The viscosity of the binary vapor mixture methanol–triethylamine at low densities and in the saturated vapor phase of the vapor–liquid equilibrium

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ARTICLE INFO

ABSTRACT

For the first time, results of precision measurements of the viscosity coefficient of the binary vapor mixture methanol–triethylamine at low densities are reported. The relative measurements with an all-quartz oscillating-disk viscometer were carried out for nearly equimolar mixtures along five isochores at densities from 0.010 to 0.033 mol dm^{-3} as well as for a mixture of the mole fraction y_{meth} = 0.3322 at a density 0.016 mol dm^{-3} in the temperature range between 298 and 498 K. The uncertainty is estimated to be ±0.2% at ambient temperature, increasing to ±0.3% at higher temperatures. Isothermal values of a mixture with the averaged mole fraction y_{meth} = 0.5002 were recalculated from the original experimental data and evaluated with a first-order expansion for the viscosity, in terms of density. A so-called individual correlation on the basis of the extended theorem of corresponding states was employed to describe the interaction viscosity in the limit of zero density. Some data points at low temperatures had to be excluded from this calculation, since the measurements were performed in the saturated vapor phase. For these data points the vapor–liquid equilibrium had to be evaluated to assign the correct mole fraction in the vapor to the measured viscosity.

1. Introduction

In principle, negative initial density dependencies of viscosity occur at sufficiently low temperatures for all gases [1,2]. In the case of polar vapors, for which associates could be formed, strongly negative initial density dependencies are to be expected. But the results of viscosity measurements on the vapors of water [3], methanol [4], and triethylamine [5] did not show an exceptionally strong initial density dependence. To investigate this field further, new viscosity measurements on the binary vapor mixture methanol–triethylamine at moderately low densities were performed and evaluated. Their results are reported in this paper. According to our knowledge, experimental viscosity data for this vapor mixture have not been published in publicly available literature.

In analogy to the correlation and prediction of the viscosity of pure gases and vapors over a restricted range of thermodynamic states, a first-order expansion, in terms of density, can also be used for mixtures of gases and vapors. Thus at moderately low densities, the viscosity is described as a function of temperature T, molar density ρ, and composition $\bar{y}$ (for a binary mixture in the form of the mole fractions y_1 and y_2):

$$\eta_{mix}(T, \rho, \bar{y}) = \eta_{mix}^{(0)}(T, \bar{y}) + \eta_{mix}^{(1)}(T, \bar{y})\rho$$
$$= \eta_{mix}^{(0)}(T, \bar{y})[1 + B_{\eta_{mix}}(T, \bar{y})\rho]. \quad (1)$$

Here, $\eta_{mix}^{(0)}$ is the viscosity coefficient in the limit of zero density, $\eta_{mix}^{(1)}$ is the initial density viscosity coefficient, and $B_{\eta_{mix}}$ is the second viscosity virial coefficient. Measurements at very low densities are influenced by slip effects, whereas experiments in the limit of zero density are not feasible. Hence $\eta_{mix}^{(0)}$ has to be determined using isotherms of the same composition with a sufficient number of experimental points at different densities and extrapolating them to the limit of zero density. The slope of the isotherms corresponds to $\eta_{mix}^{(1)}$.

2. Theory

The zero-density contribution $\eta_{mix}^{(0)}$ in Eq. (1) is comparably well founded by the formal kinetic theory and could, in principle, be evaluated in an adequate manner, even for polyatomic gas mixtures [6–8]. But the kinetic theory formulates the transport properties of dilute molecular gases on the basis of generalized cross-sections, which are determined by the dynamics of the binary collisions in the gas and are related to the intermolecular potential energy hypersurface. This hypersurface representing a particular

molecular interaction is typically developed using the zero-point vibrationally averaged configuration. This treats molecules as rigid rotors in developing predictions for the outcome of molecular collisions. At this time, the theory has been extended to asymmetric-top molecules in pure gases [9], but not to gaseous mixtures. In the case of the viscosity of pure gases, the results using the rigid-rotor assumption are consistent with the experimental data for linear molecules like carbon dioxide [10], but also for spherical-top and asymmetric-top molecules, such as methane [11] and water [12].

Unfortunately, in the case of large polyatomic molecules such as methanol and triethylamine, the corresponding large-scale procedure cannot yet be applied, neither for pure vapors nor for their vapor mixtures. Given this, the zero-density viscosity coefficients of the pure vapors of methanol [4] and triethylamine [5] were analyzed and correlated using the well-established kinetic theory of dilute monatomic gases by Chapman and Enskog [13]. For that purpose a relationship for the viscosity of a species i corresponding formally to the first-order approximation of the theory was used [8]:

$$\eta_i^{(0)}(T) = \frac{(\pi m_i k_B T)^{1/2}}{4\pi \sigma_i^2 \mathfrak{S}_\eta^*(T_i^*)} = \frac{0.021357(M_i T)^{1/2}}{\sigma_i^2 \mathfrak{S}_\eta^*(T_i^*)}, \tag{2}$$

