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# Experimental Study and Correlation of the Viscosity of 2,2,2-Trifluoroethanol (TFE)—Water Mixtures[1]

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The kinematic viscosity of pure 2,2,2-trifluoroethanol, water, and their mixtures was measured with Ubbelohde capillary viscometers at ambient pressure. The study covers the full range of compositions in the liquid region between the bubble and the freezing line. The viscosity was found to vary by a factor of 280 from 0.30 to 87.2 cSt. It exhibits a pronounced maximum at high $H_2O$ mole fractions and a flat minimum at high TFE concentrations. The temperature dependence of viscosity was correlated individually for each composition and three mixing rules were tested which are widely used for alcohol–water mixtures. The data were represented best with Dizechi's equation.

**KEY WORDS:** fluorinol; kinematic viscosity; mixing rules; mixtures; pure fluids; trifluoroethanol; water.

## 1. INTRODUCTION

Mixtures of 2,2,2-trifluoroethanol (TFE) with water appear to be favorable working fluids for Rankine cycle devices to recover low-temperature waste heat [1]. The feasibility studies carried out so far could not account for the real properties of this mixture since very few data were available. Consequently, global estimates for heat and mass transfer resistances or estimation methods for the mixture properties had to be applied.

Since the mixture involves two highly polar substances, it is questionable if estimation methods yield correct results. This holds in particular

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for the viscosity, which reflects molecular interactions usually stronger than other properties. However, the viscosity of the working fluid is a key property in the design of waste heat recovery devices [2].

Therefore, the viscosity of the TFE–$H_2O$ system was measured in the entire liquid region at ambient pressure within the priority program *Thermophysical Properties of New Working Fluids in Energy Technology* sponsored by Deutsche Forschungsgemeinschaft. The low-temperature range between the freezing line and 273.15 K was explored for the first time.

## 2. EXPERIMENTAL

### 2.1. Materials

Water was bidistilled and degassed overnight above room temperature. TFE was a special sample produced by Kali-Chemie AG (Hannover, F.R.G.). Its composition was stated by the manufacturer as 99.97% TFE with 0.03% water. The sample was kept under nitrogen to avoid further absorption of water. The mixtures were prepared on a Sartorius Type 1518 scale with an accuracy of ±0.003 g. The resulting accuracy of the mixture composition is ±0.02% in mole fraction.

### 2.2. Equipment and Procedure

The viscosity was measured with Ubbelohde glass capillary viscometers and peripheral equipment by Schott-Geräte (Hofheim a. Ts., F.R.G.). Capillary types 0, 0a, I, Ic, II, and $\mu$I were used. One capillary at a time was inserted into a measuring stand (AVS/S) and immersed in a thermostat CT 1150. The measuring stand connects to a control unit (AVS 300). The efflux time is determined with two light barriers in the measuring stand which detect the moving liquid surface and trigger an electronic timer in the control unit. The accuracy of the timing is ±0.01 s. Especially when low viscosities are measured, electronic timing offers a reduction of experimental errors as compared to manual timing [3].

The thermostat was additionally insulated so that the temperature was constant to ±0.05 K in the middle of the capillary. Cryostat K 90 SW by MGW (Lauda, F.R.G.) was used for the low-temperature measurements. Thermostating liquids were ethanol below 273.15 K and Baysilon oil M 20 above. A calibrated platinum resistance thermometer was used to determine the temperature at the capillary with an accuracy of ±0.2 K below 273.15 K and 0.1 K above.

The working equation of Ubbelohde capillary viscometers reads

$$\nu = \frac{\pi R^4 gh}{8lV}\tau - \frac{mV}{8\pi l\tau} \tag{1}$$

with $\nu$ the kinematic viscosity, $R$ the radius of the capillary, $gh$ the driving hydrostatic pressure difference, $l$ the length of the capillary, $m$ the Hagenbach–Couette correction factor, and $V$ the liquid volume which passes the capillary during the measured efflux time $\tau$. Usually the simplified equation

$$\nu = K(\tau - \vartheta) \tag{2}$$

is employed with the calibration constant $K$ of a capillary determined by the manufacturer and $\vartheta$ a tabulated correction time. To check the reliability of the manufacturer's calibration constants, the viscosity of $H_2O$ was measured from 278.15 to 368.15 K and compared with data calculated from the IAPS release [4, 5]. The agreement was better than 0.5% above 328.15 K, while at the lower temperatures discrepancies of up to 2% indicated that the calibration constant of this capillary was not correct. However, when obtained by linear interpolation between table entries at intermediate temperatures, the reference water viscosities may be already incorrect up to 0.5%. It is therefore important to *calculate* the reference data from the IAPS formulations throughout since otherwise the comparison is biased.

