

Experimental Study on the Surface Tension, Density, and Viscosity of Aqueous Poly(vinylpyrrolidone) Solutions

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ABSTRACT: Aqueous solutions of the polymer poly(vinylpyrrolidone) (PVP) were analyzed in terms of surface tension (Wilhelmy-Plate), density (vibrating tube density meter), and dynamic viscosity (falling ball viscometer) for different molar masses, concentrations, and temperatures. Surface tensions were determined for PVP 10, K25, and K90 at 298.15 K. Densities and viscosities were studied with PVP K25 and K90 in a temperature region from (293.15 to 310.15) K. The dynamic viscosity isotherms were fitted successfully to a basic polynomial function. The experimental data are discussed and compared to literature data.

INTRODUCTION

The polymer poly(vinylpyrrolidone) (PVP) acts as stabilizer in food industry and can also be used in a variety of fields such as pharmacy, cosmetics, and the detergent industry and also as an adhesive, in steel production, crop protection, or the electrical industry.^{1–3} The diversity of applications is due to the unique physical and chemical properties of PVP, especially its good solubility in both water and organic solvents and its adhesive strength on different materials as well as its enhanced cross-linking. PVP is stable in a broad range of pH values. Furthermore, PVP is nontoxic and biocompatible. In the year 2006 the worldwide production was about 31 000 tonnes whereof about 47 % were used for cosmetic and 25 % for pharmaceutical applications. Depending on the grade of polymerization, the molecular mass of PVP varies in the range of (2000 to 2 500 000) $\text{g} \cdot \text{mol}^{-1}$. The different types of PVP are characterized by their inherent viscosities, the so-called *K*-values.² Since many applications are based on the usage of aqueous PVP solutions, the knowledge of the dependency of surface tension, density, and viscosity on concentration is often required. This work was carried out with the intention to characterize PVP in terms of the mentioned parameters to apply it as stabilizing agent in the process of rapid expansion of supercritical solutions into aqueous solutions (RESSAS).⁴

EXPERIMENTAL SECTION

Materials. PVP (CAS 9003-39-8, E number E1201) is a hygroscopic amorphous powder with white color whose structure is given in Figure 1. PVP K25 and PVP K90 were purchased from Carl Roth (Germany); PVP 10 was acquired from Sigma-Aldrich (Germany). The powders were used without further purification. The water used as solvent was purified by filtration, reverse osmosis, and photo-oxidation by an Elect 50 (Elga, Germany) which produces water with a quality equal to distilled water. Dimethylacetamide and lithium bromide used in SEC had a purity of 99% and were purchased from Acros Organics (Belgium) and Sigma-Aldrich (Germany), respectively.

Methods. The determination of the molar mass distribution (MMD) was carried out with size exclusion chromatography

(SEC) using the eluent dimethylacetamide (99 %) containing 0.1 % lithium bromide. The SEC setup was calibrated using polystyrene standards (PSS) of low polydispersity.⁵ Surface tensions were measured using a conventional DIN-certified Wilhelmy-Plate technique (DCAT 11, DataPhysics Instruments, Germany) at a constant temperature of 298.15 K. Density measurements were carried out with a vibrating-tube density meter (DMA 38, Anton Paar, Austria) with a measuring inaccuracy of $0.0001 \text{ g} \cdot \text{cm}^{-3}$. The temperature of the measuring cell was automatically controlled within an uncertainty of $\pm 0.1 \text{ K}$. The equipment was calibrated with air and double-distilled water. Viscosity measurements were carried out with a falling ball viscometer (HAAKE type C, Thermo Electron, Germany), using a boron silica glass ball ($d_{\text{ball}} = 15.809 \text{ mm}$; $\rho_{\text{ball}} = 2.220 \text{ g} \cdot \text{cm}^{-3}$; $m_{\text{ball}} = 4.5923 \text{ g}$; $K_{\text{ball}} = 0.01103 \text{ mPa} \cdot \text{s} \cdot \text{cm}^3 \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) which has a reproducibility of 1.0 %. The temperature was adjusted with a thermostat (HAAKE DC5, Thermo Electron, Germany) and controlled with a resistance thermometer (Pt-100) and a digital multimeter (PREMA 8015, Prema, Germany) within an uncertainty of $\pm 0.01 \text{ K}$.

RESULTS AND DISCUSSION

Molar Mass Distribution. The weight average molar mass, M_w , and the polydispersity index PDI ($\text{PDI} = M_w/M_n$, with M_n = number average molar mass) of the different PVP samples are given in Table 1. Figures 2 and 3 show the molar mass distribution of the different charges. Concerning the difference between manufacturer's data and measured data no influence of the molar mass on this difference can be found. The PDI varies from PDI = (3.08 to 4.12) which is in the same range of sizes found in Kany et al.⁶ and Bühler.¹ PVP K25^a and PVP K25^b show almost the same curve progression, while the PVP K25 charge with the index c shows a narrower MMD and a smaller PDI. The two PVP K90 charges show differences, too. The MMD determined for PVP K90^b indicates a higher weight average molar

