

## AN EQUATION FOR VISCOSITY OF BINARY LIQUID MIXTURES

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Received April 25, 2001

Accepted June 18, 2001

An equation for the viscosity of binary liquid mixtures is presented. The equation is based on McAllister's four-body model by taking into account the viscosity dependence on temperature suggested by Goletz and Tassios.

**Keywords:** Viscosity; Binary liquid mixtures; McAllister's model; Thermodynamics.

Much attention has been attracted by viscosities of liquid mixtures, both from the practical standpoint of predicting the viscosity of a mixture from the properties of pure components and from the theoretical viewpoint of gaining a clearer insight into the behavior of liquid mixtures. Viscosity-composition curves are not simple functions of composition, that is to say, they may have minimum, maximum, neither minimum nor maximum or both. A theory for the prediction of the viscosity of a liquid mixture from the properties of the pure components has not been established yet, so the equations describing the viscosity of a mixture are empirical or semitheoretical<sup>1</sup>. It is obvious that such equations should correlate experimental data as closely as possible, the number of necessary experimental data should not be large to avoid costly experiments and the equation should also be as much applicable as possible.

On the basis of the Eyring theory of absolute reaction rates, McAllister proposed two equations taking into account interactions between a moving molecule and two neighboring molecules (three-body model, Fig. 1) or three neighboring molecules (four-body model, Fig. 2)<sup>2</sup>. McAllister's equation was tested for many systems and it was found that it fits the data better than other tested equations<sup>3-6</sup>. It has been extended also to ternary liquid mixtures<sup>7</sup>. McAllister based his approach on the Eyring theory, where

$$\nu = \frac{hN}{M} e^{\Delta G^*/RT} . \quad (1)$$

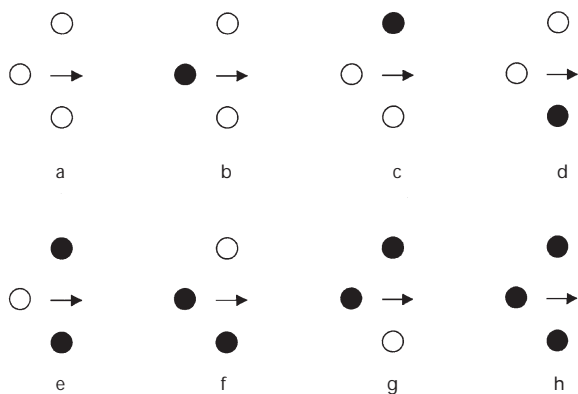


FIG. 1

The McAllister's two-body model. The arrow shows the direction of the movement. The open and full circles represent the two different types of molecules

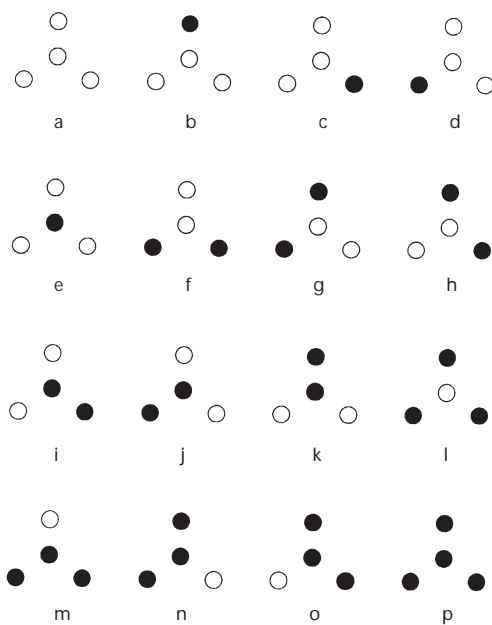


FIG. 2

The McAllister's three-body model. The direction of the movement is vertical to the plane of the page. Symbols have the same meaning as in Fig. 1

This equation assumes the Andrade-type relation between the viscosity and temperature

$$\nu = Be^{A/T} . \quad (2)$$

In the above equations  $\nu$  is the kinematic viscosity,  $h$  the Planck constant,  $N$  the Avogadro constant,  $M$  the molar mass,  $R$  the gas constant,  $\Delta G^*$  the molar Gibbs activation energy,  $T$  the absolute temperature, and  $A, B$  constants. Goletz and Tassios<sup>8</sup> proposed for the viscosity correlation to temperature an Antoine-type equation

$$\nu = Be^{A/(t+C)} , \quad (3)$$

where

$$C = 239 + Zt_b . \quad (4)$$

In the above expressions  $t$  is the temperature (in centigrades),  $t_b$  the boiling point and  $Z$  a parameter. The Goletz-Tassios equation gave very successful results for hydrocarbons and polar liquids. Dizechi and Marschall<sup>1,9</sup> followed the approach taken by Goletz and Tassios and developed the three-body model of McAllister. They introduced a new equation, giving good results, especially in polar mixtures. From this point of view, modification of the four-body model of McAllister's equation might be of interest.

