Measurement and Correlation of the Surface Tension−Temperature Relation for Methanol

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New experimental data on the surface tension of methanol are reported obtained by the Wilhelmy plate method using the Krűss K100MK2 tensiometer at 13 temperatures from (279 to 333) K. At each temperature, from 11 to 42 individual measurements have been carried out. The surface tension average values at particular temperatures are presented with the estimated overall standard uncertainty of ± 0.1 $\text{mN}\cdot\text{m}^{-1}$. An empirical surface tension−temperature equation has been developed describing the temperature dependence of the methanol surface tension from 225 K to the critical point at 512.6 K. The equation is fitted to the data of the present work and to critically assessed data of other authors compiled from the literature. The uncertainties associated with the correlation are estimated to be ± 0.3 $\text{mN}\cdot\text{m}^{-1}$.

Introduction

Methanol is often used as a low surface tension testing substance in calibration and/or testing of new apparatuses or methods to measure surface tension, while water is used as the high surface tension one. Besides water, methanol is often used as a model solvent in binary systems with various solutes.[22,23,27] Reliable values of methanol surface tension are required in evaluation of excess values of the surface tension of mixtures containing methanol and for testing of methods to predict surface tension.[28] Temperature derivative of the surface tension is necessary in evaluation of the surface entropy, which provides information on the surface layer structure.

As far as we are aware, a simple correlation providing reliable values of the surface tension−temperature relation in a broad temperature interval is missing in the open literature. The available tables and compilations do not provide the most reliable data on the methanol surface tension−temperature relation. The available experimental data[1−27] are of various quality and require critical evaluation.

The aim of the present study was to obtain new high accuracy experimental data for the methanol surface tension and to develop a reliable description of the methanol surface tension−temperature relation in a temperature interval as broad as possible, based on critically evaluated experimental data compiled from the literature. The comparison of our new data with the developed correlation equation should provide an estimation of their accuracy. We have also performed similar surface tension measurements on water and compared their result with the IAPWS correlation.[29] Our water surface tension data at temperatures from (293 to 343) K show a root-mean-square deviation of 0.03 $\text{mN}\cdot\text{m}^{-1}$ from the IAPWS correlation.

Surface Tension Measurements

In the present study, the surface tension measurements were performed by the Wilhelmy plate method using the Krűss K100MK2 tensiometer. Some additional measures were taken to increase the accuracy of the results. The thermostat vessel of the apparatus was provided with thermal insulation, using a layer of microporous polyurethane. The original glass sample vessel was replaced by a stainless steel one. To improve homogeneity of the internal temperature, to minimize natural convection in the sample, and to reduce its evaporation, the sample vessel was covered with a Teflon lid being removed only during the measuring plate action itself. The sample vessel is placed in a vessel which is thermostatted externally by a Julabo MB-5 thermostat providing bath temperature stability of ± 0.02 K. At temperatures below 20 °C, in addition, external immersion cooler ETK 30 is employed. In this way, the sample temperature stability of the order of magnitude of 10^{-2} K was achieved. The sample temperature is measured with a platinum resistance thermometer immersed into the sample. The temperature measurement standard uncertainty is specified by the manufacturer to be ± 0.02 K. Before each measurement run, the Wilhelmy plate was cleaned by heating with a Bunsen burner until it was hot red. Without this procedure the obtained values of the surface tension underestimate the correct value by an amount increasing by several millinewtons per meter with each progressive run.

Table 1. Experimental Surface Tension γ of Methanol

$T \pm 2s^a$ K	$\gamma \pm 2s^a$ $\text{mN}\cdot\text{m}^{-1}$	number of data
279.11 ± 0.02	23.87 ± 0.04	42
282.59 ± 0.02	23.63 ± 0.04	24
288.30 ± 0.02	23.14 ± 0.02	29
293.37 ± 0.04	22.73 ± 0.02	24
296.97 ± 0.01	22.43 ± 0.03	29
301.54 ± 0.02	21.99 ± 0.01	25
307.31 ± 0.03	21.43 ± 0.02	29
311.76 ± 0.06	21.00 ± 0.05	31
317.66 ± 0.06	20.43 ± 0.05	36
322.90 ± 0.09	19.83 ± 0.07	42
326.56 ± 0.05	19.42 ± 0.06	34
330.01 ± 0.10	19.09 ± 0.03	22
333.81 ± 0.06	18.63 ± 0.05	11

[a] Estimation of the experimental standard deviation.

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The dried methanol supplied by Merck KGaA under the registered mark SeccoSolv was employed for measurements. The maximal mass fraction of H_2O contained in the sample as specified by the supplier is $5 \cdot 10^{-5}$. After each period of 7 h, the measuring vessel was filled with a new dry sample. No influence of air moisture absorption was observed in repeated measurements performed within the first 7 h.

