

## Prediction of the Viscosity of Liquid Mixtures

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This paper describes the application of the theoretically based scheme of Vesovic and Wakeham, modified by making use of the hard-sphere model of Dymond and Assael, to the prediction of the viscosity of liquid mixtures. The purpose of the paper is to examine this scheme in more detail than earlier to find out in what circumstances it works well and when it fails. Hence, the scheme is employed to predict, for the first time, the viscosity of a wide range of mixtures of quite disparate liquids from groups of hydrocarbons, through combinations of alcohols and hydrocarbons, to halogenated refrigerants. It is shown that, in all cases, provided that the mass ratio of the pure components is close to unity, the predictions show excellent agreement with experiment.

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**KEY WORDS:** mixtures; prediction; viscosity.

### 1. INTRODUCTION

In a series of recent papers [1–3], the theoretically based scheme of Vesovic and Wakeham was modified by making use of the hard-sphere theory of Dymond and Assael and was applied to the prediction of the viscosity of liquid mixtures. The Vesovic–Wakeham scheme was initially developed for the prediction of the viscosity of gases, and it was applied in this new form for the first time to the prediction of the viscosity of mixtures of *n*-hexane with toluene and with cyclohexane [1]. In the case of the *n*-hexane + toluene mixture, the predicted values deviated from the experimental ones by up to 22%, while in the case of the second mixture the maximum deviation was 11%. No real explanation was put forward at that time.

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To examine the power of this scheme further, accurate measurements of the viscosity and thermal conductivity of toluene+cyclopentane mixtures were performed [2, 3]. The application of the scheme to the prediction of the viscosity of this mixture produced a maximum deviation of 60%. Careful investigation of the results, however, showed that the maximum deviation was reduced to 23% when the viscosity ratio of the two pure components was less than 4. We should, moreover, state at this point of the discussion that to calculate the viscosity of the mixture, the scheme requires the viscosity of the pure components at the same temperature and molar density as those of the mixture.

The measurements of the thermal conductivity [3] of the aforementioned toluene+cyclopentane mixture showed that the scheme can predict well the experimental values when the molar volume of each component is much higher than its close-packed volume.

In this paper, a more thorough investigation of the predictive power of this scheme is attempted, aiming to establish when the scheme works well and whether this is attributed to the molecular species, the viscosity ratio, or the mass ratio of the pure components. It is shown that the scheme works excellently provided the mass ratio of the pure components is close to unity.

## 2. THEORETICAL

The Vesovic–Wakeham scheme has been described in detail in previous papers [1–3] and is only briefly presented here. According to the Vesovic–Wakeham scheme [4, 5], the viscosity  $\eta$  of a dense-gas mixture containing  $N$  components with mole fractions  $x_i$  can be expressed by the equation [6]

$$\eta(\rho_m, T) = - \left| \begin{array}{cccc} H_{11} & \cdots & H_{1N} & Y_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & \cdots & H_{NN} & Y_N \\ Y_1 & \cdots & Y_N & 0 \end{array} \right| \left| \begin{array}{ccc} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{array} \right| + \kappa_{\text{mix}} \quad (1)$$

where  $\rho_m$  is its molar density,  $T$  the absolute temperature, and

$$Y_i = x_i \left[ 1 + \sum_{j=1}^N \frac{m_j}{(m_i + m_j)} x_j a_{ij} \bar{\chi}_{ij} \rho_m \right] \quad (2)$$

$$H_{ii} = \frac{x_i^2 \bar{\chi}_{ii}}{\eta_i^0} + \sum_{\substack{j=1 \\ j \neq i}}^N \frac{x_i x_j \bar{\chi}_{ij}}{2\eta_{ij}^0 A_{ij}^*} \frac{m_i m_j}{(m_i + m_j)^2} \left( \frac{20}{3} + \frac{4m_j}{m_i} A_{ij}^* \right) \quad (3)$$

$$H_{ij(j \neq i)} = -\frac{x_i x_j \bar{\chi}_{ij}}{2\eta_{ij}^\circ A_{ij}^*} \frac{m_i m_j}{(m_i + m_j)^2} \left( \frac{20}{3} - 4A_{ij}^* \right) \quad (4)$$

$$\kappa_{\text{mix}} = \frac{3}{\pi} \rho^2 \sum_{j=1}^N \sum_{i=1}^N x_i x_j \bar{\chi}_{ij} a_{ij}^2 \eta_{ij}^\circ \quad (5)$$

