The Viscosity of Liquid Mixtures

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The theory of viscosity of liquid mixtures presented here is based on Eyring's theory of absolute reaction rates. The most important conclusions drawn are that for liquids the free energies of activation for viscosity are additive on a number fraction or mole fraction basis and that interactions of like and unlike molecules must be considered. Methanol-toluene, benzene-toluene, and cyclohexane-heptane systems were analyzed with a three-body model and found to fit within the accuracy of the experimental data. Acetone-water mixtures fit a four-body interaction much better. Indications are that to describe acetone-water mixtures well would require consideration of seven- or eight-body interactions.

The viscosity of liquid mixtures has attracted much attention in the literature (3, 13, 14), both from the practical standpoint of wanting to be able to predict the viscosity of a mixture from the properties of the pure components and from the theoretical viewpoint of wishing to gain a clearer insight into the behavior of liquid mixtures. It has long been recognized that viscosity-composition curves are not simple functions of composition. Almost never are they linear; they may have a maximum, a minimum, neither, or both.

One of the early equations, and certainly one of the most popular, relating the absolute viscosity of a liquid to temperature (1, 2, 6) is

$$\mu = A e^{B/T} \qquad (1)$$

Eyring (5) gave the equation added theoretical significance in the following form:

$$\mu = \frac{\lambda_1 h}{\lambda_2 \lambda_3 \lambda^2} e^{\Delta G^*/RT} \qquad (2)$$

If λ is assumed equal to λ_1, and $\lambda_1 \lambda_2 \lambda_3$ is identified with the molecular volume, Equation (2) may be written as

$$\mu = \frac{hN}{V} e^{\Delta G^*/RT} \qquad (3)$$

or

$$\nu = \mu/\rho = \frac{hN}{M} e^{\Delta G^*/RT} \qquad (4)$$

Eyring's picture of shear between two layers of liquid involves the successive passage of individual molecules from one equilibrium position to another as indicated in Figure 1. Such a passage requires that either a hole or site be available. The production of such a site requires the expenditure of energy to push back other molecules. The movement of the molecule may be regarded as the passage of the system over a potential-energy barrier, related to ΔG^*.

DERIVATION OF THE CUBIC EQUATION

In a study of the viscosity of a mixture of molecules of types 1 and 2 a number of different encounters must be considered, some of which are shown in Figure 2.

The types of interaction considered in this case are only three bodied and are, in effect, all in one plane. If the two types of molecules are different in size (radius) by more than a factor of 1.5, it will probably become necessary to take into account other interactions involving more than three molecules and especially on a three-dimensional basis (instead of simply in one plane). The ratio of 1.5 to 1 in size is chosen arbitrarily. The three-body model shown in Figure 2 seems to describe the situation well for the methanol-toluene system; the ratio of molar volumes for this system is about 2.6, resulting in a ratio of the radii of approximately 1.39.

The type of interaction shown in Figure 2a would correspond to a free energy of activation of ΔG_1^*, that is for pure component 1. The interaction of Figure 2h would be characteristic of ΔG_2^*, or pure component 2. Interactions of types b, c, and d all correspond to two molecules of type 1 and one of type 2. One would expect the activation energy for types c and d to be identical; they will be referred to as ΔG_{112}^*. The free energy of activation for interaction b will be referred to as ΔG_{121}^*. Similarly energies of activation for types f and g would be equal and designated by ΔG_{122}^*, whereas type e may be designated by ΔG_{212}^*.

In any binary mixture of mole fraction x_1 the fraction of the times interactions of type a (Figure 2) would be x_1^3, as long as the number of molecules of types 1 and 2 was statistically large. Corresponding occurrences of the various types of interactions are listed below:

Type of interaction	1-1-1	1-2-1
Fraction of total occurrences	x_1^3	$x_1^2 x_2$

The assumption made here of course is that the probability for the interactions is dependent only on the concentration and not on the free energy of activation. This might well be a point to question. Perhaps the rate of each individual interaction is proportional to the energy of activation in much the same manner as the reaction rate of a

chemical reaction. It may be assumed that for the mixture there is a free energy of activation ΔG^* and further that

$$\Delta G^* = x_1^3 \Delta G_1^* + x_1^2 x_2 \Delta G_{121}^* + 2x_1^2 x_2 \Delta G_{112}^* + x_1 x_2^2 \Delta G_{212}^* + 2x_1 x_2^2 \Delta G_{122}^* + x_2^3 \Delta G_2^* \qquad (5)$$

