

# Prediction of the Viscosity of Liquid Mixtures: An Improved Approach<sup>1</sup>

M. J. Assael,<sup>2,5</sup> N. K. Dalaouti,<sup>2</sup> J. H. Dymond,<sup>3</sup> E. Perperi,<sup>2</sup>  
and W. A. Wakeham<sup>4</sup>

---

A recently developed theoretically based scheme for the prediction of the viscosity of gas mixtures is modified by making use of the hard-sphere theory and applied to the prediction of the viscosity of liquid mixtures. Preliminary results are compared with viscosity measurements of mixtures of *n*-hexane with toluene and with cyclohexane, and demonstrate the predictive power of this scheme.

---

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

## 1. INTRODUCTION

Whereas for pure liquids there exists a body of reliable experimental viscosity data, the situation for liquid mixtures is much less satisfactory with respect to experiment and correlation. This distinctive lack of experimental data over wide ranges of conditions has hindered the development of a theoretical approach and also rendered a purely empirical approach to the prediction of the transport properties impractical. To date, two approaches have been employed. The corresponding states approach [1, 2] has been widely used for mixtures of hydrocarbons or refrigerants. Its accuracy however, depends on the availability of experimental data in order to improve the correlation. Dymond and Assael employed an

---

<sup>1</sup> Paper presented at the Fifth Asian Thermophysical Properties Conference, August 30–September 2, 1998, Seoul, Korea.

<sup>2</sup> Chemical Engineering Department, Aristotle University, Thessaloniki 54006, Greece.

<sup>3</sup> Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom.

<sup>4</sup> Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, London SW2 2BY, United Kingdom.

<sup>5</sup> To whom correspondence should be addressed.

approach based on considerations of hard-sphere theory in order to predict the transport properties of liquids up to high pressures. The scheme was successfully employed for hydrocarbons [3, 4], alcohols [5], and refrigerants [6], but its application is restricted to mixtures of homologous series [7] only.

An alternative approach has recently been proposed by Vesovic and Wakeham [8, 9], who extended a theoretically based scheme [10, 11] for predicting the transport properties of fluid mixtures from those of the pure components to high-pressure gases. Vesovic and Wakeham also applied their scheme successfully to one liquid mixture—propane and methane [9].

The work presented here attempts to expand the application of the Vesovic and Wakeham scheme to calculate the viscosity of liquid mixtures.

## 2. THEORETICAL

The Vesovic and Wakeham scheme for the prediction of the mixture viscosity from the properties of its constituents has been described in detail elsewhere [8, 9], and it will only be briefly presented here together with the extensions we now propose. According to Di Pippo et al. [10], the viscosity  $\eta$  of a dense-gas mixture of  $N$  components as a function of its molar density  $\rho$  and its temperature  $T$  can be expressed as

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

where

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

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

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

and

$$\kappa_{\text{mix}} = \left( \frac{16}{5\pi} \right) \frac{15}{16} \rho^2 \sum_{j=1}^N \sum_{i=1}^N x_i x_j \bar{\chi}_{ij} a_{ij}^2 \eta_{ij}^{\circ} \quad (5)$$

**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	-0.37080	-0.0271
4	797.6900	0.00241	0.0024
5	-1221.9770	—	—
6	987.5574	—	—
7	-319.4636	—	—

In these equations,  $x_i$  and  $x_j$  are the mole fractions of species  $i$  and  $j$ , while  $m_i$  and  $m_j$  are their molecular masses. The dilute-gas limit interaction viscosity of species  $i$ - $j$ ,  $n_{ij}^o$ , can be obtained from [12]

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

where

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

Coefficients  $b_k$  are given in Table I, while  $\sigma_{ij}$  and  $\varepsilon_{ij}/k_B$  represent the length and energy scaling parameters. Equations (6) and (7) can also be employed for the calculation of the dilute-gas limit viscosity  $\eta_i^o$  of pure component  $i$ .