In the above equations  $m_i$  and  $m_j$  are molecular masses of species  $i$  and  $j$ . The viscosity  $\eta_i^\circ$  of the pure component  $i$  in the dilute-gas limit, as well as the dilute-gas limit interaction viscosity for species  $i-j$ ,  $\eta_{ij}^\circ$ , can be calculated from [7]

$$\eta_{ij}^\circ = \frac{5}{16} \left[ \frac{2m_i m_j}{(m_i + m_j)} \frac{k_B T}{\pi} \right]^{1/2} \frac{1}{\sigma_{ij}^2 \Omega_{ij}^*(T^*)} \quad (6)$$

where

$$\ln \Omega_{ij}^*(T^*) = \sum_{k=0}^4 b_k [\ln(k_B T / \varepsilon_{ij})]^k \quad (7)$$

In these equations,  $k_B$  is the Boltzmann constant,  $\sigma_{ij}$  and  $\varepsilon_{ij}/k_B$  are the length and energy scaling parameters, and coefficients  $b_k$  are given in Table I.  $A_{ij}^*$  is a weak functional of the intermolecular potential for the  $i-j$  interaction, and it is obtained from [7]

$$\ln A_{ij}^*(T^*) = \sum_{k=0}^4 c_k [\ln(k_B T / \varepsilon_{ij})]^k \quad (8)$$

The coefficients  $c_k$  are given in Table I.

**Table I.** Coefficients  $a_{\eta k}$ ,  $b_k$ , and  $c_k$

| $k$ | $a_{\eta k}$ | $b_k$    | $c_k$   |
|-----|--------------|----------|---------|
| 0   | 1.0945       | 0.46649  | 0.1281  |
| 1   | -9.26324     | -0.57015 | -0.1108 |
| 2   | 71.0385      | 0.19164  | 0.0962  |
| 3   | -301.9012    | -0.3708  | -0.0271 |
| 4   | 797.69       | 0.00241  | 0.0024  |
| 5   | -1221.9770   | —        | —       |
| 6   | 987.5574     | —        | —       |
| 7   | -319.4636    | —        | —       |

In Eqs. (2)–(5),  $\bar{\chi}_{ij}$  is the pseudo-radial distribution function for the molecules  $i$  and  $j$ , in the presence of all the other species in the mixture, obtained according to Vesovic and Wakeham [5] as

$$\bar{\chi}_{ij}(\rho_m, T) = 1 + \frac{2}{5} \sum_{k=1}^N x_k (\bar{\chi}_k - 1) + \frac{[\frac{6}{5}(\bar{\chi}_i - 1)^{1/3} (\bar{\chi}_j - 1)^{1/3} \sum_{k=1}^N x_k (\bar{\chi}_k - 1)^{2/3}]}{(\bar{\chi}_i - 1)^{1/3} + (\bar{\chi}_j - 1)^{1/3}} \quad (9)$$

The pseudo-radial distribution function for the pure fluid was expressed in terms of the experimental viscosity  $\eta_i$ , at the same molar density and temperature as

$$\bar{\chi}_i(\rho_m, T) = \frac{\beta (\eta_i - \rho_m a_{ii} \eta_i^0)}{2 \rho_m^2 a_{ii}^2 \eta_i^0} + \beta \left[ \left( \frac{(\eta_i - \rho_m a_{ii} \eta_i^0)}{2 \rho_m^2 a_{ii}^2 \eta_i^0} \right)^2 - \frac{1}{\beta \rho_m^2 a_{ii}^2} \right]^{1/2} \quad (10)$$

where  $\beta = 0.830$ . We note that in its general form Eq. (10) has two solutions, as its two terms can be combined with a positive or a negative sign [5]. In the case of liquids, only the positive sign produces physically realistic solutions [5].