The accuracy of the viscosity measurements was assessed also by analyzing the sensitivity of Eq. (1) to different experimental errors. The maximum relative error of the viscosity is obtained from

$$\left(\frac{\Delta\nu}{\nu}\right) = \pm\frac{1}{\nu}\sum_{i=1}^{6}|\Delta\nu_i| \tag{3}$$

with the individual contributions

$$|\Delta\nu_i| = \left|\left(\frac{\partial\nu}{\partial y_i}\right)_{y_{j\neq i}}\right|\Delta y_i \tag{4}$$

The calculation included the following quantities $y_i$ and their respective variations $\Delta y_i$.

| | |
|---|---|
| Hagenbach–Couette correction factor | $\Delta m = 0.1$ |
| Gravity difference between calibration and measurement | $\Delta g = 0.001\ \mathrm{m\cdot s^{-2}}$ |

| | |
|---|---|
| Accuracy of efflux time measurement | $\Delta\tau = 0.01$ s |
| Nonvertical inclination of the capillary | $\Delta\varphi = 2°$ |
| Temperature difference between calibration and experiment (accounts for thermal expansion of the capillary) | $(T - T_{\text{calib}})$ |
| Accuracy of temperature measurement | $\Delta T = 0.2$ K $(T < 273.15$ K$)$<br>$\Delta T = 0.1$ K $(T > 273.15$ K$)$ |

The last contribution has to be calculated for each liquid from the temperature dependence of its viscosity and therefore requires a correlation of the experimental results. This, however, can be established only after the measurements are completed and needs some skill in selecting an appropriate function. Yet the accuracy of the temperature determination is the predominant contribution to the total experimental accuracy as illustrated in Fig. 1 for TFE. The correlation described in Section 4 was used to calculate that contribution which decreases from 1% at 233.15 K

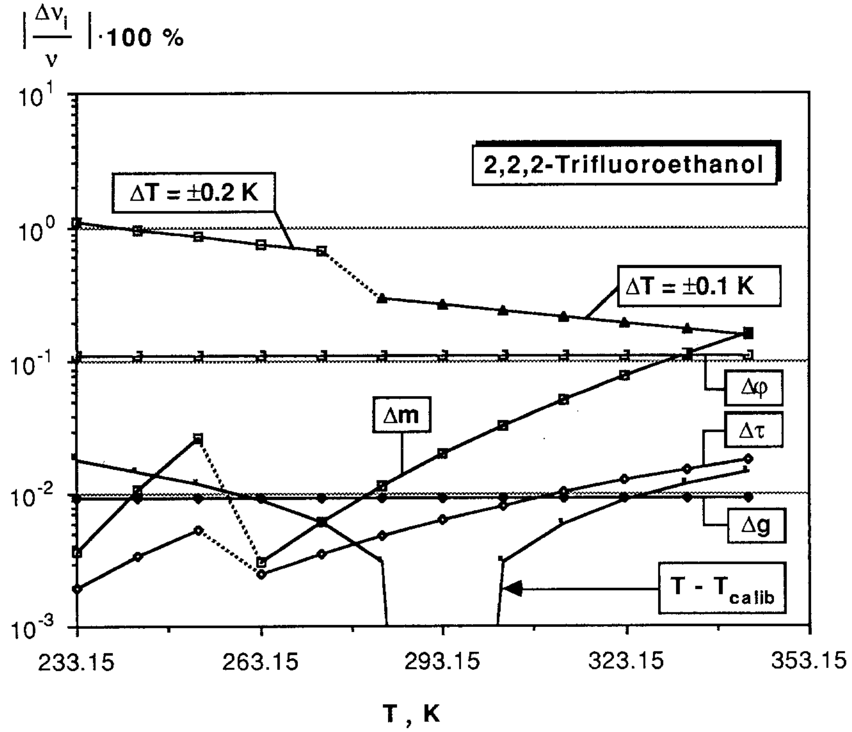

**Fig. 1.** Individual contributions to the accuracy of viscosity measurements with Ubbelohde capillary viscometers.

to 0.2% at 343.15 K due to the strong temperature dependence of the TFE viscosity. The accuracy of the measurements was also assessed by repeating certain runs with different samples after a longer period of time. For pure TFE the reproducibility was well within ±0.2%, and for the mixtures ±1%.

