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Surface Tension of Pure Liquids and Binary Liquid Mixtures

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The pendant drop method, combined with efficient temperature control of the measuring cell, allows high precision in surface tension measurements. The surface tensions of heptane, toluene, *N*,*N*-dimethylformamide, cyclohexane, *N*-methyl-2-pyrrolidone, and propanone were measured as a function of temperature using the pendant drop method. The results were compared with literature data. The surface tension and density of toluene + heptane and *N*,*N*-dimethylformamide + toluene at atmospheric pressure were measured over a temperature range. Gibbs excess surface concentrations are derived from the experimental surface tensions, and the influence of activity coefficients is discussed.

Introduction

Because of their importance in nature, interfacial phenomena have attracted the attention of scientists for more than a century. Apart from its theoretical interest, a detailed understanding of interfacial behavior is crucial to many technological processes, such as coating or adsorption, industrial separation, or tertiary oil recovery. Surface tensions have been measured for a long time, and collections of experimental data for pure liquids and some binary liquid mixtures exist.[1−3]

In a search for data of a special system, one soon realizes that some of the experimental data sets are rather old, and often no specifications for precision, measuring method, and purity of the substances are given. A critical review of the few available data reveals a considerable scattering of the measured values. High quality experimental surface and interfacial tensions form the basis for a successful modeling and for theoretical calculations of interfacial properties in fluid systems.[4−8] Therefore, further precision measurements are needed. Especially calculations of the relative Gibbs excess concentrations from surface tensions are very sensitive to the scatter in the experimental data.[9] Because of its high flexibility and precision, the pendant drop method is the favored experimental technique to investigate both interfacial and surface tensions over several orders of magnitude. It is superior to most other commonly used measuring methods such as Wilhelmy plate or spinning drop.[10−13] The amount of sample needed is small, and it is possible to measure both surface and interfacial tensions with high accuracy even under high pressure.[14−16] Extremely small interfacial tensions in the vicinity of critical solution points[17,18] can be determined where spinning drop measurements fail because of their low temperature stability.

Experimental Section

Reagents. Toluene pa. with a purity of >99.5% (by GC) and a water content of 0.03%, heptane pa. with a purity of >99.0% (by GC) and a water content of 0.01%, propanone pa. with a purity of >99.5% (by GC) and a water content of 0.2%, and 1-methyl-2-pyrrolidone pa. with a purity of >99.5% (by GC) and a water content of 0.1% were supplied by Fa. Merck, Darmstadt, Germany. *N*,*N*-Dimethylformamide pa. with a purity of >99.5% (by GC) and a water content of 0.15% was supplied by Fa. Fluka, and cyclohexane pa. with a purity of >99.5% (by GC) and a water content of 0.15% was supplied by Fa. Riedel-de Haen. All substances were dried over molecular sieves ZEOSORB A4/A3 and stored in a dark place.

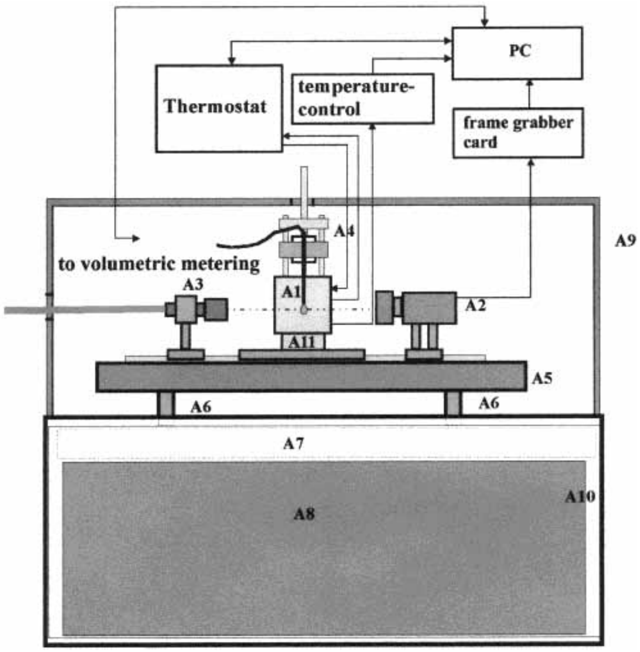

Figure 1. Pendant drop apparatus: A1, measuring cell; A2, CCD camera; A3, light source coupling; A4, capillary; A5, vibration-damped breadboard; A6, vibration-control system; A7, slab; A8, sand bed; A9, dust jacket; A10, brick base; A11, *xyz*-positioning table.