Finally, the parameter  $\alpha_{ii}$ , which accounts for the mean-free-path shortening in an  $i$ – $i$  collision in a dense gas, was originally defined [6] as

$$\alpha_{ii} = (8/15) N_A \pi \sigma_{ii}^3 \quad (11)$$

where  $N_A$  is Avogadro's constant. For the calculation of this parameter, since we are interested in applying the procedure to liquid mixtures, we have adopted an approach different from that described by Vesovic and Wakeham [4, 5]. We have related this parameter to the Enskog close-packed volume  $V_{oi}$ , given by

$$V_{oi} = N_A \sigma_{ii}^3 / \sqrt{2} \quad (12)$$

and thus

$$a_{ii} = 2.369 V_{oi} \quad (13)$$

Furthermore, instead of calculating  $V_{oi}$  directly from Eq. (12), we have adopted the hard-sphere Dymond–Assael scheme [8] and hence calculated  $V_{oi}$  from liquid-phase experimental viscosity values as

$$V_{oi} = \sum_{k=1}^5 v_k (T/T_i^c)^{k-1} \quad (14)$$

where  $T_i^c$  is the critical temperature of component  $i$ . The coefficients  $v_k$  were obtained according to the aforementioned scheme [8], by employing experimental viscosity values,  $\eta_i$ , and solving the following two equations for  $V_{oi}$ ,

$$\eta_i^* = \frac{16}{5} (2N_A)^{1/3} \pi^{1/2} \left( \frac{1}{M_i RT} \right)^{1/2} \frac{\eta_i V_i^{2/3}}{R_{\eta i}} \quad (15)$$

$$\log \eta_i^* = \sum_{k=0}^7 a_{\eta k} (V_{oi}/V_i)^k \quad (16)$$

$R_{\eta}$  is the roughness factor [8], optimized for each fluid. In Eq. (15),  $V_i$  is the molar volume,  $M_i$  is the molar mass, and  $R$  is the universal gas constant. The coefficients  $a_{\eta k}$  are given in Table I.

Finally, the interaction parameter  $a_{ij}$  was calculated by using the mixing rule proposed by Di Pippo et al. [6]

$$a_{ij} = \frac{1}{8} (a_{ii}^{1/3} + a_{jj}^{1/3})^3 \quad (17)$$

Equations (1)–(17) form a consistent set, whereby the viscosity of the mixture can be predicted from properties related only to the pure components. All required parameters are given in Table II, while the pure-component viscosities at the mixture molar density and temperature are obtained from the Dymond–Assael scheme described by Eqs. (14)–(16).

A disadvantage of this combined scheme, as already pointed out, is that to calculate the viscosity of the mixture at a specific temperature and molar density, the viscosity of the pure components at the same temperature and molar density as those of the mixture is required.

Table II. Constants and Parameters

|   | <i>n</i> -Hexane | <i>n</i> -Heptane | <i>n</i> -Hexanol | R125     | R134a    |
|---|------------------|-------------------|-------------------|----------|----------|
| $T^c$ (K)   | 507.9            | 540.15            | 610.7             | 339.4    | 374.21   |
| $M$ (g/mol)   | 86.177           | 100.203           | 102.176           | 120.022  | 102.031  |
| $\sigma_{ij}$ (nm)                                    | 0.6152           | 0.6501            | 0.6226            | 0.5066   | 0.5044   |
| $\varepsilon_{ij}/k_B$ (K)                            | 393.6            | 418.6             | 473.3             | 263.0    | 290.0    |
| $R_{\eta}$  | 1.185            | 1.255             |                   | 1.35     | 1.1      |
| $v_1$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ) | 118.874          | 134.799           |                   | 166.462  | 54.213   |
| $v_2$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ) | -128.372         | -143.059          |                   | -739.826 | -224.198 |
| $v_3$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ) | 141.363          | 159.886           |                   | 1265.157 | 362.030  |
| $v_4$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ) | -55.636          | -66.921           |                   | -974.033 | -264.893 |
| $v_5$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ ) | —                | —                 |                   | 282.842  | 73.004   |

### 3. APPLICATIONS

In the following sections the scheme is applied to mixtures of  $n$ -alkanes, hydrocarbons in general,  $n$ -alkane + alcohol mixtures, and mixtures of refrigerants.

#### 3.1. Mixtures of $n$ -Alkanes

The first mixture considered is a  $n$ -hexane +  $n$ -heptane mixture. The range of measurements covered from 293 to 323 K in a pressure range from atmospheric pressure up to 64 MPa. The results of three investigators were considered [9–11], with a total of 81 measurements (63 [9], 9 [10], 9 [11]).

The scaling parameters  $\sigma_{ij}$  and  $\varepsilon_{ij}/k_B$  were calculated from the critical constants as described elsewhere [1]. Values obtained are given in Table II. The coefficients of Eq. (14) as well as values for the roughness factor  $R_\eta$ , all obtained previously [8], are also shown in the same table.

