International Journal of Thermophysics, Vol. 12, No. 3, 1991

Initial Density Dependence of Experimental Viscosities and of Calculated Diffusion Coefficients of the Binary Vapor Mixtures Methanol–Benzene and Methanol–Cyclohexane

E. Vogel,[1] K. Dobbert,[1] K. Meissner,[1] U. Ruh,[1] and E. Bich[1]

Received July 11, 1990

The paper reports experimental results for the viscosity of the vapor mixtures methanol–benzene (five mole fractions with densities up to $1.5\,\mathrm{kg \cdot m^{-3}}$ and $0.022\,\mathrm{mol} \cdot L^{-1}$) and methanol–cyclohexane (four mole fractions with densities up to $1.9\,\mathrm{kg \cdot m^{-3}}$ and $0.026\,\mathrm{mol} \cdot L^{-1}$). In analogy to the pure components, the measurements on the mixtures were carried out with an oscillating-disk viscometer with small gaps, completely made of quartz, beginning as near as possible to room temperature and continuing to a maximum temperature of 630 K. A first evaluation by means of the Chapman–Enskog theory of dilute gases has shown differences in the resulting values of the interaction viscosity $\eta_{ij}^{(0)}$ in the limit of zero density exceeding the experimental errors. Consistent results were obtained by taking into account the initial density dependence of the viscosity within the framework of the modified Enskog theory for gaseous mixtures. The values of $\eta_{ij}^{(0)}$ were also used to estimate binary diffusion coefficients of the mixtures.

KEY WORDS: binary diffusion coefficient; gas mixtures; methanol–benzene; methanol–cyclohexane; viscosity.

1. INTRODUCTION

A description of the viscosity η of fluids or fluid mixtures over a wide range of thermodynamic states starts with the zero-density limit and extends to moderately dense gases. Modern kinetic theory [1] predicts that the density

---

[1] Fachbereich Chemie, Universitaet Rostock, Hermannstr. 14, Rostock 1, D-O-2500, Germany.

0195-928X/91/0500-0469$06.50/0

dependence of η of a pure fluid should be represented by an expansion of the form

$$\eta = \eta^{(0)} + \eta^{(1)}\rho + \eta^{(2)\prime}\rho^2 \ln \rho + \eta^{(2)}\rho^2 + \cdots \tag{1}$$

Here, only terms up to the first power of the density ρ are discussed.

The theory of the initial density dependence of viscosity, that is, the description of $\eta^{(1)}$ by the Rainwater–Friend theory [2–6], has not reached the same level yet as the theoretical basis for the zero-density viscosity $\eta^{(0)}$ given by Chapman and Enskog [7, 8]. Thus, modifications of the Enskog theory for the transport properties of the hard-sphere fluid [9, 10] as well as of its extension to binary mixtures by Thorne [10] and to multicomponent mixtures by Tham and Gubbins [11] represent practical tools for the treatment of viscosity data of real dense gases [12, 13] and for the prediction of the density and composition dependence of the viscosity of real dense gaseous mixtures [14–18]. In the modified Enskog theory (MET) for pure dense gases the hard-sphere diameter σ and the value of the radial distribution function at contact χ in the formulae of the transport coefficients of the Enskog theory are replaced by quantities depending on the pressure virial coefficients of the real gas. In the MET of mixtures it is also assumed that the formulae for the hard-sphere mixtures can be applied to real-gas mixtures provided that the hard-sphere quantities are again substituted by suitably chosen real-gas quantities. Tests of methods for computing viscosity of moderately dense gas mixtures are hampered by the limited number of experimental work in this field and, in addition, by the fact that the measurements have not been very accurate in each case.

In recent years, the Rostock group has achieved a very high level of accuracy in measuring the viscosity of gases and vapors by means of an oscillating-disk method at low and moderate densities [19–28]. The program has been extended to vapor mixtures and the results for methanol–benzene and methanol–cyclohexane are reported in this paper. First, the experimental data were evaluated with the aid of the Chapman–Enskog theory of dilute gas mixtures [7, 8], as the measurements were performed at relatively low densities. But the values of the interaction viscosity coefficient in the limit of zero density, $\eta_{ij}^{(0)}$, resulting for each individual mole fraction at fixed temperatures showed differences whose origin could not be explained by measurement errors alone. Results of our earlier measurements for the viscosity of the pure components methanol and benzene [23], as well as cyclohexane [25], revealed that even for low densities the first density correction $\eta^{(1)}\rho$ in Eq. (1) has to be taken into account. Therefore, we assumed that the values for the mixtures were influenced by a density dependence of the viscosity. As a consequence, the measurements were reevaluated by applying a correction linear in ρ. For this procedure we followed the guidelines of Kestin et al. [16] for applying the MET.

In a separate section the binary diffusion coefficients of the mixtures are presented using the obtained $\eta_{ij}^{(0)}$ values. In analogy to the viscosity coefficient the calculation of the diffusion coefficient was carried out by taking into consideration the initial density dependence. These diffusion coefficients show large differences from the values resulting from the relations between viscosity and diffusion coefficients of mixtures in the limit of zero densiy predicted by the Chapman–Enskog theory.

2. EXPERIMENTAL RESULTS

If the initial density dependence of viscosity has to be taken into account, it is necessary, in principle, to perform several series of measurements at different densities for each mole fraction of the mixture at various temperatures. However, such a measuring program is time-consuming and expensive. As the densities in our measurements are relatively small, the effect of the initial density dependence of viscosity was considered to be negligibly small when we started and we concentrated on getting data over a large temperature range for several mole fractions.

We used an all-quartz oscillating-disk viscometer whose characteristics have already been described previously [25], as well as the basic principles of design and construction [19] and the details of calibration and evaluation of the measurements [20]. We calibrated the viscometer for large ranges of the boundary-layer thickness at room temperature using reference viscosity values of noble gases and nitrogen given with an uncertainty less than 0.15% [29, 30]. Period and logarithmic decrement of the damped harmonic oscillation were determined in the traditional way, i.e., by means of a mirror attached to the oscillating system, a precision glass scale, a telescope, and a stopwatch. The performance of the viscometer was checked by determining the viscosity of the noble gases and nitrogen [21] as well as carbon dioxide [22] at low densities between room temperature and 650 K. Our data for the noble gases together with many other macroscopic and microscopic data were used by Aziz et al. [31–34] to generate new interatomic potential functions of the HFD type. On the basis of the results of this multiproperty fit for the noble gases and of the errors of the measurement, the uncertainty of our experimental data has been estimated to be between ±0.15% at room temperature and ±0.2–0.3% at the highest temperatures, whereas the reproducibility is even better.

The purification of methanol and benzene [23] as well as of cyclohexane [25] has already been described earlier. In a special glass apparatus the final products of the three compounds were dried by molecular sieve 3A or 4A, degassed, and filled into small glass ampules. Then the evacuated viscometer was filled by sublimation of the weighed samples for each mixture. Five series of measurements for the methanol–benzene system and four series for the methanol–cyclohexane system, each differing in the mole fraction as well as in density were carried out. The temperature range was started at a temperature, at which the mixture as a whole existed as vapor, and continued to approximately 630 K. To test for thermal decomposition, a check measurement was performed at a low temperature after the highest temperature had been attained. In this connection we should note the problems in viscosity measurements we found for methanol, benzene, and cyclohexane [23, 25], particularly at high temperatures and at relatively low densities.