In Eqs. (3) and (4) the symbol  $A_{ij}^*$  represents a weak function of the intermolecular potential for the  $i$ - $j$  interaction. This can readily be calculated from [12]

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

where the coefficients  $c_k$  are given in Table I.

In cases where they are not known from other sources [12], the length and energy scaling parameters for the like and unlike interactions can approximately be calculated from [13]

$$(\varepsilon_{ij}/k_B) = 0.775 T_{ij}^c \quad (9)$$

$$(2/3) \pi N_A \sigma_{ij}^3 = 0.211 (RT_{ij}^c/P_{ij}^c) \quad (10)$$

while the mixture critical properties can be obtained from the Lorentz–Berthelot mixing rules [14] as

$$\omega_{ij} = (\omega_i + \omega_j)/2 \quad (11)$$

$$Z_i^c = 0.2905 - 0.085\omega_i \quad (12)$$

$$V_i^c = Z_i^c RT_i^c / P_i^c \quad (13)$$

$$V_{ij}^c = \frac{1}{8} [(V_i^c)^{1/3} + (V_j^c)^{1/3}]^3 \quad (14)$$

$$T_{ij}^c = (1 - k_{ij}) \sqrt{T_i^c T_j^c} \quad (15)$$

$$P_{ij}^c = Z_{ij}^c RT_{ij}^c / V_{ij}^c \quad (16)$$

where  $k_{ij}$  is the binary interaction parameter, and  $\omega_i$ ,  $\omega_j$ , and  $\omega_{ij}$  are acentric factors. Note that Eq. (12) is also valid for  $Z_{ij}^c$ .

The pseudo-radial distribution function  $\bar{\chi}_{ij}$  for the molecules  $i$  and  $j$  in the presence of all other species in the mixture was obtained according to Vesovic and Wakeham [9] as

$$\bar{\chi}_{ij}(\rho, T) = 1 + \frac{2}{5} \sum_{k=1}^N x_k (\bar{\chi}_k - 1) + \frac{[\frac{6}{5}(\bar{\chi}_i - 1)^{1/3} (\bar{\chi}_j - 1)^{1/3} \sum_{k=1}^N x_k (\bar{\chi}_k - 1)^{2/3}]}{(\bar{\chi}_i - 1)^{1/3} + (\bar{\chi}_j - 1)^{1/3}} \quad (17)$$

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

$$\bar{\chi}_i(\rho, T) = \frac{\beta \eta_i - \rho a_{ii} \eta_i^0}{2 \rho^2 a_{ii}^2 \eta_i^0} + \beta \left[ \left( \frac{\eta_i - \rho a_{ii} \eta_i^0}{2 \rho^2 a_{ii}^2 \eta_i^0} \right)^2 - \frac{1}{\beta \rho^2 a_{ii}^2} \right]^{1/2} \quad (18)$$

with  $\beta = 0.830$ . It should be noted that in the case of liquid mixtures, the positive root in Eq. (18) is to be chosen, but for gaseous mixtures with lower densities the negative root has to be taken.

The parameter  $a_{ii}$  accounts for the mean-free path shortening in an  $i$ – $i$  collision in the dense gas, and is defined [10] as

$$a_{ii} = (8/15) N_A \pi \sigma_{ii}^3 \quad (19)$$

For the calculation of this parameter, since we are interested in applying the procedure to liquid mixtures we have adopted a different approach from that described by Vesovic and Wakeham [8, 9]. We have related this parameter to the Enskog close-packed volume  $V_o$  given by

$$V_{oi} = N_A \sigma_{ii}^3 / \sqrt{2} \quad (20)$$

and thus

$$a_{ii} = 0.8 \times 2.961 V_{oi} \quad (21)$$

Furthermore, we have calculated  $V_{oi}$  from liquid-phase experimental viscosity values according to the hard-sphere scheme proposed by Dymond and Assael [3]. Thus,  $V_{oi}$  was expressed as