In Table III a representative selection of the results is shown. In this case all deviations are well below 20%, notwithstanding the wide range of pressure and temperature. The explanation for this is that since the properties of the pure components need to be calculated at the same molar density as that of the mixture, the ratio of the molecular masses is very important. Indeed, as all organic liquids have similar mass densities, converting from molar density to mass density with very different molecular masses can easily result in mass density values not likely to be encountered in practice and, thus, unrealistic pure properties. Hence, we believe that the reason that the predicted values for this mixture are in close agreement with the experimental ones is that the mass ratio of the two components is very close to unity.

This statement is in full agreement with our previous observation [3] that the scheme predicts good values when the ratio  $V/V_0$  is large. When the  $V/V_0$  value for the mixture is large, similar pure-component molecular masses will retain high  $V/V_0$  ratios for the pure components, as  $V$  is the same and  $V_0$  depends on the molecular mass.

To examine this proposition further, we investigated the mixture  $n$ -hexane +  $n$ -dodecane, which is characterized by very different molecular masses. In this case converting the molar density of the mixture to the mass density of the pure component results in an unrealistic value because of the difference in molecular masses. Furthermore, the ratio  $V/V_0$  for the pure components will have very different values since the value of  $V_0$  also depends on the molecular mass. Hence, although the ratio  $V/V_0$  for