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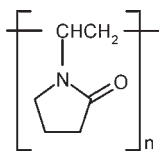
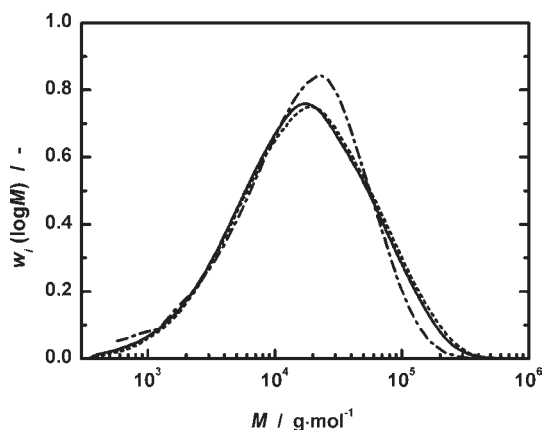
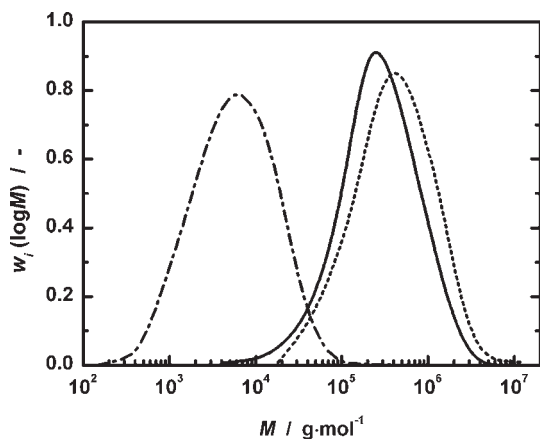


Figure 1. Chemical structure of PVP.

Table 1. Molar Mass, Weight Average Molar Mass, and PDI of the PVP Charges⁵

PVP	index	charge ^a	M^a	M_w	PDI
			$\text{g}\cdot\text{mol}^{-1}$	$\text{g}\cdot\text{mol}^{-1}$	
10		097K0107	10000	9882	3.25
K25	a	40790076	24000	31502	4.12
K25	b	28898054	24000	33318	4.05
K25	c	279106234	24000	26620	3.50
K90	a	38784380	360000	437370	3.18
K90	b	32884380	360000	665170	3.08

^a Manufacturer's data.Figure 2. MMD of used PVP charges, see Table 1: solid line, PVP K25^a; dotted line, PVP K25^b; dotted and dashed line, PVP K25^c.Figure 3. MMD of used PVP charges, see Table 1: dotted and dashed line, PVP 10; solid line, PVP K90^a; dotted line, PVP K90^b.

mass with a lower PDI compared to PVP K90^a. Molar mass literature data are presented as given by the authors either as M_w

Table 2. Surface Tension and Standard Deviation of Aqueous PVP 10 and PVP K90 Solutions at 298.15 K

c	PVP 10		PVP K90 ^a	
	γ	SD	γ	SD
	$\text{mN}\cdot\text{m}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$
$\text{g}\cdot\text{dm}^{-3}$				
0.2	67.66	0.070	67.70	0.104
0.4	67.16	0.050	67.42	0.082
0.8	67.52	0.076	66.72	0.374
1.6	66.63	0.225	66.69	0.080
3.1	66.17	0.351	67.12	0.039
6.2	67.46	0.404	66.37	0.074
12.5	66.01	0.219	66.36	0.014
25.0	66.91	0.123	66.19	0.605
50.0			66.22	0.108
100.0	64.90	0.127	65.21	0.258

Table 3. Surface Tension and Standard Deviation of Aqueous PVP K25 Solutions at 298.15 K

c	PVP K25 ^a	
	γ	SD
	$\text{mN}\cdot\text{m}^{-1}$	$\text{mN}\cdot\text{m}^{-1}$
$\text{g}\cdot\text{dm}^{-3}$		
0.9	67.79	0.083
3.5	66.52	0.096
6.1	66.42	0.217
8.6	66.63	0.439
12.0	67.17	0.054
12.5	66.95	0.778
13.8	66.83	0.097
16.3	66.84	0.080
18.9	66.80	0.156
21.4	66.53	0.138
24.0	66.83	0.098
25.0	64.43	0.304
50.0	66.69	0.150
100.0	67.20	0.385

or as M_n . In case of missing specification M is used without an index.

