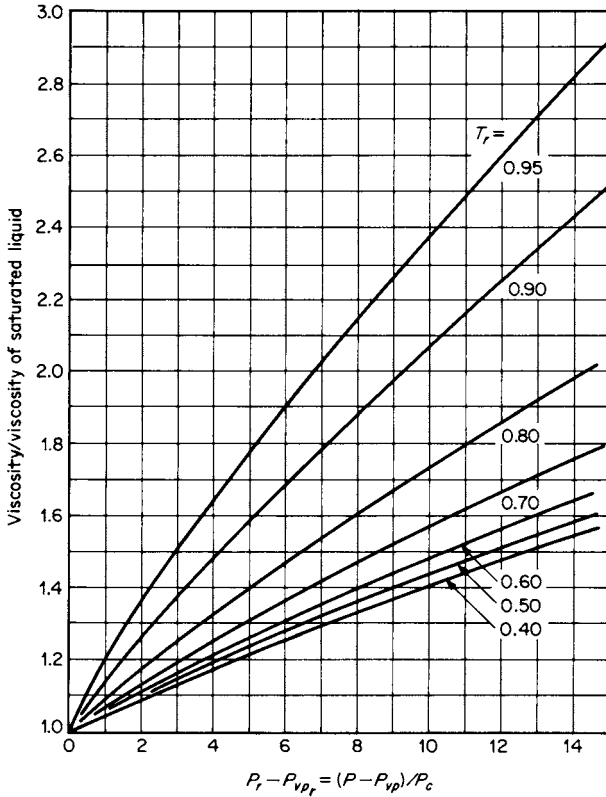


FIGURE 9-12 Effect of pressure on the viscosity of liquids; $\omega = 0.2$.

example, the viscosity of saturated liquid benzene is graphed as a function of temperature. Also, as noted in Sec. 9-8 and as illustrated in Fig. 9-10, for a temperature range from the freezing point to somewhere around the normal boiling temperature, it is often a good approximation to assume $\ln \eta_L$ is linear in reciprocal absolute temperature; i.e.,

$$\ln \eta_L = A + \frac{B}{T} \quad (9-10.1)$$

This simple form was apparently first proposed by de Guzman (1913) (O'Loane, 1979), but it is more commonly referred to as the Andrade equation (1930, 1934). Variations of Eq. (9-10.1) have been proposed to improve upon its correlation accuracy; many include some function of the liquid molar volume in either the A or B parameter (Bingham and Stookey, 1939; Cornelissen and Waterman, 1955; Eversteijn, et al., 1960; Girifalco, 1955; Gutman and Simmons, 1952; Innes, 1956; Marschalko and Barna, 1957; Medani and Hasan, 1977; Miller, 1963, 1963a; Telling, 1945; and van Wyk, et al., 1940). Another variation involves the use of a third constant to obtain the Vogel equation (1921),

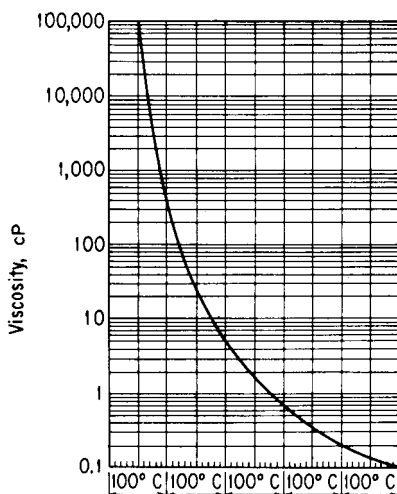


FIGURE 9-13 Lewis and Squires liquid viscosity-temperature correlation. (Lewis and Squires, 1934 as adapted in Gambill, 1959)

$$\ln \eta_L = A + \frac{B}{T + C} \quad (9-10.2)$$

Goletz and Tassios (1977) have used this form (for the kinematic viscosity) and report values of A , B , and C for many pure liquids.

Equation (9-10.1) requires at least two viscosity-temperature datum points to determine the two constants. If only one datum point is available, one of the few ways to extrapolate this value is to employ the approximate Lewis-Squires chart (1934), which is based on the empirical fact that the sensitivity of viscosity to temperature variations appears to depend primarily upon the value of the viscosity. This chart, shown in Fig. 9-13, can be used by locating the known value of viscosity on the ordinate and then extending the abscissa by the required number of degrees to find the new viscosity. Figure 9-13 can be expressed in an equation form as

$$\eta_L^{-0.2661} = \eta_K^{-0.2661} + \frac{T - T_K}{233} \quad (9-10.3)$$

where η_L = liquid viscosity at T , cP

η_K = known value of liquid viscosity at T_K , cP

T and T_K may be expressed in either °C or K. Thus, given a value of η_L at T_K , one can estimate values of η_L at other temperatures. Equation (9-10.3) or Fig. 9-13 is only approximate, and errors of 5 to 15% (or greater) may be expected. This method should not be used if the temperature is much above the normal boiling point.

Example 9-16 The viscosity of acetone at 30°C is 0.292 cP; estimate the viscosities at -90°C, -60°C, 0°C, and 60°C.

solution At -90°C , with Eq. (9-10.3),

$$\eta_L^{-0.2661} = (0.292)^{-0.2661} + \frac{-90 - 30}{233}$$

$$\eta_L = 1.7 \text{ cP}$$

For the other cases,

$T, ^{\circ}\text{C}$	η_L, cP Eq. (9-10.3)	η_L, cP Experimental	Percent error
-90	1.7	2.1	-19
-60	0.99	0.98	1
0	0.42	0.39	8
60	0.21	0.23	-9

In summary, from the freezing point to near the normal boiling point, Eq. (9-10.1) is a satisfactory temperature-liquid viscosity function. Two datum points are required. If only one datum point is known, a rough approximation of the viscosity at other temperatures can be obtained from Eq. (9-10.3) or Fig. 9-14.

Liquid viscosities above the normal boiling point are treated in Sec. 9-12.

9-11 ESTIMATION OF LOW-TEMPERATURE LIQUID VISCOSITY

Estimation methods for low-temperature liquid viscosity often employ structural-sensitive parameters which are valid only for certain homologous series or are found from group contributions. These methods usually use some variation of Eq. (9-10.1) and are limited to reduced temperatures less than about 0.75. We present two such methods in this section. We also describe a technique that employs corresponding states concepts. None of the three methods considered is particularly reliable.

Orrick and Erbar (1974) Method

This method employs a group contribution technique to estimate A and B in Eq. (9-11.1).

$$\ln \frac{\eta_L}{\rho_L M} = A + \frac{B}{T} \quad (9-11.1)$$

where η_L = liquid viscosity, cP
 ρ_L = liquid density at 20°C , g/cm^3
 M = molecular weight
 T = temperature, K

The group contributions for obtaining A and B are given in Table 9-9. For liquids that have a normal boiling point below 20°C , use the value of ρ_L at 20°C ; for liquids

TABLE 9-9 Orrick and Erbar (1974) Group Contributions for *A* and *B* in Eq. (9-11.1)

Group	<i>A</i>	<i>B</i>
Carbon atoms [†]	$-(6.95 + 0.21N)$	$275 + 99N$
$\begin{array}{c} \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	-0.15	35
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	-1.20	400
Double bond	0.24	-90
Five-membered ring	0.10	32
Six-membered ring	-0.45	250
Aromatic ring	0	20
Ortho substitution	-0.12	100
Meta substitution	0.05	-34
Para substitution	-0.01	-5
Chlorine	-0.61	220
Bromine	-1.25	365
Iodine	-1.75	400
-OH	-3.00	1600
-COO-	-1.00	420
-O-	-0.38	140
$\begin{array}{c} \\ -\text{C}=\text{O} \end{array}$	-0.50	350
-COOH	-0.90	770

[†]*N* = number of carbon atoms not including those in other groups shown above.

whose freezing point is above 20°C, ρ_L at the melting point should be employed. Compounds containing nitrogen or sulfur cannot be treated. Orrick and Erbar tested this method for 188 organic liquids. The errors varied widely, but they reported an average deviation of 15%. This is close to the average value of 16% shown in Table 9-11 for a more limited test. Since ρ_L in Eq. (9-11.1) is at 20°C and not *T*, the temperature of the liquid, Eq. (9-11.1) is the same form as the Andrade equation, Eq. (9-10.1).

Example 9-17 Estimate the viscosity of liquid *n*-butyl alcohol at 120°C with the Orrick-Erbar method. The experimental value is 0.394 cP.

solution From Table 9-9

$$A = -6.95 - (0.21)(4) - 3.00 = -10.79$$

$$B = 275 + (99)(4) + 1600 = 2271$$

From Vargaftik, et al. (1996), at 20°C, $\rho_L = 0.8096 \text{ g/cm}^3$ and $M = 74.123$. Then, with Eq. (9-11.1),

$$\ln \frac{\eta_L}{(0.8096)(74.123)} = -10.79 + \frac{2271}{T}$$

$$\text{At } T = 120^\circ\text{C} = 393 \text{ K, } \eta_L = 0.400 \text{ cP}$$

$$\text{Error} = \frac{0.400 - 0.394}{0.394} \times 100 = 1.5\%$$

Sastri-Rao Method (1992)

In this method, the pure liquid viscosity is calculated with the equation

$$\eta = \eta_B P_{vp}^{-N} \quad (9-11.2)$$

P_{vp} is the vapor pressure in atmospheres and η_B is the viscosity at the normal boiling point, T_b in mPa.s. Below T_b , Sastri and Rao determine P_{vp} with the equation

$$\ln P_{vp} = (4.5398 + 1.0309 \ln T_b) \times \left(1 - \frac{(3 - 2T/T_b)^{0.19}}{T/T_b} - 0.38(3 - 2T/T_b)^{0.19} \ln(T/T_b) \right) \quad (9-11.3)$$

Equation (9-11.3) should be used only when $T < T_b$. Equation (9-11.3) is not necessarily the most accurate equation for vapor pressure predictions but should be used with Eq. (9-11.2) because the group contributions used to estimate η_B and N have been determined when P_{vp} was calculated with Eq. (9-11.3). η_B is determined with the equation

$$\eta_B = \sum \Delta \eta_B + \sum \Delta \eta_{Bcor} \quad (9-11.4)$$

N is determined from

$$N = 0.2 + \sum \Delta N + \sum \Delta N_{cor} \quad (9-11.5)$$

Values for group contributions to determine the summations in Eqs. (9-11.4) and (9-11.5) are given in Table 9-10. The contributions of the functional groups to η_B and N are generally cumulative. However, if the compound contains more than one identical functional group, its contributions for N should be taken only once unless otherwise mentioned. Thus for branched hydrocarbons with multiple $>\text{CH}-$ groups, N is 0.25. In Table 9-10, the term alicyclic means cycloparaffins and cycloolefins and excludes aromatics and heterocyclics. In the contributions of halogen groups, "others" means aromatics, alicyclics, and heterocyclics while the carbon groups listed are meant for aliphatic compounds. Also for halogens, the values of ΔN for aliphatic, alicyclics and aromatics are not used if other non-hydrocarbon groups are present in the cyclic compound (See footnote b in the halogen section of Table 9-10). For example, the corrections for halogenated pyridines and anilines are given in footnote b and are not to be used in conjunction with the corrections listed under "aliphatic, alicyclics and aromatics." Calculation of η_B and N is illustrated in Example 9-18 and typical deviations are shown in Table 9-11.