Experimental Apparatus. The experimental setup[19] is shown in Figure 1.

Mechanical noise and vibrations, caused by vehicles, machines, or people, greatly affect the stability of the pendant drop. For that reason the apparatus was completely decoupled from the building. The whole apparatus is placed on a slab (A7) that lies in a sand bed (A8). The optical setup is mounted on a vibration-damped breadboard (A5). Additionally, a vibration control system (A6) hori-

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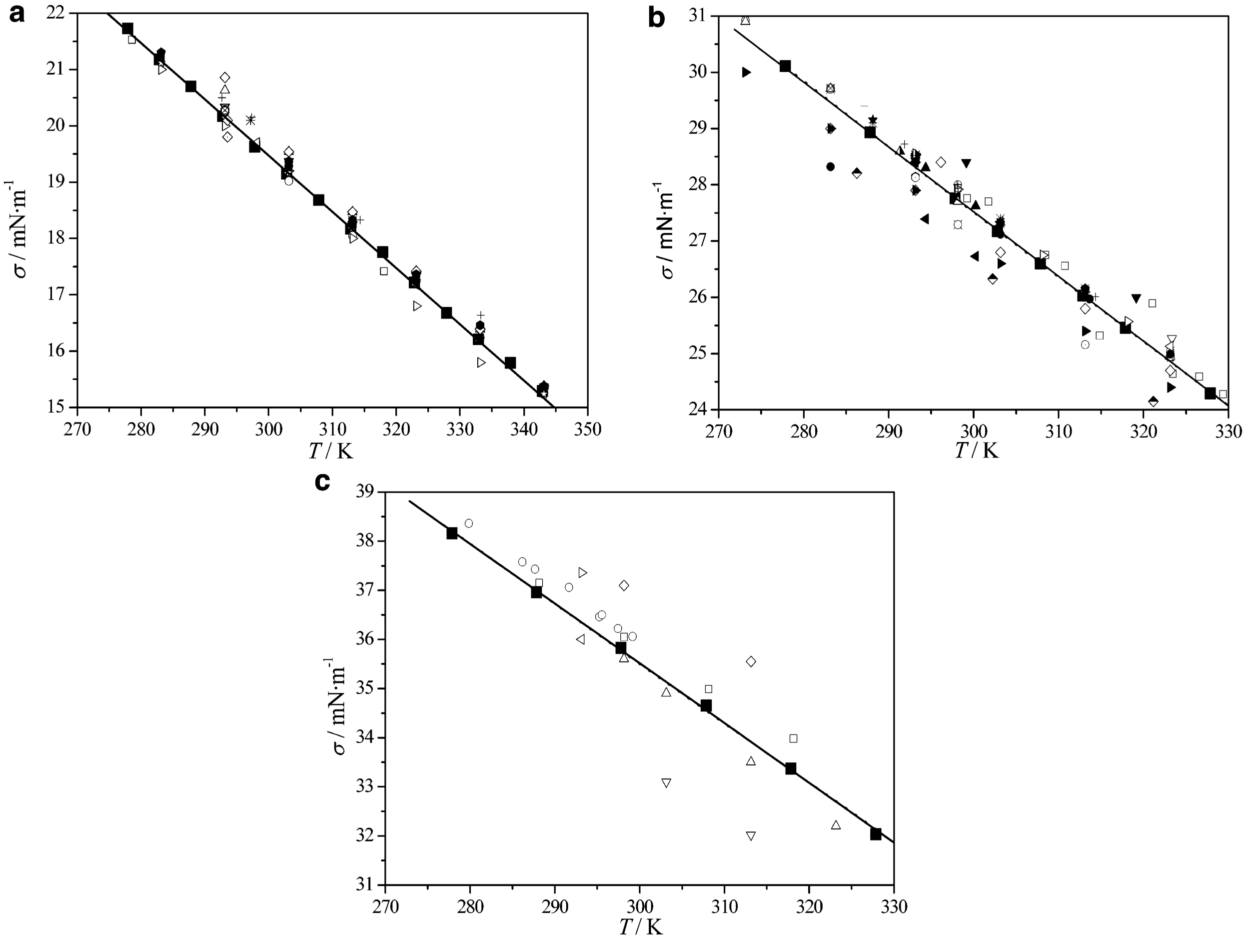