A total of 378 individual measurements were carried out at 13 temperature points between (288 and 333) K, i.e. in average 29 measurements at each temperature. Table 1 gives averages of temperature and surface tension together with the estimation of experimental standard deviations characterizing dispersion of the observed values about their mean and with the number of measurements performed at individual temperatures. But, the observed data scatter is by far not the dominant source of their uncertainty. The overall uncertainty of the present data can be estimated by comparison with the most reliable surface tension data obtained by the capillary rise method.

Correlation

Within the present study, 27 literature sources of experimental data have been collected containing a total of 118 data points on the $\gamma - T$ relation of methanol. Only original unsmoothed experimental data were included in the data used for fitting of the empirical equation. The sources of the data are listed in Table 2 together with their estimated standard uncertainties. The original values of the standard uncertainties of the surface tension data given by authors were employed for this purpose wherever available. In other cases, we estimated the standard uncertainty based on the method used to measure the data and based on comparison with the data of other authors.

Table 2. Sources of Data on the Surface Tension of Methanol

		range of values			u^a
author(s)	year	T/K	method	number of data	$\mathrm{mN \cdot m^{-1}}$
Ramsay and Shields[1]	1893	293–509	capillary rise	20	± 0.04
Morgan and McAfee[2]	1911	273–323	drop weight	5	± 0.50
Morgan and Neidle[3]	1913	303	drop weight	1	± 0.70
Richards and Cooms[4]	1915	293	capillary rise	1	± 0.04
Morgan and Scarlett[5]	1917	273–323	drop weight	3	± 0.70
Smith and Sorg[6]	1941	298	pendant drop	1	± 0.40
Teitelbaum et al.[7]	1951	263–323	capillary rise	13	± 0.04
Efremov[8]	1968	283–333	maximum bubble pressure	6	± 0.10
Konobeev and Lyapin[9]	1970	293–333	du Noüy ring	3	± 0.20
Kőrösi and Kováts[10]	1981	293–343	capillary rise	2	± 0.12
Won et al.[11]	1981	298	du Noüy ring	1	± 0.15
Strey and Schmeling[12]	1983	225–310	capillary rise	18	± 0.04
Cheong and Carr[13]	1987	298	du Noüy ring	1	± 0.15
Braslau et al.[14]	1988	293	capillary waves	1	± 0.35
Kalbassi and Biddulph[15]	1988	320–338	maximum bubble pressure	2	± 0.30
Rao and Enhorning[16]	1995	293	maximum bubble pressure	1	± 0.50
Wallenberger and Lyzenga[17]	1990	297	capillary waves	1	± 1.60
Vázquez et al.[18]	1995	293–323	Wilhelmy plate	7	± 0.08
Feenstra et al.[19]	2001	273–295	maximum bubble pressure	4	± 0.30
Santos et al.[20]	2003	303	du Noüy ring	1	± 0.01
Gao and Zeng[21]	2003	293	fiber drop analysis	2	± 0.40
Calvo et al.[22]	2004	298	drop volume	1	± 0.03
Kijevcanin et al.[23]	2004	303	du Noüy ring	1	± 0.01
Sönmez and Cebeci[24]	2004	298	drop volume	1	± 0.60
Dilmohamud et al.[25]	2005	288–313	drop weight	6	± 0.80
Tahery et al.[26]	2006	293	pendant drop	1	± 0.10
Domańska et al.[27]	2008	308–318	du Noüy ring	2	± 0.40
this work	2008	279–334	Wilhelmy plate	13	± 0.10

[a] Estimation of the experimental standard uncertainty.