Two additional assumptions are made at this point:

$$\Delta G_{121}^* \doteq \Delta G_{112}^* \equiv \Delta G_{12}^*, \text{ and} \qquad (6)$$

$$\Delta G_{212}^* \doteq \Delta G_{122}^* \equiv \Delta G_{21}^* \qquad (7)$$

Incorporating Equations (6) and (7) into Equation (5) results in

$$\Delta G^* = x_1^3 \Delta G_1^* + 3x_1^2 x_2 \Delta G_{12}^* + 3x_1 x_2^2 \Delta G_{21}^* + x_2^3 \Delta G_2^* \qquad (8)$$

It was necessary to make assumptions (6) and (7) because with the cubic Equation (5) it is not possible to determine four arbitrary constants. Even though ΔG_{121}^* and ΔG_{112}^* would be expected to be physically different, it is not possible to differentiate between them with viscosity-composition data alone. Equation (5) may be written

$$\Delta G^* = x_1^3 \Delta G_1^* + x_1^2 x_2 (\Delta G_{121}^* + 2\Delta G_{112}^*) + x_1 x_2^2 (\Delta G_{212}^* + 2\Delta G_{122}^*) + x_2^3 \Delta G_2^* \qquad (9)$$

in which case

$$\Delta G_{12}^* = \frac{\Delta G_{121}^* + 2\Delta G_{112}^*}{3} \qquad (10)$$

$$\Delta G_{21}^* = \frac{\Delta G_{212}^* + 2\Delta G_{122}^*}{3} \qquad (11)$$

It must be further emphasized that for certain systems the three-body, essentially planar model indicated here may have to be modified to incorporate three-dimensional, four-body (or more) interactions. The most important result of the theory proposed here is that the free energies of activation for viscosity are the additive quantity. The fact that the three-body model fits so well for several systems, as shown below, lends

2-1-1, 1-1-2	2-1-2	2-2-1, 1-2-2	2-2-2
$2x_1^2 x_2$	$x_1 x_2^2$	$2x_1 x_2^2$	x_2^3

support to the premise that, at least for certain cases, the one-dimensional approach is sufficient. For the acetone-water system discussed below, a four-body model was used. This approaches the multibody, three-dimensional problem. For this system the four-body model is much more reasonable than the three-body model discussed here.
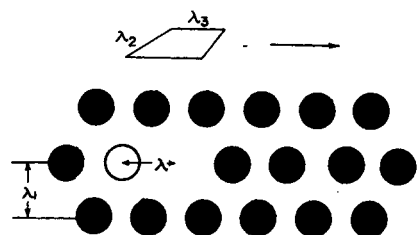
Fig. 1. Distances between molecules in a liquid (5).

The multibody model would necessitate a lengthy, if not unwieldy, equation having many constants; such an equation may be necessary for certain mixtures.

For each type of energy of activation considered here a corresponding kinematic viscosity may be assigned. For the mixture

$$\nu = \frac{hN}{M_{avg}} e^{\Delta G*/RT} \qquad (12)$$

For pure component 1

$$\nu_1 = \frac{hN}{M_1} e^{\Delta G_1*/RT} \qquad (13)$$

For interactions of types b, c, and d in Figure 2

$$\nu_{12} = \frac{hN}{M_{12}} e^{\Delta G_{12}*/RT} \qquad (14)$$

For interactions of types e, f, and g in Figure 2

$$\nu_{21} = \frac{hN}{M_{21}} e^{\Delta G_{21}*/RT} \qquad (15)$$

and for pure component 2

$$\nu_2 = \frac{hN}{M_2} e^{\Delta G_2*/RT} \qquad (16)$$

Substituting Equation (8) into (12) results in the following expression for the kinematic viscosity of the mixture:

$$\nu = \frac{hN}{M_{avg}} e^{[x_1{}^3\Delta G*_1 + 3x_1{}^2x_2\Delta G_{12}* + 3x_1x_2{}^2\Delta G_{21}* + x_2{}^3\Delta G_2*]/RT} \qquad (17)$$