Figure 2. (a) Experimental surface tension, σ (■, this work; solid line, linear fit of eq 1), of heptane obtained by the pendant drop apparatus in comparison with values from the literature: □, Grigor'ev et al.;[21] ○, Abdulagatov et al.;[22] △, Volyak et al.;[23] ▽, Aguila-Hernandez et al.;[24] ◇, Vargaftik;[25] open triangle pointing left, McLure et al.;[26] open triangle pointing right, Shukla et al.;[27] ⬢, Pugachevich et al.;[28] ☆, Jasper et al.;[29] pentagon, Jasper et al.;[30] +, Vogel;[31] ×, Quayle et al.;[32] ∗, Tillman et al.;[33] dot in a box, Shafrin et al.;[34] ⊙, Wibaut et al.;[35] dot in a diamond, Ramakrishnan et al.;[36] ⊗, Edgar et al.;[37] × in a box, Abramzon et al.[38] (b) Experimental surface tension, σ (■, this work; solid line, linear fit of eq 1), of toluene obtained by the pendant drop apparatus in comparison with experimental values from the literature: ⊗, Jasper;[2] ×, Vargaftik;[25] □, Kalbassi et al.;[39] ○, Rossini et al.;[40] ▽, Morino;[41] open triangle pointing left, Prabhakar et al.;[42] open triangle pointing right, Wanchoo et al.;[43] dot in a diamond, Korosi et al.;[44] ☆, Agarwal et al.;[45] pentagon, Donaldson et al.;[46] +, Vogel;[47] dot in a box, Buehler et al.;[48] ∗, Hennaut-Roland et al.;[49] ▲, Sugden;[50] ●, Kremann et al.;[51] ▼, Jaeger;[52] filled triangle pointing left, Walden et al.;[53] filled triangle pointing right, Watanabe et al.;[54] ⬢, Tonomura et al.;[55] ★, Mahl et al.;[56] ⊙, Herz et al.;[57] −, Green et al.;[58] |, Bartell et al.;[59] ◇, Damerell et al.;[60] ◆, Richards et al.;[61] △, Harkins et al.;[62] thin filled triangle pointing right, Voronkov;[63] slant in a circle, Trimble;[64] ⊕, Krishna et al.;[65] ⊞, Transue et al.[66] (c) Experimental surface tension, σ (■, this work; solid line, linear fit of eq 1), of *N*,*N*-dimethylformamide obtained by the pendant drop apparatus in comparison with other available experimental values from the literature: □, Wadewitz;[67] ○, Stairs et al.;[68] △, Hradetzky et al.;[69] ▽, Gopal et al.;[70] ◇, Granzhan et al.;[71] triangle pointing left, Shcherbina et al.;[72] triangle pointing right, Kreft et al.[73]

zontally aligns the breadboard. The pendant drop is formed in the measuring cell (A1) on a special steel capillary (A4) by means of a computer controlled sample supply system. A gastight PTFE-piston syringe through PTFE-tubes supplies the sample. The drop, formed at the end of the capillary, is illuminated by glass fiber optics aligned parallel by a light source coupling (A3). The CCD camera (A2) monitors pictures of the pendant drop, which are either stored on a video recorder or directly digitized on a PC. Special frame grabber software enables the automatic storage of the digitized drop images and controls both the sample size and temperature. The pendant drop profiles are extracted from the drop images and analyzed by means of the ADSA software.[11,20] This ADSA software ensures a high-quality contour extraction and a very precise interfacial tension calculation by numerical solution of the Laplace equation. To control the temperature, a Julabo type FP25MH thermostat together with a 100 Ω platinum resistance thermometer is used. An additional dust jacket (A9) enables dust protection as well as temperature control within the measuring cell of $\Delta T = \pm 0.002$ K over extended periods of time.

Preparation of Samples. All glassware and PTFE parts used in measurement and sample handling are cleaned with propanone and distilled water. To remove dust, the glassware is cleaned in a steam bath using distilled water, and after that it is carefully dried. Samples are weighed to ±0.1 mg into an Erlenmeyer flask and sealed with PTFE stoppers. To avoid the decomposition of *N*,*N*-dimethylformamide, the samples are kept in a dark place. For mixtures the mole fraction is accurate to $\pm 1 \times 10^{-4}$.