$$T_i^* = \frac{k_B T}{\varepsilon_i}. \tag{3}$$

Here $\mathfrak{S}_\eta^*$ represents a reduced effective cross-section which accounts for all the dynamic and statistical information about the binary collisions and includes the effects of different higher-order approximations for the viscosity. T_i^* is the reduced temperature, σ_i and ε_i/k_B are length and energy scaling parameters, m_i and M_i are the molecular and the molar masses of the species, k_B is the Boltzmann constant. $\eta_i^{(0)}$ is given in units of μPa s, T is in K, σ_i in nm, ε_i/k_B in K, and M_i in g mol^{-1}. The temperature dependence of $\mathfrak{S}_\eta^*$ can be represented by the following functional form:

$$\ln \mathfrak{S}_\eta^*(T_i^*) = \sum_{k=0}^{4} a_k (\ln T_i^*)^k. \tag{4}$$

The analysis of the experimental $\eta_i^{(0)}$ values for methanol and triethylamine by means of the Eqs. (2)–(4) was based on the extended corresponding states principle [13] which is strictly valid only for monatomics such as rare gases, but not for polyatomic vapors. In a first step, a universal correlation with the coefficients (a_k) of the functional $\mathfrak{S}_\eta^*$ for the rare gases reported by Bich et al. [14] was applied to deduce values of the scaling factors (σ_i and ε_i/k_B). Then, in a second step, an individual correlation was performed and new values of the coefficients (a_k) were deduced. This was carried out by fitting Eqs. (2)–(4) to the experimental zero-density viscosity values with the implicit understanding that the scaling factors (σ_i and ε_i/k_B) remain the same as in the universal correlation.

Analogously, the viscosity of an N-component polyatomic gas mixture in the limit of zero density may be formulated in the first-order approximation of the Chapman–Enskog theory as the ratio of two determinants. In doing so, it is assumed that the reduced effective cross-sections $\mathfrak{S}_\eta^*$ needed according to Eq. (2) include the effects of different higher-order approximations. With respect to the measuring procedure and the evaluation of the original experimental data, the following relationships are used for the considered two-component vapor mixture:

$$\eta_{\text{mix}}^{(0)}(T) = \frac{1 + Z_\eta}{X_\eta + Y_\eta}, \tag{5}$$

$$X_\eta = \frac{y_1^2}{\eta_1^{(0)}} + \frac{2y_1 y_2}{\eta_{12}^{(0)}} + \frac{y_2^2}{\eta_2^{(0)}}, \tag{6}$$

$$Y_\eta = \frac{3}{5} A_{12}^* \left[\frac{y_1^2}{\eta_1^{(0)}} \frac{m_1}{m_2} + \frac{2y_1 y_2}{\eta_{12}^{(0)}} \frac{(m_1 + m_2)^2}{4m_1 m_2} \frac{(\eta_{12}^{(0)})^2}{\eta_1^{(0)} \eta_2^{(0)}} + \frac{y_2^2}{\eta_2^{(0)}} \frac{m_2}{m_1} \right], \tag{7}$$

$$Z_\eta = \frac{3}{5} A_{12}^* \left\{ y_1^2 \frac{m_1}{m_2} + 2y_1 y_2 \left[\frac{(m_1 + m_2)^2}{4m_1 m_2} \left(\frac{\eta_{12}^{(0)}}{\eta_1^{(0)}} + \frac{\eta_{12}^{(0)}}{\eta_2^{(0)}} \right) - 1 \right] + y_2^2 \frac{m_2}{m_1} \right\}. \tag{8}$$

Here y_1 and y_2 are the mole fractions of the components 1 and 2. $\eta_1^{(0)}$ and $\eta_2^{(0)}$ are the zero-density viscosity coefficients of the pure components. These were correlated on the basis of the experimental data of the foregoing papers [4,5], $\eta_{12}^{(0)}$ represents the interaction viscosity of a hypothetical one-component gas with the molecular mass m_{12} and the interaction or scaling parameters of length σ_{12} and energy ε_{12}/k_B:

$$\eta_{12}^{(0)}(T) = \frac{(\pi m_{12} k_B T)^{1/2}}{4\pi \sigma_{12}^2 \mathfrak{S}_\eta^*(T_{12}^*)}, \tag{9}$$

$$m_{12} = \frac{2m_1 m_2}{(m_1 + m_2)^2}, \tag{10}$$

$$T_{12}^* = \frac{k_B T}{\varepsilon_{12}}. \tag{11}$$

The quantity A_{12}^* represents a temperature dependent ratio of reduced effective cross-sections for the hypothetical one-component gas. But it can be approximated by the value 1.1 so that Eqs. (5)–(8) can be used to derive the interaction viscosity in the limit of zero density $\eta_{12}^{(0)}$. In analogy to the pure vapors, the obtained $\eta_{12}^{(0)}$ values can subsequently be analyzed on the basis of Eqs. (9), (11) and (4) using a universal correlation followed by an individual correlation.

The Rainwater–Friend theory [1,2,15,16] was utilized to model the second viscosity virial coefficient (B_{η_i}) and consequently the initial density dependence of viscosity ($\eta_i^{(1)}$) of the pure vapors methanol [4] and triethylamine [5]. Unfortunately, this theory has not been extended to mixtures. Therefore, modifications of the Enskog theory for hard-sphere mixtures would have to be used for the prediction of the initial-density viscosity coefficient of the real dense vapor mixture under consideration [17–20]. There again the accessible gaseous density region of the mixture under consideration is restricted due to its vapor–liquid equilibrium so that we do not claim to apply any variant of the modified Enskog theory to the results of the present paper.

