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Thermodynamic Properties of Aqueous Poly(vinylpyrrolidone) Solutions from Laser-Light-Scattering, Membrane Osmometry, and Isopiestic Measurements

Hans-Peter Kany,[†] Hans Hasse,[‡] and Gerd Maurer*

Lehrstuhl für Technische Thermodynamik, Universität Kaiserslautern, D-67653 Kaiserslautern, Germany

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Thermodynamic properties of poly(vinylpyrrolidone) (PVP) were studied by laser-light-scattering, membrane osmometry, and isopiestic measurements. Four polymer samples of weight-average molecular mass between about 9000 and 1 200 000 were investigated at temperatures from (278 to 333) K. The experimental results are described with application of the osmotic virial equation and compared to literature data.

Introduction

In previous work thermodynamic properties of aqueous solutions of poly(ethylene glycol) (PEG)[1] and of dextran (DEX)[2] were investigated by laser-light-scattering, membrane osmometry, and isopiestic measurements. With the present contribution this work is extended to aqueous solutions of poly(vinylpyrrolidone) (PVP). Figure 1 shows the structural formula of PVP. Despite the importance of aqueous solutions of PVP, only a few experimental investigations of their thermodynamic properties have been carried out before. Table 1 gives a survey of that literature data. Most of the experimental work has been limited to 298 K and has been given in graphical form or as correlations. Only Vink[3] reported numerical data. In the present study, as in our previous work on PEG and DEX solutions, three different methods were applied: laser-light-scattering, membrane osmometry, and isopiestic measurements. The experimental results are presented together with the second and third osmotic virial coefficients of PVP(aq) which were determined by simultaneously evaluating the experimental data with an expanded osmotic virial equation.

Experimental Section

The experimental methods applied in the present studies are similar to those used in previous investigations on aqueous solutions of PEG[1] and of DEX.[2] Experimental details described in these earlier publications are not repeated here.

Materials. Aqueous solutions of four different PVP samples were investigated. All samples were described by the suppliers as non-cross-linked PVP. Two samples were from BASF, AG, Ludwigshafen, Germany [PVP 10 (producer's nomenclature PVP 17PF) and PVP 1000 (producer's nomenclature PVP 90F)], one was from Aldrich, Steinheim, Germany [PVP 50 (producer's nomenclature PVP K30)], and one from Fluka, Neu-Ulm, Germany [PVP 1000FL (producer's nomenclature PVP K90)]. The number following the abbreviation PVP gives the approximate weight-average molecular mass (e.g., PVP 10: $M_w \approx 10\,000$). All polymer samples were furthermore characterized with a gel permeation chromatograph (GPC) coupled with a multiangle laser-light-scattering photometer and an interferometric refractometer. Experimental details were similar to those described for DEX samples by Kany et al.[2] The numerical results have been reported by Kany.[4] Figure 2 gives the differential molecular weight distributions $d\xi/d \log M$. The results for the molecular mass distribution were evaluated to determine the number-average molecular mass M_n and the weight-average molecular mass M_w (cf. Table 2 and the explanation below). The ratio of M_w to M_n is called the polydispersity P. The polydispersities of the samples varied between 1.8 (PVP 10) and 9.32 (PVP 1000FL). The rather large numbers for the polydispersities of the high molecular weight PVP samples reveal their broad molecular mass distributions.

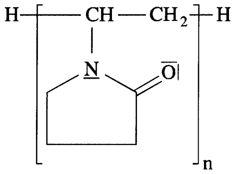

Figure 1. Structure of poly(1-vinyl-2-pyrrolidone).

Table 1. Previous Experimental Work on Aqueous Solutions of Poly(pyrrolidone)

exp method	molecular mass	T/K	ref
membrane osmometry	1.6×10^5, 1.2×10^6	295	11
	1.1×10^4, 2.3×10^4	298	15
	1.2×10^4 to 7.5×10^4 [a]	298	10
	5×10^4, 10^6	298	3[c]
light-scattering	10^5 [b]	298	16
	7.5×10^5	283, 293, 303, 313, 323	17
	1.1×10^4	298	15
sedimentation	2.3×10^4, 3.8×10^5	298	15

[a] 10 samples. [b] 15 samples. [c] Numerical data reported.

HPLC water (Merck, Darmstadt, Germany; impurities below 5 mg/kg) was used for the preparation of all aqueous solutions. Table 3 gives a survey of the experimental work.