Example 9-18 Determine the values of η_B and N to be used in Eq. (9-11.2) for o-xylene, ethanol, ethylbenzene, 2-3-dimethylbutane, and o-chlorophenol.

TABLE 9-10 Sastri and Rao (1992) Group Contributions for η_B and N in Eq. (9-11.2)

Hydrocarbon groups				
Group	$\Delta\eta_B$	ΔN	Remarks and examples	
Non-ring				
—CH ₃	0.105	0.000	For <i>n</i> -alkanes, <i>n</i> -alkenes or <i>n</i> -alkynes with C > 8 $\Delta N_{\text{cor}} = 0.050$	
>CH ₂	0.000	0.000		
>CH—	−0.110	0.050	(i) if both >CH— and >C< groups are present $\Delta N_{\text{cor}} = 0.050$ only	
>C<	−0.180	0.100	(ii) ΔN values applicable only for aliphatic hydrocarbons and halogenated derivatives of aliphatic compounds (e.g. 2,2,4 trimethyl pentane, chloroform, bromal) in other cases $\Delta N = 0.000$	
=CH ₂	0.085	0.000		
=CH—	−0.005	0.000		
=C<	−0.100	0.000		
HC≡C—	−0.115	0.075		
Ring			Examples of ΔN values	
>CH ₂	0.060	0.000		
>CH—	−0.085	0.000	ΔN for 2-methyl propane 0.050	
>C<	−0.180	0.000	2,3-dimethylbutane 0.050 (see text)	
—CH—	Alicyclic	0.040	2,2-dimethylpropane 0.100	
=CH—	Others	0.050	2,2,4,4-tetramethyl pentane 0.100	
=C<	Alicyclic	−0.100	2,2,4-trimethylpentane 0.050 (both >CH— and >C< present)	
=C<	Others	−0.120	>CH— in chloroform 0.050 but in isopropylamine 0.000 and	
=C<	Fused	−0.040	isopropylbenzene 0.000	
=CH—	Fused	−0.065		

Contributions of ring structure and hydrocarbon chains to ΔN_{cor}		
Structure	ΔN_{cor}	Remarks and examples
All monocyclic and saturated polycyclic hydrocarbon rings (unsubstituted)	0.100	cyclopentane, benzene, or cis-decahydronaphthalene
Methyl substituted compounds of the above	0.050	ethylcyclopentane, toluene
Monocyclic monoalkyl alicyclic hydrocarbons		
$1 < C_{\text{br}} \leq 5$	0.025	ethylcyclopentane, <i>n</i> -pentylcyclohexane
$C_{\text{br}} > 5$	0.050	<i>n</i> -hexylcyclopentane
Monocyclic multisubstituted alkyl alicyclic hydrocarbons	0.025	1,3,5-trimethylcyclohexane
Monoalkyl benzenes with $C_{\text{br}} > 1$	0.025	ethylbenzene
Bicyclic hydrocarbons partly or fully unsaturated	0.050	tetralin, diphenyl, diphenylmethane
Unsaturated tricyclic hydrocarbons	0.100	<i>p</i> -terphenyl, triphenylmethane
Correction for multiple substitution in aromatics by hydrocarbon groups		
ortho	0.050	<i>o</i> -xylene, <i>o</i> -nitrotoluene
meta and para	0.000	<i>p</i> -xylene
1,3,5	0.100	1,3,5-trimethylbenzene
1,2,4	0.050	1,2,4-trimethylbenzene
1,2,6	0.000	
$\Delta \eta_{\text{Bcor}}$ for multiple substitution in aromatics by hydrocarbon groups = 0.070		

TABLE 9-10 Sastri and Rao (1992) Group Contributions for η_B and N in Eq. (9-11.2) (*Continued*)

Contribution of halogen groups									
$\Delta\eta_B$ for halogen attached to carbon in							ΔN^b in halogenated hydrocarbons with no other functional groups		
Aliphatic compounds						Others			
Group	$-\text{CH}_3$ or $>\text{CH}_2$	$>\text{CH}-$	$>\text{C}<^a$	$=\text{CH}-$	$=\text{C}<$				
$-\text{F}^c$	0.185	0.155	0.115	n.d.	n.d.	0.185	0.075	0.025	0.00
$-\text{Cl}^a$	0.185	0.170	0.170	0.180	0.150	0.170	0.075	0.025	0.00
$-\text{Br}$	0.240	0.235	0.235	0.240	0.210	0.210	0.075	0.025	0.00
$-\text{I}$	0.260	0.260	n.d.	n.d.	n.d.	0.260	0.075	0.025	0.00
^a Special configurations/function group structure combination				ΔN_{cor}		Remarks and examples			
(1) $\text{X}-(\text{CH}_2)_n-\text{X}$ where X is halogen				0.050		1,3-dichloropropane			
(2) $\text{Cl}-\text{C}-\text{Cl}$ where the C is in a ring				0.050		For each group, one correction in hexachlorocyclopentadiene			
^b Case of non-hydrocarbon group present in cyclic compounds									
(1) Halogen attached to ring carbons in compounds containing									
(A) $-\text{NH}_2$ or phenolic $-\text{OH}$				-0.075		2-chloro-6-methyl aniline			
(B) oxygen-containing groups other than OH				0.050		2-chlorophenylmethyl ether			
(C) other non-oxygen functional groups				-0.050		2-chloropyridine			
(2) Halogen attached to non-hydrocarbon functional group				-0.050		benzoylbromide			
^c Fluorine groups in perfluorocompounds									
Group	$\Delta\eta_B$								
Non-ring									
$-\text{CF}_3$	0.210	$\Delta N=0.150$ for all perfluoro <i>n</i> -compounds							
$>\text{CF}_2$	0.000								
$>\text{CF}-$	-0.080	$\Delta N=0.200$ for all isocompounds							
Ring									
$-\text{CF}_2-$	0.145	$\Delta N=0.200$ for all cyclic compounds							
$>\text{CF}-$	-0.170								

Contribution of oxygen groups

Group	Structure	$\Delta\eta_B$	ΔN	Remarks
—O—	Non-ring attached to ring carbon	0.020	0.050	For multiple occurrence $\Delta\eta_{Bcor} = 0.050$ (1,3-dimethoxybenzene) In compounds containing —NH ₂ or phenolic OH group attached to ring carbon $\Delta N_{cor} = -0.050$ (<i>o</i> -anisidine, 2-methoxyphenol)
—O—	Ring (Single) (Multiple occurrence)	0.120 0.200	0.050 0.150	Combined value (dioxane, paraldehyde)
—O—	Others	0.000	0.050	(i) In aliphatic compounds containing —OH, special value for the combination $\Delta N = 0.100$ (2-methoxyethanol) (ii) $\Delta\eta_{Bcor}$ for multiple occurrence 0.05 (dimethoxymethane)
>CO	Non-ring attached to ring carbon	0.030	0.050	(i) In the cyclic compounds containing NH ₂ group (with or without other functional groups) special value $\Delta N = -0.100$ for the combination (ethylanthranilate) (ii) In cyclic compounds containing >NH group $\Delta\eta_{Bcor} = 0.080$ (acetanilide)
>CO	Ring	0.055	0.100	(i) In cyclic compounds containing >NH group $\Delta\eta_{Bcor} = 0.100$ (ii) In compounds containing —O— group special value $\Delta N = 0.125$ for the combination
>CO	Others	0.030	0.025	(i) For aliphatic compounds containing —NH ₂ or >N— groups (acetamide) $\Delta\eta_{Bcor} = 0.080$ (ii) For cyclic compounds containing >NH group (acetanilide) $\Delta\eta_{Bcor} = 0.080$ (iii) In aliphatic compounds containing —OH special value for the combination, $\Delta N = 0.125$ (diacetonealcohol)
—C(O) ₃ C—	Anhydride	0.060	0.050	
—CHO	Aldehyde	0.140	0.050	In compounds containing —OH (phenolic) special value for the combination, $\Delta N = 0.075$ (salicylaldehyde)

TABLE 9-10 Sastri and Rao (1992) Group Contributions for η_B and N in Eq. (9-11.2) (*Continued*)

Contribution of oxygen groups				
Group	Structure	$\Delta\eta_B$	ΔN	Remarks
—COO—	Ester	0.040	0.050	(i) For multiple occurrence, $\Delta N = 0.100$ (dibutylphthalate) (ii) For —H in formates $\Delta\eta_B = 0.165$ (iii) In cyclic compounds containing NH_2 group, special value for the combination, $\Delta N = 0.100$ (ethylantranilate) (iv) For aliphatic compounds containing — NH_2 or $>\text{N}$ —groups, $\Delta\eta_{\text{Bcor}} = 0.080$ (methylcarbamate)
—COOH	In aliphatics			For C = 3 or 4 $\Delta N = 0.050$
	saturated	0.220	0.100	
	unsaturated	0.250	0.100	
	In aromatics	0.195	0.175	
Contribution of hydroxyl groups				
Structure		$\Delta\eta_B$	ΔN	Remarks
—OH in aliphatics				(i) In compounds containing —O— group special value for the combination, $\Delta N = 0.100$ (2 methoxy ethanol) (ii) In compounds containing $>\text{NH}$ group, special value for the combination, $\Delta N = 0.300$ (aminoethyl ethanolamine)
saturated primary	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$ for C ≤ 10 0.095 for C > 10		0.3 for 2 < C < 12 0.15 for others	
Primary branched	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$		0.375	
Secondary straight chain	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$		0.450 for C ≤ 5 0.300 for C > 5	
Secondary branched	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$		0.450 for C ≤ 8 0.300 for C > 8	
Tertiary saturated	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$		0.650 for C ≤ 5 0.300 for C > 5	In compounds containing $>\text{CO}/\text{—O—}$ groups special value for the combination $\Delta N = 0.125$ (diacetonealcohol)
Unsaturated primary	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$		0.175	
Unsaturated tertiary	$0.615 - 0.092C + 0.004C^2 - 10^{-0.58C}$		0.425	