3. Measurements and experimental results

The measurements on the methanol–triethylamine vapor mixture were carried out using an all-quartz oscillating-disk viscometer with small gaps. Details concerning the construction and operation of the viscometer as well as the evaluation of the measurements have been described in previous papers [21–23]. The calibration of the viscometer and the implementation of the relative measurements according to the measuring theory of Newell [24], including a well-founded error analysis, were given in the previously mentioned paper for triethylamine [5]. Hence only some salient details are required here. The viscometer was calibrated using only one reference value by Kestin et al. [25] for argon at room temperature and at moderately low density. The performance of the apparatus was checked by additional measurements on argon at temperatures up to 600 K. The relative uncertainty of the intrinsic viscosity measurement is estimated due to the error analysis to be ±0.2 % at room temperature and up to ±0.3 % at higher temperatures, whereas the reproducibility does not exceed ±0.1 % in the complete temperature range.

The temperature is determined with a 10 Ω platinum resistance thermometer and a resistance measuring bridge. The uncertainty of the temperature measurement is ±30 mK at 300 K increasing up

to ± 150 mK at 500 K. The uncertainty of the density determination is $\pm 1\%$ due to the procedure to close the viscometer by fusing its filling pipe. In principle, the total uncertainty in the viscosity results from the uncertainty of the viscosity measurement itself and from the allocation errors of the temperature and density measurements considering the temperature and the density dependencies of the viscosity. It was shown in the foregoing paper for triethylamine [5] that the uncertainties of the temperature and of the density measurements are practically without influence on the uncertainty of the determined viscosity correlation.

Methanol was supplied by Riedel-de Haën, Germany with a certified purity of $\geq 99.9\%$ and a maximum water content of 0.005%, whereas triethylamine was delivered by Fluka, Germany, with a certified purity of $\geq 99.5\%$ and a maximum water content of 0.1%. In a special glass apparatus the substances were dried by means of molecular sieves 4 A, degassed, and filled into small glass ampules which were closed by fusing. The purity of the samples in the ampules was checked by gas chromatography and mass spectrometry to be better than 99.9% and 99.5%, respectively. For both components a comparably large number of ampules was prepared whose mass of substance was determined by weighing the empty and filled ampules. This large number was necessary to be able to select two or more ampules to offer suitable amounts of substance for preparing mixtures with preferably the same composition, but with different densities. Five series of a nearly equimolar mixture, each differing in density, were carried out at temperatures between 298 and 498 K and at densities from 0.010 to 0.033 mol dm^{-3}. In addition, a series was performed on a mixture of the mole fraction $z_1 = 0.3322(1-\text{methanol})$ at a density 0.016 mol dm^{-3}. The total mole fraction z is used, since at the lowest temperatures the substance cannot only have existed in the gas phase but also in the liquid one (see below). The densities and compositions were obtained from the mass of the samples and the volume of the viscometer body. Since any thermal alteration of the substance at high temperature and at low density could possibly occur, the measurements were restricted to a maximum temperature of 500 K. To prove the occurrence of thermal decomposition, a check measurement, after the highest temperature of the individual isochores had been attained, was not performed at ambient temperature, as it is the rule, but at about 366 K to make sure that both components are completely vaporized. Since the results of these check measurements are in good agreement with those of the first measurements at increasing temperature, it can be adopted that no irreversible thermal alteration occurred at higher temperatures. These findings are similar to those found in our measurements on the vapors of methanol [4] and of triethylamine [5], although it should be noted that for methanol measurements were carried out at still higher temperatures. The experimental results are summarized in Table 1. The values obtained for the check measurements are given at the end of each series of measurements.

4. Evaluation and discussion

Since the evaluation requires isothermal values at a constant mole fraction, the original experimental data of the isochores had to be recalculated by means of a first-order Taylor series, in terms of temperature (T) as well as of the mole fraction (y_1) in the gas phase:

$$\eta_{\text{mix}}(T_{\text{nom}}, y_{1\text{nom}}) = \eta_{\text{mix}}(T_{\text{exp}}, y_{1\text{exp}}) + \left(\frac{\partial \eta_{\text{mix}}}{\partial T}\right)_{\rho, y_1} \Delta T$$

$$+ \left(\frac{\partial \eta_{\text{mix}}}{\partial y_1}\right)_{\rho, T} \Delta y_1 + R_N, \tag{12}$$

$$\Delta T = T_{\text{nom}} - T_{\text{exp}}, \tag{13}$$

$$\Delta y_1 = y_{1\text{nom}} - y_{1\text{exp}}. \tag{14}$$

In doing so, it is supposed that the filled substance is completely vaporized. The nominal temperature (T_{nom}) corresponds to the average of the experimental temperatures (T_{exp}) of the five, nearly equimolar, series of measurements, whereas the nominal mole fraction ($y_{1\text{nom}} = 0.5002$) corresponds to the average of the experimental mole fractions of methanol ($y_{1\text{exp}}$). The temperature derivative of viscosity ($(\partial \eta_{\text{mix}}/\partial T)_{\rho, y_1}$) needed in Eq. (12) was obtained by means of the following relationship, whose coefficients were deduced from a fit to the original isochoric data at a constant mole fraction:

$$\eta_{\text{mix}}(T) = S \exp\left(A \ln T_R + \frac{B}{T_R} + \frac{C}{T_R^2} + \frac{D}{T_R^3} + E\right),$$

$$T_R = \frac{T}{298.15\,\text{K}}, \quad S = 10.0\,\mu\text{Pa s}. \tag{15}$$

With regard to the recalculation for the nominal mole fraction, it was assumed that the experimental viscosity data measured at comparably low density are independent of the density. This takes into account that the correction was separately performed for each isochore, what means for $\rho = \text{const}$. Hence Eq. (5) was used to get the first derivative of the viscosity with respect to the mole fraction (with $\rho = 0$):

$$\left(\frac{\partial \eta_{\text{mix}}}{\partial y_1}\right)_{\rho, T} \approx \left(\frac{\partial \eta_{\text{mix}}^{(0)}}{\partial y_1}\right)_T$$

$$= \frac{(\partial Z_\eta/\partial y_1)_T (X_\eta + Y_\eta) - (1 + Z_\eta)[(\partial X_\eta/\partial y_1)_T + (\partial Y_\eta/\partial y_1)_T]}{(X_\eta + Y_\eta)^2}. \tag{16}$$

The partial derivatives needed in Eq. (16) (with $y_2 = 1 - y_1$) follow immediately from Eqs. (6)–(8). For that purpose the viscosity coefficients of the pure components in the limit of zero density ($\eta_1^{(0)}, \eta_2^{(0)}$) were calculated from the individual correlations for methanol [4] and for triethylamine [5]. To get approximately the interaction viscosity in the limit of zero density ($\eta_{12}^{(0)}$), the scaling factors for the mixture were obtained from those of the pure components by means of the usual mixing rules:

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2), \quad \varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2}. \tag{17}$$

Then the coefficients (a_k) of the functional $\mathfrak{S}_\eta^*$ of the universal correlation for the rare gases reported by Bich et al. [14] and $A_{12}^* = 1.1$ were used to derive $\eta_{12}^{(0)}$. Finally, the required isothermal values at the constant mole fraction $y_{1\text{nom}} = 0.5002$ result by means of the first-order Taylor series according to Eq. (12). The remainder (R_N) in Eq. (12) could be neglected compared with the experimental uncertainty.

The further evaluation of the resulting quasi-experimental values of the nominal isotherms for the nearly equimolar mixture with $y_{1\text{nom}} = 0.5002$ requires that the density in the viscometer corresponds to that obtained from the sample masses and the viscometer volume. Unfortunately, some experimental points at low temperatures correspond to measurements in the saturated vapor phase so that they had to be excluded from a linear fit of Eq. (1) to the values of an isotherm. For these points it is to take into account that the actual densities at which the measurements were carried out are those of the saturated vapor, but not the filled densities of the isochores. To judge whether the experimental point was performed in the saturated vapor phase or not, the saturated vapor density needs to be known for the low-temperature isotherms. For that purpose, the saturated pressure and the composition of both phases have to be known for the corresponding temperature.

Table 1
Viscosity of the methanol–triethylamine vapor mixture[a].

Series 1, $z_{1exp} = 0.4999$ $\rho = 9.73 \times 10^{-3}$ mol dm^{-3}		Series 2 $z_{1exp} = 0.4996$ $\rho = 10.45 \times 10^{-3}$ mol dm^{-3}		Series 3 $z_{1exp} = 0.4982$ $\rho = 16.54 \times 10^{-3}$ mol dm^{-3}	
T (K)	η (μPa s)	T (K)	η (μPa s)	T (K)	η (μPa s)
299.02	7.865	297.25	7.853	298.92	7.914
310.56	8.025	310.39	8.055	310.62	8.147
325.44	8.367	324.64	8.338	325.29	8.337
325.44	8.367	324.64	8.338	325.29	8.337
338.18	8.693	338.37	8.695	338.18	8.632
352.47	9.053	352.30	9.039	352.57	9.009
366.96	9.415	366.24	9.388	366.29	9.353
381.57	9.793	383.76	9.828	381.91	9.758
395.04	10.122	394.95	10.102	395.34	10.085
409.61	10.500	410.75	10.515	409.01	10.439
425.55	10.908	423.31	10.830	423.81	10.805
438.27	11.217	436.91	11.170	437.47	11.160
453.25	11.612	452.69	11.574	451.74	11.513
467.62	11.971		[b]	467.26	11.896
482.14	12.313	481.53	12.290	481.28	12.251
496.37	12.692	494.94	12.627	497.66	12.672
366.13	9.411	298.82[c]	7.887	367.89	9.381

Series 4, $z_{1exp} = 0.5035$ $\rho = 22.98 \times 10^{-3}$ mol dm^{-3}		Series 5, $z_{1exp} = 0.4998$ $\rho = 32.73 \times 10^{-3}$ mol dm^{-3}		Series 6, $z_{1exp} = 0.3322$ $\rho = 16.37 \times 10^{-3}$ mol dm^{-3}	
T (K)	η (μPa s)	T (K)	η (μPa s)	T (K)	η (μPa s)
	[b]	296.97	7.913	298.22	7.476
310.75	8.235	310.51	8.259	311.73	7.712
326.59	8.476	324.10	8.539	324.27	7.852
338.04	8.626	338.58	8.690	337.60	8.072
353.02	9.026	352.83	8.949	352.91	8.441
366.12	9.363	366.41	9.307	366.22	8.747
381.81	9.770	380.83	9.681	379.75	9.075
394.84	10.093	394.29	10.039	394.98	9.437
410.61	10.496	409.18	10.417	408.74	9.753
423.21	10.811	423.64	10.776	422.83	10.083
436.79	11.160	436.89	11.108	441.21	10.528
451.60	11.535	452.02	11.506	451.54	10.764
466.76	11.905	466.65	11.880	467.40	11.132
482.73	12.285	481.51	12.241	480.98	11.452
495.78	12.643	495.28	12.602	495.26	11.793
365.96	9.349	365.70	9.281	366.02	8.766