$$V_{oi} = \sum_{k=1}^4 v_k (T/T_i^c)^{k-1} \quad (22)$$

The coefficients  $v_k$  were obtained by employing experimental viscosity values  $\eta_i$  and solving the following two equations for  $V_{oi}$  [3]:

$$\eta_i^* = 6.035 \times 10^8 \eta_i V_i^{2/3} (1/M_i RT)^{1/2} / R_{\eta i} \quad (23)$$

$$\log \eta_i^* = \sum_{k=0}^7 a_{\eta k} (V_{oi}/V_i)^k \quad (24)$$

with  $R_{\eta} = 1$ . In Eq. (23),  $M_i$  is the molar mass and  $R$  is the universal gas constant. The coefficients  $a_{\eta k}$  are given in Table I.

Finally, for the parameter  $a_{ij}$  the mixing rule proposed by Di Pippo et al. [10] was adopted:

$$a_{ij} = \frac{1}{8} (a_{ii}^{1/3} + a_{jj}^{1/3})^3 \quad (25)$$

### 3. APPLICATION

To apply the aforementioned scheme for the prediction of the viscosity of a liquid mixture at a particular molar density and temperature, one only requires the critical parameters and the acentric factor of the constituent

**Table II.** Critical Constants, Acentric Factor, and Coefficients  $v_k$

	<i>n</i> -Hexane	Toluene	Cyclohexane
$T^c$ (K)	507.9	591.75	553.5
$P^c$ (MPa)	3.035	4.108	4.070
$V^c$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ )	370	316	308
$\omega$	0.299	0.263	0.212
$v_1$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ )	61.275	112.550	82.890
$v_2$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ )	113.607	-186.164	-5.909
$v_3$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ )	-184.203	288.889	-10.047
$v_4$ ( $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ )	87.389	-163.262	0

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

$x_{\text{tol}}$	Mixture properties				<i>n</i> -Hexane			Toluene			Predictive values		
	$T$ (K)	$P$ (MPa)	$\rho$ (mol · m <sup>-3</sup> )	$\eta(\rho, T)$ ( $\mu\text{Pa} \cdot \text{s}$ )	$P_{\text{hex}}$ (MPa)	$\eta_{\text{hex}}(\rho, T)$ ( $\mu\text{Pa} \cdot \text{s}$ )	$P_{\text{tol}}$ (MPa)	$\eta_{\text{tol}}(\rho, T)$ ( $\mu\text{Pa} \cdot \text{s}$ )	$\eta_{\text{hex}}/\eta_{\text{tol}}$	$\eta(\rho, T)$ ( $\mu\text{Pa} \cdot \text{s}$ )	Deviation (%)		
0.75	298.28	74.9	9408.8	838	398.0	2467	5.9	580	4.3	931	11.1		
0.75	298.28	100	9548.9	972	455.3	3115	24.1	666	4.7	1115	14.7		
0.75	323.27	74.7	9233.4	655	380.6	1718	13.9	462	3.7	700	6.9		
0.75	348.35	75.6	9030.4	546	394.2	1192	17.7	368	3.2	528	-3.3		
0.75	348.35	103.9	9210.2	631	417.2	1463	37.8	442	3.3	639	1.3		
0.75	373.35	51.7	8659.8	365	271.1	763	6.6	290	2.6	385	5.5		
0.75	373.35	74.6	8845.1	446	328.3	929	22.6	335	2.8	451	1.2		
0.75	373.35	98.9	9013.9	502	381.9	1102	39.8	385	2.9	525	4.6		
0.5	298.23	151.8	9374.3	1109	384.5	2336	1.7	560	4.1	1293	16.6		
0.5	298.23	200.7	9575.1	1416	466.2	3258	27.6	683	4.8	1732	22.3		
0.5	323.24	150.9	9220.7	868	375.4	1687	12.4	457	3.7	971	11.9		
0.5	348.32	151.5	9050.2	716	356.8	1222	19.8	374	3.3	733	2.4		
0.5	348.32	201.2	9272.3	895	441.4	1559	45.5	457	3.4	922	3.0		
0.5	373.23	100.4	8608.3	447	255.6	722	2.6	280	2.6	472	5.6		
0.5	373.23	150.7	8897.6	600	345.5	983	27.5	346	2.8	621	3.4		
0.25	298.30	301	9530.5	1993	447.6	3018	21.6	654	4.6	2260	13.4		
0.25	323.25	300	9386.6	1466	444.3	2124	32.5	527	4.0	1619	10.4		
0.25	348.20	201	8893.8	779	301.1	1011	4.6	338	3.0	806	3.4		
0.25	348.20	300.1	9249.7	1148	432.4	1526	42.5	447	3.4	1191	3.7		
0.25	373.20	200.2	8753.5	672	299.4	844	14.1	310	2.7	682	1.5		
0.25	373.20	303.3	9133.4	1005	424.5	1251	53.6	424	3.0	999	-0.6		