Surface Tension. The surface tension measurements were carried out for PVP concentrations ranging from $c = (0.2$ to $100.0) \text{ g}\cdot\text{dm}^{-3}$ at 298.15 K. Each experiment was repeated at least three times or until the standard deviation (SD) was smaller than one. The average value of the surface tension data and SD for each concentration are summarized in Tables 2 and 3 and depicted in Figures 4 and 5. For comparison, surface tension data available from literature are shown too. In Figure 4 our own surface tension data for PVP K25, data from Gargallo et al.⁷ ($M = 42\,000 \text{ g}\cdot\text{mol}^{-1}$; $T = 298 \text{ K}$), and Gabrielli et al.⁸ ($M = 40\,000 \text{ g}\cdot\text{mol}^{-1}$; $T = 294.6 \text{ K}$) show nearly constant behavior over a wide range of concentration, while the data determined by Huang and Wang⁹ ($M_w = 40\,000 \text{ g}\cdot\text{mol}^{-1}$; $T = 293.15 \text{ K}$) decrease slightly with increasing concentration until a dramatic decrease occurs at $c = 49 \text{ g}\cdot\text{dm}^{-3}$. As shown in Figure 5, a similar result was obtained for PVP 10, PVP K90, and surface tension data

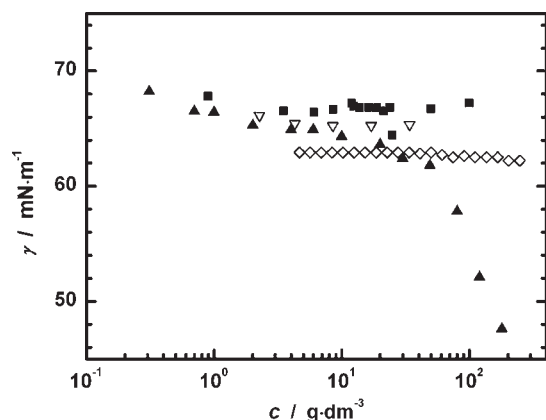


Figure 4. Surface tension versus polymer concentration in water: ■, PVP K25^a at 298.15 K; ▽, PVP $M = 42\,000\text{ g}\cdot\text{mol}^{-1}$ at 298 K;⁷ ◇, PVP $M = 40\,000\text{ g}\cdot\text{mol}^{-1}$ at 294.6 K;⁸ ▲, PVP $M_w = 40\,000\text{ g}\cdot\text{mol}^{-1}$ at 293.15 K.⁹

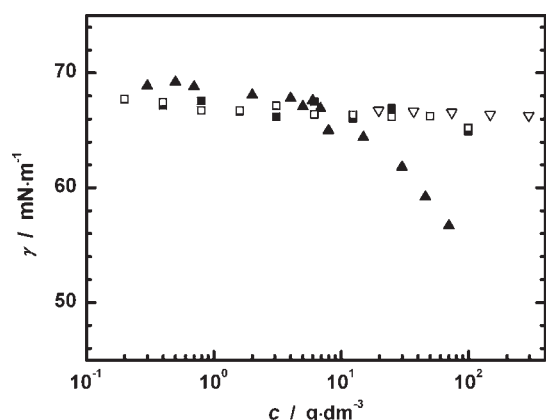


Figure 5. Surface tension versus polymer concentration in water: ■, PVP 10 at 298.15 K; □, PVP K90^a at 298.15 K; ▽, PVP $M = 365\,000\text{ g}\cdot\text{mol}^{-1}$ at 298 K;⁷ ▲, PVP $M_w = 1\,000\,000\text{ g}\cdot\text{mol}^{-1}$ at 293.15 K.⁹

published by Gargallo et al.⁷ ($M = 365\,000\text{ g}\cdot\text{mol}^{-1}$; $T = 298\text{ K}$) which are nearly constant over the concentration range investigated, whereas the surface tension data published by Huang and Wang⁹ ($M_w = 1\,000\,000\text{ g}\cdot\text{mol}^{-1}$; $T = 293.15\text{ K}$) decrease rapidly above $c = 15\text{ g}\cdot\text{dm}^{-3}$.

In case of our aqueous PVP 10, PVP K25, and PVP K90 solutions, no significant influence of molar mass on surface tension data can be observed. These results agree with those of Gargallo et al.,⁷ while the data from Huang and Wang⁹ show a slight influence of molar mass on both the absolute value of the surface tension data and the concentration at which the surface tension decreases. These differences cannot be explained by different measurement methods. Gargallo et al.⁷ and Gabrielli et al.⁸ applied a ring tensiometer, which is an analogue to the Wilhelmy-Plate used by Huang and Wang⁹ as well as in this work. Measurements done by Noskov et al.¹⁰ show that the surface tension for PVP 10 ($M = 10\,000\text{ g}\cdot\text{mol}^{-1}$; $T = 293.15\text{ K}$) and PVP 55 ($M = 55\,000\text{ g}\cdot\text{mol}^{-1}$; $T = 293.15\text{ K}$) is nearly constant for static surface tension measurements until $c \approx 0.1\%$ in mass and independent of molecular weight. For $c \approx (0.1\text{ to }3.0)\%$ in mass they made dynamic surface tension measurements with surface ages of around 500 min for PVP 10 and 1200 min for PVP

Table 4. Density and Viscosity Data for PVP K25 at Different Temperatures and Concentrations Including the Standard Deviation