## 3. RESULTS

The viscosity was determined in the entire liquid region of the TFE–$H_2O$ system from 213.15 to 368.15 K. Figure 2 shows the distribution of all 165 data points. Each data point represents an average of four independent measurements. They were carried out at 13 mixture compositions. To obtain an estimate for the freezing points, mixture samples in test tubes were cooled in the cryostat until solidification was observed. For $x_{TFE} = 0.85$ the viscosity could not be measured below 218.15 K since it exceeded the measuring range of capillary type II (100 cSt).

The bubble and dew line determined by Hengerer [6] are included in Fig. 2. They coincide nearly at mole fractions $x_{TFE} > 0.8$, accompanied by

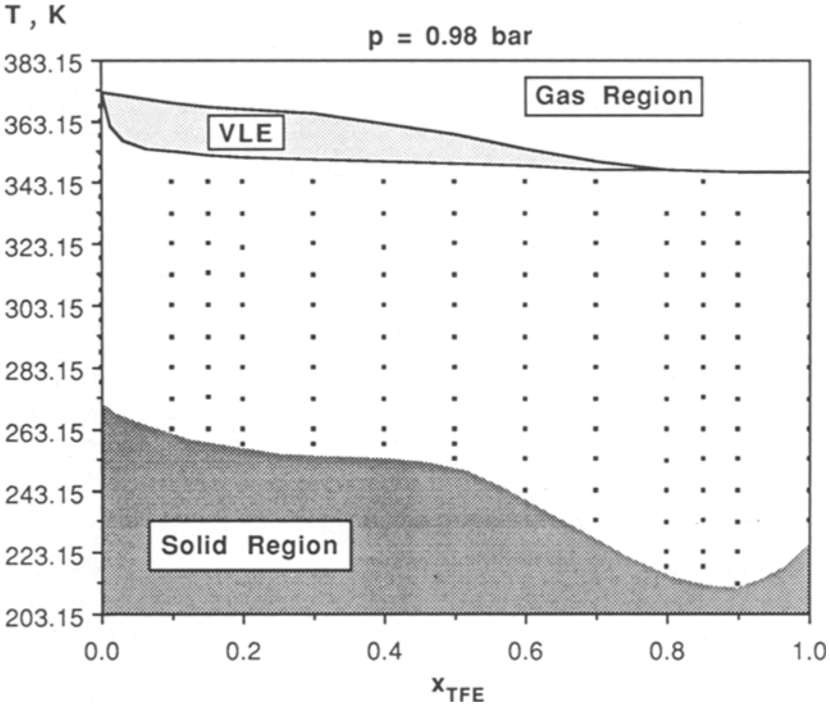

**Fig. 2.** Phase diagram of the TFE–$H_2O$ system with loci of viscosity measurements.

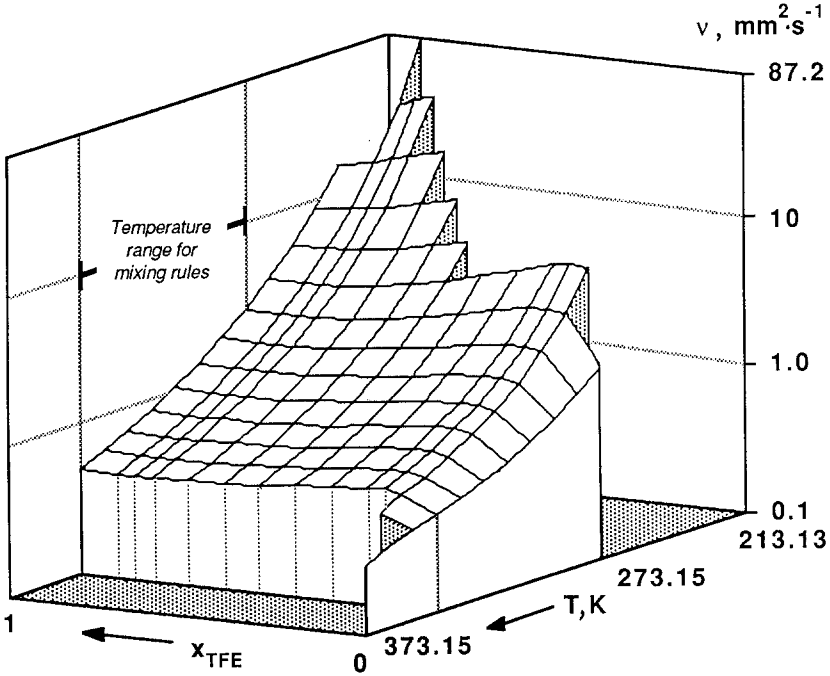

Fig. 3. Liquid viscosity of the system TFE–$H_2O$ at ambient pressure as a function of temperature and composition.

a considerable reduction of the freezing temperature which suggests that a "liquification" effect is taking place. This is reflected also in the viscosity by a flat minimum in that range of compositions down to 263.15 K. The entire viscosity surface is depicted in Fig. 3 as a function of temperature and mole fraction. Between $x_{TFE} = 0.1$ and $x_{TFE} = 0.3$ the viscosity exhibits a pronounced maximum considerably higher than even the viscosity of pure TFE. Similar characteristics occur in the viscosity of other alcohol–water mixtures [13].