All experimental points are reported, together with the density and the mole fraction x_i of each series, in Table I for methanol–benzene and in Table II for methanol–cyclohexane. For both vapor mixtures all data of the check measurements showed a tendency to increased values in comparison with the direct measurements as a consequence of a small thermal decomposition. As there was no clear evidence of the temperature at which the decomposition started, all experimental points apart from the check measurements were included in the further evaluation. Therefore, the uncertainty of the experimental data at the highest temperatures could be larger than $\pm 0.3\,\%$. The experimental data of each individual series of measurements were represented by

$$\eta(T) = S \exp(A \ln T_R + B/T_R + C/T_R^2 + D) \tag{2}$$

with

$$S = 10\ \mu\text{Pa}\cdot\text{s}, \qquad T_R = T/298.15$$

The parameters of Eq. (2), the standard deviations σ_η, and the root-mean-square deviations (rms) are given in Table III. Viscosity values calculated at fixed temperatures are presented as filled circles for three isotherms in Figs. 1 and 2 for methanol–benzene and methanol–cyclohexane, respectively. Viscosity coefficients of the pure vapors are plotted as open circles. These values are extrapolated to zero density [23, 25], in contrast to the data for the mixtures which correspond to the actual densities of the measurements. The lines in both figures are not fitted to the data; they are only a guide for the eyes. The included uncertainties of 0.5 % are much greater than the measurement error. Two special features clearly emerge from Fig. 1. First, the viscosity value for the mixture $x_{\text{METH}} = 0.2233$ for the 603 K isotherm is large in comparison with those for the other mixtures. This probably was

Table I. Viscosity of Methanol–Benzene Vapor Mixtures

Series 1

$x_{\mathrm{METH}} = 0.2233$
$\rho' = 1.498\ \mathrm{kg \cdot m^{-3}}$
$\rho = 22.08 \times 10^{-3}\ \mathrm{mol \cdot L^{-1}}$

Temperature T (K)	Viscosity η (μPa · s)
345.74	9.184
372.00	9.882
403.03	10.708
441.02	11.720
479.52	12.735
520.19	13.821
561.06	14.940
601.21	16.038
637.03	16.988
344.71	9.170[a]

Series 2

$x_{\mathrm{METH}} = 0.4071$
$\rho' = 0.893\ \mathrm{kg \cdot m^{-3}}$
$\rho = 15.05 \times 10^{-3}\ \mathrm{mol \cdot L^{-1}}$

Temperature T (K)	Viscosity η (μPa · s)
333.46	9.280
346.82	9.653
378.00	10.522
414.56	11.545
452.73	12.610
497,36	13.848
536.29	14.926
580.96	16.179
627.68	17.514
332.56	9.264[a]

Series 3

$x_{\mathrm{METH}} = 0.5840$
$\rho' = 0.553\ \mathrm{kg \cdot m^{-3}}$
$\rho = 10.79 \times 10^{-3}\ \mathrm{mol} \cdot L^{-1}$

Temperature T (K)	Viscosity η (μPa · s)
314.77	9.170
334.58	9.755
363.21	10.592
396.37	11.569
433.88	12.672
470.94	13.754
514.91	15.044
557.93	16.308
604.38	17.693
626.65	18.353
320.85	9.356[a]

Series 4

$x_{\mathrm{METH}} = 0.8011$
$\rho' = 0.557\ \mathrm{kg \cdot m^{-3}}$
$\rho = 13.51 \times 10^{-3}\ \mathrm{mol \cdot L^{-1}}$

Temperature T (K)	Viscosity η (μPa · s)
320.74	9.851
342.11	10.532
369.33	11.396
400.23	12.377
436.94	13.523
478.47	14.831
518.76	16.088
555.66	17.250
595.42	18.520
637.82	19.863
318.14	9.767[a]

Series 5

$x_{\mathrm{METH}} = 0.8097$
$\rho' = 0.824\ \mathrm{kg \cdot m^{-3}}$
$\rho = 20.20 \times 10^{-3}\ \mathrm{mol \cdot L^{-1}}$

Temperature T (K)	Viscosity η (μPa · s)
329.66	10.130
364.67	11.261
398.32	12.333
436.44	13.546
515.66	16.071
558.25	17.427
604.62	18.907
628.89	19.670
328.79	10.114[a]

[a] Excluded from further evaluation.

caused by thermal decomposition. Second, the results of the two series of measurements for the mole fraction $x_{\mathrm{METH}} \approx 0.8$ show different behavior for the isotherms of low and high temperature, respectively. Whereas the slightly higher value of the mixture $x_{\mathrm{METH}} = 0.8097$ for the 603 K isotherm could again be influenced by thermal decomposition, neither errors of the viscosity measurement nor thermal alteration can be responsible for the

Table II. Viscosity of Methanol–Cyclohexane Vapor Mixtures

Temperature T (K)	Viscosity η (μPa · s)	Temperature T (K)	Viscosity η (μPa · s)
Series 1		Series 3	
$x_{\mathrm{METH}} = 0.2068$ $\rho' = 1.921\ \mathrm{kg \cdot m^{-3}}$ $\rho = 26.17 \times 10^{-3}\ \mathrm{mol \cdot L^{-1}}$		$x_{\mathrm{METH}} = 0.5087$ $\rho' = 0.996\ \mathrm{kg \cdot m^{-3}}$ $\rho = 17.27 \times 10^{-3}\ \mathrm{mol \cdot L^{-1}}$	
359.93	8.810	335.00	9.156
374.27	9.140	363.16	9.894
413.26	10.028	394.84	10.722
451.30	10.891	435.45	11.776
502.77	12.041	474.11	12.767
546.69	13.010	513.51	13.781
591.00	14.066	558.18	14.977
633.97	15.044	603.03	16.236
366.99	8.980[a]	628.86	16.919
		319.98	8.766[a]
Series 2		Series 4	
$x_{\mathrm{METH}} = 0.4121$ $\rho' = 1.135\ \mathrm{kg \cdot m^{-3}}$ $\rho = 18.10 \times 10^{-3}\ \mathrm{mol \cdot L^{-1}}$		$x_{\mathrm{METH}} = 0.7984$ $\rho' = 0.517\ \mathrm{kg \cdot m^{-3}}$ $\rho = 12.14 \times 10^{-3}\ \mathrm{mol \cdot L^{-1}}$	
356.69	9.391	313.84	9.469
378.44	9.941	333.87	10.092
411.31	10.761	362.03	10.946
453.39	11.797	396.44	11.987
498.26	12.910	433.56	13.097
538.91	13.926	474.01	14.318
579.87	14.951	512.28	15.469
626.79	16.110	561.75	17.002
363.81	9.590[a]	606.02	18.401
		630.95	19.148
		313.66	9.470[a]

[a] Excluded from further evaluation.