Taking logarithms of Equations (13) through (17), combining to eliminate the free energies of activation, and rearranging yields

$$\ln\nu = x_1{}^3\ln\nu_1 + 3x_1{}^2x_2\ln\nu_{12} + 3x_1x_2{}^2$$
$$\ln\nu_{21} + x_2{}^3\ln\nu_2 + \ln\frac{hN}{M_{avg}} - x_1{}^3\ln\frac{hN}{M_1}$$
$$- 3x_1{}^2x_2\ln\frac{hN}{M_{12}} - 3x_1x_2{}^2\ln\frac{hN}{M_{21}}$$
$$- x_2{}^3\ln\frac{hN}{M_2} \qquad (18)$$

When one recalls that $x_1{}^3 + 3x_1{}^2x_2 + 3x_1x_2{}^2 + x_2{}^3 = (x_1 + x_2)^3 = 1.0$, Equation (18) may be written

$$\ln\nu = \theta(x) - \ln M_{avg} + x_1{}^3\ln M_1$$
$$+ 3x_1{}^2x_2\ln M_{12} + 3x_1x_2{}^2\ln M_{21}$$
$$+ x_2{}^3\ln M_2 \qquad (19)$$

The various molecular weights may be assumed to be as follows:

$$M_{avg} = x_1M_1 + x_2M_2$$

$M_{12} = (2M_1 + M_2)/3$ since these interactions involve two molecules of type 1 and one molecule of type 2.

$M_{21} = (M_1 + 2M_2)/3$ since the three-body interactions involve two molecules of type 2 and one of type 1. Substituting these quantities into Equation (19) and condensing the equation results in

$$\ln\nu = x_1{}^3\ln\nu_1 + 3x_1{}^2x_2\ln\nu_{12} + 3x_1x_2{}^2\ln\nu_{21}$$
$$+ x_2{}^3\ln\nu_2 - \ln[x_1 + x_2M_2/M_1]$$
$$+ 3x_1{}^2x_2\ln[(2 + M_2/M_1)/3]$$
$$+ 3x_1x_2{}^2\ln[(1 + 2M_2/M_1)/3]$$
$$+ x_2{}^3\ln[M_2/M_1] \qquad (20)$$

It is noted that the entire equation involves only two undetermined constants, ν_{12} and ν_{21}. Other features of the equation include the possibility of having a maximum, a minimum, neither, or both for ν as a function of x.

If $M_2/M_1 = 1.0$, the last four terms of the equation vanish. Every term of the equation contains the logarithm to the base e, and hence each term may be replaced by the logarithm to the base 10, with which it is often more convenient to work.

Further development of the equations may be made by using

$$\Delta G* = \Delta H* - T\Delta S* \qquad (21)$$

at a given temperature. Substitution of Equation (21) into Equation (12) results in

$$\nu = \frac{hN}{M_{avg}} e^{-\Delta S*/R} e^{\Delta H*/RT} \qquad (22)$$

Furthermore

$$\nu_1 = \frac{hN}{M_1} e^{-\Delta S_1*/R} e^{\Delta H_1*/RT} \qquad (23)$$

$$\nu_{12} = \frac{hN}{M_{12}} e^{-\Delta S_{12}*/R} e^{\Delta H_{12}*/RT} \qquad (24)$$

$$\nu_{21} = \frac{hN}{M_{21}} e^{-\Delta S_{21}*/R} e^{\Delta H_{21}*/RT} \qquad (25)$$

and

$$\nu_2 = \frac{hN}{M_2} e^{-\Delta S_2*/R} e^{\Delta H_2*/RT} \qquad (26)$$
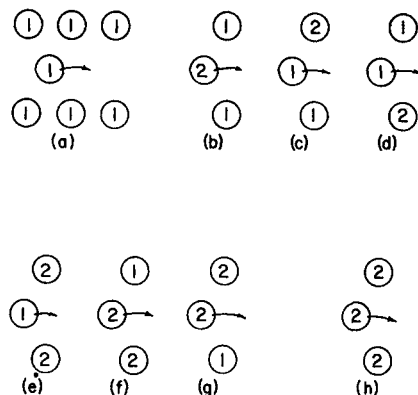

Fig. 2. Types of viscosity interactions in a binary mixture, three-body model.