## 4. CORRELATION OF TEMPERATURE DEPENDENCE

In the first step of the evaluation, temperature functions at constant mole fraction were established for the experimental viscosities. In many cases, simple exponential functions are employed which are based on the kinetic theory of liquids. However, when a wider temperature range is considered, an accurate representation of the viscosity requires more complicated functions. Schwen and Puhl [7] studied the temperature

**Table I.** Parameters of Viscosity Correlations (5)–(7) for TFE–$H_2O$ Mixtures

| $x_{TFE}$ | Eq. | $b_1$ | $b_2$ | $b_3$ | $b_4$ | $b_5$ | $b_6$ |
|---|---|---|---|---|---|---|---|
| 0.1 | (5) | 30.73657 | −113.3837 | −2.735527 | 0.1625736 | −4.215800 | 0.3954048 |
| 0.15 | (5) | 34.4118 | −129.679 | −3.87070 | 0.914678 | −5.53700 | 0.497203 |
| 0.2 | (5) | 30.37031 | −113.1502 | −2.304374 | 0.04225815 | −4.230988 | 0.4043298 |
| 0.3 | (5) | 28.58122 | −107.3751 | 3.052752 | −2.162682 | −3.856539 | 0.3742780 |
| 0.4 | (6) | −3.59172 | 536.229 | 111.955 | 950.996 | −3697.07 | |
| 0.5 | (5) | 1.60227 | −7.87845 | −12.0300 | 3.52869 | −520.705 | 33.2901 |
| 0.6 | (5) | 28.5513 | −112.301 | 5.43488 | −3.20666 | −3.69786 | 0.348814 |
| 0.7 | (5) | 31.3790 | −127.107 | −2.83984 | 0.148394 | −4.08790 | 0.373161 |
| 0.8 | (5) | 30.0201 | −121.367 | 1.38600 | −3.03770 | −3.59194 | 0.337095 |
| 0.85 | (7) | −9.509606 | 0.6238286 | −3.619876 | 0.3160892 | −5.298701 | 0.3238067 |
| 0.9 | (5) | 52.7647 | −237.914 | −6.22052 | 1.79930 | −6.31989 | 0.480172 |
| 1.0 | (5) | 34.99809 | −150.1359 | −1.725899 | −0.8809222 | −3.582061 | 0.3391575 |

dependence of more than 200 liquids with widely different viscosities as well as suitable functional expressions. They found that a set of 25 functions was sufficient to correlate their entire data within the experimental accuracy.