Table III. Parameters of Eq. (2) for the Series of Measurements on Methanol–Benzene and Methanol–Cyclohexane Vapor Mixtures

Series	A	B	C	D	SD $10^3 \sigma_\eta$ (μPa · s)	Root mean square deviation 10^2 rms (%)
			Methanol–benzene			
1	1.11507	0.267400	−0.0750570	−0.424791	11.04	5.65
2	1.26669	0.789890	−0.287825	−0.693041	6.14	3.62
3	1.14343	0.398041	−0.140662	−0.399660	3.87	2.34
4	1.20504	0.600960	−0.233760	−0.459865	4.76	2.51
5	1.03298	0.0870655	−0.0570831	−0.122706	4.50	2.20
$\eta_{ij}^{(0)}$	0.689847	−0.995386	0.399172	0.420881	4.37	3.02
			Methanol–cyclohexane			
1	1.61400	2.01396	−0.737943	−1.59274	14.92	7.97
2	1.08375	0.338677	−0.107111	−0.465023	6.27	3.58
3	1.74921	2.19739	−0.753383	−1.65125	15.33	7.71
4	1.37633	1.04898	−0.359868	−0.796614	12.34	5.46
$\eta_{ij}^{(0)}$	1.92159	2.54067	−0.808551	−1.94979	2.29	2.01

difference at 343 K, and we attribute these effects to the differences in density. Hence, the initial density dependence of the viscosity has to be taken into account as described below.

According to our knowledge there are no data in the open literature for the viscosity of the methanol–benzene and methanol–cyclohexane vapor mixtures.

3. THEORY

In practice, viscosity data at low densities are often interpreted as zero-density values. That is, it is assumed that the influence of the initial density dependence is small and negligible in comparison with the experimental uncertainties. This assumption ceases to be valid at low reduced temperatures T^*. It was shown in the framework of the Rainwater–Friend theory that even for noble gases for $T^* < 1$ the effect of the initial density dependence of viscosity amounts to some percentage when data at atmospheric pressure are compared with zero-density values [6]. In the present paper, we identify data at low densities with values for which a linear-density contribution has to be taken into account.

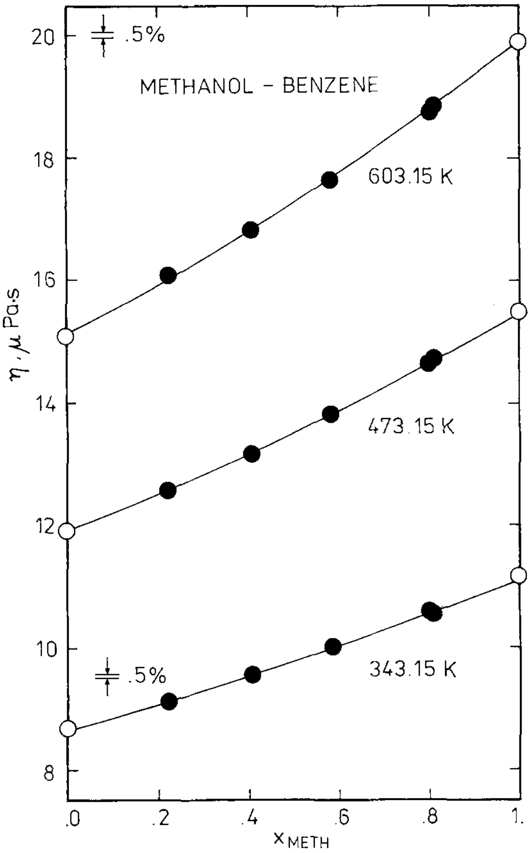

Fig. 1. Viscosity of methanol–benzene vapor mixtures as a function of mole fraction for three isotherms. (●) At densities according to Table 1; (○) at zero density, calculated.

As already mentioned, the methods of prediction of the density and composition dependence of real dense gaseous mixtures are based on the Enskog theory [9–11]. The viscosity coefficient η_i of a dense gas of hard spheres deduced by solving the Enskog kinetic equation can be expressed in terms of the viscosity in the limit of zero density $\eta_i^{(0)}$ given by the Chapman–Enskog solution of the Boltzmann equation. If the density expansion is terminated after terms linear in ρ, one obtains

$$\eta_i = \eta_i^{(0)} + \eta_i^{(1)}\rho + \cdots \tag{3}$$

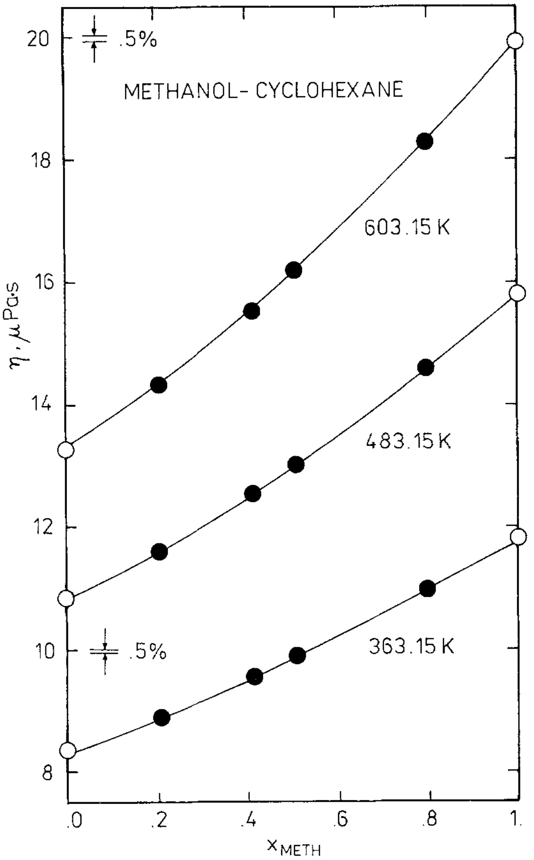

Fig. 2. Viscosity of methanol–cyclohexane vapor mixtures as a function of mole fraction for three isotherms. (●) At densities according to Table II; (○) at zero density, calculated.

with

$$\eta_i^{(0)} = \frac{5(\pi m_i kT)^{1/2}}{16\pi\sigma_i^2}, \tag{4}$$

$$\eta_i^{(1)} = \eta_i^{(0)}\left(\frac{4}{5}b_i - \chi_i^{(1)}\right) = \eta_i^{(0)} B_{\eta_i}, \tag{5}$$

$$b_i = \frac{2}{3}\pi N\sigma_i^3, \tag{6}$$

$$\chi_i = 1 + \chi_i^{(1)}\rho + \cdots = 1 + \frac{c}{b}\rho + \cdots \tag{7}$$

$$\chi_i^{(1)} = \frac{5}{12}\pi N\sigma_i^3 \tag{8}$$

Since the formulae for the mixtures refer to the first approximation in the corresponding solution, Eqs. (3) and (4) are also written in the first approximation of the perturbation solution. Here, m_i, σ_i, b_i, and c_i are molecular mass, diameter, and second and third pressure virial coefficients of hard spheres, respectively. Furthermore, N is Avogadro's number, B_{η_i} is the second viscosity virial coefficient, and the quantity χ_i is the radial distribution function of the hard spheres of diameter σ_i at contact.