Measuring Procedure and Calibration. To avoid surface contamination and surface distortion due to evaporation, all surface tension measurements were performed with a drop developed in a closed measuring cell with a volume of about 40 cm^3. The empty cell was filled with a certain amount of sample, and it was allowed to saturate

Table 1. Surface Tension, σ, from 277.3 K to 337.88 K for Heptane, Toluene, *N*,*N*-Dimethylformamide, Cyclohexane, *N*-Methyl-2-pyrrolidone, and Propanone Measured with the Pendant Drop Apparatus

T/K	σ/mN·m^{-1}
Heptane	
277.93	21.73 ± 0.04
282.83	21.18 ± 0.04
287.81	20.70 ± 0.02
292.81	20.17 ± 0.04
297.82	19.63 ± 0.05
302.83	19.15 ± 0.04
307.86	18.68 ± 0.03
312.86	18.17 ± 0.02
317.86	17.76 ± 0.05
322.86	17.22 ± 0.05
327.88	16.68 ± 0.03
332.91	16.21 ± 0.08
337.88	15.79 ± 0.10
342.92	15.29 ± 0.10
Toluene	
277.85	30.11 ± 0.05
287.81	28.93 ± 0.03
297.82	27.76 ± 0.05
302.83	27.17 ± 0.05
307.86	26.60 ± 0.05
312.87	26.03 ± 0.03
317.86	25.46 ± 0.04
327.88	24.29 ± 0.04
337.88	23.22 ± 0.10
N,*N*-Dimethylformamide (DMF)	
277.85	38.16 ± 0.05
287.81	36.96 ± 0.07
297.82	35.83 ± 0.07
307.86	34.65 ± 0.05
317.86	33.37 ± 0.10
327.89	32.03 ± 0.10
Cyclohexane	
279.33	26.37 ± 0.08
282.82	25.99 ± 0.04
287.81	25.34 ± 0.04
297.82	24.20 ± 0.02
307.86	23.02 ± 0.03
317.86	21.84 ± 0.04
327.88	20.71 ± 0.03
337.93	19.57 ± 0.05
N-Methyl-2-pyrrolidone (NMP)	
277.84	42.61 ± 0.04
287.80	41.35 ± 0.10
297.81	40.25 ± 0.06
307.85	39.10 ± 0.02
317.85	37.91 ± 0.05
327.89	36.80 ± 0.07
337.88	35.66 ± 0.09
Propanone	
287.81	23.94 ± 0.06
297.82	22.78 ± 0.01
307.86	21.59 ± 0.01
317.86	20.33 ± 0.01
327.88	19.01 ± 0.03

with sample vapor. The temperature of the cell was continuously monitored until thermal equilibrium was achieved. The measurements started at the lowest temperature. For each sample we developed four different drops in this saturated atmosphere and recorded 10 images of each drop. The density differences needed for the numerical solution of the Laplace equation are determined using a vibrating tube densimeter (DMA 60 Fa. Anton Paar) with temperature control to ±0.01 K. For its calibration at each temperature we used twice distilled water and pure heptane. The accuracy of the measured densities is considered to be $\Delta\rho = \pm 0.0001$ g cm^{-3}.

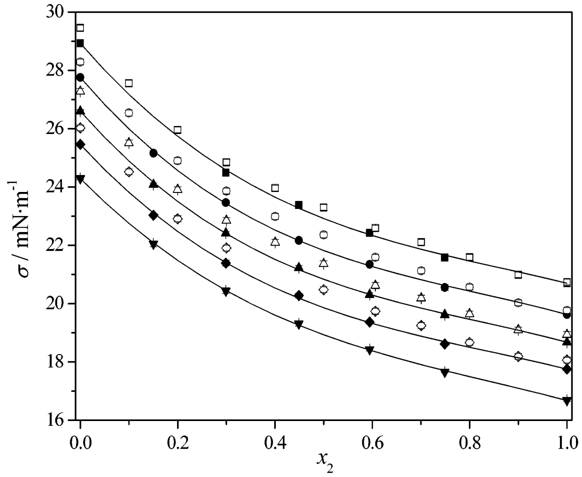

Figure 3. Experimental surface tension, σ, of the binary mixtures toluene (1) + heptane (2) measured with the pendant drop apparatus at different temperatures: ■, T = 287.15 K; ●, T = 297.81 K; ▲, T = 307.86 K; ◆, T = 317.86 K; ▼, T = 327.88 K. The full lines are the model calculations according to eq 2. Open symbols show further experiments using the ring method of Wadewitz:[67] □, T = 288.15 K; ○, T = 298.15 K; △, T = 308.15 K; ◇, T = 318.15 K.