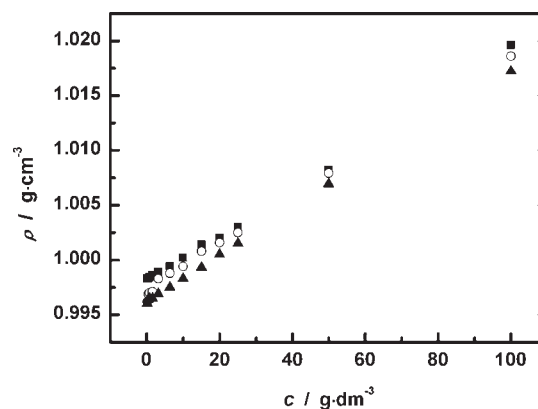
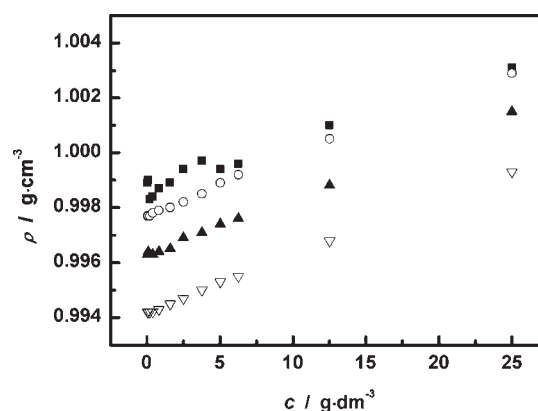
PVP	T	c	ρ	SD	η	SD
	K	$\text{g}\cdot\text{dm}^{-3}$	$\text{g}\cdot\text{cm}^{-3}$	$\text{g}\cdot\text{cm}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{mPa}\cdot\text{s}$
K25 ^b	293.15	0.20	0.998	0	1.003	$1.2\cdot 10^{-3}$
		0.40	0.998	0	1.002	$3.1\cdot 10^{-3}$
		0.80	0.998	0	1.002	$4.4\cdot 10^{-3}$
		1.60	0.999	$5.00\cdot 10^{-5}$	1.011	$4.5\cdot 10^{-3}$
		3.21	0.999	$5.00\cdot 10^{-5}$	1.031	$2.4\cdot 10^{-3}$
		6.42	0.999	$1.00\cdot 10^{-4}$	1.087	$2.3\cdot 10^{-3}$
		10.02	1.000	$5.00\cdot 10^{-5}$	1.165	$3.3\cdot 10^{-3}$
		15.00	1.001	0	1.301	$1.9\cdot 10^{-3}$
		20.05	1.002	$3.60\cdot 10^{-4}$	1.378	$2.1\cdot 10^{-3}$
		25.00	1.003	$5.85\cdot 10^{-4}$	1.515	$2.9\cdot 10^{-3}$
K25 ^c	298.15	50.02	1.008	0	2.251	$4.7\cdot 10^{-3}$
		100.00	1.020	$1.03\cdot 10^{-4}$	4.386	$1.5\cdot 10^{-2}$
K25 ^b	298.15	0.20	0.996	0	0.872	$1.9\cdot 10^{-3}$
		0.40	0.997	$5.00\cdot 10^{-5}$	0.869	$1.8\cdot 10^{-3}$
		0.80	0.997	0	0.878	$2.6\cdot 10^{-3}$
		1.60	0.997	0	0.887	$1.5\cdot 10^{-3}$
		3.21	0.998	0	0.915	$1.8\cdot 10^{-3}$
		6.42	0.999	$1.10\cdot 10^{-4}$	0.965	$2.8\cdot 10^{-3}$
		10.02	0.999	$8.94\cdot 10^{-5}$	1.027	$3.2\cdot 10^{-3}$
		15.00	1.001	$8.94\cdot 10^{-5}$	1.123	$4.3\cdot 10^{-3}$
		20.05	1.002	$5.00\cdot 10^{-5}$	1.220	$2.5\cdot 10^{-3}$
		25.00	1.003	0	1.361	$4.3\cdot 10^{-3}$
K25 ^c	303.15	50.02	1.008	0	1.961	$4.4\cdot 10^{-3}$
		100.00	1.019	$1.97\cdot 10^{-4}$	3.813	$7.2\cdot 10^{-3}$
K25 ^b	303.15	0.20	0.996	$1.41\cdot 10^{-4}$	0.790	$2.2\cdot 10^{-3}$
		0.40	0.996	$5.48\cdot 10^{-5}$	0.786	$3.5\cdot 10^{-3}$
		0.80	0.996	$5.00\cdot 10^{-5}$	0.787	$2.2\cdot 10^{-3}$
		1.60	0.997	0	0.799	$3.5\cdot 10^{-3}$
		3.21	0.997	$5.00\cdot 10^{-5}$	0.832	$2.9\cdot 10^{-3}$
		6.42	0.998	0	0.862	$1.4\cdot 10^{-3}$
		10.02	0.998	$5.00\cdot 10^{-5}$	0.913	$2.2\cdot 10^{-3}$
		15.00	0.999	0	1.001	$1.7\cdot 10^{-3}$
		20.05	1.001	0	1.102	$3.1\cdot 10^{-3}$
		25.00	1.001	$2.50\cdot 10^{-4}$	1.208	$3.5\cdot 10^{-3}$
K25 ^c	303.15	50.02	1.007	$1.79\cdot 10^{-4}$	1.735	$2.6\cdot 10^{-3}$
		100.00	1.017	$1.00\cdot 10^{-4}$	3.318	$1.4\cdot 10^{-3}$