The theoretical formulae for the viscosity of a dense binary mixture of hard spheres up to terms linear in ρ become

$$\eta_{\text{mix}} = \eta_{\text{mix}}^{(0)} + \eta_{\text{mix}}^{(1)} \rho + \cdots \tag{9}$$

with

$$\begin{aligned} \eta_{\text{mix}}^{(0)} = {} & [x_1^2 H_{22}^{(0)} + x_2^2 H_{11}^{(0)} - 2x_1 x_2 H_{12}^{(0)}] \\ & \times [H_{11}^{(0)} H_{22}^{(0)} - H_{12}^{(0)2}]^{-1} \end{aligned} \tag{10}$$

$$\begin{aligned} \eta_{\text{mix}}^{(1)} = {} & \{ [x_1^2 H_{22}^{(1)} + x_2^2 H_{11}^{(1)} - 2x_1 x_2 H_{12}^{(1)} + 2x_1\, y_1^{(1)} H_{22}^{(0)} \\ & + 2x_2\, y_2^{(1)} H_{11}^{(0)} - 2x_1\, y_2^{(1)} H_{12}^{(0)} - 2x_2\, y_1^{(1)} H_{12}^{(0)}] \\ & - \eta_{\text{mix}}^{(0)} [H_{11}^{(0)} H_{22}^{(1)} + H_{11}^{(1)} H_{22}^{(0)} - 2H_{12}^{(0)} H_{12}^{(1)}] \} \\ & \times [H_{11}^{(0)} H_{22}^{(0)} - H_{12}^{(0)2}]^{-1} \end{aligned} \tag{11}$$

$$H_{ij} = H_{ij}^{(0)} + H_{ij}^{(1)} \rho + \cdots \tag{12}$$

$$H_{ii}^{(1)} = \frac{x_i^2 \chi_{ii}^{(1)}}{\eta_i^{(0)}} + \sum_{j=1, j \neq i}^{2} \frac{2x_i x_j \chi_{ij}^{(1)}}{\eta_{ij}^{(0)}} \frac{m_i m_j}{(m_i + m_j)^2} \left(\frac{5}{3A_{ij}^*} + \frac{m_j}{m_i} \right) \tag{13}$$

$$H_{ij}^{(1)}\ (j \neq 1) = -\frac{2x_i x_j \chi_{ij}^{(1)}}{\eta_{ij}^{(0)}} \frac{m_i m_j}{(m_i + m_j)^2} \left(\frac{5}{3A_{ij}^*} - 1 \right) \tag{14}$$

$$H_{ij}^{(0)} = H_{ij}^{(1)} \qquad \text{with} \qquad [\chi_{ij}^{(1)} = 1] \tag{15}$$

$$\eta_{ij}^{(0)} = \frac{5(\pi m_{ij} kT)^{1/2}}{16\pi\sigma_{ij}^2} \tag{16}$$

$$m_{ij} = \frac{2m_i m_j}{m_i + m_j} \tag{17}$$

$$b_{ij} = \frac{2}{3} \pi N \sigma_{ij}^3 \tag{18}$$

$$\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj}) \tag{19}$$

$$\chi_{ij} = 1 + \chi_{ij}^{(1)} \rho + \cdots \tag{20}$$

$$\chi_{ij}^{(1)} = \zeta_3 + \frac{3\sigma_{ii}\sigma_{jj}}{2\sigma_{ij}}\zeta_2 \tag{21}$$

$$\zeta_k = \frac{\pi}{6} N \sum_{i=1}^{2} x_i \sigma_{ii}^k \tag{22}$$

$$y_i = x_i + y_i^{(1)}\rho + \cdots \tag{23}$$

$$y_i^{(1)} = \frac{4}{5} x_i \sum_{j=1}^{2} \frac{m_j}{m_i + m_j} x_j b_{ij} \tag{24}$$

The interaction viscosity $\eta_{ij}^{(0)}$ in the limit of zero density is the viscosity of a hypothetical one-component hard-sphere gas with molecules of mass m_{ij} and diameter σ_{ij}, where σ_{ij} corresponds to the usual combining rule of hard spheres and is further used to express the second pressure virial coefficients b_{ij} and the values of the radial distribution function χ_{ij} of mixtures at contact by means of the quantities of the pure components. The term A_{ij}^* is a dimensionless ratio of collision integrals that is exactly unity for hard spheres.

An ad hoc adaptation of the Enskog theory to real gases was already proposed by Enskog himself [35]. He assumed that the transport coefficients of simple real gases are of the same functional form as those of hard spheres. If η_i of Eq. (3) is identified with the viscosity of a real gas, it can be reproduced with a suitable choice of the diameter σ_i in $\eta_i^{(0)}$, b_i, and $\chi_i^{(1)}$. Three different effective values, σ_i^η, σ_i^b, and σ_i^χ are possibly needed in order to take into account the interactions in real dense gases. Thus, σ_i^η, or better $\eta_i^{(0)}$, is replaced by the experimentally obtained zero-density viscosity coefficient, whereas σ_i^b and σ_i^χ are substituted under the condition that the thermal pressure $T(\partial P/\partial T)_\rho$ of the real gas is used instead of the pressure P in the equation of state of the hard-sphere gas. The parameter b_i then becomes [12]

$$b_i = B_i + T\, dB_i/dT \tag{25}$$

and $\chi_i^{(1)}$ in Eq. (7) can be chosen by using a relation analogous to Eq. (25) (complete MET [12, 23]),

$$c_i = C_i + T\, dC_i/dT \tag{26}$$

where B_i and C_i are the second and third pressure virial coefficient of the real gas, respectively.

It has been shown that values of the reduced second viscosity virial coefficient B_η^* as a function of the reduced temperature T^* resulting from the complete MET for the Lennard-Jones 12-6 potential are approximately in agreement with experimental data for benzene [23], cyclohexane and neopentane [25], *n*-hexane [26], and sulfur hexafluoride [28]. The reduced quantities are defined by

$$B_\eta^* = B/\sigma_r^3 \tag{27}$$

$$T^* = kT/\varepsilon_r \tag{28}$$

where σ_r and ε_r are the distance and energy parameters of the real intermolecular potential.

To modify the Enskog–Thorne theory for binary hard-sphere gaseous mixtures, η_{mix} of Eq. (9) is assumed to be the viscosity of the real dense gaseous mixture. The diameter σ_{ij} in $\eta_{ij}^{(0)}$ for the hard-sphere mixture is replaced by means of the experimentally obtained interaction viscosity of the real-gaseous mixture in the limit of zero density. The diameters σ_{ij}^b in b_{ij} and σ_{ij}^χ in $\chi_{ij}^{(1)}$ can be substituted following the guidelines of Kestin et al. [14, 16]. In this procedure σ_i^b and σ_i^χ are determined so that the experimental viscosities of the dense pure gases are reproduced. A suitably chosen value of b_i or σ_i^b could not be obtained by means of second pressure virial coefficients of the real pure gas via Eqs. (25) and (6), since there is not a real solution of the complete equation of the Enskog theory for the viscosity of a dense one-component gas of hard spheres [equivalent to Eq. (3)] at all densities by using this b_i in order to determine χ_i:

$$\eta_i = \eta_i^{(0)} \left[\left(1 + \frac{2}{5} b_i \rho\, \chi_i\right)^2 \chi_i^{-1} + \frac{48}{25\pi} (b_i \rho)^2 \chi_i \right] \tag{29}$$

Further complications were solved by Sandler and Fiszdon [15] in order to ensure that χ_i is a real, continuous, and monotonically increasing function of ρ. In this procedure the fact is used that η/ρ according to Eq. (29) has a minimum at a certain density ρ_{min}. Finally, the interaction values b_{ij} and χ_{ij} were obtained from relations following from the combining rule for hard spheres. In this connection it should be mentioned that Kestin et al. [16], in determining χ_i or σ_i^χ as well as χ_{ij}, used the same density expansions of Eqs. (7) and (20) which are terminated after terms linear in ρ. This choice seems to have been adequate as Kestin et al. found a reasonable estimate within a few tenths of a percent for the viscosity of He–Ne and Ne–Ar mixtures in the density range of their experimental data. In systems for which the density dependence of viscosity is stronger, such a choice would not be sufficient.