Structure		$\Delta\eta_B$	ΔN	Remarks
In cyclic alcohols	0.270		0.150	
Phenolic	0.270		0.200	(i) In compounds containing $-\text{NH}_2$ or $-\text{CHO}$ groups in ortho position, special value for the combination, $\Delta N = 0.075$ (2-nitrophenol, salicylaldehyde) (ii) In compounds containing $-\text{O}-$ $\Delta N_{\text{cor}} = 0.050$ (4-methoxyphenol)
Contribution of nitrogen groups				
Group	Structure	$\Delta\eta_B^a$	ΔN	Remarks
$-\text{NH}_2$	In aliphatic <i>n</i> -amines	0.170	0.100	(i) $\Delta\eta_{\text{Bcor}} = 0.100$ in $\text{NH}_2 - (\text{CH}_2)_n - \text{NH}_2$ (ethylenediamine) (ii) in compounds containing $>\text{COO}$ $\Delta\eta_{\text{Bcor}} = 0.080$ (acetamide) (iii) In compounds containing $-\text{COO}$, $\Delta N_{\text{cor}} = 0.100$ (ethyl carbamate)
$-\text{NH}_2$	Aliphatic isoamines attached to $>\text{CH}$	0.200	0.100	(isopropylamine)
$-\text{NH}_2$	In monocyclic compounds, attached to side chain	0.170	0.100	(benzylamine)
$-\text{NH}_2$	In monocyclic compounds, attached to ring carbon	0.205	0.150	(i) For compounds containing $-\text{O}-$ $\Delta N_{\text{cor}} = -0.050$ (2-methoxyaniline) (ii) In cyclic compounds containing $-\text{COO}-$ group, special value for the combination, $\Delta N = 0.100$ (ethylantranilate)
$-\text{NH}_2$	In other aromatics	0.150	0.100	(1-naphthylamine)
$>\text{NH}$	In aliphatics	0.020	0.075	In compounds containing $-\text{OH}$ special value for the combination, $\Delta N = 0.300$ (aminoethyl ethanolamine)
$>\text{NH}$	In aromatic compounds, attached to side chain	0.020	0.075	(dibenzylamine)
$>\text{NH}$	In aromatic compounds, attached to ring carbon	0.020	0.100	
$>\text{NH}$	Ring	0.160	0.100	

TABLE 9-10 Sastri and Rao (1992) Group Contributions for η_B and N in Eq. (9-11.2) (*Continued*)

Contribution of nitrogen groups (continued)				
Group	Structure	$\Delta\eta_B^a$	ΔN	Remarks
>N—	In aliphatics	-0.115	0.050	For aliphatic compounds containing >CO $\Delta\eta_{Bcor} = 0.080$ (dimethyl acetamide)
>N—	In aromatic compounds, attached to side chain	-0.115	0.050	(tribenzylamine)
>N—	In aromatic compounds, attached to ring carbon	-0.060	0.050	
>N—	Ring	0.100	0.050	In compounds containing —CN or halogen, $\Delta N_{cor} = -0.050$
—NO ₂	In aliphatics	0.180	0.050	For multiple occurrences $\Delta N_{cor} = 0.050$
	In aromatics	0.160	0.050	(i) for multiple occurrences $\Delta N_{cor} = 0.050$ and $\Delta\eta_{Bcor} = 0.070$ (<i>m</i> -dinitrobenzene) (ii) In compounds containing —OH (phenolic) in ortho position, special value for the combination, $\Delta N = 0.075$ (2-nitrophenol)
—CN		0.135	0.025	(i) For multiple occurrence, $\Delta N_{cor} = 0.075$ (ii) With N in ring, $\Delta N_{cor} = -0.050$
^a $\Delta\eta_B = 0.080$ for —H in compounds containing hydrocarbon functional groups (e.g. formanilide)				
Contribution of sulphur groups				
Functional group/structure		$\Delta\eta_B$	ΔN	
—S— Non-ring		0.045	0.000	
—S— ring		0.150	0.050	
—SH		0.150	0.025	

TABLE 9-11 Comparison of Calculated and Experimental Viscosities of Liquids

Compound	<i>T</i> , K	η (exp.) cP**	Percent error* in liquid viscosity calculated by the method of		
			Orrick and Erbar	Sastri and Rao	Przezdziecki and Sridhar
Acetone	183	2.075	-25	-3.5	-11
	213	0.982	-6.7	1.9	-4.6
	273	0.389	-8.3	3.6	-2.3
	303	0.292	-9.4	1.6	-1.2
	333	0.226	-8.3	1.9	0.2
Acetic acid	283	1.450	-22	-15	8.6
	313	0.901	-15	-15	0
	353	0.561	-9.5	-17	-1.3
	383	0.416	-5.3	-16	0.3
Aniline	263	13.4	—	-24	—
	293	4.38	—	-4.8	—
	333	1.520	—	8.1	-49
	393	0.658	—	-9.6	-33
Benzene	278	0.826	-45	-8.5	1.1
	313	0.492	-35	-6.6	7.3
	353	0.318	-26	-5.5	12
	393	0.219	-46	-5.7	18
	433	0.156	-7.1	-6.4	23
	463	0.121	5.1	-9.5	28
<i>n</i> -Butane	183	0.630	-14	1.6	-9
	213	0.403	-20	-2.8	-8.9
	273	0.210	-23	-0.4	-5.8
1-Butene	163	0.79	-22	0.9	-13
	193	0.45	-20	-2.9	-9.6
	233	0.26	-18	-2.5	-3.3
<i>n</i> -Butyl alcohol	273	5.14	-2.1	0.3	—
	313	1.77	-1.6	-3.4	—
	353	0.762	0.5	-2	—
	393	0.394	-1.4	1.4	—
Carbon tetrachloride	273	1.369	20	-4.4	-24
	303	0.856	22	-2	-15
	343	0.534	20	-0.1	-6.7
	373	0.404	19	-0.7	-2.8
Chlorobenzene	273	1.054	1.4	2.7	-8.3
	313	0.639	-0.6	0.8	-7
	353	0.441	-0.9	-1.2	-5.2
	393	0.326	-5.1	-0.9	-3.8
Chloroform	273	0.700	40	7.4	-11
	303	0.502	34	5.7	-8.1
	333	0.390	27	3.6	-7.9
Cyclohexane	278	1.300	-51	-29.7	-38
	333	0.528	-38	-16.4	-22
Cyclopentane	293	0.439	-32	-5.1	-33
	323	0.323	-28	-7.8	-29

TABLE 9-11 Comparison of Calculated and Experimental Viscosities of Liquids
(Continued)

Compound	<i>T</i> , K	η (exp.) cP**	Percent error* in liquid viscosity calculated by the method of		
			Orrick and Erbar	Sastri and Rao	Przeddziecki and Sridhar
2,2-Dimethylpropane	258	0.431	-3.5	-24.3	20
	283	0.281	-0.8	-15.1	30
Ethane	98	0.985	30	53.6	-24
	153	0.257	-12	26.4	-14
	188	0.162	-22	21.3	-13
Ethylene chloride	273	1.123	-43	-20.7	—
	313	0.644	-35	-15.3	—
	353	0.417	-27	-8.8	—
Ethyl alcohol	273	1.770	27	-14.1	—
	313	0.826	3.5	-6	—
	348	0.465	-5.4	7.7	—
Ethyl acetate	293	0.458	-4.2	-5.5	-16
	353	0.246	0.4	-1.2	-5.3
	413	0.153	7.4	-9.7	-1.8
	463	0.0998	27	-2.2	4.8
Ethylbenzene	253	1.240	-2.9	19.7	-33
	313	0.535	-1.2	7.3	-23
	373	0.308	-1.7	0.1	-16
	413	0.231	-1.2	-1.9	-13
Ethyl bromide	293	0.395	27	0	-23
	333	0.269	32	2.2	-17
	373	0.199	36	4.6	-16
Ethylene	103	0.70	-25	-0.7	25
	133	0.31	-27	-2.3	-17
	173	0.15	-22	4.8	-6.4
Ethyl ether	273	0.289	0	2.7	0
	293	0.236	0	1.6	2.2
	333	0.167	2	-3.5	4
	373	0.118	1	5.5	7.4
Ethyl formate	273	0.507	-18	6.8	-16
	303	0.362	-17	6.6	-11
	328	0.288	-16	7	-9.6
<i>n</i> -Heptane	183	3.77	-21	-33.2	-1.7
	233	0.965	-0.5	-11.3	-27
	293	0.418	-1.9	-7.2	-21
	373	0.209	-3.3	-1	-17
<i>n</i> -Hexacontane (C ₆₀ H ₁₂₂)	408	7.305	18	37	—
	466	3.379	-63	19	—
<i>n</i> -Hexane	213	0.888	2.9	-2.3	-8.3
	273	0.381	-2.4	-2.4	-8.2
	343	0.205	-4.9	1.2	-7.1

TABLE 9-11 Comparison of Calculated and Experimental Viscosities of Liquids
(Continued)

Compound	T, K	η (exp.) cP**	Percent error* in liquid viscosity calculated by the method of		
			Orrick and Erbar	Sastri and Rao	Przedzdiecki and Sridhar
Isobutane	193	0.628	-23	1.1	-37
	233	0.343	-25	-12.2	-29
	263	0.239	-24	-17.1	-23
Isopropyl alcohol	283	3.319	-24	-16.2	—
	303	1.811	-15	9.8	—
	323	1.062	-10	4.5	—
Methane	88	0.226	60	1.5	-11
	113	0.115	23	-20.1	-4.3
2-Methylbutane	223	0.550	-13	-10.8	-30
	253	0.353	-12	0.3	-21
	303	0.205	-10	-1.9	-12
<i>n</i> -Pentane	153	2.35	-1	-1.7	11
	193	0.791	3.8	0.1	-7
	233	0.428	-3.3	7.3	-6
	273	0.279	-8.2	2.9	-4.7
	303	0.216	-11	0.6	-4.9
Phenol	323	3.020	0	1.5	-50
	373	0.783	37	12.5	-5.4
Propane	133	0.984	-1.5	45.4	-23
	193	0.327	-22	14	-19
	233	0.205	-25	-1.7	-16
<i>n</i> -Propyl alcohol	283	2.897	-9.1	0.8	—
	313	1.400	-9.8	-6.1	—
	373	0.443	-6.5	-7.4	—
Toluene	253	1.070	-19	0.4	-33
	293	0.587	-13	0.7	-24
	333	0.380	-10	-2.1	-16
	383	0.249	-6.8	-5.1	-10
<i>o</i> -Xylene	273	1.108	3.1	-5.1	-5.5
	313	0.625	5	-4.5	-4.8
	373	0.345	3.7	4.5	-0.3
	413	0.254	3.6	1.8	1.9
<i>m</i> -Xylene				-2.7	
	273	0.808	1.1	-2.6	1.9
	313	0.492	1.4	-0.4	1.8
	353	0.340	0.3	2	2.9
	413	0.218	1.4	3.4	4.6

*[(calc - exp)/exp] \times 100.