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* To whom all correspondence should be addressed. Fax: +49 631 205 3835. E-mail: gmaurer@rhrk.uni-kl.de.

[†] Present address: Groβhandels- und Lagerei-Berufsgenossenschaft, M 5,7 D-68161 Mannheim, Germany.

[‡] Present address: Institut für Technische Thermodynamik und Thermische, Verfahrenstechnik, Universität Stuttgart, D-70550 Stuttgart, Germany.

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Table 2. Poly(pyrrolidone) Samples

				M_w			M_n		
					LLS + ISO + MO			LLS + ISO + MO	
abbrev	supplier's abbrev	supplier	supplier's charge no.	GPC	method I	method II	GPC	method I	method II
PVP 10	PVP 17PF	BASF	93-0024	9 411	9 377	8 894	3 882	4 856	4 606
PVP 50	PVP K30	Aldrich	73-095	57 980	54 090	48 480	17 750	22 690	22 610
PVP 1000	PVP 90F	BASF	73-3990	973 500	1 045 600	1 189 300	210 400	162 900	169 400
PVP 1000FL	PVP K90	Fluka	336382/1495	1 146 000	1 028 000	1 171 000	138 600	125 600	127 000

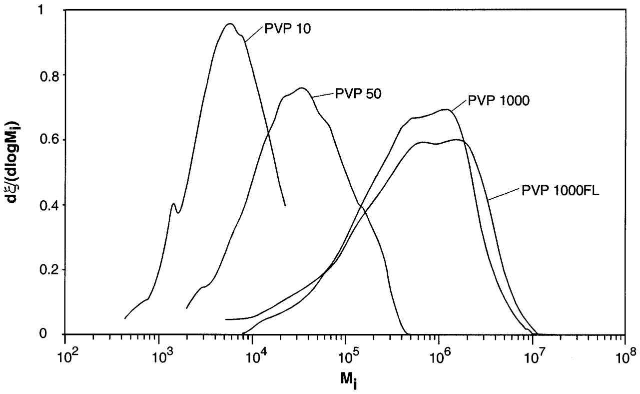

Figure 2. Differential molecular weight distribution of poly(vinylpyrrolidone) samples from gel permeation chromatography.

Table 3. Survey of the Experimental Work

		polymer mass fraction ($100\xi_s$/g·g^{-1})			
polymer	T/K	LLS	MO	ISO	density
PVP 10	278	0.40−5.1		35−42	0.50−30
	293	0.30−1.5		25−40	1.2−37
	333	0.38−4.8		44−54	1.2−37
PVP 50	278	0.40−1.5		38−42	0.61−29
	293	0.81−2.0		26−40	0.10−39
	303		0.52−2.8		
	333	0.40−1.0		45−54	0.10−39
PVP 1000	278	0.017−0.17			0.51−4.8
	293	0.015−0.14			0.61−20
	303		2.0−4.0		
	333	0.032−0.12	0.63−2.1		0.61−9.5
PVP 1000FL	278	0.0092−0.16			
	293	0.020−0.15			
	303		0.48−3.9		
	333	0.033−0.12	0.58−3.0		

Laser-Light-Scattering. Laser-light-scattering experiments were performed with aqueous solutions of all PVP samples at temperatures between (278 and 333) K and polymer mass fractions of about (0.3 to 5) mass % (for PVP 10) and (0.015 to 0.17) mass % (for PVP 1000). The experimental results are given in Tables 4−6. The uncertainty of these investigations was checked by repeating some experiments, as indicated, for example, in Table 5.

Membrane Osmometry. Membrane osmometry experiments were carried out with commercially available equipment (membrane osmometer type Osmomat 090, Gonotec, Berlin, Germany). Experiments could not be carried out for the low molecular weight PVPs due to the lack of suitable membranes. With the exception of a single data point, the experimental results for the osmotic pressure could be reproduced within ±5%, which is also the estimated experimental uncertainty. The experimental results are given in Tables 7 and 8.

Isopiestic Method. The apparatuses and the experimental procedures used for the isopiestic investigations have been described before.[5] Isopiestic investigations were performed with aqueous solutions of PVP 10 and PVP 50 at polymer mass fractions up to about 50%. Experimental work was not possible for the high molecular weight PVPs, as the aqueous solutions were too viscous and equilibration could not be achieved within a reasonable period of time. The experimental results are summarized in Table 9. The maximum uncertainty of that data is ±0.1 K in temperature, ±0.002 g·g^{-1} in polymer concentration, and ±0.001 in water activity.