4. DETERMINATION AND RESULTS OF THE INTERACTION VISCOSITY IN THE LIMIT OF ZERO DENSITY

The further evaluation of the data of our measurements on the methanol–benzene and methanol–cyclohexane vapor mixtures involved the determination of the zero-density interaction viscosity $\eta_{ij}^{(0)}$. As already mentioned in Section 2, the measurements on the mixtures were probably influenced like that on the pure vapors by the initial density dependence of viscosity. Thus, the usual evaluation by means of the Chapman–Enskog theory becomes insufficient.

The treatment of the experimental data in the limit of zero density according to Chapman and Enskog implies that only $\eta_{\mathrm{mix}}^{(0)}$ has to be kept in Eq. (9) including Eq. (10) as well as Eqs. (13) and (14) under the condition given by Eq. (15). A_{ij}^* should be taken in a good approximation to be 1.10 [16]. Then exactly the same values of $\eta_{ij}^{(0)}$ ought to be obtained from η_{mix} of different mole fractions for isotherms as a criterion of consistency.

In our treatment of the initial density dependence, b_i values for the pure substances were determined by means of experimental second pressure virial coefficients according to Eq. (25). This is based on the fact that the measurements were performed at relatively low densities so that the minimum of η/ρ as a function of ρ is not attained and χ_i is a real and monotonically increasing function in any case. Then $\chi_i^{(1)}$ was obtained from Eq. (5) with b_i and the experimentally determined $\eta_i^{(1)}$ and $\eta_i^{(0)}$ for the pure substances from Refs. 23 and 25. σ_i^b and σ_i^χ were deduced from Eqs. (6) and (8). Finally, values of b_{ij} and $\chi_{ij}^{(1)}$ were obtained from Eqs. (18) and (21) using the combining rule given by Eq. (19) for σ_{ij}^b and σ_{ij}^χ. Apart from the determination of b_i our procedure is consistent with that of Kestin et al. [16] with regard to the linear density expansion of χ_{ij}.

We determined the second pressure virial coefficients B_i and their temperature derivatives dB_i/dT for methanol, benzene, and cyclohexane on the basis of own experimental data and their theoretical evaluation including data from the literature.

Bich et al. [36] reported B_i values for methanol in the temperature range from 356 up to 623 K which were experimentally based and were extrapolated down to a temperature of 298 K with the aid of an 12–6–8–3 intermolecular potential. The values calculated from this potential model between 298 and 623 K (see last column in Table 2 of Ref. 36) were used in order to fit the coefficients of the following polynomial in $1/T$:

$$B_i = \sum_{k=0}^{5} a_k/T^k \tag{30}$$

The coefficients a_k thus obtained are given in Table IV.

Table IV. Coefficients of the Polynomial Given by Eq. (30) for the Second Pressure Virial Coefficients, B and B_{ij} in $\mathrm{L \cdot mol^{-1}}$

Coefficient	Methanol	Benzene	Cyclohexane	Methanol–benzene
a_0	1.27787	0.0816286	0.	0.0459421
a_1	−3.25548 (3)[a]	0.0214401 (3)	1.20746 (3)	0.0274675 (3)
a_2	3.30677 (6)	−0.199242 (6)	−2.13346 (6)	−0.0705704 (6)
a_3	−1.71730 (9)	0.0531628 (9)	1.24989 (9)	0.
a_4	0.445539 (12)	−0.0109625 (12)	−0.335554 (12)	0.
a_5	−0.0489585 (15)	0.	0.0318016 (15)	0.

[a] $(z) = 10^z$.

Bich and Opel [37] analyzed and evaluated the experimental temperature function of B_i for the vapors of aromatic compounds, including benzene between 303 and 635 K, by means of m–6–8 potential models. Values, following from the 100–6–8 potential parameters given in the last row for benzene in Table 5 of Ref. 37, were used in determining the coefficients a_k of Eq. (30) for benzene given in Table IV.

Finally, the coefficients a_k for cyclohexane in Table IV were directly taken from Bich et al. [38]. They were deduced by means of own experimental data between 372 and 622 K and of some from the literature in the range 315 up to 348 K.

In Fig. 3 the results for the interaction viscosity $\eta_{ij}^{(0)}$ in the limit of zero density are shown for five isotherms of both systems as deviations of the values for each individual mixture from that of the average $\overline{\eta_{ij}^{(0)}}$. The percentage deviations between the values recalculated with $\overline{\eta_{ij}^{(0)}}$ and the experimental data for η_{mix} are presented in Fig. 4. For temperatures below the third isotherm shown for both systems, significant differences clearly emerge between the values with taking into account the initial density dependence of viscosity and those without. To give an example, for methanol–benzene at 343 K it becomes obvious that the results of $\eta_{ij}^{(0)}$ and $\eta_{\mathrm{mix,exp}}$ for the mole fractions at higher densities are too small and the result for the mole fraction at the lowest density is too large in comparison with $\overline{\eta_{ij}^{(0)}}$ and $\eta_{\mathrm{mix,recalc}}$, respectively. These results following from the evaluation without considering the initial density dependence are in agreement with the findings for the pure vapors that at low temperatures the viscosity coefficient decreases with increasing density. These differences clearly exceed the reproducibility of the experiments (±0.1 up to ±0.15%). But the experimental data apart from only a few values are reproduced within ±0.1 % by taking into consideration this effect for all isotherms up to 433 K.

For temperatures near and above the third isotherm, significant differences do not occur in Figs. 3 and 4 for both systems because of the relatively small initial density dependence of the viscosity for the three pure vapors and, hence, also the vapor mixtures in that temperature range. For all three pure vapors the values of the initial density dependence are positive at the highest temperatures, decrease with decreasing temperature, pass through zero for approximately the fourth isotherm and become negative [23, 25].