Table 2. Parameters *A* and *B* for the Correlation of the Temperature Dependence of Surface Tension, Eq 1

substance	A/mN·m^{-1}	B/mN·m^{-1}·K^{-1}
heptane	49.06 ± 0.18	−0.098 62 ± 0.000 6
toluene	62.03 ± 0.18	−0.115 04 ± 0.000 6
DMF	71.99 ± 0.56	−0.121 58 ± 0.002 0
cyclohexane	58.86 ± 0.16	−0.116 37 ± 0.000 5
NMP	74.55 ± 0.24	−0.115 18 ± 0.000 8
propanone	59.36 ± 0.59	−0.122 88 ± 0.002 0

Table 3. Parameters σ_{112} and σ_{122} for the Correlation of the Composition Dependence of the Binary Mixtures Toluene (1) + Heptane (2) and DMF (1) + Toluene (2) (Eq 2) from 287.81 K to 327.88 K

T/K	σ_{112}	$\Delta\sigma_{112}$	σ_{122}	$\Delta\sigma_{122}$
Toluene (1) + Heptane (2)				
287.81	66.21	0.08	67.52	0.07
297.82	63.41	0.10	63.79	0.09
307.86	60.46	0.10	60.94	0.09
317.86	57.38	0.10	58.28	0.12
327.88	54.48	0.06	56.02	0.05
DMF (1) + Toluene (2)				
287.81	91.45	0.59	97.25	0.56
297.82	88.63	0.44	93.84	0.42
307.86	85.83	0.50	89.79	0.47
317.86	80.81	0.60	87.92	0.57
327.88	77.62	0.57	84.79	0.50

High accuracy results from the drop profile analysis require that parallel light enters perpendicular to the CCD camera and the drop is correctly aligned in the optical axis. To calibrate the pixel coordinates of the drop profile image and to map this image to the physical length scale, we use the image of a grid with a width of 0.025 mm exactly at the position of the drop. For the calculation of the surface tension, a drop size of 80−90% from the apex is used to exclude possible asymmetries in the upper part of the drop around the mouth of the capillary due to wetting at the solid−liquid phase boundary. Once the density difference is known, the interfacial tension is extracted from the drop profile by numerically solving the modified Laplace equation. We applied the algorithm of Neumann et al.[11,20] that uses a Bulirsch−Stoer procedure instead of the standard fourth-order Runge−Kutta method. The apparatus pro-

Table 4. Surface Tension, σ, versus Mole Fractions, x_1, from 287.81 K to 327.88 K for Mixtures of Toluene (1) + Heptane (2) Measured with the Pendant Drop Apparatus

	σ/mN·m^{-1} for the following values of T/K				
x_1	287.81	297.82	307.86	317.86	327.88
0.000	28.93 ± 0.03	27.76 ± 0.05	26.60 ± 0.05	25.46 ± 0.04	24.29 ± 0.04
0.150		25.16 ± 0.07	24.08 ± 0.05	23.03 ± 0.06	22.05 ± 0.10
0.299	24.49 ± 0.08	23.47 ± 0.07	22.42 ± 0.05	21.39 ± 0.10	20.44 ± 0.09
0.449	23.38 ± 0.04	22.17 ± 0.03	21.23 ± 0.08	20.28 ± 0.08	19.31 ± 0.08
0.595	22.41 ± 0.06	21.35 ± 0.05	20.31 ± 0.06	19.37 ± 0.05	18.43 ± 0.05
0.749	21.58 ± 0.04	20.56 ± 0.10	19.62 ± 0.02	18.62 ± 0.04	17.66 ± 0.02
1.000	20.70 ± 0.02	19.63 ± 0.05	18.68 ± 0.03	17.76 ± 0.05	16.68 ± 0.03

Table 5. Liquid Densities, ρ, versus Mole Fractions, x_1, from 278.15 K to 333.15 K for Mixtures of Toluene (1) + Heptane (2) Measured with the Vibration Tube Densimeter

