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Part II. Mixtures

The free volume equation for liquid viscosities is generalized to multicomponent mixtures. No experimental mixture data are needed in order to use the correlation. Calculated viscosities for liquid mixtures composed of molecules which approximately obey the Lennard-Jones 6, 12 potential law show very good agreement with experimental data for eight binary systems.

A method of estimating the viscosity of liquid mixtures should represent an extension of a satisfactory treatment of pure liquids (*1*), and its use should require only pure component data. In Part I of this work (*2*), the viscosity equation (1) proposed by Macedo and Litovitz (*3*) was shown to predict viscosities of simple liquids for $\rho \geqq 2\rho_c$, provided that allowance was made for the temperature dependence of V_o and for the volume dependence of E_v. In this part the theory is extended to mixtures. As before, attention is restricted to liquids composed of simple, nonpolar molecules, whose potential interactions may be expected to approximately obey the Lennard-Jones 6, 12 law.

MIXING RULE FOR E_v

A mixture containing molecular species 1, 2, ... i, j .... r is assumed. The simple model of a molecular jump used for pure components in part I is used here for mixtures (Figure 3 of part I), with the following additional assumptions:

1. The molecules are randomly mixed. This assumption is known to be a good approximation for many simple liquid mixtures (*4*).
2. The intermolecular distances r_1 and r_2 are independent of the molecular species involved. However, these distances will vary with composition as the molal volume changes.

Consider a molecule of species i in the process of making a jump. The most probable number of molecules of type j contained in the ring of surrounding molecules will be $x_j z$, using assumption 1. The activation energy is

$$e_v{}^i = \sum_{j=1}^{r} x_j e_v{}^{ij}$$

where

$$e_v{}^{ij} = z\,[\phi_{ij}(r_2) - \phi_{ij}(r_1)] \qquad (1)$$

and $\phi_{ij}(r)$ is the intermolecular potential energy for an $i - j$ pair at a separation r. The fraction of such jumps that involve molecules of type i is x_i, so that the average activation energy for the mixture is

$$e_v = \sum_{i=1}^{r} x_i e_v{}^i = \sum_{i=1}^{r} \sum_{j=1}^{r} x_i x_j e_v{}^{ij}$$

$$E_v = \sum_i \sum_j x_i x_j E_v{}^{ij} \qquad (2)$$

When $i = j$ the terms $E_v{}^{ij}$ are those for the pure components and they may be estimated by methods previously described (*2*). The cross-terms $E_v{}^{ij}$ arise from unlike pair interactions, and are

$$e_v^{ij} = K\epsilon_{ij}z\left\{\left[\left(\frac{\sigma_{ij}}{r_2}\right)^n - \left(\frac{\sigma_{ij}}{r_2}\right)^6\right] - \left[\left(\frac{\sigma_{ij}}{r_1}\right)^n - \left(\frac{\sigma_{ij}}{r_1}\right)^6\right]\right\} \qquad (3)$$

Define

$$\delta = \alpha\sigma_{ij}^3/v_m^{ij}$$

$$\psi = KT_m^{ij}/\epsilon_{ij}$$

The last two equations serve to define melting parameters characteristic of unlike pair interactions. Introducing these relationships in Equation (3),

$$e_v^{ij} = \frac{KkT_m^{ij}z}{\psi}\left\{\left[\left(\frac{\delta v_m^{ij}}{\beta v}\right)^{n/3} - \left(\frac{\delta v_m^{ij}}{\beta v}\right)^2\right] - \left[\left(\frac{\delta v_m^{ij}}{v}\right)^{n/3} - \left(\frac{\delta v_m^{ij}}{v}\right)^2\right]\right\}$$

If n, β, δ, ψ, and z are constant for a group of molecules it follows that

$$E_v^{ij*} = E_v^{ij*}\ (V^*) \qquad (4)$$

where

$$E_v^{ij*} = E_v^{ij}/RT_m^{ij}, \quad V^* = V/V_m^{ij} \qquad (5)$$

It is therefore possible to calculate E_v^{ij} from the corresponding states relationship presented for pure components (Figure 4 of part I) if T_m^{ij} and V_m^{ij} are available. Assuming the usual mixing rules for the potential parameters,