Substitution of Equations (23) through (26) into Equation (20) results in an equation relating the viscosity of a liquid mixture to both composition and temperature. In such an equation the only constants not known a priori or not involving the pure components are $\Delta S_{12}*$, $\Delta S_{21}*$, $\Delta H_{12}*$, and $\Delta H_{21}*$. If these constants are assumed independent of temperature, a method is provided for extrapolating viscosity-composition data at two temperatures to other temperatures.

Forerunners to Equation (20) are those by Kendall (11); Glasstone, Laidler, and Eyring (5); Hirschfelder, Curtiss, and Bird (8); and Frenkel (3, 4). The latter was one of the first to consider interactions of molecules of 1 with 2. Frenkel's equation is

$$\ln\mu = x_1{}^2\ln\mu_1 + 2x_1x_2\ln\mu_{12} + x_2{}^2\ln\mu_2 \qquad (27)$$

Kendall's equation is

$$\ln(1/\mu) = x_1\ln(1/\mu_1) + x_2\ln(1/\mu_2) \qquad (28)$$

or

$$\ln\mu = x_1\ln\mu_1 + x_2\ln\mu_2 \qquad (29)$$

The similarity of Equations (27) and (29) to Equation (20) is at once apparent. For Equation (27) or (29) to hold, however, requires that the molal volumes of the mixture, component 1, and component 2 all be equal. This condition seldom obtains. Equation (27) can have a maximum or a minimum, but not both, as required by the experimental data for methanol-toluene mixtures (7).

TABLE 1. ENTHALPIES AND ENTROPIES OF ACTIVATION FOR VISCOSITY FOR THE METHANOL-TOLUENE SYSTEM

$\Delta H_1* = 2.27$ kcal./g.mole	$\Delta S_1* = -0.000369$ kcal./g.mole °K.
$\Delta H_{12}* = 2.64$ kcal./g.mole	$\Delta S_{12}* = -0.000511$ kcal./g.mole °K.
$\Delta H_{21}* = 2.04$ kcal./g.mole	$\Delta S_{21}* = -0.00246$ kcal./g.mole °K.
$\Delta H_2* = 1.88$ kcal./g.mole	$\Delta S_2* = -0.00364$ kcal./g.mole °K.

These constants were determined for the temperature range from 20° to 60°C.

TABLE 2. KINEMATIC VISCOSITIES FOR THE METHANOL-TOLUENE SYSTEM

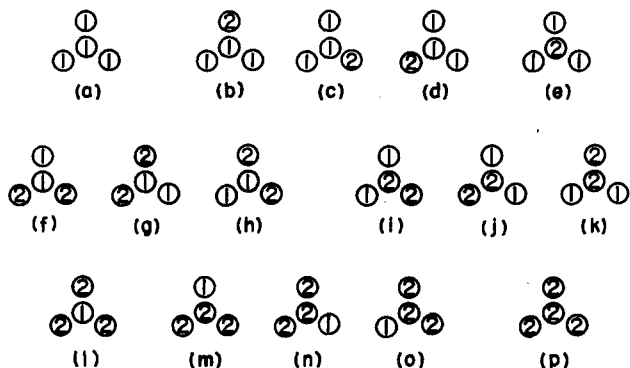|	20.00°C.	25.00°C.	37.80°C.	50.05°C.	60.11°C.
v_1, cs.	0.7373	0.6914	0.5908	0.5138	0.4590
v_{12}, cs.	0.9093	0.8609	0.7080	0.6004	0.5359
v_{21}, cs.	0.6420	0.5850	0.5195	0.4595	0.4159
v_2, cs.	0.6786	0.6414	0.5621	0.5009	0.4592

DERIVATION OF THE QUARTIC EQUATION

When one considers the movement of a molecule in a mixture from one equilibrium position to another, the three-body interactions considered above may not always be realistic. This would be especially true where the size of one component molecule is much greater than the size of the other component molecule.