Table IV. Prediction of the Viscosity of *n*-Hexane + Cyclohexane Mixtures

$x_{\text{hex}}$	Mixture properties				<i>n</i> -Hexane			Cyclohexane			Predictive values	
	$T$ (K)	$P$ (MPa)	$\rho$ (mol · m <sup>-3</sup> )	$\eta(\rho, T)$ ( $\mu\text{Pa} \cdot \text{s}$ )	$P_{\text{hex}}$ (MPa)	$\eta_{\text{hex}}(\rho, T)$ ( $\mu\text{Pa} \cdot \text{s}$ )	$P_{\text{cyc}}$ (MPa)	$\eta_{\text{cyc}}(\rho, T)$ ( $\mu\text{Pa} \cdot \text{s}$ )	$\eta_{\text{hex}}/\eta_{\text{cyc}}$	$\eta(\rho, T)$ ( $\mu\text{Pa} \cdot \text{s}$ )	Deviation (%)	
0.799	298.15	300	9408.7	2062	397.7	2469	23.4	1202	2.1	2181	5.8	
0.799	348.15	200	8814.1	792	275.4	920	14.2	514	1.8	829	4.6	
0.799	348.15	300	9163.9	1205	398.8	1392	48.0	749	1.9	1205	3.3	
0.799	348.15	400	9443.7	1742	510.5	1813	84.7	1047	1.7	1642	-5.7	
0.6	298.15	200	9359.2	1625	377.9	2276	17.6	1118	2.0	1768	8.8	
0.6	348.15	200	9031.2	995	349.3	1195	33.8	638	1.9	952	-4.8	
0.6	348.15	300	9370.9	1561	481.2	1712	74.3	953	1.8	1383	-11.4	
0.4	298.15	100	9227.1	1173	327.9	1851	3.2	929	2.0	1264	7.8	
0.4	298.15	200	9639.0	2259	492.6	3629	54.9	1727	2.1	2414	6.9	
0.4	348.15	100	8874.0	674	294.5	987	19.2	543	1.8	706	4.7	
0.4	348.15	200	9368.3	1215	479.8	1707	73.8	949	1.8	1227	1.0	
0.2	298.15	50	9247.4	1087	335.2	1908	5.3	955	2.0	1123	3.3	
0.2	348.15	50	8833.5	610	281.3	940	15.8	523	1.8	597	-2.1	
0.2	348.15	100	9188.3	908	408.3	1430	50.9	761	1.9	880	-3.1	

liquids and their viscosity, but at the same molar density and temperature. The satisfaction of the latter requirement made the literature search very difficult for testing the scheme. Only two mixtures were found for which the viscosity was measured at a molar density and temperature where the viscosity of the constituent liquids was also available. The mixtures were *n*-hexane + toluene [15] and *n*-hexane + cyclohexane [16], and the viscosity of the constituents had also been measured—*n*-hexane [17], toluene [15], and cyclohexane [18]. Table II gives the critical constants, the acentric factor, and the coefficients  $v_k$  of Eq. (22), obtained as described.