#### MODIFICATION OF THE EQUATION

With the assumption that the cases b-e as well as the cases f-k and l-o of Fig. 2 are equivalent, the activation energy for each of the cases a-p would be defined as

$$\begin{aligned} \Delta G_1^* & \text{ for case a,} \\ \Delta G_{1112}^* & \text{ for cases b-e,} \\ \Delta G_{1122}^* & \text{ for cases f-k,} \\ \Delta G_{2221}^* & \text{ for cases l-o,} \\ \Delta G_2^* & \text{ for case p.} \end{aligned} \quad (5)$$

The activation energy of the mixture would be

$$\Delta G_1^* = x_1^4 \Delta G_1^* + 4x_1^3 x_2 \Delta G_{1112}^* + 6x_1^2 x_2^2 \Delta G_{1122}^* + 4x_1 x_2^3 \Delta G_{2221}^* + x_2^4 \Delta G_2^*, \quad (6)$$

where  $x$  is the mole fraction and the subscripts 1 and 2 correspond to the two components. By accepting for the correlation of the kinematic viscosity to temperature the approach (3) used by Goletz and Tassios

$$v = \frac{Nh}{M} e^{\frac{\Delta G^*}{R(C+t)}}, \quad (7)$$

the kinematic viscosity for each cases a-p would be

$$\begin{aligned} v_1 &= \frac{Nh}{M_1} e^{\frac{\Delta G_1^*}{R(C_1+t)}} \\ v_{1112} &= \frac{Nh}{M_{1112}} e^{\frac{\Delta G_{1112}^*}{R(C_{1112}+t)}} \\ v_{1122} &= \frac{Nh}{M_{1122}} e^{\frac{\Delta G_{1122}^*}{R(C_{1122}+t)}} \\ v_{2221} &= \frac{Nh}{M_{2221}} e^{\frac{\Delta G_{2221}^*}{R(C_{2221}+t)}} \\ v_2 &= \frac{Nh}{M_2} e^{\frac{\Delta G_2^*}{R(C_2+t)}}, \end{aligned} \quad (8)$$

where

$$M_{1112} = (3M_1 + M_2)/4$$

$$M_{1122} = (M_1 + M_2)/2$$

$$M_{2221} = (M_1 + 3M_2)/4$$

and

$$C_i = 239 + Z_i(t_b)_i$$

$$C_{1112} = (3C_1 + C_2)/4$$

$$C_{1122} = (C_1 + C_2)/2$$

$$C_{2221} = (C_1 + 3C_2)/4.$$

By taking the logarithm of Eq. (7) and substituting  $\Delta G^*$  from Eq. (6), one gets for the kinematic viscosity of the mixture

$$\ln v = \ln \frac{hN}{M_{av}} + \frac{1}{R(C_{av} + t)} (x_1^4 \Delta G_1^* + 4x_1^3 x_2 \Delta G_{1112}^* + 6x_1^2 x_2^2 \Delta G_{1122}^* + 4x_1 x_2^3 \Delta G_{2221}^* + x_2^4 \Delta G_2^*), \quad (9)$$

where  $M_{av} = x_1 M_1 + x_2 M_2$  and  $C_{av} = x_1 C_1 + x_2 C_2$ . Finally, taking into account Eqs (8), Eq. (9) results in

$$\begin{aligned} \ln v = & x_1^4 \frac{(C_1 + t)}{(C_{av} + t)} \ln v_1 M_1 + 4x_1^3 x_2 \frac{(C_{1112} + t)}{(C_{av} + t)} \ln v_{1112} M_{1112} + \\ & 6x_1^2 x_2^2 \frac{(C_{1122} + t)}{(C_{av} + t)} \ln v_{1122} M_{1122} + 4x_1 x_2^3 \frac{(C_{2221} + t)}{(C_{av} + t)} \ln v_{2221} M_{2221} + \\ & x_2^4 \frac{(C_2 + t)}{(C_{av} + t)} \ln v_2 M_2 - \ln M_{av} - \\ & \frac{\ln hN}{(C_{av} + t)} (x_1^4 C_1 + 4x_1^3 x_2 C_{1112} + 6x_1^2 x_2^2 C_{1122} + 4x_1 x_2^3 C_{2221} + x_2^4 C_2 - C_{av}). \end{aligned} \quad (10)$$