Density. For the conversion of polymer mass fractions ξ_s ($=m_s/(m_s + m_w)$) into mass density c_s ($=m_s/V$), the specific density ρ^* ($=(m_s + m_w)/V$) of the aqueous PVP solution has to be known:

$$c_s = \rho^* \xi_s$$

The specific densities of the aqueous solutions of PVP 10, PVP 50, and PVP 1000 were measured at (278, 293, and 333) K with a vibrating tube densimeter. The experimental results are given in Table 10.

Correlation

Model. The osmotic virial equation is used to describe the thermodynamic properties of aqueous solutions of PVP in a similar way as it was used before for describing aqueous solutions of PEG[1] and DEX,[2] respectively. For a better understanding, the basic ideas are repeated here. It is common practice to use that equation also for solutions of polydisperse polymers, but neglecting any polydispersity. However, this can result in serious deficiencies when the osmotic virial coefficients depend on the polymer molecular mass. In the present work two different evaluations of the experimental data (from light-scattering, membrane osmometry, and isopiestic measurements) were applied. In one evaluation, the influence of polydispersity on the osmotic virial coefficients is taken into account (method I) whereas, in the other one (method II), it is neglected. The polydispersity of the polymer samples was approximated by assuming that the polydisperse polymer consists of (i = 2, ..., N), that is, (N − 1), monodisperse polymers. The distribution is characterized by the mass fraction ξ_i of (each) monodisperse polymer in the polydisperse polymer sample. The osmotic virial equation is based on a Taylor series expansion of the activity coefficients of the solutes, $\ln \gamma_i$, in concentration c_i, that is, mass of polymer per volume, around the ideal solution ($\ln \gamma_i = 0$ at $c_i = 0$ in pure solvent), where the chemical potential μ_i of solute i is normalized according to Henry's law ($c_i \rightarrow 0$ for interactions and $c_i \rightarrow 1$ g·cm^{-3} for concentration, both in pure solvent):

$$\ln \gamma_i = \sum_{j=2}^{N} \left(\frac{\partial \ln \gamma_i}{\partial c_j}\right)_{\text{pure solvent}} c_j + \frac{1}{2}\sum_{j=2}^{N}\sum_{k=2}^{N}\left(\frac{\partial^2 \ln \gamma_i}{\partial c_j\, \partial c_k}\right)_{\text{pure solvent}} c_j c_k + ... \quad (1)$$