**Data from Aasen, et al. (1990), Amdur and Mason (1958), and Landolt-Bornstein (1955).

solution o-xylene has 4=CH— (ring, not alicyclic), 2=C< (ring, not alicyclic) and 2 —CH₃ groups. There is a correction to η_{Bcor} of 0.07 for multiple substitution. With values from Table 9-10:

$$\eta_B = 4 \times 0.05 - 2 \times 0.12 + 2 \times 0.105 + 0.07 = 0.24 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.05 = 0.25$$

ethanol has one —CH₃, one >CH₂ (non-ring) and one —OH. With values from Table 9-10:

$$\eta_B = 0.105 + 0.615 - 0.092 \times 2 + 0.004 \times 4 - 10^{-0.58 \times 2} = 0.483 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.15 = 0.35$$

ethylbenzene has 5 =CH— (ring, not alicyclic), one =C< (ring not alicyclic), one —CH₃, and one —CH₂— (non-ring). There is a branching correction to ΔN of 0.025. With values from Table 9-10:

$$\eta_B = 5 \times 0.05 - 0.12 + 0.105 = 0.235 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.025 = 0.225$$

2-3 dimethylbutane has 4 —CH₃ and 2 >CH— (non-ring). The value of ΔN of 0.05 is applied only once. With values from Table 9-10:

$$\eta_B = 4 \times 0.105 - 2 \times 0.11 = 0.2 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.05 = 0.25$$

o-chlorophenol has 4=CH— (ring, not alicyclic), 2=C< (ring, not alicyclic), one —Cl attached to an “other”, and one —OH (phenolic). Note that the —Cl contribution to ΔN of 0.025 is not used. Footnote b in the halogen section of Table 9-10 applies because of the presence of the non-hydrocarbon —OH group. With values from Table 9-10:

$$\eta_B = 4 \times 0.05 - 2 \times 0.12 + 0.17 + 0.27 = 0.4 \text{ mPa}\cdot\text{s}$$

$$N = 0.2 + 0.2 - 0.075 = 0.325$$

Przedziecki and Sridhar (1985) Method

In this technique, the authors propose using the Hildebrand-modified Batschinski equation (Batschinski, 1913; Hildebrand, 1971; Vogel and Weiss, 1981)

$$\eta_L = \frac{V_o}{E(V - V_o)} \quad (9-11.6)$$

where η_L = liquid viscosity, cP
 V = liquid molar volume, cm³/mol

and the parameters E and V_o are defined below.

$$E = -1.12 + \frac{V_c}{12.94 + 0.10 M - 0.23 P_c + 0.0424 T_{fP} - 11.58(T_{fP}/T_c)} \quad (9-11.7)$$

$$V_o = 0.0085\omega T_c - 2.02 + \frac{V_m}{0.342(T_{fp}/T_c) + 0.894} \quad (9-11.8)$$

where T_c = critical temperature, K

P_c = critical pressure, bar

V_c = critical volume, cm³/mol

M = molecular weight, g/mol

T_{fp} = freezing point, K

ω = acentric factor

V_m = liquid molar volume at T_{fp} , cm³/mol

Thus, to use Eq. (9-11.6), one must have values for T_c , P_c , V_c , T_{fp} , ω , and V_m in addition to the liquid molar volume V at the temperature of interest. The authors recommend that V_m and V be estimated from T_{fp} and T by the Gunn-Yamada (1971) method. In the Gunn-Yamada method, one accurate value of V is required in the temperature range of applicability of Eq. (9-11.6). We define this datum point as V^R at T^R ; then at any other temperature T ,

$$V(T) = \frac{f(T)}{f(T^R)} V^R \quad (9-11.9)$$

where

$$f(T) = H_1(1 - \omega H_2) \quad (9-11.10)$$

$$H_1 = 0.33593 - 0.33953T_r + 1.51941T_r^2 - 2.02512T_r^3 + 1.11422T_r^4 \quad (9-11.11)$$

$$H_2 = 0.29607 - 0.09045T_r - 0.04842T_r^2 \quad (9-11.12)$$

Equation (9-11.6) was employed with Eqs. (9-11.7) to (9-11.12) to estimate liquid viscosities for the compounds in Table 9-11. The values of T_c , P_c , V_c , T_{fp} , and ω , were obtained from Appendix A. The reference volume for each compound was calculated from the liquid density datum value given in Appendix A. Large errors were noted for alcohols, and those results are not included in the table. For other compounds, the errors varied widely and, except for a few materials, the technique underestimated the liquid viscosity. Larger errors were normally noted at low temperatures, but that might have been expected from the form of Eq. (9-11.6). That is, because V_o is of the order of the volume at the freezing point and $\eta_L \propto (V - V_o)^{-1}$, the estimated value of η_L becomes exceedingly sensitive to the choice of V . This problem was emphasized by Lucas and Lucas (1986), who suggest that Eq. (9-11.6) should not be used below T_r values of about 0.55.

Example 9-19 Use the Przedzicki and Sridhar correlation to estimate the liquid viscosity of toluene at 383 K. The experimental value is 0.249 cP (Vargaftik, et al., 1996).

solution From Appendix A, for toluene (slightly different values were used to calculate the results shown in Table 9-11)

$$\begin{aligned}T_c &= 591.75 \text{ K} \\P_c &= 41.08 \text{ bar} \\V_c &= 316 \text{ cm}^3/\text{mol} \\T_{fp} &= 178 \text{ K} \\M &= 92.14 \text{ g/mol} \\\omega &= 0.264 \\V_L &= 106.87 \text{ cm}^3/\text{mol at } 298.15 \text{ K}\end{aligned}$$

With $T^R = 298.15 \text{ K}$, and with Eqs. (9-11.9) to (9-11.12),

$$T_r^R = \frac{298.15}{591.75} = 0.504$$

$$\begin{aligned}H_1(T_r^R) &= 0.33593 - (0.33953)(0.504) + (1.51941)(0.504)^2 - (2.02512)(0.504)^3 \\&\quad + (1.11422)(0.504)^4 = 0.363\end{aligned}$$

$$H_2(T_r^R) = 0.29607 - (0.09045)(0.504) - (0.04842)(0.504)^2 = 0.238$$

$$f(T^R) = 0.363[1 - (0.264)(0.238)] = 0.340$$

Similarly,

	$T, \text{ K}$	T_r	H_1	H_2	$f(T)$
T_{fp}	178	0.301	0.325	0.264	0.303
T	383	0.647	0.399	0.217	0.376

$$V_m = \frac{0.303}{0.340} (106.87) = 95.2 \text{ cm}^3/\text{mol}$$

Then

$$V = \frac{0.376}{0.340} (106.87) = 118.2 \text{ cm}^3/\text{mol}$$

This value for V agrees with that given in Vargaftik, et al. (1996). With Eqs. (9-11.7) and (9-11.8)

$$\begin{aligned}E &= -1.12 + 316/[12.94 + (0.10)(92.14) - (0.23)(41.08) + (0.0424)(178) \\&\quad - (11.58)(178/591.8)] = 17.72\end{aligned}$$

$$\begin{aligned}V_o &= (0.0085)(0.264)(591.75) - 2.02 + \frac{95.2}{[(0.342)(178/591.8) + 0.894]} \\&= 94.8 \text{ cm}^3/\text{mol}\end{aligned}$$

Then, with Eq. (9-11.6)

$$\eta_L = \frac{94.8}{17.72(118.2 - 94.8)} = 0.229 \text{ cP}$$

$$\text{Error} = \frac{0.229 - 0.249}{0.249} \times 100 = -8\%$$

Other Correlations

Other viscosity-correlating methods have been proposed, and a number of these are summarized in Mehrotra, et al. (1996) and Monnery, et al. (1995). Other recent correlations are given in Mehrotra (1991), and the earlier literature was reviewed in the 4th Edition of this book.

Recommendations for Estimating Low-temperature Liquid Viscosities

Three estimation methods have been discussed. In Table 9-11, calculated liquid viscosities are compared with experimental values for 36 different liquids (usually of simple structure). Large errors may result, as illustrated for all methods. The method of Przedziecki and Sridhar should not be used for alcohols.

The method of Sastri and Rao assumes that the temperature dependence of η_L is related to the temperature dependence of the vapor pressure, whereas the Orrick and Erbar method is slightly modified to include the liquid density. Neither is reliable for highly branched structures or for inorganic liquids and the Orrick-Erbar method cannot be used for sulfur compounds. Both are limited to a temperature range from somewhat above the freezing point to about $T_r \approx 0.75$. Przedziecki and Sridhar's method employs the Hildebrand equation, which necessitates knowledge of liquid volumes.

It is recommended that, in general, the method of Sastri and Rao be used to estimate low-temperature liquid viscosities. Errors vary widely, but should be less than 10 to 15% in most instances.

9-12 ESTIMATION OF LIQUID VISCOSITY AT HIGH TEMPERATURES

Low-temperature viscosity correlations as covered in Sec. 9-10 usually assume that $\ln \eta_L$ is a linear function of reciprocal absolute temperature. Above a reduced temperature of about 0.7, this relation is no longer valid, as illustrated in Fig. 9-10. In the region from about $T_r = 0.7$ to near the critical point, many estimation methods are of a corresponding states type that resemble or are identical with those used in the first sections of this chapter to treat gases. For this temperature range, Sastri (1998) recommends

$$\ln \eta = \left[\frac{\ln \eta_B}{\ln(\alpha \eta_B)} \right]^\phi \ln(\alpha \eta_B) \quad (9-12.1)$$

where η is in mPa · s

η_B = viscosity at T_b in mPa · s, from contributions in Table 9-10
 $\alpha = 0.1175$ for alcohols and 0.248 for other compounds

$$\phi = \frac{1 - T_r}{1 - T_{br}} \quad (9-12.2)$$

where $T_r = T/T_c$
 $T_{br} = T_b/T_c$

Sastri reports average deviations of 10% for $T_r > 0.9$ and 6% for $T_{br} < T_r < 0.9$.