The four-body model approaches more nearly a three-dimensional treatment. The interactions to be considered are shown in Figure 3. Types a and p are seen to correspond to the pure components 1 and 2 respectively. Types b, c, and d would be expected to be identical, whereas type e should be different from the previous three. Since, however, types b through e all involve three molecules of component 1 and one molecule of component 2, it is not possible to differentiate between the interactions with viscosity data alone. Six interactions are involved with two molecules of each component, interactions f through k; and four interactions are discerned with three molecules of component 2 and one of component 1, types l through o.

As before, the energies of activation for the four-body interactions are added in proportion to the fraction of the total occurrences for each interaction shown in Figure 3:

$$\Delta G^* = x_1^4 \Delta G_1^* + 4x_1^3 x_2 \Delta G_{1112}^{*\prime}$$

$$+ 6x_1^2 x_2^2 \Delta G_{1122}^{*\prime} + 4x_1 x_2^3 \Delta G_{2221}^{*\prime}$$

$$+ x_2^4 \Delta G_2^* \qquad (30)$$

In this equation $\Delta G_{1112}^{*\prime}$ is an equivalent free energy for interactions of types b, c, d, and e and does not differentiate between the first three and the last interaction. Likewise $\Delta G_{1122}^{*\prime}$ and $\Delta G_{2221}^{*\prime}$ are combinations similar to those made in Equations (10) and (11). $\Delta G_{1122}^{*\prime}$ combines the free energies of activation for types f, g, and h with those of i, j, and k. $\Delta G_{2221}^{*\prime}$ combines the free energies of activation for type l with those of types m, n, and o.

By techniques entirely analogous to the method given above, the following equation is derived:.

$$\ln v_{mix} = x_1^4 \ln v_1 + 4x_1^3 x_2 \ln v'_{1112}$$

$$+ 6x_1^2 x_2^2 \ln v'_{1122} + 4x_1 x_2^3 \ln v'_{2221}$$

$$+ x_2^4 \ln v_2 - \ln(x_1 + x_2 M_2/M_1)$$

$$+ 4x_1^3 x_2 \ln[(3 + M_2/M_1)/4]$$

$$+ 6x_1^2 x_2^2 \ln[(1 + M_2/M_1)/2]$$
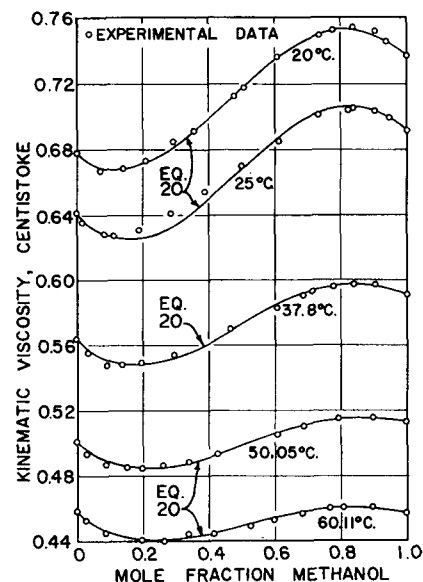
$$+ 4x_1 x_2^3 \ln[(1 + 3M_2/M_1)/4]$$

Fig. 4. Viscosity of liquid methanol-toluene mixtures.

$$+ x_2^4 \ln(M_2/M_1) \qquad (31)$$

RESULTS

Methanol-Toluene System

Equation (20) was tested first with the experimentally obtained data for the viscosity of mixtures of methanol-toluene solutions (7). The data for each temperature were used in Equation (20), and the constants v_{12} and v_{21} were determined by the method of least squares. Then, with these constants, $\ln v$ was calculated at each composition given. Noting that

The molecule in the center of each group is considered to be moving perpendicular to the page between the other three molecules