Table III. Prediction of the Viscosity of *n*-Hexane + *n*-Heptane Mixtures

| Ref. | Mixture property |            |              |                                    |                              | Predicted values       |                           |                        |                           |                              |                  |
|------|------------------|------------|--------------|------------------------------------|------------------------------|------------------------|---------------------------|------------------------|---------------------------|------------------------------|------------------|
|      | $x_{\text{hex}}$ | $T$<br>(K) | $P$<br>(MPa) | $\rho_m$<br>(mol·m <sup>-3</sup> ) | $\eta(\rho_m, T)$<br>(μPa·s) | $(V/V_0)_{\text{hex}}$ | $\bar{\chi}_{\text{hex}}$ | $(V/V_0)_{\text{hep}}$ | $\bar{\chi}_{\text{hep}}$ | $\eta(\rho_m, T)$<br>(μPa·s) | Deviation<br>(%) |
| [9]  | 0.64             | 293.35     | 0.1          | 7326.3                             | 349.7                        | 1.70                   | 17.0                      | 1.46                   | 44.3                      | 395.8                        | -11.7            |
| [9]  | 0.64             | 303.15     | 0.1          | 7234.2                             | 317.2                        | 1.73                   | 15.6                      | 1.49                   | 37.7                      | 352.6                        | -10.0            |
| [9]  | 0.64             | 303.15     | 15.6         | 7389.8                             | 369.1                        | 1.69                   | 16.8                      | 1.45                   | 44.6                      | 415.0                        | -11.1            |
| [9]  | 0.64             | 303.15     | 30.9         | 7526.7                             | 422.0                        | 1.66                   | 18.1                      | 1.42                   | 52.6                      | 484.6                        | -12.9            |
| [9]  | 0.64             | 303.15     | 51.2         | 7685.6                             | 494.1                        | 1.63                   | 19.8                      | 1.40                   | 64.9                      | 588.8                        | -16.1            |
| [9]  | 0.64             | 303.15     | 71.7         | 7824.7                             | 569.9                        | 1.60                   | 21.5                      | 1.37                   | 79.5                      | 708.9                        | -19.6            |
| [9]  | 0.64             | 312.26     | 0.1          | 7145.5                             | 289.8                        | 1.76                   | 14.6                      | 1.51                   | 32.7                      | 318.8                        | -9.1             |
| [9]  | 0.64             | 323.15     | 0.1          | 7037.1                             | 262.9                        | 1.79                   | 13.5                      | 1.54                   | 28.1                      | 285.3                        | -7.9             |
| [9]  | 0.64             | 323.15     | 15.5         | 7211.2                             | 309.3                        | 1.75                   | 14.5                      | 1.51                   | 32.9                      | 334.7                        | -7.6             |
| [9]  | 0.64             | 323.15     | 30.8         | 7363.5                             | 355.2                        | 1.71                   | 15.5                      | 1.47                   | 38.4                      | 389.1                        | -8.7             |
| [9]  | 0.64             | 323.15     | 50.8         | 7532.2                             | 415.8                        | 1.68                   | 16.9                      | 1.44                   | 46.5                      | 466.2                        | -10.8            |
| [9]  | 0.64             | 323.15     | 64.2         | 7630.8                             | 455.1                        | 1.65                   | 17.8                      | 1.42                   | 52.5                      | 522.9                        | -12.9            |
| [9]  | 0.33             | 288.28     | 0.1          | 7117.6                             | 403.4                        | 1.75                   | 15.7                      | 1.50                   | 36.6                      | 439.2                        | -8.2             |
| [9]  | 0.33             | 294.31     | 0.1          | 7067.3                             | 377.6                        | 1.76                   | 15.0                      | 1.51                   | 33.6                      | 409.2                        | -7.7             |
| [9]  | 0.33             | 303.15     | 0.1          | 6990.9                             | 344.0                        | 1.79                   | 14.1                      | 1.54                   | 29.8                      | 370.6                        | -7.2             |
| [9]  | 0.33             | 303.15     | 15.5         | 7135.4                             | 400.9                        | 1.75                   | 15.0                      | 1.51                   | 34.1                      | 432.6                        | -7.3             |
| [9]  | 0.33             | 303.15     | 30.8         | 7265.2                             | 459.2                        | 1.72                   | 15.9                      | 1.48                   | 38.9                      | 502.2                        | -8.6             |
| [9]  | 0.33             | 303.15     | 46.1         | 7381.3                             | 519.5                        | 1.70                   | 16.8                      | 1.46                   | 44.2                      | 578.8                        | -10.2            |
| [9]  | 0.33             | 303.15     | 61.7         | 7488.1                             | 583.3                        | 1.67                   | 17.7                      | 1.44                   | 50.2                      | 664.9                        | -12.3            |
| [9]  | 0.33             | 313.28     | 0.1          | 6900.9                             | 311.4                        | 1.82                   | 13.2                      | 1.57                   | 26.3                      | 333.4                        | -6.6             |
| [9]  | 0.33             | 323.15     | 0.1          | 6810.9                             | 283.8                        | 1.85                   | 12.4                      | 1.59                   | 23.5                      | 302.7                        | -6.1             |
| [9]  | 0.33             | 323.15     | 15.6         | 6975.2                             | 351.1                        | 1.81                   | 13.2                      | 1.56                   | 26.7                      | 353.7                        | -5.5             |
| [9]  | 0.33             | 323.15     | 30.7         | 7117.6                             | 383.2                        | 1.77                   | 13.9                      | 1.53                   | 30.2                      | 408.8                        | -6.3             |
| [9]  | 0.33             | 323.15     | 40.9         | 7202.4                             | 417.2                        | 1.75                   | 14.4                      | 1.51                   | 32.7                      | 447.7                        | -6.8             |
| [9]  | 0.33             | 323.15     | 53.0         | 7292.4                             | 457.2                        | 1.73                   | 15.0                      | 1.49                   | 35.7                      | 495.3                        | -7.7             |
| [10] | 0.09             | 293.15     | 0.1          | 6901.0                             | 400.7                        | 1.80                   | 14.1                      | 1.55                   | 29.1                      | 419.4                        | -4.5             |
| [10] | 0.30             | 293.15     | 0.1          | 7058.9                             | 379.8                        | 1.76                   | 15.0                      | 1.51                   | 33.6                      | 420.7                        | -9.7             |
| [10] | 0.50             | 293.15     | 0.1          | 7226.4                             | 359.2                        | 1.72                   | 16.2                      | 1.48                   | 39.7                      | 414.9                        | -13.4            |
| [10] | 0.70             | 293.15     | 0.1          | 7403.4                             | 338.9                        | 1.68                   | 17.6                      | 1.44                   | 48.5                      | 395.0                        | -14.2            |
| [10] | 0.91             | 293.15     | 0.1          | 7586.2                             | 319.3                        | 1.64                   | 19.5                      | 1.41                   | 61.3                      | 350.0                        | -8.8             |
| [11] | 0.11             | 298.15     | 0.1          | 6860.4                             | 379.2                        | 1.82                   | 13.6                      | 1.56                   | 27.4                      | 393.7                        | -3.7             |
| [11] | 0.30             | 298.15     | 0.1          | 7010.4                             | 358.0                        | 1.78                   | 14.5                      | 1.53                   | 31.2                      | 392.4                        | -8.8             |
| [11] | 0.51             | 298.15     | 0.1          | 7173.4                             | 340.9                        | 1.74                   | 15.5                      | 1.49                   | 36.5                      | 384.6                        | -11.4            |
| [11] | 0.70             | 298.15     | 0.1          | 7340.3                             | 322.7                        | 1.70                   | 16.8                      | 1.46                   | 43.6                      | 365.5                        | -11.7            |
| [11] | 0.90             | 298.15     | 0.1          | 7511.0                             | 307.5                        | 1.66                   | 18.3                      | 1.43                   | 53.5                      | 327.4                        | -6.1             |