Tables III and IV show the values of the viscosity predicted by this new scheme. Values of the viscosity of the pure components at the same molar density and temperature are also shown.

The following two points must be considered: (1) In order to achieve the same molar density for the pure liquids, very high pressure measurements had to be included; and (2) in some cases the ratio of the viscosities of the two pure components was as large as 4.8.

With these two points in mind, the deviations between the predicted values and the measured ones, as shown in the last columns in Tables III and IV, are considered as very satisfactory. We note that, in general, deviations are within  $\pm 5\%$  and only rise above that value if the viscosity ratio is larger than 4 or the pressure is very high.

Although these results should be considered as preliminary, it is worth noting that the simple mole-fraction average of the pure component viscosities at the same pressure and temperature yields discrepancies of some 35% (*n*-hexane + cyclohexane) from the experimental mixture viscosity. The computer package SUPERTRAPP, based on a corresponding-states principle, yields viscosity data that underestimate the experimental values for the mixtures by as much as 30%. This, however, is most probably attributed to the very high pressures involved.

## 4. CONCLUSION

The scheme proposed in this paper for the prediction of the viscosity of liquid mixtures seems to be promising. Preliminary results compared with viscosity measurements of mixtures of *n*-hexane with toluene and with cyclohexane demonstrate the predictive power of this scheme.

## REFERENCES

1. J. F. Ely and J. J. M. Hanley, *Ind. Eng. Chem. Fund.* **20**:323 (1981).
2. M. L. Huber and J. F. Ely, *Fluid Phase Equil.* **80**:239 (1992).



3. M. J. Assael, J. H. Dymond, M. Papadaki, and P. M. Patterson, *Int. J. Thermophys.* **13**:269 (1992).
4. M. J. Assael, J. H. Dymond, and P. M. Patterson, *Int. J. Thermophys.* **13**:895 (1992).
5. M. J. Assael, J. H. Dymond, and S. K. Polimatidou, *Int. J. Thermophys.* **15**:189 (1994).
6. M. J. Assael, N. K. Dalaouti, J. H. Dymond, and E. Feleki, *Int. J. Thermophys.* **21**:367 (2000).
7. M. J. Assael, J. H. Dymond, M. Papadaki, and P. M. Patterson, *Int. J. Thermophys.* **13**:659 (1992).
8. V. Vesovic and W. A. Wakeham, *Int. J. Thermophys.* **10**:125 (1988).
9. V. Vesovic and W. A. Wakeham, *Chem. Eng. Sci.* **44**:2181 (1989).
10. R. Di Pippo, J. R. Dorfman, J. Kestin, H. E. Khalifa, and E. A. Mason, *Physica A* **86**:205 (1977).
11. E. A. Mason, H. E., Khalifa, J. Kestin, and J. R. Dorfman, *Physica A* **91**:377 (1978).
12. G. C. Maitland, E. B. Smith, M. Rigby, and W. A. Wakeham, *Intermolecular Forces* (Clarendon Press, Oxford, 1981), pp. 564–567.
13. R. S. Brokaw, *NASA Tech. Rep. TR R-81*, Washington (1960), pp. 1–34.
14. S. M. Walas, *Phase Equilibria in Chemical Engineering* (Butterworths, London, 1965).
15. J. H. Dymond, M. A. Awan, N. F. Glen, and J. D. Isdale, *Int. J. Thermophys.* **12**:275 (1991).
16. J. D. Isdale, J. H. Dymond, and T. A. Brawn, *High Temp. High Press.* **11**:571 (1979).
17. J. H. Dymond, K. J. Young, and J. D. Isdale, *Int. J. Thermophys.* **1**:345 (1980).
18. Y. Tanaka, H. Hosokawa, H. Kubota, and T. Makita, *Int. J. Thermophys.* **12**:245 (1991).