[a] Subscript 1 – methanol.
[b] An outlier had to be left out.
[c] Check measurement at different temperature.

The saturated vapor pressure of the mixture (p_s) is dependent on the composition of the phases and results in:

$$p_s = \frac{x_i \gamma_i p_{si}^*}{y_i}. \tag{18}$$

Here, x_i and y_i, respectively, characterize the mole fractions of component i in the liquid and vapor phases, while γ_i is the activity coefficient in the liquid phase, and p_{si}^* is the saturated vapor pressure of the pure component i.

The determination of the saturated vapor pressure and the composition of the phases was founded on results for the vapor–liquid equilibrium of methanol and triethylamine obtained by Copp and Findlay [26] at 313 K and 333 K as well as by Chun and Davison [27] for temperatures between 283 K and 313 K. These authors determined the saturated vapor pressure of the mixture in dependence of the composition in the liquid phase and used their experimental data to derive empiric equations for the molar excess Gibbs function G_m^E. First, we determined the activity coefficients γ_i of both components on the basis of these equations by applying elementary thermodynamic relationships. Then, the mole fraction in the vapor phase y_i resulted from Eq. (18) using the experimental data for the saturated vapor pressure and the composition of the liquid phase of the mixture given in [26,27] as well as the saturated vapor pressure of the pure components, taken for methanol from the equation of

state [28] and for triethylamine as described in [5]. Subsequently, this information was used to infer relationships which describe the saturated vapor pressure of the mixture as function of temperature and of the mole fraction of methanol in the vapor phase $p_s(T, y_1)$ and in the liquid phase $p_s(T, x_1)$, respectively. In addition, a relationship was established for the mole fraction in the vapor phase as a function of temperature and of the mole fraction in the liquid phase $y_1(T, x_1)$ (see further details given by Teske [29]).

To obtain the saturated vapor density (ρ_s) it was assumed that the thermodynamic behavior of the mixture can be represented by means of a virial equation of state restricted to the second order, in terms of density:

$$p_s = \rho_s RT[1 + B_{mix}(T)\rho_s], \tag{19}$$

$$\rho_s = -\frac{1}{2B_{mix}(T)} - \left(\left[\frac{1}{2B_{mix}(T)} \right]^2 + \frac{p_s}{B_{mix}(T)RT} \right)^{1/2}. \tag{20}$$

The second pressure virial coefficient for the binary mixture (B_{mix}) is related to the respective coefficients of the pure components B_{11} and B_{22} as well as to the second cross virial coefficient (B_{12}):