55. The surface tension decreases rapidly in this concentration range. Noskov et al.¹⁰ describe the abrupt surface tension drop in the range of relatively concentrated solutions as a general phenomenon for polymer solutions. By doing further investigations they figured out that impurities cause the effect of abrupt decrease at certain PVP concentrations. In this way the discrepancies in the compared data can be explained, whereas the PVP used by Huang and Wang⁹ shows the same effects as described by Noskov et al.¹⁰ and probably contains traces of impurities. The PVP used by the other authors and in this work contains less or no impurities affecting the surface tension. The marginal decrease in surface tension compared to water is probably based on a small tendency toward migration of PVP to the interface which could be anticipated, because the pyrrolidone ring structure is strongly hydrated.⁷

Table 5. Density and Viscosity Data for PVP K90 at Different Temperatures and Concentrations Including the Standard Deviation

PVP	T	c	ρ	SD	η	SD		
	K	$\text{g} \cdot \text{dm}^{-3}$	$\text{g} \cdot \text{cm}^{-3}$	$\text{g} \cdot \text{cm}^{-3}$	$\text{mPa} \cdot \text{s}$	$\text{mPa} \cdot \text{s}$		
K90 ^b	293.15	0.05	0.999	0	1.078	$1.04 \cdot 10^{-2}$		
		0.09	0.999	0	0.987	$1.62 \cdot 10^{-3}$		
		0.20	0.998	0	1.014	$1.66 \cdot 10^{-3}$		
		0.40	0.998	$5.00 \cdot 10^{-5}$	1.101	$1.23 \cdot 10^{-2}$		
		0.81	0.999	$8.94 \cdot 10^{-5}$	1.078	$3.75 \cdot 10^{-2}$		
		1.60	0.999	$8.94 \cdot 10^{-5}$	1.218	$2.22 \cdot 10^{-3}$		
		2.50	0.999	0	1.375	$2.17 \cdot 10^{-3}$		
		3.75	1.000	$1.10 \cdot 10^{-4}$	1.627	$8.76 \cdot 10^{-3}$		
		5.01	0.999	$1.00 \cdot 10^{-4}$	1.890	$3.43 \cdot 10^{-3}$		
		6.27	1.000	$5.00 \cdot 10^{-5}$	2.190	$4.29 \cdot 10^{-3}$		
		12.51	1.001	$5.00 \cdot 10^{-5}$	4.004	$4.11 \cdot 10^{-3}$		
		25.01	1.003	0	9.658	$9.31 \cdot 10^{-3}$		
		K90 ^b	298.15	0.05	0.998	0	0.984	$3.27 \cdot 10^{-3}$
				0.09	0.998	0	0.875	$4.06 \cdot 10^{-3}$
0.20	0.998			0	0.901	$2.01 \cdot 10^{-3}$		
0.40	0.998			0	1.033	$3.87 \cdot 10^{-3}$		
0.81	0.998			0	0.970	$2.87 \cdot 10^{-3}$		
1.60	0.998			0	1.075	$2.77 \cdot 10^{-3}$		
2.50	0.998			0	1.213	$3.46 \cdot 10^{-3}$		
3.75	0.999			0	1.427	$2.63 \cdot 10^{-3}$		
5.01	0.999			0	1.652	$4.87 \cdot 10^{-3}$		
6.27	0.999			0	1.909	$3.19 \cdot 10^{-3}$		
12.51	1.000			$1.00 \cdot 10^{-4}$	3.462	$6.92 \cdot 10^{-3}$		
25.01	1.003			0	8.370	$1.89 \cdot 10^{-2}$		
K90 ^b	303.15			0.05	0.996	0	0.885	$7.49 \cdot 10^{-3}$
				0.09	0.996	$5.00 \cdot 10^{-5}$	0.784	$2.58 \cdot 10^{-3}$
		0.20	0.996	$5.77 \cdot 10^{-5}$	0.811	$2.83 \cdot 10^{-3}$		
		0.40	0.996	0	0.921	$6.23 \cdot 10^{-3}$		
		0.81	0.996	0	0.866	$2.60 \cdot 10^{-3}$		
		1.60	0.997	0	0.954	$3.61 \cdot 10^{-3}$		
		2.50	0.997	0	1.074	$2.99 \cdot 10^{-3}$		
		3.75	0.997	0	1.265	$3.19 \cdot 10^{-3}$		
		5.01	0.997	0	1.456	$1.92 \cdot 10^{-3}$		
		6.27	0.998	$5.00 \cdot 10^{-5}$	1.679	$2.67 \cdot 10^{-3}$		
		12.51	0.999	$1.00 \cdot 10^{-4}$	3.021	$6.44 \cdot 10^{-3}$		
		25.01	1.001	$5.00 \cdot 10^{-5}$	7.236	$1.43 \cdot 10^{-2}$		
		K90 ^b	310.15	0.05	0.994	0	0.766	$4.00 \cdot 10^{-3}$
				0.09	0.994	$5.00 \cdot 10^{-5}$	0.680	$3.25 \cdot 10^{-3}$
0.20	0.994			$5.77 \cdot 10^{-5}$	0.702	$2.23 \cdot 10^{-3}$		
0.40	0.994			$5.00 \cdot 10^{-5}$	0.800	$1.12 \cdot 10^{-3}$		
0.81	0.994			0	0.747	$1.55 \cdot 10^{-3}$		
1.60	0.995			0	0.819	$2.20 \cdot 10^{-3}$		
2.50	0.995			$5.00 \cdot 10^{-5}$	0.915	$1.41 \cdot 10^{-3}$		
3.75	0.995			0	1.080	$3.46 \cdot 10^{-3}$		
5.01	0.995			0	1.235	$2.39 \cdot 10^{-3}$		
6.27	0.995			$3.00 \cdot 10^{-4}$	1.417	$1.56 \cdot 10^{-3}$		
12.51	0.997			0	2.515	$4.81 \cdot 10^{-3}$		
25.01	0.999			0	5.948	$5.08 \cdot 10^{-3}$		