Furthermore, one has to take into consideration an increasing thermal alteration and decomposition of the substances. From the highest isotherms in Figs. 3 and 4 it can be seen that $\eta_{ij}^{(0)}$ for the methanol–benzene vapor

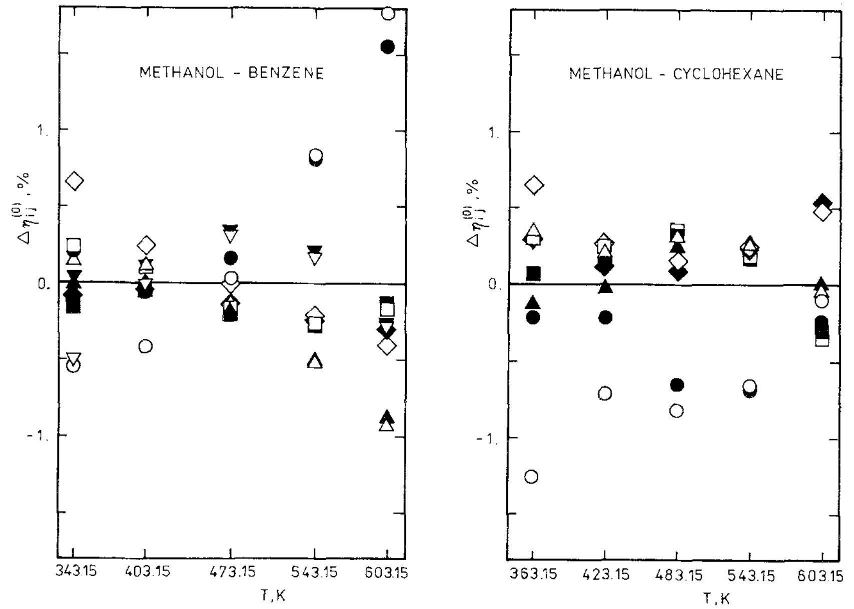

Fig. 3. Deviations of the results for each individual mixture from the average of the interaction viscosity in the limit of zero density as a function of temperature. $\Delta\eta_{ij}^{(0)} = 100\,[\eta_{ij}^{(0)} - \overline{\eta_{ij}^{(0)}}]/\overline{\eta_{ij}^{(0)}}$. Open symbols, without initial density dependence; filled symbols, including initial density dependence. Methanol–benzene: (○, ●) $x_{\mathrm{METH}} = 0.2233$, $\rho = 22.08 \times 10^{3}\,\mathrm{mol \cdot L^{-1}}$; (□, ■) $x_{\mathrm{METH}} = 0.4071$, $\rho = 15.05 \times 10^{-3}\,\mathrm{mol \cdot L^{-1}}$; (◇, ◆) $x_{\mathrm{METH}} = 0.5840$, $\rho = 10.79 \times 10^{-3}\,\mathrm{mol \cdot L^{-1}}$; (△, ▲) $x_{\mathrm{METH}} = 0.8011$, $\rho = 13.51 \times 10^{-3}\,\mathrm{mol \cdot L^{-1}}$; (▽, ▼) $x_{\mathrm{METH}} = 0.8097$, $\rho = 20.20 \times 10^{-3}\,\mathrm{mol \cdot L^{-1}}$. Methanol–cyclohexane: (○, ●) $x_{\mathrm{METH}} = 0.2068$, $\rho = 26.17 \times 10^{-3}\,\mathrm{mol \cdot L^{-1}}$; (□, ■) $x_{\mathrm{METH}} = 0.4121$, $\rho = 18.10 \times 10^{-3}\,\mathrm{mol \cdot L^{-1}}$; (◇, ◆) $x_{\mathrm{METH}} = 0.5087$, $\rho = 17.27 \times 10^{-3}\,\mathrm{mol \cdot L^{-1}}$; (△, ▲) $x_{\mathrm{METH}} = 0.7984$, $\rho = 12.14 \times 10^{-3}\,\mathrm{mol \cdot L^{-1}}$.

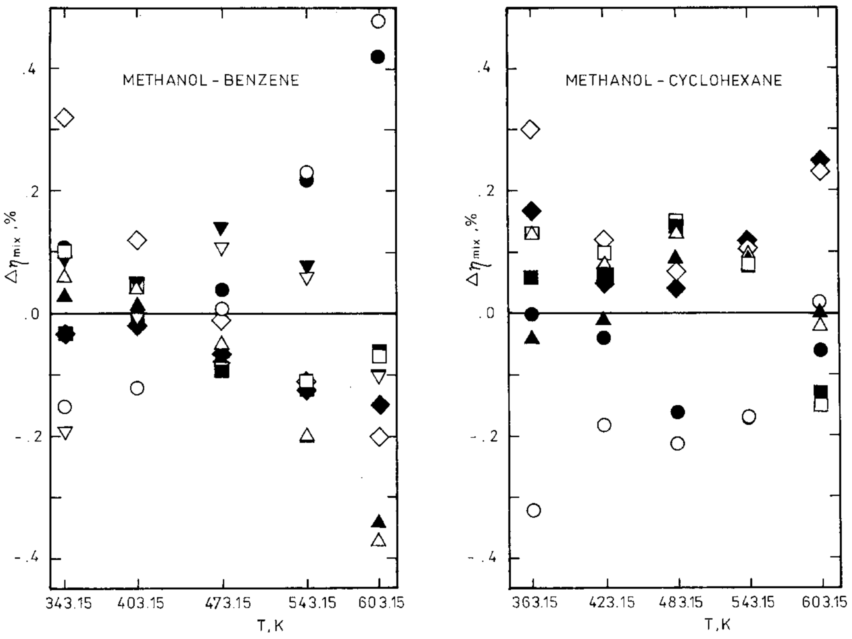

Fig. 4. Deviations of the experimental results from values recalculated with $\overline{\eta_{ij}^{(0)}}$ for the viscosity of each individual mixture as a function of temperature. $\Delta\eta_{\mathrm{mix}} = 100\,(\eta_{\mathrm{mix,exp}} - \eta_{\mathrm{mix,recalc}})/\eta_{\mathrm{mix,exp}}$. Symbols for Fig. 3.

mixture with $x_{\mathrm{METH}} = 0.2233$ is large in comparison with $\overline{\eta_{ij}^{(0)}}$ as a consequence of an increased experimental value of η_{mix}. It is evident that thermal alteration is responsible for it. Therefore, we excluded the $\eta_{ij}^{(0)}$ values for this mixture at temperatures above 523 K from the calculation of $\overline{\eta_{ij}^{(0)}}$. All other experimental data were included in the determination of the interaction viscosity in the limit of zero density because it was impossible to distinguish between the effects of experimental error, thermal alteration, and initial density dependence.

In Table V we list $\overline{\eta_{ij}^{(0)}}$ values of the methanol–benzene and methanol–cyclohexane vapor mixtures corrected for the initial density dependence of viscosity for several isotherms. Equation (2) was fitted to the $\overline{\eta_{ij}^{(0)}}$ values at fixed temperatures in 10 K intervals. The parameters in Eq. (2) for both systems are included in Table III.