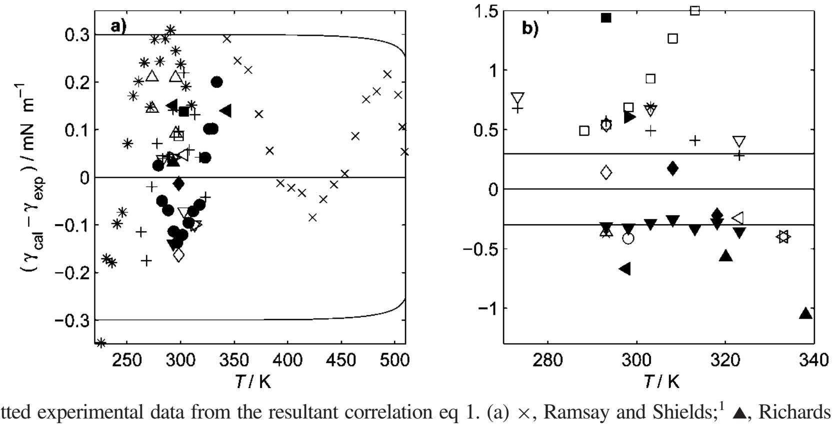

Figure 1. Deviations of the fitted experimental data from the resultant correlation eq 1. (a) ×, Ramsay and Shields;[1] ▲, Richards and Cooms;[4] +, Teitelbaum et al.;[7] ▽, Efremov;[8] open right-pointing triangle, Konobeev and Lyapin;[9] filled left-pointing triangle, Kőrösi and Kováts;[10] ◆, Won et al.;[11] ∗, Strey and Schmeling;[12] ◇, Cheong and Carr;[13] △, Feenstra et al.;[19] ■, Santos et al.;[20] □, Calvo et al.;[22] open left-pointing triangle, Kijevcanin et al.;[23] ▼, Tahery et al.;[26] •, this work. (b) ×, Ramsay and Shields;[1] +, Morgan and McAfee;[2] ∗, Morgan and Neidle;[3] ▽, Morgan and Scarlett;[5] open left-pointing triangle, Efremov;[8] open right-pointing triangle, Konobeev and Lyapin;[9] △, Braslau et al.;[14] ▲, Kalbassi and Biddulph;[15] ■, Rao and Enhorning;[16] filled left-pointing triangle, Wallenberger and Lyzenga;[17] ▼, Vázquez et al.;[18] filled right-pointing triangle, Sönmez and Cebeci;[24] □, Dilmohamud et al.;[25] ◆, Domańska et al.[27]

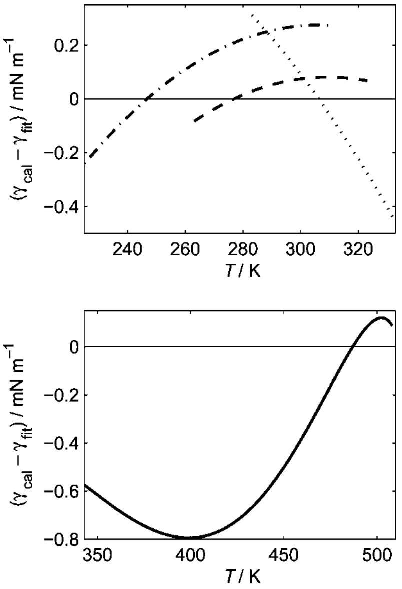

Figure 2. Deviations of the $\gamma - T$ correlations by other authors from eq 1. - - -, Teitelbaum et al.;[7] - • - • -, Strey and Schmeling;[12] —, ICT;[30] ••••, Jasper.[31]

Table 3. Coefficients *B*, *b*, and Exponent *μ* of Equation *1* with Estimated Standard Uncertainties[a]

$B \pm u$ N·m^{-1}	$b \pm u$	$\mu \pm u$
0.06603 ± 0.00030	−0.364 ± 0.001	1.062± 0.005

[a] $T_c = 512.6$ K.

Though the temperature scale corrections are of the order of the experimental uncertainties, all the temperatures given in ITS-48 and IPTS-68 have been converted to ITS-90. Twelve of the cited literature sources provide only one data point. Temperatures of almost all measurements lie within the temperature interval from (263 to 323) K covered by the 13 data points by Teitelbaum et al.[7] Temperatures below 263 K down to 226 K are covered by only one data set by Strey and Schmeling.[12] Similarly, temperatures above the boiling temperature of 337.8 K up to the critical point at 512.6 K cover 18 points measured by Ramsay and Shields[1] and one point reported by Kőrösi and Kováts.[10]

To correlate data on surface tension at the air−liquid boundary in limited temperature intervals, a linear function of temperature is quite sufficient. The functional form of a $\gamma(T) = B\tau^{\mu}$, where $\tau = 1 - T/T_c$, is usually used to correlate $\gamma - T$ data at the vapor−liquid boundary up to critical point. To describe the $\gamma - T$ relation within broader temperature intervals comparable with the temperature interval from the triple point to the critical point of the substance, the form of eq 1

$$\gamma(T) = B\tau^{\mu}(1 + b\tau) \tag{1}$$

is appropriate, employed, for example, for the IAPWS correlation of the surface tension of water.[29] The coefficients B, b, and μ were determined by minimizing the following sum of squares:

$$\chi^2 = \sum_{i=1}^{N}\left[\frac{\gamma_{i,\exp} - \gamma(T_i)}{u_i}\right]^2$$

where N is the number of the data points, $\gamma_{i,\exp}$ is the ith experimental value of surface tension, and $\gamma(T_i)$ is the value calculated from eq 1 at temperature T_i. Reciprocal values of estimates of the experimental uncertainties u_i of the data given in Table 2 were used as the weights. Table 3 gives the resultant coefficients B, b, and the exponent μ of eq 1 for methanol together with estimates of their standard uncertainties calculated from the uncertainty estimates in the fitted data using the rule of propagation of uncertainties.