Example 9-20 Estimate the saturated liquid viscosity of *n*-propanol at 433.2 K by using Eq. (9-12.1). The experimental value is 0.188 cP.

solution From Appendix A, $T_b = 370.93$ K and $T_c = 536.78$ K. With contributions from Table 9-10, $\eta_B = 0.105 + 0.615 - 0.092 \times 3 + 0.004 \times 9 - 10^{-3 \times 0.58} = 0.462$ mPa · s = 462 μ Pa · s. From Eq. (9-12.2)

$$\phi = \frac{1 - 433.2/536.78}{1 - 370.93/536.78} = 0.624$$

With $\alpha = 0.1175$, Eq. (9-12.1) gives

$$\ln \eta = \ln(0.1175 \times 462) \left[\frac{\ln(462)}{\ln(0.1175 \times 462)} \right]^{0.624}$$

$$\eta = 185 \mu\text{Pa} \cdot \text{s} = 0.185 \text{ cP}$$

$$\text{Error} = \frac{0.185 - 0.188}{0.188} \times 100 = -1.6\%$$

A more general estimation method would logically involve the extension of the high-pressure gas viscosity correlations described in Sec. 9-6 into the liquid region. Two techniques have, in fact, been rather widely tested and found reasonably accurate for reduced temperatures above about 0.5. These methods are those of Chung, et al. (1988) and Brulé and Starling (1984). Both methods use Eq. (9-6.16), but they have slightly different coefficients to compute some of the parameters. The Chung, et al. form is preferable for simple molecules and will treat polar as well as nonpolar compounds. The Brulé and Starling relation was developed primarily for complex hydrocarbons, and the authors report their predictions are within 10% of experimental values in the majority of cases. The Chung, et al. method has a similar accuracy for most nonpolar compounds, but significantly higher errors can occur with polar, halogenated, or high-molecular weight compounds. In both cases, one needs accurate liquid density data, and the reliability of the methods decreases significantly for T_r less than about 0.5. The liquids need not be saturated; subcooled compressed liquid states simply reflect a higher liquid density. The Chung, et al. technique was illustrated for dense gas ammonia in Example 9-12. The procedure is identical when applied to high-temperature liquids.

Discussion

The quantity of accurate liquid viscosity data at temperatures much above the normal boiling point is not large. In addition, to test estimation methods such as those of Chung, et al. or Brulé and Starling, one needs accurate liquid density data under

the same conditions which apply to the viscosity data. This matching makes it somewhat difficult to test the methods with many compounds. However, Brulé and Starling developed their technique so that they would be coupled to a separate computation program using a modified BWR equation of state to provide densities. They report relatively low errors, and this fact appears to confirm the general approach (See also Brulé and Starling, 1984). Hwang, et al. (1982) have proposed viscosity (as well as density and surface tension) correlations for coal liquids.

Regardless of what high-temperature estimation method is chosen, there is the problem of joining both high- and low-temperature estimated viscosities should that be necessary.

9-13 LIQUID MIXTURE VISCOSITY

Essentially all correlations for liquid mixture viscosity refer to solutions of liquids below or only slightly above their normal boiling points; i.e., they are restricted to reduced temperatures (of the pure components) below about 0.7. The bulk of the discussion below is limited to that temperature range. At the end of the section, however, we suggest approximate methods to treat high-pressure, high-temperature liquid mixture viscosity.

At temperatures below $T_r \approx 0.7$, liquid viscosities are very sensitive to the structure of the constituent molecules (See Sec. 9-11). This generality is also true for liquid mixtures, and even mild association effects between components can often significantly affect the viscosity. For a mixture of liquids, the shape of the curve of viscosity as a function of composition can be nearly linear for so-called ideal mixtures. But systems that contain alcohols and/or water often exhibit a maximum or a minimum and sometimes both (Irving, 1977a).

Almost all methods to estimate or correlate liquid mixture viscosities assume that values of the viscosities of the pure components are available. Thus the methods are interpolative. Nevertheless, there is no agreement on the best way to carry out the interpolation. Irving (1977) surveyed more than 50 equations for binary liquid viscosities and classified them by type. He points out that only very few do not have some adjustable constant that must be determined from experimental mixture data and the few that do not require such a parameter are applicable only to systems of similar components with comparable viscosities. In a companion report from the National Engineering Laboratory, Irving (1977a) has also evaluated 25 of the more promising equations with experimental data from the literature. He recommends the one-constant Grunberg-Nissan (1949) equation [see Eq. (9-13.1)] as being widely applicable yet reasonably accurate except for aqueous solutions. This NEL report is also an excellent source of viscosity data tabulated from the literature. Other data and literature sources for data may be found in Aasen et al. (1990), Aucejo, et al. (1995), supplementary material of Cao, et al. (1993), Franjo, et al. (1995), Kouris and Panayiotou (1989), Krishnan, et al. (1995, 1995a), Kumagai and Takahashi (1995), Petrino, et al. (1995), Stephan and Hildwein (1987), Stephan and Heckenberger (1988), Teja, et al., (1985), and Wu, et al. (1998).

Method of Grunberg and Nissan (1949)

In this procedure, the low-temperature liquid viscosity for mixtures is given as

$$\ln \eta_m = \sum_i x_i \ln \eta_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n x_i x_j G_{ij} \quad (9-13.1)$$

or, for a binary of 1 and 2,

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (9-13.2)$$

since $G_{ii} = 0$. In Eqs. (9-13.1) and (9-13.2), x is the liquid mole fraction and G_{ij} is an interaction parameter which is a function of the components i and j as well as the temperature (and, in some cases, the composition). This relation has probably been more extensively examined than any other liquid mixture viscosity correlation. Isdale (1979) presents the results of a very detailed testing using more than 2000 experimental mixture datum points. When the interaction parameter was regressed from experimental data, nonassociated mixtures and many mixtures containing alcohols, carboxylic acids, and ketones were fitted satisfactorily. The overall root mean square deviation for the mixtures tested was 1.6%. More recently, Isdale, et al. (1985) proposed a group contribution method to estimate the binary interaction parameter G_{ij} at 298 K.

The procedure to be followed is:

1. For a binary of i and j , select i by following the priority rules below. (j then becomes the second component.)

- a. i = an alcohol, if present
- b. i = an acid, if present
- c. i = the component with the most carbon atoms
- d. i = the component with the most hydrogen atoms
- e. i = the component with the most $-\text{CH}_3$ groups

$G_{ij} = 0$ if none of these rules establish a priority.

2. Once the decision has been made which component is i and which is j , calculate $\Sigma\Delta_i$ and $\Sigma\Delta_j$ from the group contributions in Table 9-12.

3. Determine the parameter W . (If either i or j contains atoms other than carbon and hydrogen, set $W = 0$ and go to step 4.) Let the number of carbon atoms in i be N_i and that in j be N_j .

$$W = \frac{(0.3161)(N_i - N_j)^2}{N_i + N_j} - (0.1188)(N_i - N_j) \quad (9-13.3)$$

4. Calculate G_{ij} from

$$G_{ij} = \Sigma\Delta_i - \Sigma\Delta_j + W \quad (9-13.4)$$

G_{ij} is sometimes a function of temperature. However, existing data suggest that, for alkane-alkane solutions or for mixtures of an associated component with an unassociated one, G_{ij} is independent of temperature. However, for mixtures of non-associated compounds (but not of only alkanes) or for mixtures of associating compounds, G_{ij} is a mild function of temperature. Isdale, et al. (1985) suggest for these latter two cases,

$$G_{ij}(T) = 1 - [1 - G_{ij}(298)] \frac{573 - T}{275} \quad (9-13.5)$$

where T is in kelvins.

Example 9-21 Estimate the viscosity of a mixture of acetic acid and acetone at 323 K (50°C) that contains 70 mole percent acetic acid. Isdale, et al. quote the experimental value to be 0.587 cP, and, at 50°C, the viscosities of pure acetic acid and acetone are 0.798 and 0.241 cP, respectively.

TABLE 9-12 Group Contributions for G_{ij} at 298 K

Group	Notes	Value of Δ_i
—CH ₃		−0.100
>CH ₂		0.096
>CH—		0.204
>C<		0.433
Benzene ring		0.766
Substitutions:		
Ortho		0.174
Meta		—
Para		0.154
Cyclohexane ring		0.887
—OH	Methanol	0.887
	Ethanol	−0.023
	Higher aliphatic alcohols	−0.443
>C=O	Ketones	1.046
—Cl		0.653−0.161 N_{Cl}
—Br		−0.116
—COOH	Acid with:	
	Nonassociated liquids	−0.411 + 0.06074 N_{C}
	Ketones	1.130
	Formic acid with ketones	0.167

N_{Cl} = number of chlorine atoms in the molecule.

N_{C} = total number of carbon atoms in both compounds.

solution First we must estimate G_{ij} at 298 K. Component i is acetic acid (priority rule b). Since the mixture contains atoms other than carbon and hydrogen (i.e., oxygen), $W = 0$. Then, with Table 9-12,

$$\Sigma\Delta_i (\text{acetic acid}) = \text{—CH}_3 + \text{—COOH} = -0.100 + 1.130 = 1.030$$

$$\Sigma\Delta_j (\text{acetone}) = (2)(\text{—CH}_3) + \text{>C=O} = (2)(-0.100) + 1.046 = 0.846$$

With Eq. (9-13.4),

$$G_{ij} = 1.030 - 0.846 = 0.184 \text{ at } 298 \text{ K}$$

At 50°C = 323 K, we need to adjust G_{ij} with Eq. (9-13.5).

$$G_{ij}(323 \text{ K}) = 1 - \frac{(1 - 0.184)(573 - 323)}{275} = 0.258$$

Then, using Eq. (9-13.2),

$$\ln \eta_m = (0.7) \ln (0.798) + (0.3) \ln (0.241) + (0.7)(0.3)(0.258) = -0.531$$

$$\eta_m = 0.588 \text{ cP}$$

This estimated value is essentially identical with the experimental result of 0.587 cP.