This set of 25 functions was also applied to correlate the experimental results of this study. It turned out that, with two exceptions, the viscosity of the mixtures could be expressed best by

$$\nu = e^{[b_1 + b_2(T/1000)]} + e^{[b_3 + b_4(1000/T)]} + e^{[b_5 + b_6(1000/T)^2]} \tag{5}$$

For the mixture $x_{\mathrm{TFE}} = 0.4$ a correlation with five adjustable parameters was sufficient,

$$\nu = e^{[b_1 + b_2/(T + b_3 - 273.15)]} + e^{[b_4 + b_5(T/1000)]} \tag{6}$$

while for the mixture with the highest viscosity, $x_{\mathrm{TFE}} = 0.85$, also a six parameter correlation was necessary to achieve the best representation,

$$\nu = e^{[b_1 + b_2(1000/T)^2]} + e^{[b_3 + b_4(1000/T)^2]} + e^{[b_5 + b_6(1000/T)^2]} \tag{7}$$

The program to determine the adjustable parameters $b_1$–$b_6$ by a nonlinear least-squares fit included a procedure to check how many digits of the final parameter values are necessary so that the standard deviation between calculated and experimental viscosities remains smaller than 0.1%. Table I presents the parameter values for Eqs. (5)–(7) for each mixture.[4]

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[4] The original experimental data can be obtained from the authors upon request. Inquiries may be sent to ALSO at NBS in the BITNET domain.

**Table II.** Accuracy of Correlations (5)–(7) for TFE–$H_2O$ Mixtures

| $x_{\mathrm{TFE}}$ | $f_{\mathrm{av}}$ (%) | $f_{\mathrm{std}}$ (%) | $+f_{\max}$ (%) | $-f_{\max}$ (%) |
|---|---|---|---|---|
| 0.1 | 0.04 | 0.24 | 0.44 | −0.41 |
| 0.15 | −0.002 | 0.42 | 0.70 | −0.81 |
| 0.2 | 0.02 | 0.16 | 0.23 | −0.30 |
| 0.3 | 0.01 | 0.15 | 0.29 | −0.19 |
| 0.4 | −0.03 | 0.32 | 0.5 | −0.56 |
| 0.5 | −0.02 | 0.42 | 0.56 | −1.04 |
| 0.6 | −0.02 | 0.27 | 0.53 | −0.51 |
| 0.7 | −0.01 | 0.61 | 1.4 | −0.98 |
| 0.8 | −0.11 | 0.86 | 0.97 | −1.6 |
| 0.85 | 0.06 | 0.31 | 0.83 | −0.49 |
| 0.9 | −0.02 | 0.43 | 0.88 | −0.87 |
| 1.0 | −0.002 | 0.05 | 0.07 | −0.12 |

When the absolute temperature $T$ (in K) is inserted, the viscosity is obtained in $10^{-6}\,\mathrm{m}^2 \cdot \mathrm{s}^{-1}$.

Table II summarizes the accuracy with which the experimental data are represented by correlations (5)–(7). Besides the average deviation $f_{\mathrm{av}}$ and its standard deviation $f_{\mathrm{std}}$, also the maximum positive and negative deviations $+f_{\max}$ and $-f_{\max}$ are listed. They provide a measure of the internal consistency of the experimental data. Except for the mixtures $x_{\mathrm{TFE}} = 0.5$, 0.7, and 0.8, the maximum deviations between measured and correlated viscosities are less than 1%.

Comparisons with literature data are presented in Figs. 4 to 6. Data for pure TFE are reported in Refs. 2 and 8–10. The relative deviations to the present results are within the combined accuracies of the experiments. The total accuracy of the present data is indicated in Fig. 4 by the shaded area, which was calculated from Eq. (3). Data calculated from the correla-