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad \text{and} \quad \epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$$

the melting parameters for unlike pair interactions are

$$V_m^{ij} = \frac{\tilde{N}\alpha}{\delta}\sigma_{ij}^3 = \left(\frac{V_m^{ii\ 1/3} + V_m^{jj\ 1/3}}{2}\right)^3 \qquad (6)$$

$$T_m^{ij} = \frac{\psi}{k}\epsilon_{ij} = (T_m^{ii}T_m^{jj})^{1/2} \qquad (7)$$

MIXING RULE FOR V_o

The term V_o is determined by the separation distance between molecules on collision, which is in turn determined by the pair interaction. Suppose that V_o^{ij} represents a value characteristic of $i - j$ interactions. For a molecule of species i jumping, the average value of V_o will be

$$V_o^i = \sum_{j=1}^{r} x_jV_o^{ij}$$

and the average value of V_o for the mixture will be

$$V_o = \sum_{i=1}^{r}\sum_{j=1}^{r} x_ix_jV_o^{ij} \qquad (8)$$

For $i = j$, V_o^{ij} is the value for the pure component, and may be obtained from the corresponding states correlation presented previously (*2*). For unlike pair collisions, the distance separating molecular centers should be given by the arithmetic mean of the molecular diameters, to a good approximation. A satisfactory mixing rule for V_o^{ij} should therefore be

$$V_o^{ij} = \left(\frac{V_o^{ii\ 1/3} + V_o^{jj\ 1/3}}{2}\right)^3 \qquad (9)$$

MIXING RULE FOR A_o

The derivation of the free volume equation for viscosity does not clearly specify the nature of the pre-exponential factor (*2, 5*), and it is not possible to establish an *a priori* mixing rule for A_o. However, it is possible to write an *ad hoc* relationship. Thus, a mole fraction average may be used,

$$A_o = \sum_{i=1}^{r} x_iA_o^{ii} \qquad (10)$$

where A_o^{ii} is the value for pure i.

COMPARISON WITH EXPERIMENT

Reported experimental studies of the viscosity of simple liquid mixtures appear to be limited to binary systems at atmospheric pressure, or along the liquid saturation curve. In testing the free volume equations for mixtures the following step-by-step procedure was used:

1. Values of T_m^{12} and V_m^{12} were calculated from pure component melting parameters using Equations (6) and (7).
2. The reduced volume, V/V_m, was calculated for each type of potential interaction. Only in a few instances are experimental values of the solution molal volume V available for these systems. In such cases the excess volumes are small, amounting to less than 0.5% of the molal volume in all cases. Values of V were therefore estimated from pure component data by assuming excess volumes to be zero.
3. Using these reduced volumes together with the melting temperatures, values of E_v^{11}, E_v^{12}, and E_v^{22} were obtained from curve A in Figure 4 of part I, and the mixture activation energy obtained from Equation (2).
4. Values of V_o^{11} and V_o^{22} were determined at $T^* = 1$ from

TABLE 1. DATA SOURCES AND COMPARISON WITH THEORY

Mixture	Temperature range (°K.)	Molal volume range (cc. mole^1)	Density reference	Viscosity reference	Number of points	Avg. % error
Ar-CH_4	81-96	28-36	*6, 12, 13, 15*	*7*	33	3.4
Ar-Kr	84-123	28-35	*6, 12, 13*	*8*	29	1.9
Kr-CH_4	91-123	34-38	*6, 12, 13*	*7*	39	2.7
Ar-O_2	75-92	26-29	*6, 12, 13, 16*	*9, 10*	76	10.6
CH_4-CD_4	91-114	35-38	*6, 9, 13*	*9*	22	4.9
N_2-O_2	65-110	33-45	*6, 13, 14*	*11*	23	15.2
N_2-CH_4	65-131	32-45	*6, 13, 14*	*11*	29	8.5
N_2-CO	65-112	32-46	*6, 13, 14*	*11*	35	6.0

$$V_o^* = \frac{V_o(T^* = 1)}{V_m} = 0.554 \qquad (11)$$

V_o^{11} and V_o^{22} at the temperature in question were then calculated from Equation (4) of part I. V_o^{12} at this temperature was obtained from Equation (9), and V_o for the mixture calculated from Equation (8).