To summarize the Isdale modification of the Grunberg-Nissan equation, for each possible binary pair in the mixture, first decide which component is to be labeled i and which j by the use of the priority rules. Determine $\Sigma\Delta_i$ and $\Sigma\Delta_j$ by using

Table 9-12 and W from Eq. (9-13.3), if necessary. Use Eq. (9-13.4) to calculate G_{ij} . Correct for temperatures other than 298 K, if necessary, with Eq. (9-13.5). With the values of G_{ij} so determined, use either Eq. (9-13.1) or (9-13.2) to determine the viscosity of the liquid mixture. This technique yields quite acceptable estimates of low-temperature liquid mixture viscosities for many systems, but Table 9-12 does not allow one to treat many types of compounds. Also, the method does not cover aqueous mixtures.

UNIFAC-VISCO Method (Chevalier, et al., 1988; Gaston-Bonhomme, et al., 1994)

Gaston-Bonhomme, Petrino and Chevalier have modified the UNIFAC activity coefficient method (described in Chap. 8) to predict viscosities. In this method, viscosity is calculated by

$$\ln \eta_m = \sum_i x_i \ln(\eta_i V_i) - \ln V_m + \frac{\Delta^* g^{EC}}{RT} + \frac{\Delta^* g^{ER}}{RT} \quad (9-13.6)$$

The combinatorial term is the same as in the UNIQUAC model (see Table 8-8) and is calculated by

$$\frac{\Delta^* g^{EC}}{RT} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} \quad (9-13.7)$$

where z is the coordination number, equal to 10, θ_i and ϕ_i are the molecular surface area fraction and molecular volume fraction, respectively, given by

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (9-13.8)$$

and

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (9-13.9)$$

where q_i , the van der Waals' surface area, and r_i , the van der Waals' volume of component i , are found by summation of the corresponding group contributions. Thus, if $n_k^{(i)}$ is the number of groups of type k in the molecule i ,

$$q_i = \sum_k n_k^{(i)} Q_k \quad (9-13.10)$$

$$r_i = \sum_k n_k^{(i)} R_k \quad (9-13.11)$$

where Q_k and R_k are the constants representing the group surface and size and are given in Table 9-13. These values match the UNIFAC values in Table 8-23 in cases where groups are defined the same. The residual term in Eq. (9-13.6) is calculated by

TABLE 9-13 UNIFAC-VISCO, Group Volume and Surface Area Parameters

Group k	R_k	Q_k
CH ₂ , CH _{2cy}	0.6744	0.540
CH ₃	0.9011	0.848
CH _{ar}	0.5313	0.400
Cl	0.7910	0.724
CO	0.7713	0.640
COO	1.0020	0.880
OH	1.0000	1.200
CH ₃ OH	1.4311	1.432

$$\frac{\Delta^*g^{ER}}{RT} = - \sum x_i \ln \gamma_i^{*R} \quad (9-13.12)$$

where

$$\ln \gamma_i^{*R} = \sum_k n_k^{(i)} [\ln \gamma_k^* - \ln \gamma_k^{*(i)}] \quad (9-13.13)$$

and

$$\ln \gamma_k^* = Q_k \left[\left(1 - \ln \left(\sum_m \Theta_m \Psi_{mk}^* \right) \right) - \sum_m \frac{\Theta_m \Psi_{km}^*}{\sum_n \Theta_n \Psi_{nm}^*} \right] \quad (9-13.14)$$

$$\Theta_m = \frac{Q_m X_m}{\sum_k X_k Q_k} \quad (9-13.15)$$

In Eq. (9-13.15), Θ_m is the surface area fraction in the mixture of groups and X_m is the mole fraction in the mixture of groups. Except for the minus sign in Eq. (9-13.12), these last four equations are identical to those in the UNIFAC method described in Chap 8. However, the groups are chosen differently and the interaction parameters are different and are calculated by

$$\Psi_{nm}^* = \exp \left(- \frac{\alpha_{nm}}{298} \right) \quad (9-13.16)$$

Values of α_{nm} are given in Table 9-14. γ_k^* is the activity coefficient of group k in a mixture of groups in the actual mixture, and $\gamma_k^{*(i)}$ is the activity coefficient of group k in a mixture of groups formed from the groups in pure component i . Groups in branched hydrocarbons and substituted cyclic and aromatic hydrocarbons are chosen as follows

TABLE 9-14 UNIFAC-VISCO Group Interaction Parameters, α_{nm}

n/m	CH ₂	CH ₃	CH _{2cy}	CH _{ar}	Cl	CO	COO	OH	CH ₃ OH
CH ₂	0	66.53	224.9	406.7	60.30	859.5	1172.0	498.6	-219.7
CH ₃	-709.5	0	-130.7	-119.5	82.41	11.86	-172.4	594.4	-228.7
CH _{2cy}	-538.1	187.3	0	8.958	215.4	-125.4	-165.7	694.4	-381.53
CH _{ar}	-623.7	237.2	50.89	0	177.2	128.4	-49.85	419.3	-88.81
Cl	-710.3	375.3	-163.3	-139.8	0	-404.3	-525.4	960.2	-165.4
CO	586.2	-21.56	740.6	-117.9	-4.145	0	29.20	221.5	55.52
COO	541.6	-44.25	416.2	-36.17	240.5	22.92	0	186.8	69.62
OH	-634.5	1209.0	-138	197.7	195.7	664.1	68.35	0	416.4
CH ₃ OH	-526.1	653.1	751.3	51.31	-140.9	-22.59	-286.2	-23.91	0

Type of compound	Actual group	Representation
branched cyclic	$>\text{CH}-\text{CH}_3$	2 CH_2 groups
	$>\text{CH}_{\text{cy}}-\text{CH}_3$	1 $\text{CH}_{2\text{cy}}$ + 1 CH_2
	$>\text{C}_{\text{cy}}-(\text{CH}_3)_2$	1 CH_{acy} + 2 CH_2
aromatic	$>\text{C}_{\text{ar}}-\text{CH}_3$	1 CH_{ar} + 1 CH_2

Table 9-15 compares results calculated with the UNIFAC-VISCO method to experimental values. Of all the methods evaluated, the UNIFAC-VISCO method was the only one that demonstrated any success in predicting viscosities of mixtures of compounds with large size differences. The method has also been successfully applied to ternary and quaternary alkane systems. The average absolute deviation for 13 ternary alkane systems was 2.6%, while for four quaternary systems it was 3.6%. The method is illustrated in Example 9-22.

Example 9-22 Use the UNIFAC-VISCO method to estimate the viscosity of a mixture of 35.4 mole% *n*-decane (1) and 64.6 mole% *n*-tetratetracontane, $\text{C}_{44}\text{H}_{90}$ (2) at 397.49 K. The experimental viscosity and density (Aasen, et al., 1990) are 3.278 cP and 0.7447 g/cm³.

solution From Aasen, et al. (1990), $\eta_1 = 0.2938$ cP, $\eta_2 = 4.937$ cP, $V_1 = 220$ g/cm³, and $V_2 = 815.5$ g/cm³.

$$V_m = \frac{\sum_i x_i M_i}{\rho_m} = \frac{0.354 \times 142.28 + 0.646 \times 619.16}{0.7447} = 604.7 \text{ cm}^3/\text{mol}$$

In decane, there are 8 CH_2 groups and 2 CH_3 groups. In tetratetracontane, there are 42 CH_2 groups and 2 CH_3 groups. Equations (9-13.10) and (9-13.11) give

TABLE 9-15 Comparison of Calculated and Experimental Liquid Mixture Viscosities

1 st component	2 nd component	x_1	T , K	η_{exp} mPa·s	Ref*	η_{calc} mPa·s	% deviation
<i>n</i> -C ₁₀ H ₂₂	<i>n</i> -C ₆₀ H ₁₂₂	0.749	384.1	3.075	1	2.309	-25
		0.749	446.4	1.423	1	1.275	-10
		0.354	368.8	5.286	1	5.256	-0.6
		0.354	464.1	1.465	1	1.654	13
		0.695	374.1	2.318	1	1.960	-15
butane	squalane	0.839	293.1	1.060	2	0.8812	-17
ethanol	benzene	0.5113	298.1	0.681	3	0.6403	-6.0
acetone	benzene	0.3321	298.1	0.4599	4	0.4553	-1.0
acetone	ethanol	0.3472	298.1	0.5133	5	0.4860	-5.3

*References: 1, Aasen, et al. (1990); 2, Kumagai and Takahashi (1995); 3, Kouris and Panayiotou (1989); 4, Petrino, et al. (1995); 5, Wei, et al. (1985)

$$r_1 = 8 \times 0.6744 + 2 \times 0.9011 = 7.1974$$

$$r_2 = 42 \times 0.6744 + 2 \times 0.9011 = 30.127$$

$$q_1 = 8 \times 0.54 + 2 \times 0.848 = 6.016$$

$$q_2 = 42 \times 0.54 + 2 \times 0.848 = 24.376$$

Equations (9-13.8) and (9-13.9) give

$$\theta_1 = \frac{0.354 \times 6.016}{0.354 \times 6.016 + 0.646 \times 24.376} = 0.1191, \quad \theta_2 = 0.8809$$

$$\phi_1 = \frac{0.354 \times 7.1974}{0.354 \times 7.1974 + 0.646 \times 30.127} = 0.1158, \quad \phi_2 = 0.8842$$

Equation (9-13.7) is used to calculate the combinatorial contribution

$$\begin{aligned} \frac{\Delta^* g^{EC}}{RT} &= 0.354 \ln \frac{0.1158}{0.354} + 0.646 \ln \frac{0.8842}{0.646} + 5 \left[0.354 \times 6.016 \ln \frac{0.1191}{0.1158} \right. \\ &\quad \left. + 0.646 \times 24.376 \ln \frac{0.8809}{0.8842} \right] \\ &= 0.1880 \end{aligned}$$

In the mixture of groups, with CH_2 designated by subscript 1 and CH_3 by subscript 2:

$$\begin{aligned} X_1 &= \frac{8 \times 0.354 + 42 \times 0.646}{8 \times 0.354 + 42 \times 0.646 + 2 \times 0.354 + 2 \times 0.646} = 0.9374, \\ X_2 &= 0.0626 \end{aligned}$$

Equation (9-13.15) gives

$$\Theta_1 = \frac{0.9374 \times 0.54}{0.9374 \times 0.54 + 0.0626 \times 0.848} = 0.9051, \quad \Theta_2 = 0.0949$$