*n*-hexane was around 2, for *n*-dodecane it was very near 1, thus resulting in the failure of the scheme as the molar volume becomes equal to the characteristic close-packed volume. Consequently, the pseudo-radial distribution function for *n*-dodecane was unrealistically large, resulting in very high deviations of the predicted values from the experimental ones.

The case was similar for all other *n*-alkanes considered. When the molecular masses of the pure species were near each other, the predicted values were in excellent agreement with the experimental ones.

### 3.2. Mixtures of Hydrocarbons

The idea put forward in the previous section explains very well all our previous observations [1, 2]. In a previous publication [1] we examined the prediction of the *n*-hexane+cyclohexane mixture. In that case the deviations were less than 11% over a very wide range of temperatures, 298 to 348 K, and pressures 0.1 to 300 MPa. This is simply because these two fluids have very similar molecular masses.

In the same paper [1] we examined the viscosity of the *n*-hexane+toluene mixture. Over a similar very wide range, the deviation showed only one point at 22% at the highest pressure, while most of the deviations were below 10%. Again, the molecular masses are similar, although slightly wider apart than in the previous mixture.

Furthermore, this idea explains very well the large deviations observed in the prediction of the viscosity of the toluene+cyclopentane mixture [2]. Although the picture might look slightly different depending on the ranges of temperatures and pressures, the main influencing factor is the difference in the molecular masses of the two components.

### 3.3. Mixtures of *n*-Alkane+*n*-Alcohol

We have so far established that the Vesovic–Wakeham scheme combined with the Dymond–Assael scheme can predict very well the viscosity of hydrocarbon mixtures, provided their molecular masses are similar. To test this idea further, it is interesting to apply it to a *n*-alkane+*n*-alcohol mixture. To our knowledge there is no other theoretically based scheme that can predict the viscosity of such mixtures.

We considered the *n*-hexanol+*n*-heptane mixture [12] at atmospheric pressure. The scaling parameters  $\sigma_{ij}$  and  $\varepsilon_{ij}/k_B$  were calculated from the critical constants as described elsewhere [1]. Values obtained are given in Table II. The coefficients of Eq. (14) for *n*-heptane as well as values for the roughness factor  $R_\eta$ , all obtained previously [8], are also listed in Table II. In the case of *n*-hexanol, the characteristic close-packed volume,  $V_o$ , was calculated [13] as described by Eqs. (14)–(16), with  $R_\eta = 3$ , as

$$\begin{aligned} V_o (\times 10^6 \text{ m}^3 \text{ mol}^{-1}) = & 380.57 - 2759.26T^{-0.5} + 84.994T^{0.5} - 23.664T \\ & + 2.497T^{1.5} - 0.1325T^2 + 3.4745 \times 10^{-3}T^{2.5} \\ & - 3.5785 \times 10^{-5}T^3 \end{aligned} \quad (18)$$

The deviations of the predicted values from the experimental ones [12] are shown in Table IV. All deviations are less than 8%, low as expected, since