Density. Density measurements were carried out with aqueous PVP K25 and K90 solutions of different concentrations.

**Figure 6.** Density versus polymer concentration in water for PVP K25 at: ■, 293.15 K; ○, 298.15 K; ▲, 303.15 K.**Figure 7.** Density versus polymer concentration in water for PVP K90 at: ■, 293.15 K; ○, 298.15 K; ▲, 303.15 K; ▽, 310.15 K.

The concentration of PVP K25 in water was varied from $c = (0 \text{ to } 100) \text{ g} \cdot \text{dm}^{-3}$, while the concentration of PVP K90 ranges from $c = (0 \text{ to } 25) \text{ g} \cdot \text{dm}^{-3}$. The effect of temperature on density was investigated from $T = (293.15 \text{ to } 303.15) \text{ K}$ for PVP K25 and from $T = (293.15 \text{ to } 310.15) \text{ K}$ for PVP K90. All measurements were carried out at least three times. After calibrating of the equipment, the density of the pure solvent (purified water) was determined and compared to values published in VDI-Wärmeatlas¹¹ for all temperatures investigated. The comparison shows a deviation of $\Delta\rho \leq 0.0002 \text{ g} \cdot \text{cm}^{-3}$ which is twice as big as the inaccuracy given by the manufacturer of the density meter. The densities and standard deviations determined for the aqueous PVP solutions at different concentrations and temperatures are given in Tables 4 and 5, respectively. The usage of PVP K25 with the index c for the concentration $100 \text{ g} \cdot \text{dm}^{-3}$ is due to the run out of PVP K25^b. Plots of density versus concentration are illustrated in Figures 6 and 7. The density increases almost linearly with increasing concentration. Variations of the linear behavior appear in the low concentration region for PVP K90 at 293.15 K and PVP K25 at 298.15 K. As expected, the density decreases with increasing temperature in all cases. A comparison at constant temperature and concentration shows that no significant influence of molar mass on density can be observed in the range investigated. Comparable data of Kany et al.⁶ for PVP 10 ($M_w = 9411 \text{ g} \cdot \text{mol}^{-1}$), PVP 50 ($M_w = 57\,980 \text{ g} \cdot \text{mol}^{-1}$), and PVP 1000 ($M_w = 1\,146\,000 \text{ g} \cdot \text{mol}^{-1}$) at (278.15, 293.15, and 333.15) K confirm that there is no connection between

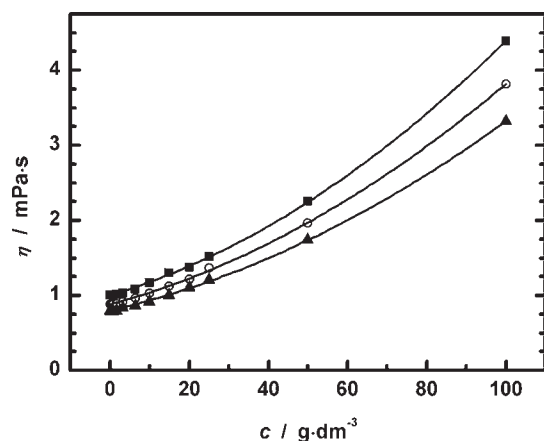


Figure 8. Dynamic viscosity versus polymer concentration in water for PVP K25 at: ■, 293.15 K; ○, 298.15 K; ▲, 303.15 K; solid line, polynomial fit.