5. The value of A_o for the mixture was obtained from Equation (10), using pure component values tabulated in part I.

6. The viscosity was calculated from Equation (1) of part I.

The resulting comparison with experimental data is shown in Table 1, together with the ranges of temperature and molal volume covered. The average deviation between theory and experiment is less than 10% with the exception of the two systems containing oxygen. The somewhat larger deviations in these cases arise from discrepancies between theory and experiment for pure liquid oxygen at high densities, rather than from an unsatisfactory fit of the concentration dependence.

Figure 1 illustrates the agreement obtained between theory and experiment for the krypton-methane system. The fit to the concentration dependence is excellent, the deviations between theory and experiment arising primarily from discrepancies for pure component data.

CONCLUSIONS

The mixing rules proposed give satisfactory results for binary mixtures of simple liquids, and no experimental mixture data is needed in order to use the correlation. The present lack of experimental data precludes a comparison for multicomponent mixtures. Experimental measurements of the viscosity of liquid mixtures as a function of density (or pressure) as well as temperature are also lacking at present but would be particularly welcome, since in addition to providing a wider range of conditions over which to test the correlation they would make possible a direct test of the combining rule for activation energy.

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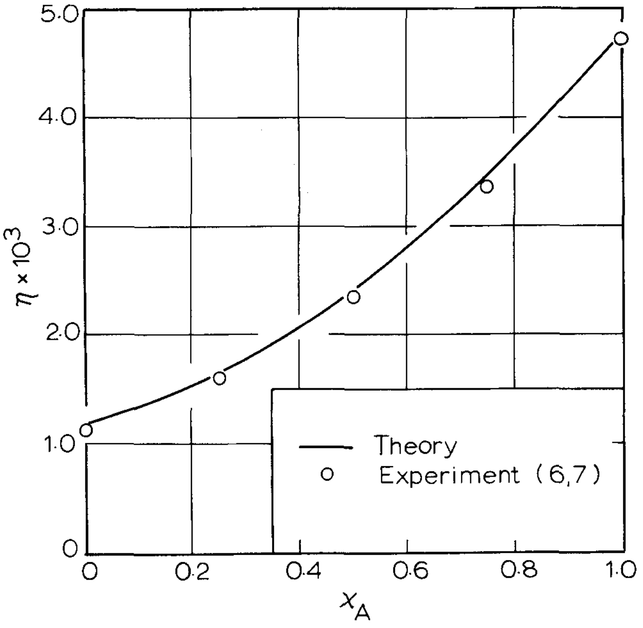

Fig. 1. Viscosity of liquid krypton-methane mixtures at 113°K.

NOTATION

A = pre-exponential factor
A_o = $A/T^{1/2}$
E_v = activation energy per mole for mixture
E_v^* = E_v/RT_m
E_v^{ij} = activation energy per mole characteristic of interactions
e_v^{ij} = activation energy per molecule characteristic of $i-j$ interactions
K = $(n/n-6)\ (n/6)^{6/(n-6)}$
k = Boltzmann constant
$\tilde{N}$ = Avogadro's number
n = repulsive exponent in $(6, n)$ potential
R = gas constant
r = distance separating two molecules
T = temperature
V = molal volume of solution = $\tilde{N}\, v$
V^* = V/V_m
V_o = minimum free volume per mole needed for molecular flow to occur
V_o^{ij} = value of V_o characteristic of $i-j$ interactions
x = mole fraction
z = number of nearest neighbors in ring

Greek Letters

α = (v/r_1^3) = constant
β = $(r_2/r_1)^3$ = constant
δ = $(\alpha\sigma^3/v_m)$ = constant
ϵ = energy parameter in $(6, n)$ potential
η = viscosity
ρ = density
ρ_c = density at critical point
σ = distance parameter in $(6, n)$ potential
ϕ = intermolecular pair potential energy
ψ = (kT_m/ϵ) = constant

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