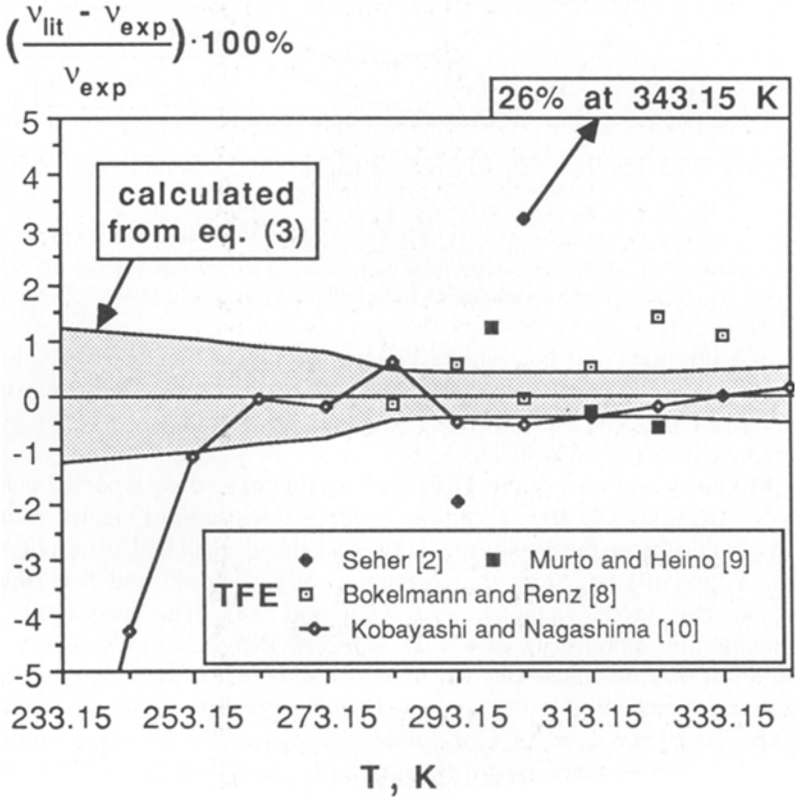

Fig. 4. Comparison of experimental viscosities with literature data for TFE.

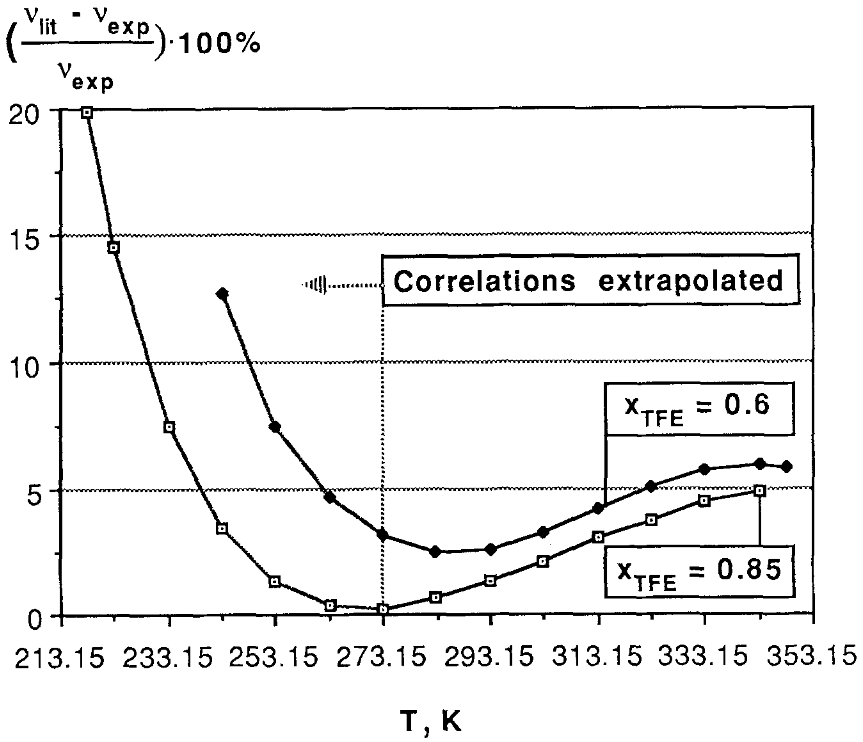

Fig. 5. Comparison of data calculated from correlations given by Eqs. (5) and (7) of this work and the correlation of Kobayashi and Nagashima [10].

tion of Kobayashi and Nagashima [10] deviate from this study systematically at lower temperatures since the correlation is based on viscosities above 273.15 K. The data of Seher [2] have to be rejected, as they yield discrepancies up to 26% at 343.15 K.