	ρ/g·cm^{-3} at the following values of T/K											
x_1	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
0.000	0.8803	0.8759	0.8714	0.8669	0.8624	0.8578	0.8532	0.8486	0.8439	0.8392	0.8345	0.8298
0.150	0.8437	0.8393	0.8349	0.8305	0.8260	0.8215	0.8170	0.8124	0.8078	0.8031	0.7985	0.7938
0.299	0.8113	0.8070	0.8027	0.7983	0.7941	0.7894	0.7849	0.7804	0.7758	0.7712	0.7665	0.7618
0.449	0.7820	0.7778	0.7735	0.7691	0.7647	0.7603	0.7558	0.7513	0.7468	0.7422	0.7376	0.7330
0.595	0.7564	0.7522	0.7479	0.7436	0.7392	0.7348	0.7304	0.7259	0.7214	0.7169	0.7123	0.7077
0.749	0.7326	0.7284	0.7242	0.7199	0.7156	0.7112	0.7068	0.7024	0.6979.	0.6934	0.6888	0.6842
1.000	0.6963	0.6922	0.6880	0.6838	0.6795	0.6752	0.6709	0.6665	0.6621	0.6577	0.6532	0.6487

duces reliable data with a reproducibility of better than $\Delta\sigma = \pm 0.25\%$ at a 95% confidence level under exactly defined conditions. At higher temperatures and low surface tension values the standard deviation increased up to $\Delta\sigma = \pm 0.65\%$ for heptane at 342.92 K.

Results and Discussion

Pure Substances. To test the correct operation of the pendant drop apparatus, we compared the surface tension values of selected pure organic liquids with available reference values.[1,2] Figure 2 shows experimental surface tensions of the pure liquids heptane, toluene, and *N*,*N*-dimethylformamide versus temperature in a range from about 280 K to 330 K (solid squares). The solid line shows the linear fit of surface tension versus temperature according to eq 1.[4] More sophisticated models which include the critical temperature were not applied, because our experimentally covered temperature range is far below the critical range.

$$\sigma = A + BT \tag{1}$$

Our values are compared with literature data that came from different data sets.[1] In the case of toluene (Figure 2b) at a given temperature the surface tension scatters up to about 2 mN/m. Measurements of surface tensions of water-sensitive substances such as *N*,*N*-dimethylformamide are rather rare. The available literature data show a wide scatter, especially at higher temperatures (Figure 2c). In this case, measurements using the pendant drop method should be preferred. Here the isolated sample drop cannot absorb water from the surroundings, which is always the experimentalist's problem when using ring or plate methods. Table 1 summarizes the experimental surface tensions of the pure liquids together with the respective standard deviation. Table 2 shows the parameters of linear fitting of the six experimentally investigated substances. These results demonstrate that the pendant drop method can be recommended for high precision measurements.

Binary Mixtures. After the measurements on pure substances, surface tension measurements of two binary mixtures were made. We investigated mixtures of toluene with both heptane and *N*,*N*-dimethylformamide versus concentrations at different temperatures.

In Figure 3 experimental surface tension data of the system toluene (1) + heptane (2) in comparison with other results, obtained by ring-method measurements,[67] are shown as a function of mole fraction at five temperatures. Solid symbols denote our results obtained by the pendant drop method, whereas open symbols show those results from the ring method. The experimental data are parametrized by the following empirical functional form (full line), which can easily be extended to describe results in ternary mixtures, too.

$$\sigma = \sigma_1{}^{\circ} x_1{}^3 + \sigma_{112} x_1{}^2 x_2 + \sigma_{122} x_1 x_2{}^2 + \sigma_2{}^{\circ} x_2{}^3 \tag{2}$$

Parameters of the pure substances ($\sigma_1{}^{\circ}$, $\sigma_2{}^{\circ}$) are represented by the surface tension values of the pure components, whereas the binary parameters (σ_{112}, σ_{122}), which were fitted to experimental data, are given in Table 3.

The raw experimental data for the system heptane + toluene are given in the following tables: Table 4 contains the surface tension data, whereas Table 5 gives the necessary liquid densities, obtained by a vibration tube densimeter. For the system toluene (1) + *N*,*N*-dimethylformamide (2) the corresponding results are given in Table 6 (surface tension measurements), and the appropriate liquid densities can be found in Table 7.