If the kinematic viscosities of the pure components  $v_1$  and  $v_2$ , the molar masses  $M_1$  and  $M_2$ , and the coefficients  $C_1$  and  $C_2$  are known, Eq. (10) includes three unknown coefficients  $v_{1112}$ ,  $v_{1122}$ , and  $v_{2221}$ , which can be easily determined by transforming Eq. (10) into the form

$$\begin{aligned} & \frac{(C_{av} + t)}{4x_1^3 x_2 (C_{1112} + t)} [\ln v - x_1^4 \frac{(C_1 + t)}{(C_{av} + t)} \ln v_1 M_1 - 4x_1^3 x_2 \frac{(C_{1112} + t)}{(C_{av} + t)} \ln M_{1112} - \\ & 6x_1^2 x_2^2 \frac{(C_{1122} + t)}{(C_{av} + t)} \ln M_{1122} - 4x_1 x_2^3 \frac{(C_{2221} + t)}{(C_{av} + t)} \ln M_{2221} - \\ & x_2^4 \frac{(C_2 + t)}{(C_{av} + t)} \ln v_2 M_2 + \ln M_{av} + \\ & \frac{\ln hN}{(C_{av} + t)} (x_1^4 C_1 + 4x_1^3 x_2 C_{1112} + 6x_1^2 x_2^2 C_{1122} + 4x_1 x_2^3 C_{2221} + x_2^4 C_2 - C_{av})] = \\ & \ln v_{1112} + \frac{3(C_{1122} + t)}{2(C_{1112} + t)} (\ln v_{1122}) \left( \frac{x_2}{x_1} \right) + \frac{(C_{2221} + t)}{(C_{1112} + t)} (\ln v_{2221}) \left( \frac{x_2}{x_1} \right)^2. \end{aligned} \quad (11)$$

The physical meaning of  $\nu_{1112}$ ,  $\nu_{1122}$ , and  $\nu_{2221}$  is that they represent the kinematic viscosity for the cases b–e, f–k, and l–o of Fig. 2, respectively. The parameter  $Z$ , if not known from literature, may be obtained as a value that gives the lowest deviation between the experimental and the calculated using Eq. (10) values of  $\nu$ .

Equation (10) was tested for the methanol–water system at 20 °C with data taken from ref.<sup>10</sup>.  $Z$  values were also taken from the literature<sup>8</sup>, being equal to  $-1.1$  for water and  $+0.4$  for methanol. The applicability of Eq. (10) can be seen in Fig. 3. The mean percentage deviation was 0.46% for Eq. (10), whereas it was 6.15 and 1.05% for McAllister's three- and four-body equations, respectively. Hence, the results are very encouraging.

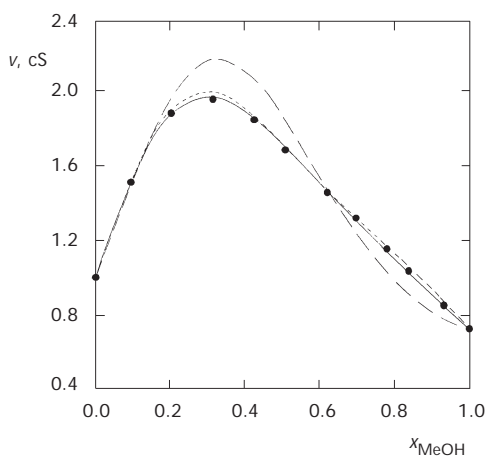


FIG. 3

Dependence of kinematic viscosity,  $\nu$ , on mole fraction,  $x_{\text{MeOH}}$ , for methanol–water system.

● Experimental points, (---) McAllister's three-body equation, (- - -) McAllister's four-body equation, (—) Eq. (10)

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