$$B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}. \tag{21}$$

In the case of methanol, the second pressure virial coefficient given by the equation of state [28] was used, while the correlation devel-
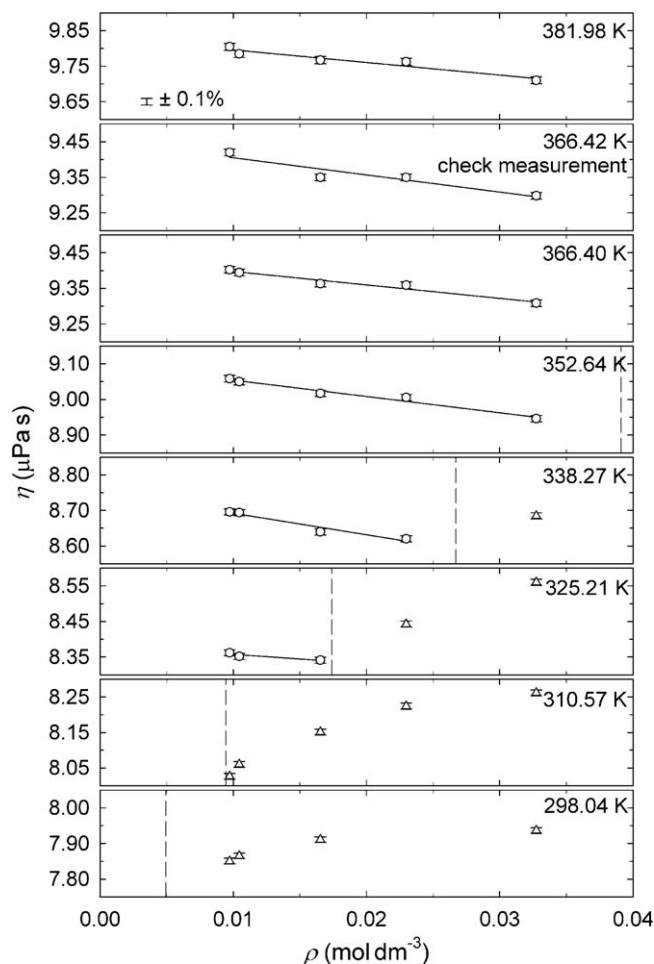
Fig. 1. Viscosity of the binary vapor mixture methanol–triethylamine with the mole fraction $z_1 = 0.5002$ as a function of the filled molar density for isotherms at low temperature. $\eta_{mix} = \eta_{mix}^{(0)} + \eta_{mix}^{(1)}\rho$. (○) Quasi-experimental values; (△) values measured in the saturated vapor phase of the vapor–liquid equilibrium; and (⋮) saturated vapor density.
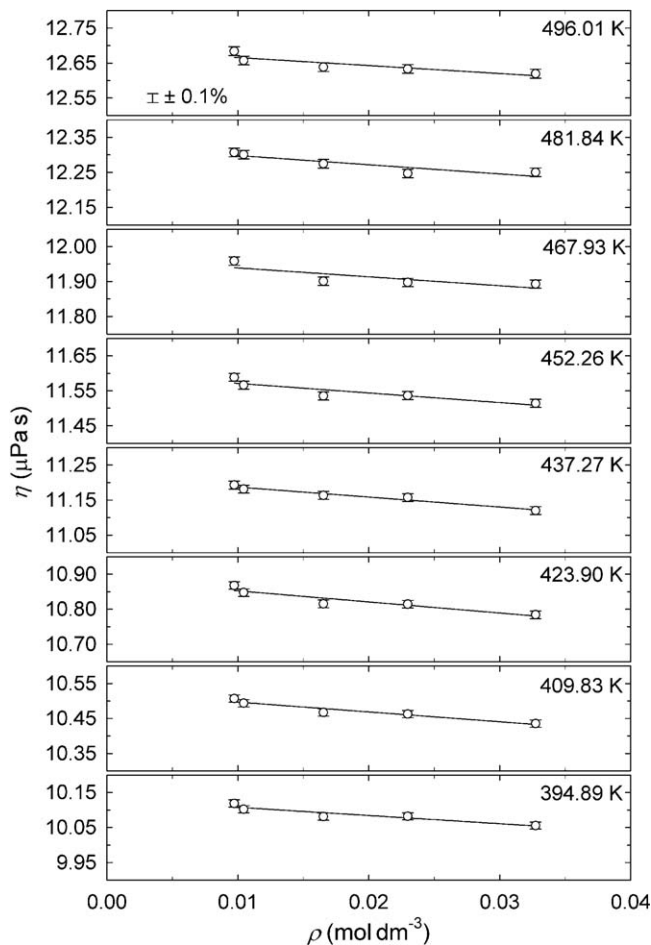

Fig. 2. Viscosity of the binary vapor mixture methanol–triethylamine with the mole fraction $z_1 = y_1 = 0.5002$ as a function of the molar density for isotherms at high temperature. $\eta_{mix} = \eta_{mix}^{(0)} + \eta_{mix}^{(1)}\rho$. (○) Quasi-experimental values.

oped by Tsonopoulos et al. [30] was applied for triethylamine. Since the Tsonopoulos correlation had also been adopted to describe the second pressure virial coefficient of methanol, B_{12} should be characterized by the same temperature dependence so that it was made use of this correlation for the representation of B_{12}, too. The required parameters for the mixture were derived from the respective values of the pure components by means of mixing rules.

Finally, the resulting quasi-experimental viscosity values for all nominal temperatures are illustrated as a function of the filled density in Figs. 1 and 2. The dashed vertical lines drawn for the five lowest isotherms in Fig. 1 represent the density of the saturated vapor (ρ_s) which results from Eq. (20). Fig. 1 demonstrates that those viscosity values, allocated to measurements in the saturated vapor phase of the vapor–liquid equilibrium, are raised with increasing density, while a negative density dependence of viscosity is observed for values at densities below the saturated vapor density (ρ_s). As already noted above, the results of the check measurements are in good agreement with the first measurements so that it can be supposed that no irreversible thermal alteration has occurred.

For all isotherms with a sufficient number of data points, a linear regression according to Eq. (1) was performed to determine the viscosity coefficient of the mixture in the limit of zero density ($\eta_{mix}^{(0)}$) as well as the initial density dependence of viscosity of the mixture ($\eta_{mix}^{(1)}$). The results derived for all nominal temperatures including

their standard deviations are summarized in Table 2. The initial density dependence of viscosity is especially pronounced at low temperatures, while it is nearly the same in the range of higher temperatures. Furthermore, it is of note that the negative value of $\eta_{mix}^{(1)}$ derived for the isotherm at 325.21 K does not correlate due to its low value, compared to the results at higher temperatures. Given that $\eta_{mix}^{(0)}$ was too low for the same temperature, both values have been excluded from the further analysis. Finally, $\eta_{mix}^{(0)}$ was used to determine the interaction viscosity $\eta_{12}^{(0)}$ by means of Eq. (5)–(8), the results are also shown in Table 2.