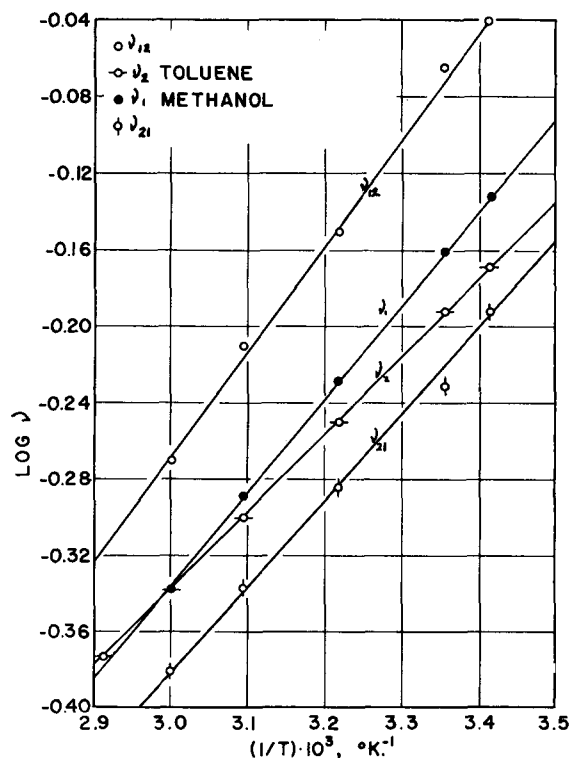Fig. 3. Types of viscosity interactions in a binary mixture, four-body model.

Fig. 5. Kinematic viscosity as a function of temperature.
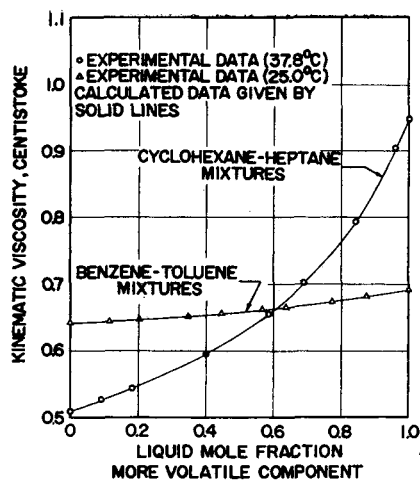
Fig. 6. Kinematic viscosities of mixtures as a function of composition.

$$\ln \nu_{calc.} - \ln \nu_{expt'l.} = \Delta \ln \nu$$

$$\dot{=} \frac{\Delta \nu}{\nu} = \frac{\nu_{calc} - \nu_{expt'l}}{\nu}$$

one can compare calculated and experimental viscosity determinations by calculating a percentage difference as 100 times $\Delta \ln \nu$. The average percentage difference at each temperature was calculated by averaging the absolute value of the difference at each composition without regard to sign. Except for three data points at 25°C. and one at 37.8°C., all the calculated viscosity values agree with the experimental data with a maximum difference of ± 0.5%. The average difference, again excepting the three points at 25°C., is about ± 0.2%, which is the same magnitude as the reported accuracy of the data (7). It may therefore be concluded that for the methanol-toluene system Equation (20) correlates the data with a high degree of precision. Figure 4 shows the viscosity-composition curves for the methanol-toluene system. The solid lines in Figure 4 were calculated from Equation (20) by the use of the ν_{12} and ν_{21} determined by the method of least squares. The circles represent the experimental data.

TABLE 3. KINEMATIC VISCOSITIES OF BENZENE-TOLUENE MIXTURES AT 25.00°C.

Mole fraction benzene x_1	Kinematic viscosity, centistoke ν
0.0000	0.6414
0.1159	0.6439
0.2032	0.6468
0.3445	0.6509
0.4476	0.6546
0.5677	0.6608
0.6394	0.6645
0.7741	0.6730
0.8772	0.6807
1.0000	0.6915

Differentiation of Equation (22) results in

$$\frac{d \ln \nu}{d(1/T)} = \Delta H^* / R + (1/RT)$$

$$\frac{d \Delta H^*}{d(1/T)} - \frac{1}{R} \frac{d \Delta S^*}{d(1/T)} \quad (32)$$

If the last two terms are negligible,

$$\frac{d \ln \nu}{d(1/T)} = \Delta H^* / R \quad (32a)$$

If both ΔH^* and ΔS^* are independent of temperature, $\ln \nu$ is a linear function of $1/T$. Figure 5 shows $\log \nu_1$, $\log \nu_2$, $\log \nu_{12}$, and $\log \nu_{21}$ as functions of $1/T$. The fact that the lines are straight over the 40-odd degrees centigrade indicates that the enthalpies and entropies of activation for viscosity are independent of temperature over this range for the methanol-toluene system.