5. BINARY DIFFUSION COEFFICIENTS

The zero-density interaction viscosity values $\eta_{ij}^{(0)}$ represent alternative data of the binary diffusion coefficients of these systems. According to the

Table V. Average Values of the Interaction Viscosity $\overline{\eta_{ij}^{(0)}}$ in the Limit of Zero Density of Methanol–Benzene and Methanol–Cyclohexane Vapor Mixtures with Taking into Account the Initial Density Dependence

	Methanol–benzene		Methanol–cyclohexane	
Temperature T (K)	Number of points (n)	Zero-density interaction viscosity $\overline{\eta_{ij}^{(0)}}$ (μPa · s)	Number of points (n)	Zero-density interaction viscosity $\overline{\eta_{ij}^{(0)}}$ (μPa · s)
333.15	4	9.290	2	8.959
363.15	5	10.092	4	9.698
393.15	5	10.903	4	10.445
423.15	5	11.723	4	11.184
453.15	5	12.553	4	11.928
483.15	5	13.389	4	12.684
513.15	5	14.229	4	13.454
543.15	4	15.042	4	14.245
573.15	4	15.870	4	15.049
603.15	4	16.697	4	15.882

Chaman–Enskog theory of dilute gases, interaction viscosity and binary diffusion coefficient can mutually be expressed so that only the collision integral ratio A_{ij}^* remains as a nonexperimental quantity which is relatively independent of the choice of the intermolecular potential model and is insensitive to inelastic collisions [39]. The relation can be written in first approximation as

$$(\rho\, D_{ij})^{(0)} = \frac{3}{5} \frac{M_i + M_j}{M_i M_j} A_{ij}^* \eta_{ij}^{(0)} \tag{31}$$

where $(\rho\, D_{ij})^{(0)}$ corresponds to the limit $\rho \to 0$. For historical reasons the proportionality constant between the molecular flux and the composition gradient is arbitrarily chosen to be $(\rho\, D_{ij})$, so that D_{ij} is inversely proportional to ρ. In practice the values of D_{ij} at atmospheric pressure are obtained using the ideal-gas law and identifying with the zero-density limit:

$$D_{ij}^{(0)} = \frac{3}{5} \frac{M_i + M_j}{M_i M_j} A_{ij}^* \frac{RT}{p} \eta_{ij}^{(0)} \tag{32}$$

The diffusion coefficients calculated according to Eqs. (31) or (32) are not true values of D_{ij}, because they have a small composition dependence in higher approximations of the kinetic theory due to Chapman and

Enskog. But they are also not exact for the first approximation, as experimental mixture viscosity data are used in order to get $\eta_{ij}^{(0)}$. Marrero and Mason [39] discussed in detail the reliability of D_{ij} obtained from mixture viscosity data. Thus, the uncertainty of the viscosity measurement enters into that of D_{ij} with a factor of five, whereas the uncertainty of A_{ij}^* is directly reproduced in D_{ij}. The value of $A_{ij}^* = 1.10$ for the systems under discussion should be reliable to about 1–2%, so that the total uncertainty of D_{ij} following from Eq. (31) or (32) is estimated to be 2–3%.

In principle, the real-gas behavior has to be taken into account if values of the diffusion coefficient at atmospheric pressure are needed. When the second pressure virial coefficient B_{mix}

$$B_{\mathrm{mix}} = x_i^2 B_{ii} + 2x_i x_j B_{ij} + x_j^2 B_{jj} \tag{33}$$

of the equation of state

$$\frac{p}{RT} = \rho + B_{\mathrm{mix}} \rho^2 + \cdots \tag{34}$$

is relatively large, the real-gas density ρ is larger than that implied by the ideal gas. Thus, diffusion coefficients obtained by using the real-gas density are smaller than the $(D_{ij})^{(0)}$ values from Eq. (32). This systematic departure can only be neglected within the uncertainty mentioned above.

The density dependence of the proportionality constant of the mass flux (ρD_{12}), which is not taken into account in Eq. (31), ought to be treated in the framework of the Enskog theory of hard-sphere mixtures and its modification. Kincaid et al. [40] examined in detail the differences between the standard Enskog theory (SET) due to Tham and Gubbins [11] and the revised Enskog theory (RET) due to van Beijeren and Ernst [41, 42]. The differences which exist between the diffusion coefficients following from both theories at higher densities do not appear in the terms linear in ρ. Thus, it should be adequate to make use of Eq. (35) for the densities corresponding to atmospheric pressure:

$$(\rho D_{ij}) = (\rho D_{ij})^{(0)} \frac{1 - 4x_i x_j \{B_{ij} - [(B_{ii} + B_{jj})/2]\} \rho + \cdots}{1 + \chi_{ij}^{(1)} \rho + \cdots} \tag{35}$$

The first density coefficient of the contact value of the radial distribution function $\chi_{ij}^{(1)}$ was again taken from the initial density dependence of the viscosity coefficient of the pure components via Eq. (21) and combining rule given by Eq. (19) within the MET. The numerator of Eq. (35) comes from a comparison of the diffusion coefficients given by the SET or RET with values obtained from the experiment. Values of the interaction second pressure virial coefficient B_{ij} are needed for the calculation of this nonideality thermodynamic factor as well as of the density by means of Eqs. (33) and (34). Experimental values of B_{ij} are available only for the vapor mixture methanol–benzene. The coefficients a_k of Eq. (30) published by Pietsch and Opel [43] are also given for this system in Table IV. In addition, values of B_{ij} for both systems were calculated by means of Eq. (18) and cobining rule (19). Although the differences between the calculated values of B_{ij} and the experimental data in the case of methanol–benzene are large at low temperatures, their influence on the nonideality thermodynamic factor and on the density mutually compensates to a certain degree, so that the choice of B_{ij} has only a relatively small effect on the diffusion coefficient resulting from Eq. (35). But the dependence of the diffusion coefficient on the mole fraction is of more importance. The differences of the calculated values of D_{ij} for $x_{\mathrm{METH}} = 0.1$ and $x_{\mathrm{METH}} = 0.9$ amount to 3.5% at the lowest temperatures and decrease with increasing temperature.

In Table VI values of the diffusion coefficient at a pressure of 1 atm calculated with Eq. (32) are compared with those resulting from Eq. (35) for the mole fraction $x_{\mathrm{METH}} = 0.5$ and for calculated values of B_{ij}. Above

Table VI. Values of the Diffusion Coefficient at Atmospheric Pressure for Methanol–Benzene and Methanol–Cyclohexane Vapor Mixtures[a]

	Methanol–benzene		Methanol–cyclohexane	
Temperature T(K)	Zero-density limit $10^4\,(D_{ij})^{(0)}$ ($\mathrm{m^2 \cdot s^{-1}}$)	Initial density dependence $10^4\,D_{ij}$ ($\mathrm{m^2 \cdot s^{-1}}$)	Zero-density limit $10^4\,(D_{ij})^{(0)}$ ($\mathrm{m^2 \cdot s^{-1}}$)	Initial density dependence $10^4\,D_{ij}$ ($\mathrm{m^2 \cdot s^{-1}}$)
333.15	0.0738	0.0649	0.0696	0.0604
363.15	0.0873	0.0808	0.0822	0.0754
393.15	0.1022	0.0971	0.0958	0.0906
423.15	0.1183	0.1141	0.1104	0.1062
453.15	0.1356	0.1321	0.1261	0.1226
483.15	0.1542	0.1511	0.1430	0.1400
513.15	0.1739	0.1711	0.1611	0.1585
543.15	0.1948	0.1923	0.1806	0.1781
573.15	0.2168	0.2147	0.2013	0.1991
603.15	0.2400	0.2382	0.2235	0.2215

[a] $(D_{ij})^{(0)}$ calculated via Eq. (32) in the limit of zero density. D_{ij} takes into account the initial density dependence according to Eq. (35) for $x_{\mathrm{METH}} = 0.5$ and for calculated values of B_{ij}.

423 K the differences between $(D_{ij})^{(0)}$ and D_{ij} are comparable or smaller than the uncertainty of $(D_{ij})^{(0)}$ resulting from its determination by means of the interaction viscosity $\eta_{ij}^{(0)}$ via the Chapman–Enskog theory. With decreasing temperature the differences increase up to more than 10%.