Table IV. Prediction of the Viscosity of Hexanol + *n*-Heptane Mixtures

| Mixture property                            |  |  | Predicted values       |                           |                        |                           |  |                  |
|---|--|--|------------------------|---------------------------|------------------------|---------------------------|--|------------------|
| $x_{\text{hexanol}}$                        | $\rho_m$<br>( $\text{mol} \cdot \text{m}^{-3}$ ) | $\eta(\rho_m, T)$<br>( $\mu\text{Pa} \cdot \text{s}$ ) | $(V/V_0)_{\text{hex}}$ | $\bar{\chi}_{\text{hex}}$ | $(V/V_0)_{\text{hep}}$ | $\bar{\chi}_{\text{hep}}$ | $\eta(\rho_m, T)$<br>( $\mu\text{Pa} \cdot \text{s}$ ) | Deviation<br>(%) |
| $T = 298.15 \text{ K}, P = 0.1 \text{ MPa}$ |  |  |                        |                           |                        |                           |  |                  |
| 0.0567                                      | 6835.5   | 440.5  | 1.59                   | 61.6                      | 1.57                   | 26.9                      | 433.0  | 1.7              |
| 0.1134                                      | 6894.6   | 454.1  | 1.58                   | 64.4                      | 1.56                   | 28.2                      | 480.5  | -5.5             |
| 0.2217                                      | 7012.1   | 547.3  | 1.55                   | 70.6                      | 1.53                   | 31.2                      | 591.3  | -7.4             |
| 0.3279                                      | 7131.4   | 683.1  | 1.53                   | 78.2                      | 1.50                   | 35.0                      | 733.1  | -6.8             |
| 0.4307                                      | 7251.6   | 874.5  | 1.50                   | 87.4                      | 1.48                   | 39.5                      | 915.8  | -4.5             |
| 0.5294                                      | 7371.0   | 1141.6   | 1.48                   | 98.6                      | 1.45                   | 45.1                      | 1150.8   | -0.8             |
| 0.6292                                      | 7495.7   | 1523.2   | 1.45                   | 112.9                     | 1.43                   | 52.5                      | 1474.2   | 3.3              |
| 0.7248                                      | 7618.6   | 2047.3   | 1.43                   | 130.6                     | 1.41                   | 61.6                      | 1900.8   | 7.7              |
| 0.8643                                      | 7802.1   | 2930.4   | 1.40                   | 166.2                     | 1.37                   | 80.1                      | 2837.7   | 3.3              |
| 0.9526                                      | 7921.0   | 3788.5   | 1.37                   | 197.0                     | 1.35                   | 96.6                      | 3730.8   | 1.5              |
| $T = 308.15 \text{ K}, P = 0.1 \text{ MPa}$ |  |  |                        |                           |                        |                           |  |                  |
| 0.0567                                      | 6749.7   | 396.0  | 1.63                   | 53.7                      | 1.60                   | 24.0                      | 387.9  | 2.1              |
| 0.1134                                      | 6808.9   | 402.1  | 1.62                   | 55.8                      | 1.58                   | 25.1                      | 427.5  | -6.0             |
| 0.2217                                      | 6927.6   | 478.8  | 1.60                   | 60.6                      | 1.56                   | 27.6                      | 519.3  | -7.8             |
| 0.3279                                      | 7048.1   | 586.3  | 1.56                   | 66.2                      | 1.53                   | 30.6                      | 634.5  | -7.6             |
| 0.4307                                      | 7169.5   | 737.8  | 1.54                   | 73.1                      | 1.50                   | 34.3                      | 780.1  | -5.4             |
| 0.5294                                      | 7291.0   | 954.1  | 1.51                   | 81.3                      | 1.47                   | 38.8                      | 964.9  | -1.1             |
| 0.6292                                      | 7415.9   | 1201.2   | 1.49                   | 91.6                      | 1.45                   | 44.5                      | 1210.8   | -0.8             |
| 0.7248                                      | 7539.9   | 1573.7   | 1.46                   | 104.1                     | 1.43                   | 51.7                      | 1529.4   | 2.9              |
| 0.8643                                      | 7725.6   | 2299.3   | 1.43                   | 128.8                     | 1.39                   | 66.1                      | 2209.5   | 4.1              |
| 0.9526                                      | 7846.6   | 2920.6   | 1.41                   | 150.1                     | 1.37                   | 78.9                      | 2841.8   | 2.8              |

their molecular masses are very close. The agreement is excellent considering that the viscosity of *n*-hexanol is about 10 times larger than that of *n*-heptane. We also note that in such cases the simple mole fraction average rule for the prediction of the mixture viscosity that is employed in some engineering practice, produces maximum errors of 60%.

It should be pointed out that upon examining all the aforementioned mixtures, it becomes obvious that the reason that the prediction is excellent is attributed to the fact that the mass ratio of the pure components is close to unity and certainly not to the earlier assumption [2] that the viscosity ratio needs to be close to unity.