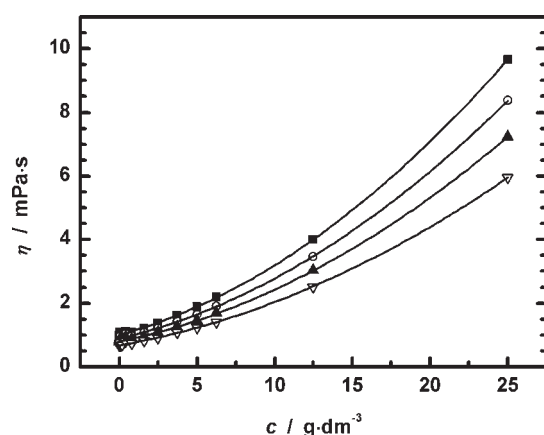


Figure 9. Dynamic viscosity versus polymer concentration in water for PVP K90 at: ■, 293.15 K; ○, 298.15 K; ▲, 303.15 K; ▽, 310.15 K; solid line, polynomial fit.

molar mass and density. The data of Kany et al.⁶ at 293.15 K and Foroutan¹² who measured the density of PVP K15 ($M = 10000 \text{ g} \cdot \text{mol}^{-1}$; $T = 298.15 \text{ K}$) result in similar density values as the data measured in this work. In contrast the density data obtained at 298.15 K by Mutalik et al.¹³ for PVP with unknown molar mass are almost independent from PVP concentration.

Dynamic Viscosity. To determine the viscosity of a fluid with a falling ball viscosimeter the falling time t of the ball has to be detected between two markings. Thus the viscosity can be calculated applying eq 1, where K_{ball} is the ball constant, ρ_{ball} is the density of the applied ball and ρ_{fluid} is the density of the fluid.

$$\eta = K_{\text{ball}} \cdot (\rho_{\text{ball}} - \rho_{\text{fluid}}) \cdot t \quad (1)$$

The viscosity measurements were carried out with the same solutions used for density measurements at the same temperatures to ensure the use of the related fluid density ρ_{fluid} . Each single experiment was repeated at least six times. At all adjusted temperatures, the equipment was tested by measurements with the pure solvent (purified water). Compared to data published in VDI-Wärmeatlas,¹¹ the maximum deviation was $\Delta\eta = 0.01 \text{ mPa} \cdot \text{s}$. The dynamic viscosities and standard deviations determined for the aqueous PVP solutions at different

Table 6. Parameters for the Polynomial Fit of Dynamic Viscosity from eq 2

PVP	T/K	η_0	x_1	x_2	R^2
K25	293.15	1.002	0.01579	$1.80761 \cdot 10^{-4}$	0.9998
K25	298.15	0.880	0.01421	$1.51520 \cdot 10^{-4}$	0.9997
K25	303.15	0.798	0.01226	$1.29643 \cdot 10^{-4}$	0.9995
K90	293.15	1.002	0.13396	0.00848	0.9998
K90	298.15	0.880	0.11622	0.00732	0.9995
K90	303.15	0.798	0.09910	0.00633	0.9996
K90	310.15	0.675	0.08591	0.00499	0.9993

concentrations and temperatures are given in Tables 4 and 5, respectively. The experimental data were fitted to the polynomial function eq 2, wherein η_0 is the dynamic viscosity of the pure solvent, and they are illustrated in Figures 8 and 9. As it is expected for liquid solutions the dynamic viscosity decreases with increasing temperature.^{14,15}

$$\eta = \eta_0 + x_1 \cdot c + x_2 \cdot c^2 \quad (2)$$

The parameters x_1 and x_2 of eq 2 are obtained from fitting the experimental data to eq 2 using the Levenberg–Marquardt algorithm and are summarized in Table 6 together with the coefficient of determination R^2 . Obviously, this simple equation is able to describe the dependency of dynamic viscosity on PVP concentration up to $c = 25 \text{ g} \cdot \text{dm}^{-3}$ for PVP K90 and up to $c = 100 \text{ g} \cdot \text{dm}^{-3}$ for PVP K25 in a satisfying way. A comparison at constant temperature and concentration shows, that $\eta_{\text{K25}} \leq \eta_{\text{K90}}$ in the range investigated. This is in accordance with the fact that the viscosity average molar mass M_η is proportional to the intrinsic viscosity $[\eta]$ as shown by the Mark–Houwink equation (eq 3). In eq 3 K_i and α are constants which can be found for common polymer/solvent combinations.³

$$[\eta] = K_i \cdot M_\eta^\alpha \quad (3)$$

To compare with literature data, which are often presented in diverse types of viscosity, it is necessary to transform the own dynamic viscosity data in the corresponding forms of viscosity. The relative viscosity (eq 4) describes the quotient of dynamic viscosity η and the dynamic viscosity of the pure solvent η_0 . The specific viscosity η_{sp} is a measure of the thickening effect of the polymer solution compared to the pure solvent (eq 5). While η_0 and η_{sp} are concentration-dependent, the reduced viscosity η_{red} is independent of concentration (eq 6). If η_{red} is plotted against polymer concentration, a straight line is usually obtained. As shown in eq 7, the extrapolation of η_{sp} to $c = 0 \text{ g} \cdot \text{dm}^{-3}$ results in the intrinsic viscosity.³

$$\eta_{\text{rel}} = \frac{\eta}{\eta_0} \quad (4)$$

$$\eta_{\text{sp}} = \frac{\eta - \eta_0}{\eta_0} = \eta_{\text{rel}} - 1 \quad (5)$$