6. CONCLUSIONS

We have demonstrated that the initial density dependence influences the viscosity data at the densities of our measurements. The evaluation of the data according to the procedure proposed guarantees that the interaction viscosity $\eta_{ij}^{(0)}$ is in fact that in the limit of zero density. Furthermore, $\eta_{ij}^{(0)}$ should be the same for different mole fractions as a criterion of the consistency of the measurements.

The described formalism can be used in order to calculate exactly the density dependence of the viscosity coefficient of binary gas mixtures up to the first order in ρ. Data of the density dependence of the viscosity for the pure components as well as of the viscosity coefficient of only one binary mixture at a single moderate density are needed. The extension to multicomponent mixtures is straightforward because further information apart from that for each individual binary mixture is not necessary. Only binary terms appear in the corresponding formalism as a consequence of the use of the hard-sphere combining rule [14].

The results of the calculation of binary diffusion coefficients at atmospheric pressure for the mixtures under discussion clearly show that for low temperatures the effect of initial density dependence cannot be neglected. Therefore, the usual procedure to determine binary diffusion coefficients by means of the interaction viscosity via Eq. (32) [39] can be accepted only if the influence of the initial density dependence is lower than the uncertainty of D_{ij}, which amounts to 3–5% essentially dependent on the uncertainty of the viscosity measurement. But a calculation on a high level needs reliable values of the interaction viscosity $\eta_{ij}^{(0)}$ in the limit of zero density and values of the real-gas density including the second pressure virial coefficients and, furthermore, has to take into consideration the initial density dependence via the Enskog theory and its modification according to Eq. (35). These findings are also of importance for a critical assessment of experimental data for the diffusion coefficient of binary gas-vapor mixtures obtained at pressures of some atmospheres.

A further improvement of the evaluation of our data could be attained if the calculations according to the Rainwater–Friend theory would have been extended to the integrals which are necessary in the case of viscosity and diffusion of gas mixtures. Bennett and Curtiss [44] have already given corrections for these transort properties of mixtures linear in density, but unlike Rainwater and Friend, they have used the full B rather than the free part of B and have not included monomer–dimer terms.

REFERENCES

1. Y. Kan, J. R. Dorfman, and J. V. Sengers, in *Proc. 7th Symp. Thermophys. Props.*, A. Cezairliyan, ed. (American Society of Mechanical Engineers, New York, 1977), p. 652.
2. J. C. Rainwater, *J. Chem. Phys.* **81**:495 (1984).
3. D. G. Friend and J. C. Rainwater, *Chem. Phys. Lett.* **107**:590 (1984).
4. D. G. Friend, *J. Chem. Phys.* **79**:4553 (1983).
5. J. C. Rainwater and D. G. Friend, *Phys. Rev.* **A36**:4062 (1987).
6. E. Bich and E. Vogel, *Int. J. Thermophys.* **12**:27 (1991).
7. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964), Chap. 8.
8. G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces—Their Origin and Determination* (Clarendon, Oxford, 1987).
9. Ref. 7, Chap. 9.
10. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1952), Chap. 16.
11. M. K. Tham and K. E. Gubbins, *J. Chem. Phys.* **55**:268 (1971).
12. H. J. M. Hanley, R. D. McCarty, and E. G. D. Cohen, *Physica* **60**:322 (1972).
13. H. J. M. Hanley and E. G. D. Cohen, *Physica* **A83**:215 (1976).
14. R. DiPippo, J. R. Dorfman, J. Kestin, H. E. Khalifa, and E. A. Mason, *Physica* **A86**:205 (1977).
15. S. I. Sandler and J. K. Fiszdon, *Physica* **A95**:602 (1979).
16. J. Kestin, Ö. Korfali, J. V. Sengers, and B. Kamgar-Parsi, *Physica* **A106**:415 (1981).
17. J. M. Kincaid, S. Perez, and E. G. D. Cohen, *Phys. Rev.* **A38**:3628 (1988).
18. S. Perez and J. M. Kincaid, *Int. J. Thermophys.* **10**:963 (1989).
19. E. Vogel, *Wiss. Z. Univ. Rostock* **21**(M2):169 (1972).
20. E. Vogel, E. Bastubbe, and S. Rohde, *Wiss. Z. W.-Pieck-Univ. Rostock* **33**(N8):34 (1984).
21. E. Vogel, *Ber. Bunsenges. Phys. Chem.* **88**:997 (1984).
22. E. Vogel and L. Barkow, *Z. Phys. Chem. Leipzig* **267**:1038 (1986).
23. E. Vogel, E. Bich, and R. Nimz, *Physica* **A139**:188 (1986).
24. T. Strehlow, E. Vogel, and E. Bich, *Wiss. Z. W.-Pieck-Univ. Rostock* **35**(N7):5 (1986).
25. E. Vogel, B. Holdt, and T. Strehlow, *Physica* **A148**:46 (1988).
26. E. Vogel and T. Strehlow, *Z. Phys. Chem. Leipzig* **269**:897 (1988).
27. E. Vogel, T. Strehlow, J. Millat, and W. A. Wakeham, *Z. Phys. Chem. Leipzig* **270**:1145 (1989).
28. T. Strehlow and E. Vogel, *Physica* **A161**:101 (1989).
29. J. Kestin, S. T. Ro, and W. A. Wakeham, *J. Chem. Phys.* **56**:4119 (1972).
30. J. Kestin, E. Paykoc, and J. V. Sengers, *Physica* **54**:1 (1971).
31. R. A. Aziz, F. R. W. McCourt, and C. C. K. Wong, *Mol. Phys.* **61**:1487 (1987).
32. R. A. Aziz and M. J. Slaman, *Chem. Phys.* **130**:187 (1989).
33. R. A. Aziz and M. J. Slaman, *Mol. Phys.* **58**:679 (1986).
34. R. A. Aziz and M. J. Slaman, *Mol. Phys.* **57**:825 (1986).
35. D. Enskog, *Kgl. Svenska Ventensk. Handl.*, Vol. 63, No. 4 (1922).
36. E. Bich, R. Pietsch, and G. Opel, *Z. Phys. Chem. Leipzig* **265**:396 (1984).
37. E. Bich and G. Opel, *Z. Phys. Chem. Leipzig* **263**:470 (1982).

38. E. Bich, G. Opel, R. Pietsch, R. Schmal, and E. Vogel, *Z. Phys. Chem. Leipzig* **265**:101 (1984).
39. T. R. Marrero and E. A. Mason, *J. Phys. Chem. Ref. Data* **1**:3 (1972).
40. J. M. Kincaid, M. Lopez de Haro, and E. G. D. Cohen, *J. Chem. Phys.* **79**:4509 (1983).
41. H. van Beijeren and M. H. Ernst, *Physica* **68**:437 (1973).
42. H. van Beijeren and M. H. Ernst, *Physica* **70**:220 (1973).
43. R. Pietsch and G. Opel, *Z. Phys. Chem. Leipzig* **269**:705 (1988).
44. D. E. Bennett and C. F. Curtiss, *J. Chem. Phys.* **51**:2811 (1969).