Mixture viscosities of the TFE–$H_2O$ system have been reported before only in Refs. 9 and 10 at certain compositions and/or temperatures. Figure 5 illustrates the deviations between values calculated from correlations (5) and (7) and from the correlation of Kobayashi and Nagashima [10] at two mole fractions, $x_{TFE} = 0.6$ and 0.85. The deviations are systematic and amount up to 6% at 343.15 K. Below 273.15 K, where the correlation of Kobayashi and Nagashima has been extrapolated, substantial discrepancies of up to 20% occur. Figure 6 presents a comparison with the viscosities measured in Ubbelohde viscometers by the same authors. The relative deviations range systematically from −0.25 to 4.2% and exceed the combined accuracy of the experiments. Eventually, these discrepancies result from increasing evaporation of TFE during the present

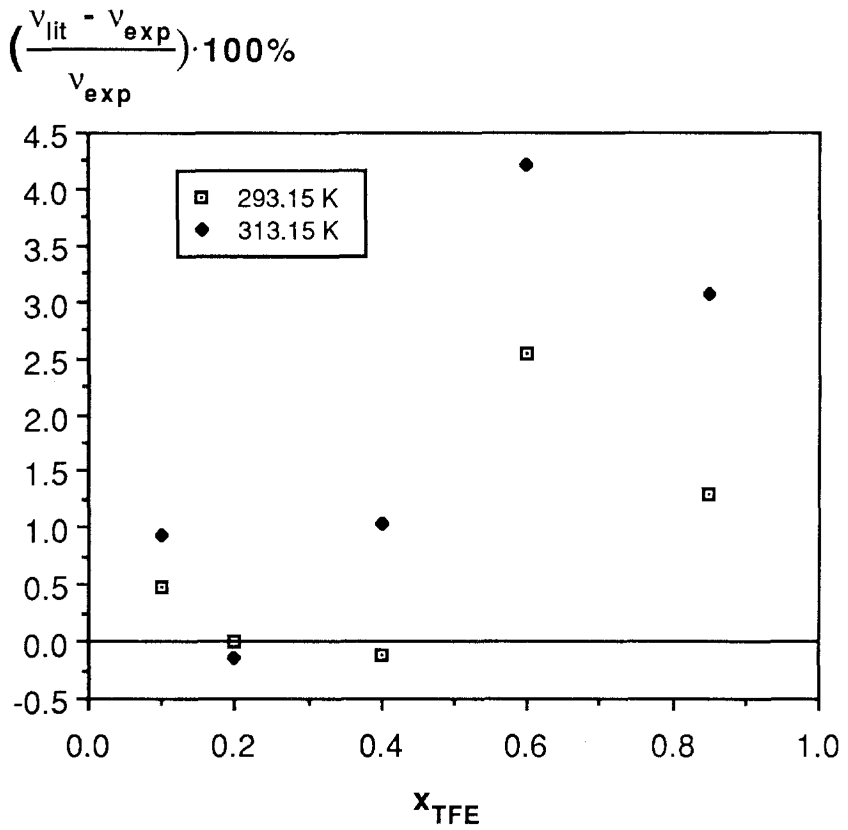

**Fig. 6.** Comparison of experimental viscosities with data of Kobayashi and Nagashima [10].

measurements at temperatures from 283.15 to 343.15 K. Due to this change in composition an additional uncertainty of 1–3% has to be assigned to the viscosity data in the range $0.5 \leqslant x_{TFE} \leqslant 0.9$.

## 5. REPRESENTATION OF CONCENTRATION DEPENDENCE

In none of the previous publications on the viscosity of the TFE–$H_2O$ system was an attempt made to represent the concentration dependence. Consequently, the final part of this study included a test of mixing rules. Three formulations for the concentration dependence of mixture viscosities were considered. The McAllister equation [11] is often used for alcohol–water mixtures and includes two adjustable parameters. Dizechi and Marschall [12, 13] improved this formulation by introducing an additional adjustable parameter. It was simplified recently by Soliman and Marschall [14]:

$$\ln \nu_{\text{mix}} = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1x_2 \ln \nu_{12} + \frac{B_{12}x_1x_2}{(M_1/M_2)^2\, x_1 + x_2} \tag{8}$$

Again, only two adjustable parameters, $\nu_{12}$ and $B_{12}$, are required and the mixture viscosity can be calculated relatively straightforward.