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{c} \quad (6)$$

$$[\eta] = \left(\frac{\eta_{\text{sp}}}{c} \right)_{c=0} \quad (7)$$

In Figures 10 and 11 the experimental data for PVP K25 and K90 are compared to the data from Yang et al.¹⁶ at (293.15 and 298.15) K in

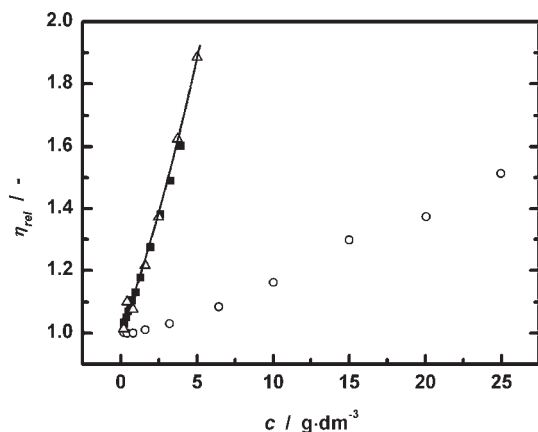


Figure 10. Relative viscosity versus polymer concentration in water at 293.15 K for PVP: O, K25; Δ , K90; \blacksquare , $M_w = 3.6 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$;¹⁶ solid line, eq 2.

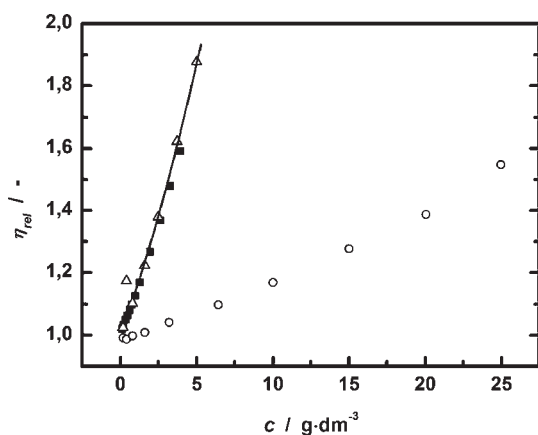


Figure 11. Relative viscosity versus polymer concentration in water at 298.15 K for PVP: O, K25; Δ , K90; \blacksquare , $M_w = 3.6 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$;¹⁶ solid line, eq 2.

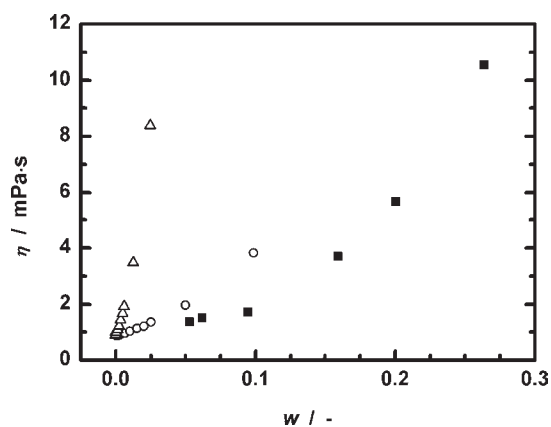


Figure 12. Dynamic viscosity versus polymer mass fraction in water at 298.15 K for PVP: O, K25; Δ , K90; \blacksquare , K15 $M_w = 1.0 \cdot 10^4 \text{ g} \cdot \text{mol}^{-1}$.¹²

terms of relative viscosity. It can be discovered that the data determined for PVP K90 and the data from Yang et al.¹⁶ for $M_w = 3.6 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$ are consistent for both temperatures. A comparison of the different literature data with eq 2 leads to deviations $\leq 4 \%$. Figure 12 illustrates a comparison of the

dynamic viscosity of PVP K25, K90, and viscosity data published by Foroutan¹² for PVP K15. Obviously, at a certain concentration, the viscosity is increasing with increasing molar mass.

CONCLUSIONS

Experimental surface tension, density, and dynamic viscosity data of aqueous PVP solutions are reported, and the obtained results were compared with data available from literature. The surface tension data were determined for aqueous PVP 10, K25, and K90 solutions at 298.15 K and PVP concentrations up to $100 \text{ g} \cdot \text{dm}^{-3}$. The density and viscosity data of the aqueous PVP K25 solutions were measured at (293.15, 298.15, and 303.15) K and for PVP concentrations up to $100 \text{ g} \cdot \text{dm}^{-3}$ and for the K90 solutions at (293.15, 298.15, 303.15, and 310.15) K and PVP concentrations up to $25 \text{ g} \cdot \text{dm}^{-3}$. In opposite to the results reported by Huang and Wang,⁹ the surface tension data show no clear effect of PVP concentration, while density and viscosity of the aqueous solution increase with increasing PVP concentration. In addition, the dynamic viscosity isotherms are successfully fitted to a simple polynomial function.

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