Analogous to the values for the zero-density viscosity coefficient of the pure components ($\eta_i^{(0)}$), the interaction viscosity in the limit of zero density ($\eta_{12}^{(0)}$) was correlated based on the kinetic theory of dilute gases. First, a universal correlation was performed and the following scaling factors were derived:

$$\sigma = 0.51309\,nm, \quad \frac{\varepsilon}{k_B} = 341.82\,K.$$

In a second step, the coefficients a_k of the functional $\mathfrak{S}_\eta^*$ (see Eq. (4)) were newly determined by means of an individual correlation to be:

$$a_0 = 0.21709707; \quad a_1 = -0.37239569;$$

$$a_2 = -0.54707267; \quad a_3 = 0.87547019; \quad a_4 = 0.0.$$

Assuming that the interaction viscosity is independent of the composition, the results can be used to calculate the viscosity of the

Table 2
Zero-density and initial-density viscosity coefficients of the equimolar binary mixture methanol–triethylamine ($z_1 = y_1 = 0.5002$) and the interaction viscosity in the limit of zero-density.

T (K)	$\eta_{mix}^{(0)} \pm$ s.d.$_{\eta_{mix}^{(0)}}$ (μPa s)	$\eta_{mix}^{(1)} \pm$ s.d.$_{\eta_{mix}^{(1)}}$ (μPa s dm^3 mol^{-1})	$10^3 \times$ s.d.$_{\eta_{mix}}$ (μPa s)	$\eta_{12}^{(0)}$ (μPa s)
325.21	8.383 ± 0.014	-2.556 ± 1.096	5.80	[a]
338.27	8.753 ± 0.016	-6.037 ± 0.999	10.69	8.345
352.64	9.100 ± 0.009	-4.580 ± 0.421	8.08	8.660
366.40	9.435 ± 0.009	-3.778 ± 0.454	8.70	8.967
381.98	9.831 ± 0.012	-3.531 ± 0.581	11.15	9.348
394.89	10.131 ± 0.010	-2.331 ± 0.506	9.70	9.605
409.83	10.525 ± 0.009	-2.810 ± 0.452	8.68	9.998
423.90	10.884 ± 0.014	-3.169 ± 0.685	13.15	10.343
437.27	11.216 ± 0.007	-2.842 ± 0.347	6.66	10.652
452.26	11.599 ± 0.016	-2.742 ± 0.766	14.69	11.019
467.07	11.964 ± 0.030	-2.539 ± 1.342	22.75	11.353
481.84	12.324 ± 0.014	-2.619 ± 0.704	13.51	11.678
496.01	12.689 ± 0.015	-2.284 ± 0.712	13.66	12.029

[a] Only three points for linear fit, results excluded from evaluation.

binary mixture as a function of temperature, density, and composition.

In the case of the pure components methanol [4] and triethylamine [5], the viscosity values obtained from measurements in the saturated vapor phase at different densities are not characterized by any density dependence so that they could be averaged to get a viscosity value in the saturated vapor. As already noted above, the results for the isotherms of the nominal equimolar mixture show a tendency to enlarge with increasing filled density. The reason for this behavior is that methanol has a lower boiling point and a higher vapor pressure than triethylamine. Hence methanol is enriched in the vapor phase at low temperatures, and the mole fraction of methanol in the vapor phase (y_1) increases when the density is raised. As the viscosity of methanol is greater than that of triethylamine, the viscosity coefficient of the mixture is increasing with increasing density.

In order to determine the amounts of the two phases and consequently the composition of the vapor phase, the lever rule can be used. In doing so, the total mole fraction of methanol z_1 is related to the amounts of substance in the liquid (n_l) and in the vapor (n_v) phases and to the total amount (n) as well as to the mole fractions in the liquid (x_1) and in the vapor (y_1) phases:

$$z_1 = \frac{n_v}{n} y_1 + \frac{n_l}{n} x_1 \quad \text{with} \quad n = n_v + n_l. \tag{22}$$

Whereas n was known for each series of measurements from the filled mass of the substances, n_v was obtained from the volume of the viscometer V and the density of the saturated vapor (ρ_s) resulting from Eq. (20):

$$n_v = \rho_s V. \tag{23}$$

Following this, the mole fraction of the vapor phase y_1 was iteratively determined for all temperatures by varying x_1, while the relationships for the saturated vapor pressure $p_s(T, x_1)$ and the mole fraction of the saturated vapor phase $y_1(T, x_1)$ (see above) had to be adhered. The iteration was finished when the total mole fraction of methanol z_1 resulting from Eq. (22) was equal to the mole fraction z_{1exp} of the respective isochore resulting from the mass of the samples and the viscometer volume. Finally, the viscosity coefficient for the vapor phase of the vapor–liquid equilibrium of the binary mixture methanol–triethylamine could be determined as function of the mole fraction of methanol in the vapor phase. The results are illustrated in Fig. 3 and summarized in Table 3.

Furthermore, viscosity coefficients for the pure vapors of methanol and triethylamine, calculated for the nominal temperatures using results from [4,5], are given in Table 3 and Fig. 3. In addition, values for the nominal mole fraction $y_{1nom} = 0.5002$

were calculated for the two highest temperatures by means of Eq. (1) with the saturated vapor density ρ_s and the $\eta_{mix}^{(0)}$ and $\eta_{mix}^{(1)}$ values of the present paper. The results, also shown in Table 3 and Fig. 3, are in good agreement with the values determined by iteration.