The application of mixing rules, which are based on the pure-component viscosities, encounters a similar problem as the calculation of gas solubilities. Without extrapolation of pure-component viscosities, mixing rules can be used only between the higher freezing point and the lower boiling point of either mixture constituent. If these are not considerably different, a mixing rule describes only a small part of the mixture viscosity

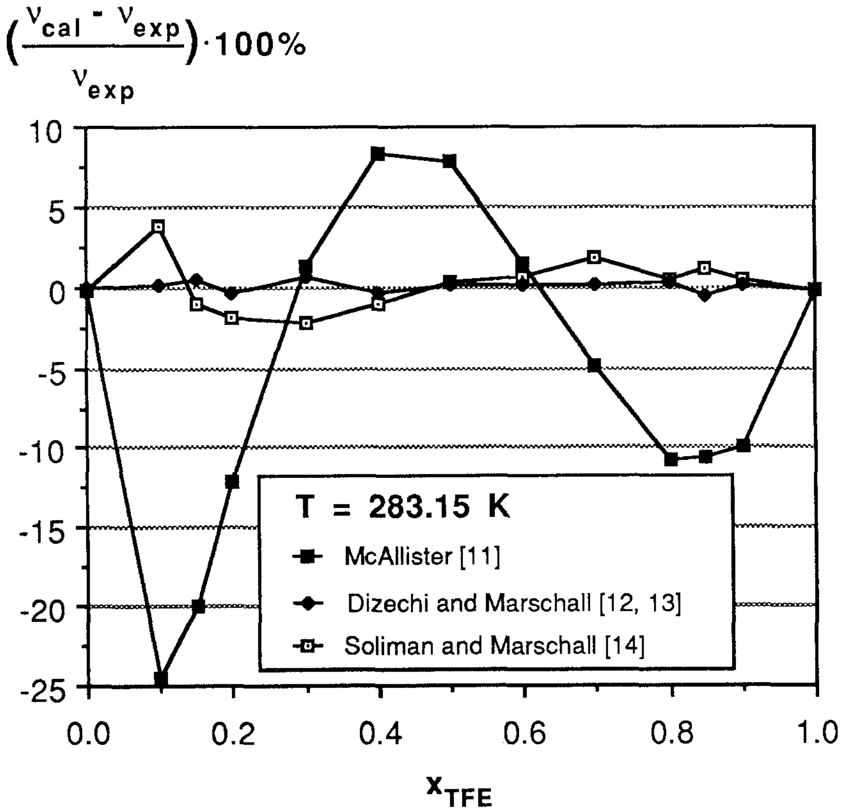

Fig. 7. Comparison of experimental viscosities with the mixing rules tested.

surface. For the TFE–$H_2O$ system the temperature range is limited by the freezing point of water and the boiling point of TFE as indicated in Fig. 3.

The interaction parameters of the three formulations were obtained from the experimental data in conjunction with correlations (5)–(7) by a nonlinear least-squares fit. A typical example of the performance of the tested mixing rules is given in Fig. 7 at 283.15 K. In all comparisons it was found that the McAllister equation is not adequate for the TFE–$H_2O$ mixture since it yields substantial discrepancies between −25 and 10%. Much better is the representation by Dizechi's and Soliman's equations, which deviate up to 5% but mostly agree with the data to 2.5%. As shown in Fig. 7 the agreement between Dizechi's equation and the data is almost excellent at 283.15 K.

## 6. SUMMARY

In this work the viscosity of the mixture TFE–$H_2O$ was measured in the entire liquid region. Data below 273.15 K are reported for the first time. The viscosity exhibits characteristics similar to those of other alcohol–water mixtures. The wide range of viscosities and their strong temperature dependence in this system require a detailed analysis of experimental inaccuracies. The accuracy of the temperature measurement is shown to contribute significantly to the overall accuracy. This factor can be assessed only when reliable correlations for the viscosity temperature dependence are established.

Three mixing rules are tested to represent the concentration dependence of the viscosity. While McAllister's equation is inadequate, the equations of Dizechi and Soliman are recommended for this system. Mixing rules are limited tools to describe mixture viscosities since they can be applied only between the higher freezing point and the lower boiling point of either mixture constituent. A description of the entire mixture viscosity requires methods which include phase equilibria information besides the viscosities of the pure components.

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Hannover, F.R.G. Unpublished material on Soliman's mixing rule was made available by Professor E. Marschall, University of California at Santa Barbara.

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