In Figure 1a and b, deviations are depicted of the experimental data points used in the fitting from the resultant correlation eq 1. A band of standard uncertainties calculated from the correlation eq 1 is plotted in Figure 1a and b using the solid line. The uncertainties follow from the reported estimated uncertainties of the correlation equation parameters. In Figure 2, plots of deviations of the correlation equations proposed by other authors from eq 1 are shown.

The present description of the $\gamma - T$ relation for methanol is based especially on the data of Ramsay and Shields,[1] Teitelbaum et al.,[7] and Strey and Schmeling[12] which are highly consistent with each others (Figure 1a). They were all obtained by the capillary rice method that provides the most reliable results in surface tension measurements. An evident systematic deviations from the correlation curve show the data sets[2,5,15,18,25] (Figure 1b).

The data by Ramsay and Shields[1] and by Kőrösi and Kováts[10] for the surface tension of methanol at the vapor−liquid boundary

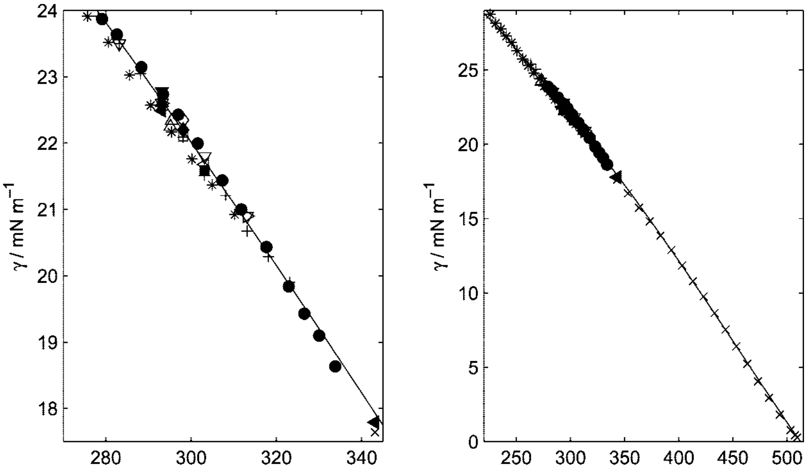

Figure 3. Distribution of the data points used in correlation along the resultant correlation curve. ×, Ramsay and Shields;[1] ▲, Richards and Cooms;[4] +, Teitelbaum et al.;[7] ▽, Efremov;[8] open right-pointing triangle, Konobeev and Lyapin;[9] filled left-pointing triangle, Kőrösi and Kováts;[10] ◆, Won et al.;[11] ∗, Strey and Schmeling;[12] ◇, Cheong and Carr;[13] △, Feenstra et al.;[19] ■, Santos et al.;[20] □, Calvo et al.;[22] open left-pointing triangle, Kijevcanin et al.;[23] ▼, Tahery et al.;[26] •, this work.

at temperatures above the boiling temperature of 337.8 K show a good consistency with the air−liquid boundary data obtained at temperatures below the boiling temperature (Figure 1a). In Figure 3 the resultant $\gamma-T$ correlation is depicted together with the data used for fitting, to give an idea how they are distributed along the correlation curve.

The overall standard uncertainty of our surface tension data for methanol, which follows from the comparison with the most reliable data obtained by the capillary rise method, should be estimated to be of $\pm$ 0.1 $\mathrm{mN \cdot m^{-1}}$.

Conclusion

The experimental data points on the methanol surface tension−temperature relation obtained in the present work at 13 temperatures from (279 to 333) K proved to be consistent with the data of other authors evaluated as the most reliable ones. An empirical equation describing the $\gamma-T$ relation of methanol has been developed based upon a body of critically assessed experimental data compiled from literature. The absolute uncertainty associated with the data correlation is estimated to be $\pm$ 0.3 $\mathrm{mN \cdot m^{-1}}$.

The present results for methanol appear to be somewhat less accurate than those obtained for water using the same apparatus and measuring procedure. Most probably, it should be ascribed to influence of evaporation of the more volatile methanol after the sample vessel is open for the Wilhelmy plate can be immersed into the sample.

Comparisons of the available measurements on the methanol surface tension have shown that the amount of available experimental data is far less valuable to establish a description of that property than it might appear at a first glance. Some of the available data sets are only of limited value, because they show large scatter or systematic deviations when compared to other data. Thus, 12 data sets containing about 30 % of the data points show an evident systematic deviation from the data evaluated as the most reliable (Figure 1b). The largest gap in the data on the methanol surface tension is clearly found outside the temperature region (263 to 323) K.

Similar data assessments and correlations are desirable to be performed for other alcohols and water substance.

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