As mentioned earlier, only one series of measurements could be carried out for another composition of the binary system methanol–triethylamine ($z_{1exp} = 0.3322$) so that an evaluation of the viscosity as function of the molar density could not be performed. Nevertheless, the experimental data of this series were recalculated to the nominal temperatures of the equimolar vapor mixture by means of Eq. (15). Then the measurements carried out in the vapor phase of the vapor–liquid equilibrium at low temperatures were evaluated with the previously explained iterative procedure and further viscosity values for the vapor phase of the vapor–liquid equilibrium were deduced in the range of smaller values of the mole fraction y_1. Fig. 3 makes evident that these results are in good agreement with those of the other series of measurements. Although Fig. 3 illustrates a slight curvature of the isotherms for the lowest temperatures, the composition dependence of the viscosity coefficient in the vapor phase of the vapor–liquid equilibrium is so weak that no further conclusions about the association in the methanol–triethylamine system can be drawn.
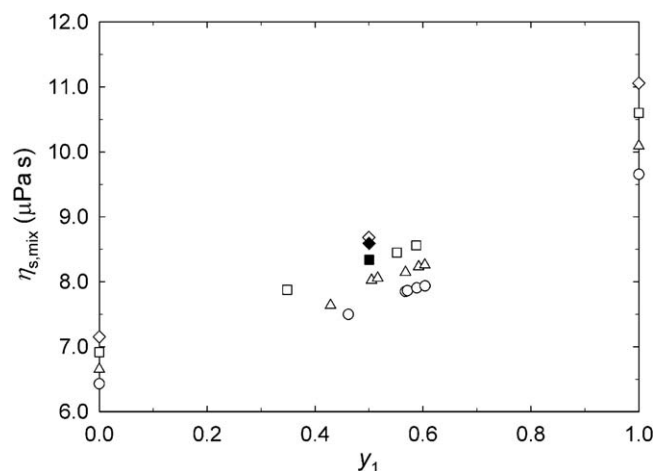

Fig. 3. Viscosity in the vapor phase of the vapor–liquid equilibrium of the binary mixture methanol–triethylamine as a function of the mole fraction of methanol in the vapor phase. (○) 298.04 K; (△) 310.57 K; (□, ■) 325.21 K; and (◇, ♦) 338.27 K. Filled symbols correspond to values calculated by means of Eq. (1) for the nominal mole fraction y_{1nom}.

Table 3
Viscosity coefficient of the binary vapor mixture methanol–triethylamine in the vapor phase of the vapor–liquid equilibrium.

T (K)	z_{1exp}	y_{1cal}	$\eta_{s,mix}$ (μPa s)	T (K)	z_{1exp}	y_{1cal}	$\eta_{s,mix}$ (μPa s)
298.04	0.0000	0.0000	6.430	325.21	0.0000	0.0000	6.917
	0.3322	0.4617	7.497		0.3322	0.3485	7.875
	0.4999	0.5676	7.850		0.5002	0.5002	8.339
	0.4996	0.5713	7.864		0.5035	0.5517	8.449
	0.4982	0.5887	7.905		0.4998	0.5875	8.559
	0.4998	0.6039	7.936		1.0000	1.0000	10.603
	1.0000	1.0000	9.656				
310.57	0.0000	0.0000	6.655	338.27	0.0000	0.0000	7.152
	0.3322	0.4287	7.639		0.5002	0.5002	8.592
	0.4999	0.5046	8.025		0.4998	0.5453	8.684
	0.4996	0.5161	8.058		1.0000	1.0000	11.058
	0.4982	0.5677	8.146				
	0.5035	0.5921	8.232				
	0.4998	0.6035	8.261				
	1.0000	1.0000	10.092				

5. Conclusions

Relative viscosity measurements were performed with an all-quartz oscillating-disk viscometer at low densities in the unsaturated vapor phase as well as in the saturated vapor phase of the vapor–liquid equilibrium of the binary mixture methanol–triethylamine.

The results in the unsaturated vapor phase, recalculated for isotherms of a nearly equimolar mixture with the mole fraction of methanol $y_{meth} = 0.5002$ at densities from 0.010 to 0.033 mol dm^{-3}, were used to determine the zero-density viscosity coefficient ($\eta_{mix}^{(0)}$) and the initial-density viscosity coefficient ($\eta_{mix}^{(1)}$). The interaction viscosity $\eta_{12}^{(0)}$ was inferred from $\eta_{mix}^{(0)}$ and represented with an individual correlation based on the kinetic theory of dilute monatomic gases and on the extended theorem of corresponding states. The $\eta_{mix}^{(1)}$ values of this particular binary mixture are negative and only pronounced at low temperatures. The comparison with the initial density dependence of the viscosity for the pure components makes evident that it is more pronounced in the case of methanol and less for triethylamine. Hence, the effect of intermolecular hydrogen bonds on the initial density dependence of viscosity is comparably large for pure methanol vapor.

Probably for the first time, viscosity measurements were carried out in the saturated vapor phase of the vapor–liquid equilibrium of a binary mixture. This concerns some recalculated values of the nearly equimolar mixture and several data points of the mixture with the mole fraction $z_{meth} = 0.3322$ at low temperatures. For these points the vapor–liquid equilibrium was evaluated to assign the correct mole fraction in the vapor y_{meth} to the measured viscosity. It was found that the resulting composition dependence of the viscosity coefficient in the vapor phase of the vapor–liquid equilibrium is only weakly pronounced.

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