Equation (9-13.16) gives

$$\Psi_{12}^* = \exp\left(-\frac{66.53}{298}\right) = 0.7999, \quad \Psi_{21}^* = \exp\left(\frac{709.5}{298}\right) = 10.81$$

Equation (9-13.14) gives

$$\begin{aligned} \ln \gamma_1^* &= 0.54 \left[1 - \ln(0.9051 + 0.0949 \times 10.81) - \frac{0.9051}{0.9051 + 0.0949 \times 10.81} \right. \\ &\quad \left. - \frac{0.0949 \times 0.7999}{0.9051 \times 0.7999 + 0.0949} \right] \\ &= -0.1185 \end{aligned}$$

Similarly, $\ln \gamma_2^* = -3.3791$

In the mixture of groups from pure component 1, $X_1^{(1)} = 0.8$, and $X_2^{(1)} = 0.2$. Using Eq. (9-13.15) for pure component 1 then gives

$$\Theta_1^{(1)} = \frac{0.8 \times 0.54}{0.8 \times 0.54 + 0.2 \times 0.848} = 0.7181, \quad \Theta_2^{(1)} = 0.2819$$

$$\ln \gamma_i^{*(1)} = 0.54 \left[1 - \ln(0.7181 + 0.2819 \times 10.81) - \frac{0.7181}{0.7181 + 0.2819 \times 10.81} - \frac{0.2819 \times 0.7999}{0.7181 \times 0.7999 + 0.2819} \right]$$

$$= -0.4212$$

Similarly, $\gamma_2^{*(1)} = -1.0479$. In pure component 2, the results are $\Theta_1^{(2)} = 0.9304$, $\Theta_2^{(2)} = 0.0696$, $\ln \gamma_1^{*(2)} = -0.07655$, and $\ln \gamma_2^{*(2)} = -4.1201$. Equation (9-13.13) gives

$$\ln \gamma_i^{*R} = 8 \times (-0.1185 + 0.4212) + 2(-3.3791 + 1.0479) = -2.241$$

$$\ln \gamma_2^{*R} = 42(-0.1185 + 0.07655) + 2(-3.3791 + 4.1201) = -0.2799$$

Finally, the residual contribution is calculated with Eq. (9-13.12)

$$\frac{\Delta^* g^{ER}}{RT} = -(-0.354 \times 2.241 - 0.646 \times 0.2799) = 0.9741$$

Equation (9-13.6) is now used to calculate the mixture viscosity

$$\begin{aligned} \ln \eta_m &= 0.354 \ln (0.2938) + 0.646 \ln (4.937) + 0.354 \ln (220) \\ &\quad + 0.646 \ln (815.5) - \ln (604.7) - 0.1880 + 0.9741 \\ \eta_m &= 3.385 \text{ cP} \\ \text{Error} &= \frac{3.385 - 3.278}{3.278} \times 100 = 3.26\% \end{aligned}$$

Method of Teja and Rice (1981, 1981a)

Based on a corresponding-states treatment for mixture compressibility factors (Teja, 1980; Teja and Sandler, 1980) (See chap. 5), Teja and Rice proposed an analogous form for liquid mixture viscosity.

$$\ln(\eta_m \varepsilon_m) = \ln(\eta \varepsilon)^{(R1)} + [\ln(\eta \varepsilon)^{(R2)} - \ln(\eta \varepsilon)^{(R1)}] \frac{\omega_m - \omega^{(R1)}}{\omega^{(R2)} - \omega^{(R1)}} \quad (9-13.17)$$

where the superscripts (R1) and (R2) refer to two reference fluids. η is the viscosity, ω the acentric factor, and ε is a parameter similar to ξ in Eq. (9-4.15) but defined here as:

$$\varepsilon = \frac{V_c^{2/3}}{(T_c M)^{1/2}} \quad (9-13.18)$$

The variable of composition is introduced in four places: the definitions of ω_m , V_{cm} ,

T_{cm} , and M_m . The rules suggested by the authors to compute these mixture parameters are:

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \quad (9-13.19)$$

$$T_{cm} = \frac{\sum_i \sum_j x_i x_j T_{cij} V_{cij}}{V_{cm}} \quad (9-13.20)$$

$$M_m = \sum_i x_i M_i \quad (9-13.21)$$

$$\omega_m = \sum_i x_i \omega_i \quad (9-13.22)$$

$$V_{cij} = \frac{(V_{ci}^{1/3} + V_{cj}^{1/3})^3}{8} \quad (9-13.23)$$

$$T_{cij} V_{cij} = \psi_{ij} (T_{ci} T_{cj} V_{ci} V_{cj})^{1/2} \quad (9-13.24)$$

ψ_{ij} is an interaction parameter of order unity which must be found from experimental data.

It is important to note that, in the use of Eq. (9-13.17) for a given mixture at a specified temperature, the viscosity values for the two reference fluids $\eta^{(R1)}$ and $\eta^{(R2)}$ are to be obtained *not at T* , but at a temperature equal to $T[(T_c)^{(R1)}/T_{cm}]$ for (R1) and $T[(T_c)^{(R2)}/T_{cm}]$ for (R2). T_{cm} is given by Eq. (9-13.20).

Whereas the reference fluids (R1) and (R2) may be chosen as different from the actual components in the mixture, it is normally advantageous to select them from the principal components in the mixture. In fact, for a binary of 1 and 2, if (R1) is selected as component 1 and (R2) as component 2, then, by virtue of Eq. (9-13.22), Eq. (9-13.17) simplifies to

$$\ln(\eta_m \varepsilon_m) = x_1 \ln(\eta \varepsilon)_1 + x_2 \ln(\eta \varepsilon)_2 \quad (9-13.25)$$

but, as noted above, η_1 is to be evaluated at $T(T_{c1}/T_{cm})$ and η_2 at $T(T_{c2}/T_{cm})$.

Our further discussion of this method will be essentially limited to Eq. (9-13.25), since that is the form most often used for binary liquid mixtures and, by this choice, one is assured that the relation gives correct results when $x_1 = 0$ or 1.0. In addition, the assumption is made that the interaction parameter ψ_{ij} is not a function of temperature or composition.

The authors claim good results for many mixtures ranging from strictly nonpolar to highly polar aqueous-organic systems. For nonpolar mixtures, errors averaged about 1%. For nonpolar-polar and polar-polar mixtures, the average rose to about 2.5%, whereas for systems containing water, an average error of about 9% was reported.

In comparison with the Grunberg-Nissan correlation [Eq. (9-13.1)], with G_{ij} found by regressing data, Teja and Rice show that about the same accuracy is achieved for both methods for nonpolar-nonpolar and nonpolar-polar systems, but their technique was significantly more accurate for polar-polar mixtures, and particularly for aqueous solutions for which Grunberg and Nissan's form should not be used.

Example 9-23 Estimate the viscosity of a liquid mixture of water and 1,4-dioxane at 60°C when the mole fraction water is 0.83. For this very nonideal solution, Teja and Rice suggest an interaction parameter $\psi_{ij} = 1.37$. This value was determined by regressing data at 20°C.

solution From Appendix A, for water, $T_c = 674.14$ K, $V_c = 55.95$ cm³/mol, and $M = 18.02$; for 1,4-dioxane, $T_c = 587$ K, $V_c = 238$ cm³/mol, and $M = 88.11$. Let 1 be water and 2 be 1,4-dioxane. With Eq. (9-13.18), $\varepsilon_1 = (55.95)^{2/3}/[(647.14)(18.02)]^{1/2} = 0.135$; $\varepsilon_2 = 0.169$. From Eq. (9-13.19),

$$V_{cm} = (0.830)^2(55.95) + (0.170)^2(238) + (2)(0.830)(0.170) \times \frac{[(55.95)^{1/3} + (238)^{1/3}]^3}{8}$$

$$= 80.93 \text{ cm}^3/\text{mol}$$

and with Eq. (9-13.20),

$$T_{cm} = \{ (0.830)^2(647.14)(55.95) + (0.170)^2(587)(238) + (2)(0.830)(0.170)(1.37) [(647.14)(55.95)(587)(238)]^{1/2} \} / 81.29 = 697.9 \text{ K}$$

$$M_m = (0.830)(18.02) + (0.170)(88.11) = 29.94$$

So, with Eq. (9-13.18),

$$\varepsilon_m = \frac{(80.93)^{2/3}}{[(697.9)(29.94)]^{1/2}} = 0.129$$

Next, we need to know the viscosity of water not at 333.2 K (60°C), but at a temperature of $(333.2)(647.14)/697.9 = 309.0$ K (35.8°C). This value is 0.712 cP (Irving, 1977a). [Note that, at 60°C, η (water) = 0.468 cP.] For 1,4-dioxane, the reference temperature is $(333.2)(587)/697.9 = 280.3$ K (7.1°C), and at that temperature, $\eta = 1.63$ cP (Irving, 1977a). Again this value is quite different from the viscosity of 1,4-dioxane at 60°C, which is 0.715 cP. Finally, with Eq. (9-13.25),

$$\ln[(\eta_m)(0.129)] = (0.830) \ln[(0.712)(0.135)] + (0.170) \ln[(1.63)(0.169)]$$

$$= -2.163$$

$$\eta_m = 0.891 \text{ cP}$$

The experimental viscosity is 0.89 cP.

Although the agreement between the experimental and estimated viscosity in Example 9-23 is excellent, in other composition ranges, higher errors occur. In Fig. 9-14, we have plotted the estimated and experimental values of the mixture viscosity over the entire range of composition. From a mole fraction water of about 0.8 (weight fraction = 0.45) to unity, the method provides an excellent fit to experimental results. At smaller concentrations of water, the technique overpredicts η_m . Still, for such a nonideal aqueous mixture, the general fit should be considered good.