For those systems for which $\ln \nu$ is not a linear function of the reciprocal temperature, Equation (32) must be used or else the liquid does not fit Eyring's basic model as exemplified by Equation (4). For those systems for which $\ln \nu$ is a linear function of the reciprocal temperature, Equation (32a) may be used to interpolate accurately the viscosity as a function of temperature. Table 1 presents the enthalpies and entropies of activation for viscosity for the methanol-toluene system calculated by the use of Equations (22) and (32a). Table 2 gives all the kinematic viscosities at the five temperatures listed.

Benzene-Toluene System

Precise experimental data for the kinematic viscosity of benzene-toluene mixtures at 25.00°C. are given in Table 3. The precision with which Equation (20) fits the data with a maximum difference of 0.06% and an average difference of 0.02% is certainly within the accuracy of the data. For the system at 25.00°C. ν_{12} and ν_{21} are 0.6616 and 0.6493 centistoke respectively. Figure 6 shows a line calculated from Equation (20) and gives the experimental data points (9).

Cyclohexane-Heptane System

Kinematic viscosity data are given in Table 4 for the cyclohexane-heptane system at 37.8°C. The average percentage difference is ± 0.2%, and the maximum difference is 0.5%, which is the same magnitude as the experimental accuracy of the data. For this system at 37.8°C. ν_{12} and ν_{21} are 0.6272 and 0.5782 centistoke respectively.

Acetone-Water System

One of the most nonideal systems insofar as viscosity-composition data are concerned is acetone-water. Figure 7 shows the acetone-water viscosity ex-

TABLE 4. KINEMATIC VISCOSITIES OF CYCLOHEXANE-HEPTANE MIXTURES AT 37.8°C. (9)

Mole fraction cyclohexane x_1	Kinematic viscosity, centistoke ν
0.000	0.510
0.092	0.527
0.184	0.544
0.402	0.595
0.585	0.655
0.690	0.702
0.841	0.792
0.960	0.904
1.000	0.947

perimental data (10), the data calculated according to the cubic Equation (20), and the data according to the quartic Equation (31). In each case the unknown constants were determined by the method of least squares. Equation (20) fits the data with an average deviation of 6.4%; the maximum deviation is 15.8%. Equation (31), however, has an average deviation of only 2.1% and a maximum deviation of 4.8%. It is important to notice that it is in the low acetone concentrations that both Equations (20) and (31) fit the poorest.

DISCUSSION

The accuracy with which Equation (20) fits the data for the first three systems presented is encouraging. For these three systems, at least, the model proposed seems adequate. More important, however, is the indication that it is the free energy of activation that is the additive quantity in the viscosity of mixtures. Equation (31) was not used for the data of the methanol-toluene, benzene-toluene, or cyclohexane-heptane systems. Mathematically this equation must fit the data at least
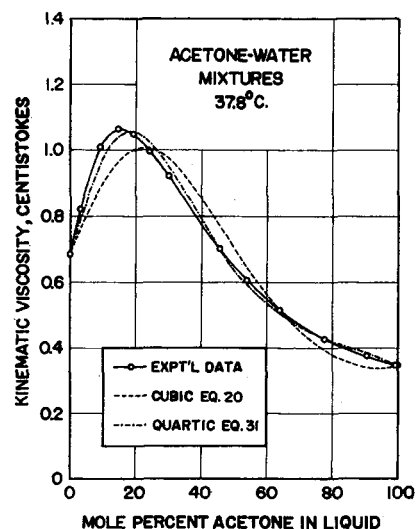

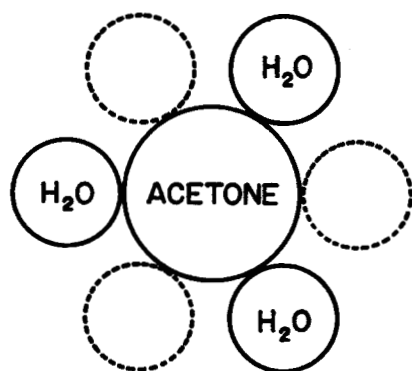Fig. 7. Comparison of acetone-water mixtures with two theoretical models.

Fig. 8. Interaction of an acetone molecule with water molecules.

as well and probably better than Equation (20). Since Equation (20) already fits within the accuracy of the experimental data, nothing could be gained by applying the quartic equation.