The results of the surface tension measurements for that system are shown in Figure 4. We compare our pendant drop measurements (solid symbols) with previous data from a ring tensiometer (open symbols).[67] The solid lines represent the parametrization of our pendant drop data using eq 2; the corresponding parameters are given in Table 2. These data are more consistent than ring tensiometer data. In both systems the experimental surface tension data show negative derivation from additivity, indicating an enrichment of one component in the 3-dimensional liquid–vapor interface. A quantitative description of this phenomenon can be achieved by the Gibbs adsorption isotherm. It relates the Gibbs excess concentration Γ_{21} to the gradient $(\partial\sigma/\partial x_2)_{T,P}$.

$$\Gamma_{21} = -\left(\frac{\partial\sigma}{\partial x_2}\right)_{T,p} \frac{x_2}{RT}\left(1 + \frac{\partial \ln \gamma_2}{\partial \ln x_2}\right)_{T,p}^{-1} \tag{3}$$

Table 6. Surface Tension, σ, versus Mole Fractions, x_1, from 287.81 K to 327.88 K for the Binary System DMF(1) + Toluene(2) Measured with the Pendant Drop Apparatus

	σ/m·N m^{-1} at the following values of T/K				
x_1	287.81	297.82	307.86	317.86	327.88
0.0000	36.96 ± 0.07	35.83 ± 0.07	34.65 ± 0.05	33.37 ± 0.10	32.03 ± 0.10
0.1502	35.22 ± 0.04	33.97 ± 0.02	32.84 ± 0.02	31.70 ± 0.03	30.50 ± 0.08
0.3000	33.42 ± 0.02	32.50 ±0.02	31.20 ± 0.05	30.21 ± 0.05	29.04 ± 0.15
0.4492	32.15 ± 0.06	31.04 ± 0.09	29.86 ± 0.02	28.77 ± 0.04	27.62 ± 0.06
0.5998	31.20 ± 0.02	30.04 ± 0.04	28.98 ± 0.01	27.61 ± 0.02	26.59 ± 0.05
0.7548	30.17 ± 0.07	29.17 ± 0.03	28.06 ± 0.02	26.85 ± 0.02	25.70 ± 0.03
1.0000	28.93 ± 0.03	27.76 ± 0.05	26.60 ± 0.05	25.46 ± 0.04	24.29 ± 0.04

Table 7. Liquid Densities, ρ, versus Mole Fractions, x_1, from 278.15 K to 333.15 K of Binary Mixtures of DMF(1) + Toluene(2) Measured with the Vibration Tube Densimeter

	ρ/g·cm^{-3} at the following values of T/K											
x_1	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
0.0000	0.9630	0.9583	0.9537	0.9491	0.9445	0.9399	0.9354	0.9309	0.9263	0.9217	0.9179	0.9132
0.1502	0.9491	0.9444	0.9399	0.9353	0.9306	0.9261	0.9215	0.9170	0.9124	0.9078	0.9033	0.8990
0.3000	0.9357	0.9311	0.9266	0.9220	0.9174	0.9129	0.9083	0.9038	0.8992	0.8946	0.8901	0.8857
0.4492	0.9231	0.9186	0.9141	0.9095	0.9050	0.9004	0.8959	0.8913	0.8867	0.8820	0.8775	0.8730
0.5998	0.9110	0.9065	0.9020	0.8975	0.8929	0.8884	0.8838	0.8792	0.8746	0.8699	0.8653	0.8607
0.7548	0.8989	0.8945	0.8900	0.8855	0.8809	0.8764	0.8718	0.8672	0.8625	0.8579	0.8532	0.8485
1.0000	0.8803	0.8759	0.8714	0.8669	0.8624	0.8578	0.8532	0.8486	0.8439	0.8392	0.8345	0.8298

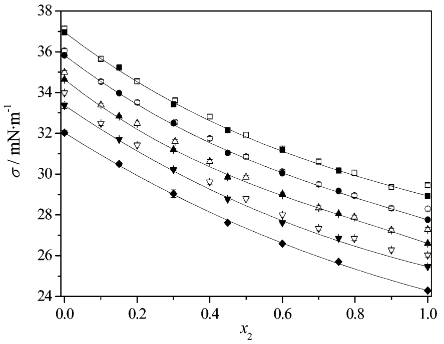

Figure 4. Experimental surface tension, σ, of the binary mixtures N,N-dimethylformamide (1) + toluene (2) measured with the pendant drop apparatus at different temperatures: ■, $T = 287.81$ K; ●, $T = 297.81$ K; ▲, $T = 307.86$ K; ▼, $T = 317.86$ K; ◆, $T = 327.88$ K. The full lines are the model calculations according to eq 2. Open symbols show further experiments using the ring method:[67] □, $T = 288.15$ K; ○, $T = 298.15$ K; △, $T = 308.15$ K; ▽, $T = 318.15$ K.