### 3.4. Mixtures of Refrigerants

As already stated in the case of *n*-alkane + *n*-alcohol mixtures, there is no theoretically based scheme that can predict their viscosity. The same

**Table V.** Prediction of the Viscosity of R125+R134a Refrigerant Mixtures at Saturation Pressure

| Mixture property |            |                                    |                              | Predicted values |                     |                   |                      |                              |                  |
|------------------|------------|------------------------------------|------------------------------|------------------|---------------------|-------------------|----------------------|------------------------------|------------------|
| $x_{R125}$       | $T$<br>(K) | $\rho_m$<br>(mol·m <sup>-3</sup> ) | $\eta(\rho_m, T)$<br>(μPa·s) | $(V/V_0)_{R125}$ | $\bar{\chi}_{R125}$ | $(V/V_0)_{R134a}$ | $\bar{\chi}_{R134a}$ | $\eta(\rho_m, T)$<br>(μPa·s) | Deviation<br>(%) |
| 0.493            | 251.83     | 12587.9                            | 315.1                        | 1.75             | 14.8                | 1.77              | 12.2                 | 300.2                        | 5.0              |
| 0.492            | 258.43     | 12391.5                            | 287.6                        | 1.79             | 13.6                | 1.81              | 11.4                 | 276.1                        | 4.2              |
| 0.491            | 263.75     | 12231.1                            | 270.0                        | 1.83             | 12.8                | 1.84              | 10.8                 | 258.7                        | 4.4              |
| 0.490            | 268.57     | 12070.7                            | 251.9                        | 1.86             | 12.2                | 1.86              | 10.3                 | 243.1                        | 3.6              |
| 0.488            | 275.43     | 11840.0                            | 231.7                        | 1.91             | 11.3                | 1.91              | 9.6                  | 222.9                        | 3.9              |
| 0.487            | 280.75     | 11661.4                            | 216.6                        | 1.96             | 10.8                | 1.94              | 9.2                  | 209.0                        | 3.6              |
| 0.486            | 281.81     | 11618.2                            | 214.5                        | 1.97             | 10.6                | 1.95              | 9.1                  | 205.8                        | 4.2              |
| 0.485            | 286.39     | 11448.5                            | 203.1                        | 2.01             | 10.2                | 1.98              | 8.7                  | 194.0                        | 4.7              |
| 0.484            | 289.05     | 11351.1                            | 195.8                        | 2.03             | 9.9                 | 2.00              | 8.5                  | 187.7                        | 4.3              |
| 0.484            | 290.47     | 11296.9                            | 192.5                        | 2.05             | 9.8                 | 2.01              | 8.4                  | 184.3                        | 4.5              |
| 0.483            | 293.38     | 11163.2                            | 181.3                        | 2.08             | 9.5                 | 2.04              | 8.1                  | 176.3                        | 2.8              |
| 0.482            | 298.32     | 10984.4                            | 175.2                        | 2.13             | 9.2                 | 2.08              | 7.8                  | 166.2                        | 5.4              |
| 0.480            | 304.40     | 10734.9                            | 159.9                        | 2.20             | 8.7                 | 2.14              | 7.4                  | 153.5                        | 4.2              |
| 0.478            | 309.89     | 10494.4                            | 151.2                        | 2.27             | 8.4                 | 2.20              | 7.1                  | 142.4                        | 6.2              |
| 0.478            | 311.04     | 10440.1                            | 148.0                        | 2.29             | 8.3                 | 2.21              | 7.0                  | 140.1                        | 5.6              |

certainly applies to the prediction of the viscosity of halogenated refrigerants. To test the present scheme we chose a mixture of refrigerants R125+R134a [14], which again have very similar molecular masses.

The scaling parameters  $\sigma_{ij}$  and  $\varepsilon_{ij}/k_B$  were calculated from the critical constants as described elsewhere [1]. Values obtained are given in Table II. The coefficients of Eq. (14) for the two refrigerants as well as the values for the roughness factor [15] are also shown in the same table.

The deviations of the experimental values of the viscosity of the mixture from the predicted ones are shown in Table V. The maximum deviation is 6%, which is excellent and was expected since their molecular masses are very similar.

#### 4. CONCLUSION

The Vesovic–Wakeham scheme as modified by the Dymond–Assael proposal has been successfully employed for the prediction of the viscosity of a wide range of mixtures of quite disparate liquids from groups of hydrocarbons, through combinations of alcohols and hydrocarbons to halogenated refrigerants. It was shown that, in all cases, provided that the mass ratio of the pure components is close to unity, the predictions show excellent agreement with experiment.

We further note that this is the only scheme that can predict the viscosity of mixtures with such a wide range of components with such accuracy. Its only drawback, that the pure components must have similar molecular masses, needs further study.

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