Discussion

Three methods have been introduced to estimate the viscosity of liquid mixtures: the Grunberg-Nissan relation [Eq. (9-13.1)], the UNIFAC-VISCO method [Eq. (9-13.6)] and the Teja-Rice form [Eq. (9-13.24)]. The Grunberg-Nissan and Teja-Rice forms contain one adjustable parameter per binary pair in the mixture. The

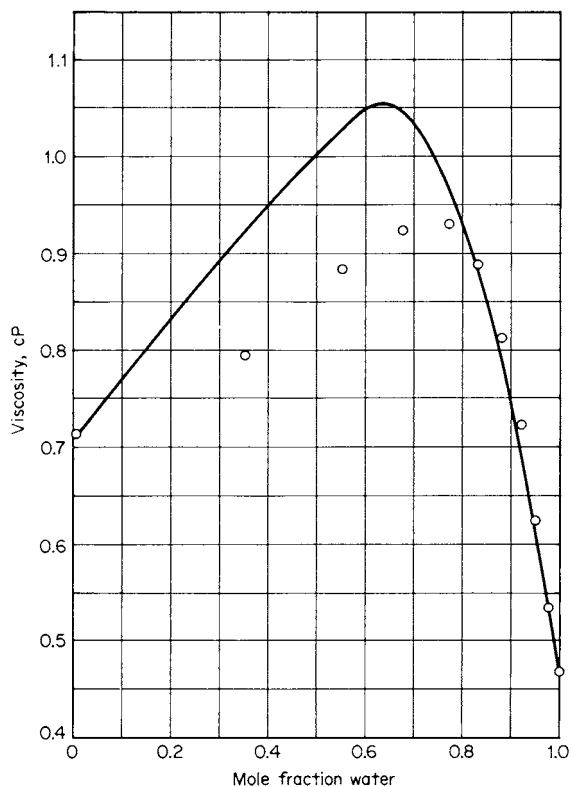


FIGURE 9-14 Viscosity of water and 1,4-dioxane at 333 K. Line is Eq. (9-13.25) with $\psi_{ij} = 1.37$; o experimental. (Irving, 1977a)

UNIFAC-VISCO method is predictive, but limited in the types of compounds to which it can be applied. The method correctly predicts the behavior of the methanol-toluene system which demonstrates both a maximum and minimum in the viscosity vs. concentration curve (Hammond, et al., 1958). An approximate technique is available to estimate the Grunberg-Nissan parameter G_{ij} as a function of temperature [Eq. (9-13.5)] for many types of systems. Teja and Rice suggest that their parameter ψ_{ij} is independent of temperature—at least over reasonable temperature ranges. This latter technique seems better for highly polar systems, especially if water is one of the components, and it has also been applied to undefined mixtures of coal liquids (Teja, et al., 1985; Thurner, 1984) with the introduction of reference components [See Eq. (9-13.16)]. The UNIFAC-VISCO method has been successfully applied to ternary and quaternary alkane mixtures (Chevalier, et al., 1988) but otherwise, evaluation of the above methods for multicomponent mixtures has been limited.

The above three methods are by no means a complete list of available methods. For example, Twu (1985, 1986) presents an equation to estimate the viscosity of petroleum fractions based on the specific gravity and boiling point. This method is

particularly useful for cases where the exact chemical composition of a mixture is unknown. Allan and Teja (1991) have also presented a method applicable to petroleum fractions and (Chhabra, 1992) presents a method for mixtures of hydrocarbons. Chhabra and Sridhar (1989) extend Eq. (9-11.6) to mixtures. For the treatment of electrolyte solutions, the reader is referred to Lencka, et al. (1998). Cao, et al. (1993) presented a UNIFAC-based method but our testing did not reproduce their excellent results in a number of cases. Other mixture correlations are reviewed in Monnery, et al. (1995) as well as the 4th edition of this book. For an example of gases dissolved in liquids under pressure, see Tilly, et al. (1994).

An equation developed by McAllister (1960) has been used successfully to correlate data for binary as well as multicomponent mixtures (Aminabhavi, et al., 1982; Aucejo, et al, 1995; Dizechi and Marschall, 1982a; Noda, et al., 1982). For binaries, the McAllister (1960) equation has been written to contain either two or three adjustable parameters. For ternary mixtures, the equation has been used with one (Dizechi and Marschall, 1982a) or three (Noda, et al., 1982) ternary parameters in addition to the binary parameters. Dizechi and Marschall (1982) have extended the equation to mixtures containing alcohols and water and Asfour, et al. (1991) have developed a method to estimate the parameters in the McAllister equation from pure component properties. Because of the variable number of parameters that can be introduced into the McAllister equation, it has had considerable success in the correlation of mixture viscosity behavior.

Lee, et al. (1999) used an equation of state method to successfully correlate the behavior of both binary and multicomponent mixtures. Nonaqueous mixtures required one parameter per binary while aqueous mixtures required two parameters per binary. One drawback of their method is the non-symmetrical mixing rule used for multicomponent aqueous mixtures (Michelsen and Kistenmacher, 1990). The equation of state structure allowed the method to be successfully applied to liquid mixtures at high pressure.

To finish this section, we again reiterate that the methods proposed should be limited to situations in which the reduced temperatures of the components comprising the mixture are less than about 0.7, although the exact temperature range of the Teja-Rice procedure is as yet undefined.

Should one desire the viscosity of liquid mixtures at high pressures and temperatures, it is possible to employ the Chung, et al. (1988) method described in Sec. 9-7 to estimate high-pressure gas mixture viscosities. This recommendation is tempered by the fact that such a procedure has been only slightly tested, and usually with rather simple systems where experimental data exist.

Recommendations to Estimate the Viscosities of Liquid Mixtures

To estimate low-temperature liquid mixture viscosities, either the Grunberg-Nissan equation [Eq. (9-13.1) or (9-13.2)], the UNIFAC-VISCO method [Eq. (9-13.6)] or the Teja-Rice relation [Eq. (9-13.17) or (9-13.25)] may be used. The Grunberg-Nissan and Teja-Rice methods require some experimental data to establish the value of an interaction parameter specific for each binary pair in the mixture. In the absence of experimental data, the UNIFAC-VISCO method is recommended if group interaction parameters are available. The UNIFAC-VISCO method is particularly recommended for mixtures in which the components vary greatly in size. It is possible to estimate the Grunberg-Nissan interaction parameter G_{ij} by a group contribution technique and this technique can be applied to more compounds than can the UNIFAC-VISCO method. All three methods are essentially interpolative in

nature, so viscosities of the pure components comprising the mixture must be known (or in the Teja-Rice procedure, one may instead use reference fluids of similar structure rather than the actual mixture components). The errors to be expected range from a few percent for nonpolar or slightly polar mixtures to 5 to 10% for polar mixtures. With aqueous solutions, neither the Grunberg-Nissan form nor the UNIFAC-VISCO method is recommended.

NOTATION

a^*	group contribution sum; Eq. (9-4.22)
b_o	excluded volume, $(2/3)\pi N_o \sigma^3$, Eq. (9-6.1)
C_v	heat capacity at constant volume, J/(mol·K); C_i , structural contribution in Eq. (9-4.22) and Table 9-3 C_{br} , number of carbon atoms in a branch
D	diffusion coefficient, cm^2/s or m^2/s
F_c	shape and polarity factor in Eq. (9-4.11); F_p^o , low-pressure polar correction factor in Eq. (9-4.18); F_Q^o , low-pressure quantum correction factor in Eq. (9-4.19); F_p , high-pressure polar correction factor in Eq. (9-6.10); F_Q , high-pressure quantum correction factor in Eq. (9-6.11)
g_{ij}	radial distribution function, Eq. (9-7.14)
G_1, G_2	parameters in Eqs. (9-6.21) and (9-6.22); G_{ij} parameter in Eq. (9-13.1)
$\Delta^* g^{EC}$	combinatorial contribution to viscosity in Eq. (9-13.6)
$\Delta^* g^{ER}$	residual contribution to viscosity in Eq. (9-13.6)
k	Boltzmann's constant
L	mean free path
m	mass of molecule
M	molecular weight
n	number density of molecules; number of components in a mixture
N	number of carbon atoms or parameter in Eq. (9-11.2); ΔN , structural contribution in Eq. (9-11.5) and Table 9-10; N_o , Avogadro's number
P	pressure, N/m ² or bar (unless otherwise specified); P_c , critical pressure; P_r , reduced pressure, P/P_c ; P_{vp} , vapor pressure; $\Delta P_r = (P - P_{vp})/P_c$
q_i	surface area parameter for molecule i
Q	polar parameter in Eq. (9-6.5); Q_k , surface area parameter of group k
r	distance of separation; r_i , volume of molecule i
R	gas constant, usually 8.314 J/(mol · K), R_η , parameter in Eq. (9-6.4); R_k , volume parameter of group k
T^*	kT/ϵ
T	temperature, K; T_c , critical temperature; T_r , reduced temperature, T/T_c ; T_b , boiling point temperature; T_{fp} , melting point temperature
v	molecular velocity
V	volume, cm^3/mol ; V_c , critical volume; V_r , reduced volume, V/V_c , or in Eq. (9-6.3), V/V_o ; V_o , hard packed volume used in Eq. (9-6.3) or parameter in Eq. (9-11.6)
x	mole fraction, liquid
y	mole fraction, vapor; parameter in Eq. (9-6.20)

Y	parameter in Eq. (9-6.9)
Z	compressibility factor; Z_c , critical compressibility factor; Z_1 , Z_2 , parameters in Eqs. (9-6.6) to (9-6.8)

Greek

γ	orientation factor in the Brulé-Starling method, Table 9-8, or obtain from Brulé-Starling (1984)
Δ	correction term in Eq. (9-6.17)
ε	energy-potential parameter; variable defined in Eq. (9-13.18)
η	viscosity (usually in micropoises for gas and in centipoises for liquids); η^o , denotes value at low-pressure (about 1 bar); η_c , at the critical point; η_c^* , at the critical temperature but at about 1 bar; η^* , η^{**} , parameters in Eqs. (9-6.19) and (9-6.23), η_r , reduced viscosity, defined in either Eq. (9-4.13) or (9-6.4), η_b , at the normal boiling point temperature
θ_i, Θ_k	surface area fraction of molecule i or group k
κ	polar correction factor in Eq. (9-4.11), see Table 9-1
λ	thermal conductivity, W/(m · K)
μ	dipole moment, debyes; μ_r , dimensionless dipole moment defined in either Eq. (9-4.12) or Eq. (9-4.17)
ν	kinematic viscosity, η/ρ , m ² /s
ξ	inverse viscosity, defined in Eq. (9-4.14) or Eq. (9-4.15); ξ_T , inverse viscosity defined in Eq. (9-6.13)
ϕ_i	volume fraction of molecule i
ρ	density (usually mol/cm ³); ρ_c critical density; ρ_r , reduced density, ρ/ρ_c
σ	molecular diameter, Å
ψ	intermolecular potential energy as a function of r
Ψ	radial distribution function
ψ_{ij}	interaction parameter in Eq. (9-13.24)
ω	acentric factor, Sec. 2-3
Ω_v	collision integral for viscosity

Subscripts

i, j, k	components i, j, k
1, 2	components 1, 2
L	liquid
m	mixture
SL	saturated liquid

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