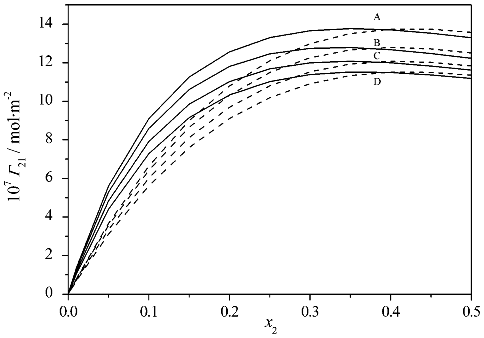

Figure 5. Influence of the activity coefficients on the Gibbs excess concentration, Γ_{21}, of heptane in the system toluene (1) + heptane (2) obtained by surface tension measurements: using eq 3 (full lines, Γ_{real}) and eq 4 (dashed lines, Γ_{ideal}). (A) $T = 287.81$ K; (B) $T = 297.81$ K; (C) $T = 307.86$ K; (D) $T = 317.86$ K.

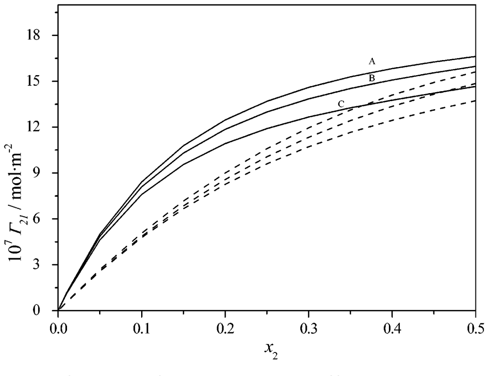

Figure 6. Influence of the activity coefficients on the relative Gibbs excess concentration, Γ_{21}, of toluene in the system DMF (1) + toluene (2) obtained by surface tension measurements: using eq 3 (full line, Γ_{real}) and eq 4 (dashed line, Γ_{ideal}). (A) $T = 287.81$ K; (B) $T = 297.82$ K; (C) $T = 307.86$ K.

Under the assumption of an ideal mixture eq 3 simplifies to

$$\Gamma_{21} = -\left(\frac{\partial\sigma}{\partial x_2}\right)_{T,p}\frac{x_2}{RT} \qquad (4)$$

which is often applied to systems where the assumption of γ_2 being 1 is not fulfilled. In addition to that, the expression for Γ_{21} is derived under the assumption that there is no enrichment of substance 1 in the interface ($\Gamma_1 = 0$). Therefore, eq 3 should only be applied in the concentration range $0 \le x_2 \le 0.5$, where component 2 is the solute.

In Figures 5 and 6 the relative Gibbs excess concentration Γ_{21} is shown for both binary systems. For a given x_2 at different temperatures the gradient $(\partial\sigma/\partial x_2)_{T,P}$ is nearly constant. Therefore, the relative Gibbs excess concentration Γ_{21} will decrease with increasing temperature. To demonstrate the effect of the thermodynamic activity coefficients, γ_2, values of Γ_{21} are calculated according to eq 3 (solid line) and eq 4 (dotted line). The activity coefficients γ_2 were obtained from the NRTL model.[74] When we compare the "real" Γ_{21} values with the "ideal" ones, we find a significant difference in the slopes, especially in the system N,N-dimethylformamide + toluene (Figure 6). This indicates that at lower concentration the toluene is slightly enriched in the interface.

Conclusions

Surface tensions of pure liquids and binary liquid mixtures versus temperature are measured with high precision using a pendant drop apparatus. The efficient tempering regime and the low substance consumption are profitable. Standard deviations of $\Delta\sigma = 0.25\%$, which increased up to $\Delta\sigma = \pm 0.65\%$ at high temperatures, can be obtained. Experimental surface tensions of binary mixtures were parametrized using a simple empirical cubic functional form. Gibbs excess concentrations are obtained from the experimental surface tensions.

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