For those systems which do not fit Equation (20) well, as for example the acetone-water systems discussed here, a more general equation is necessary. Equation (20) is concerned only with the interactions of three molecules at a time. This is rather like a flatland description of a three-dimensional occurrence. The four-body interactions are a more accurate representation of the physical facts for mixtures whose component molecules are approximately the same size. The four-body model also enjoys the three-dimensional representation of the problem. Figure 8, however, shows that even a four-body model is unrealistic for molecules differing in size as much as acetone and water. In Figure 8 the size ratio is 1.61, which is the cube root of the ratio of the molar volumes of acetone and water. The three water molecules circled with solid lines in this figure can hardly be descriptive of the interactions involved in the movement of an acetone molecule when three additional water molecules, shown as dashed circles, do not fill all the available space around the periphery of the acetone molecule. Again the illustration shows a two-dimensional representation. On a three-dimensional basis perhaps a dozen or more molecules are affected by the movement of a single acetone molecule.

TABLE 5. SIZE RATIOS OF SYSTEMS STUDIED

System	Volumetric size ratio (molal)	Volumetric size ratio
Methanol-toluene	1/2.62	1/1.38
Benzene-toluene	1/1.20	1/1.06
Cyclohexane-heptane	1/1.21	1/1.07
Acetone-water	4.16/1	1.61/1

Where such interactions are an important fraction of the total occurrences, as in the low acetone concentrations, one would expect that at least a seventh- or eighth-order equation would be necessary to describe viscosity-concentration data accurately

For the acetone-water system it is also interesting to note that the quartic equation fits the data above 50 mole % fairly well. This might indicate that a fifth-order equation is satisfactory in this region, but an eighth-order equation might be required for the low acetone concentrations.

Not enough systems have been investigated here to indicate when it is permissible to use the cubic equation and when a more complicated equation is called for. As a rough guide, however, if the component molecules in a mixture are close to the same size, a cubic or quartic equation should adequately describe the mixtures. If the size ratio of the molecules is more than 1.5, one may expect to employ a higher order equation to describe the mixtures accurately. Table 5 gives the size ratios for the systems treated here.

The use of the kinematic viscosity in most of the equations presented here instead of the absolute viscosity has the obvious advantage of avoiding equations containing volume fractions, or volume changes on mixing, quantities which are not always known.

While it is true that many liquids do not follow Equation (3) or (4) well over the entire range of temperature possible for the liquid, there is usually some temperature range for which viscosities may be described by the methods presented here.

Many attempts have been made to relate ΔG^* to chemical structure (12, 14) for pure liquids. These attempts have been either unsuccessful or at best not entirely satisfactory. Prediction of ΔG_{12}^* and ΔG_{21}^* (or the corresponding ΔH^*'s and ΔS^*'s) is not possible at this time.

It is granted that the approach presented here is highly oversimplified, but the accuracy obtained for even the three systems discussed here is sufficiently good to make further examination and development of the theory worthwhile.

NOTATION

A, B = empirical constants
ΔG^* = molal free energy of activation for viscosity, cal./g.mole

R = gas constant, 1.987 cal./(g. mole) (°K.)
T = absolute temperature
N = Avogadro number, 6.023×10^{23} molecules/g.mole
h = Planck constant, 6.6240×10^{-27} erg.-sec./molecule
M = molecular weight, g./g.mole
e = base of natural logarithms, 2.71828 . . .
V = molal volume, cc./g.mole
x_i = mole fraction of component i in the liquid

Greek Letters

μ = absolute viscosity, poise or centipoise
ν = kinematic viscosity, stoke or centistoke. All numerical values given in this paper are in centistoke.
ρ = liquid density, g. mass/cc.
λ = average intermolecular distances between adjacent liquid molecules (Figure 1)
$\theta(x) = x_1{}^3\ln\nu_1 + 3x_1{}^2x_2\ln\nu_{12} + 3x_1x_2{}^2\ln\nu_{21} + x_2{}^3\ln\nu_2$
$\Psi(x) = -\ln[x_1 + x_2 M_2/M_1] + 3x_1{}^2x_2\ln[(2 + M_2/M_1)/3] + 3x_1x_2{}^2\ln[(1 + 2M_2/M_1)/3] + x_2{}^3\ln M_2/M_1$

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