Introducing abbreviations for partial derivatives similar to

Table 4. Experimental Results for the Excess Rayleigh Ratio at 278.15 K

100c_{s}/g·cm^{-3}	$10^4(Kc_{\mathrm{s}}/R_{\Theta}^{\mathrm{E}})$/mol·g^{-1}										
	Θ = 44.5°	Θ = 54.0°	Θ = 64.9°	Θ = 77.1°	Θ = 90.0°	Θ = 102.9°	Θ = 115.1°	Θ = 126.0°	Θ = 135.5°	Θ = 143.8°	Θ = 151.3°
PVP 10											
0.403		1.1079	1.1114		1.1009	1.0906		1.0975	1.0739	1.0839	
0.758		1.2038	1.2038		1.1907	1.1738		1.1822	1.1634	1.1696	
1.50		1.3804	1.3789		1.3616	1.3392		1.3489	1.3365	1.3365	
2.27		1.5751	1.5763		1.5564	1.5299		1.5406	1.5299	1.5275	
3.03		1.7845	1.7821		1.7607	1.7272		1.7409	1.7317	1.7294	
3.72		1.9826	1.9826		1.9574	1.9190		1.9339	1.9190	1.9032	
4.56		2.2495	2.2495		2.2192	2.1778		2.1934	2.1826	2.1778	
5.07		2.3859	2.3872		2.3616	2.3193		2.3390	2.3291	2.3267	
PVP 50											
0.400	2.1665	2.1651		2.1387	2.1143	2.1076		2.0865	2.0710	2.0697	2.0506
0.400	2.2228	2.2213		2.1764	2.1567	2.1401		2.1103	2.1010	2.0891	2.0839
0.604	2.5237	2.5148		2.4692	2.4369	2.4229		2.3918	2.3782	2.3771	2.3682
0.604	2.4986	2.5073		2.4560	2.4287	2.4078		2.3715	2.3626	2.3494	2.3374
0.800	2.7579	2.7499		2.7009	2.6621	2.6462		2.6120	2.5947	2.5917	2.5777
0.800	2.7218	2.7218		2.6642	2.6358	2.6079		2.5678	2.5599	2.5404	2.5317
1.00	3.1255	3.1231		3.0634	3.0158	2.9984		2.9580	2.9340	2.9392	2.9084
1.00	3.0691	3.0668		3.0006	2.9664	2.9361		2.8873	2.8714	2.8362	2.7214
1.50	3.7798	3.7912		3.7168	3.6721	3.6384		3.5592	3.5211	3.4693	3.1622
PVP 1000											
0.0149	1.0428	1.0955	1.1527	1.2736	1.3265	1.3968	1.4857	1.5306	1.5804	1.5521	
0.0284	1.0933	1.1436	1.2012	1.3228	1.3730	1.4423	1.5311	1.5749	1.6235	1.6022	
0.0546	1.2031	1.2529	1.3155	1.4399	1.4821	1.5481	1.6358	1.6778	1.7246	1.7015	
0.0546	1.2129	1.2636	1.3214	1.4488	1.4941	1.5601	1.6504	1.6918	1.7408	1.7186	
0.0837	1.3588	1.4064	1.4673	1.6017	1.6359	1.7012	1.7872	1.8280	1.8752	1.8513	
0.0837	1.3518	1.3986	1.4569	1.5920	1.6288	1.6944	1.7826	1.8221	1.8727	1.8453	
0.112	1.5009	1.5480	1.6088	1.7505	1.7778	1.8438	1.9293	1.9667	2.0181	1.9851	
0.112	1.5105	1.5580	1.6148	1.7573	1.7879	1.8507	1.9392	1.9770	2.0311	1.9977	
0.140	1.6540	1.7486	1.7567	1.9062	1.9274	1.9900	2.0777	2.1131	2.1657	2.1289	
0.140	1.6555	1.7546	1.7638	1.9126	1.9327	1.9949	2.0811	2.1159	2.1682	2.1246	
PVP 1000FL											
0.00920	0.9916		1.1304	1.2391	1.3432	1.4272	1.5311	1.5952			
0.0169	0.9484		1.1147	1.2379	1.3569	1.4507	1.5602	1.6294			
0.0323	1.1443		1.2931	1.4072	1.5159	1.6016	1.7057	1.7725			
0.0457	1.1798		1.3331	1.4494	1.5630	1.6500	1.7574	1.8245			
0.0654	1.3566		1.4967	1.6076	1.7149	1.7968	1.9014	1.9693			
0.0817	1.4367		1.5832	1.6963	1.8064	1.8881	1.9953	2.0638			
0.121	1.7012		1.8431	1.9556	2.0647	2.1443	2.2533	2.3225			
0.162	1.9965		2.1333	2.2434	2.3494	2.4239	2.5334	2.6032			

those for a binary system

$$a_{ij} = \left(\frac{\partial \ln \gamma_i}{\partial c_j}\right)_{\text{pure solvent}} \tag{2}$$

$$a_{ijk} = \left(\frac{\partial^2 \ln \gamma_i}{\partial c_j\, \partial c_k}\right)_{\text{pure solvent}} \tag{3}$$

leads to the osmotic virial equation for the activity coefficient of the polydisperse polymer i

$$\ln \gamma_i = \sum_{j=2}^{N} a_{ij} c_j + \frac{1}{2}\sum_{j=2}^{N}\sum_{k=2}^{N} a_{ijk} c_j c_k + \ldots \tag{4}$$

The activity of the solvent follows from an integration of the Gibbs−Duhem equation, taking into account the symmetry of the virial coefficients as well as assuming $\rho_{\text{solution}} \approx \rho_{\text{pure solvent}}$:

$$\ln a_1 = -\frac{c_{\mathrm{s}}}{\rho_1}\left(\frac{1}{M_{\mathrm{n}}} + A_2^{\mathrm{osm}} c_{\mathrm{s}} + A_3^{\mathrm{osm}} {c_{\mathrm{s}}}^2 + \ldots\right) \tag{5}$$

where

$$A_2^{\mathrm{osm}} = \sum_{i=2}^{N}\sum_{j=2}^{N} \xi_i \xi_j A_{ij} \tag{6}$$

$$A_3^{\mathrm{osm}} = \sum_{i=2}^{N}\sum_{j=2}^{N}\sum_{k=2}^{N} \xi_i \xi_j \xi_k A_{ijk} \tag{7}$$

$$c_{\mathrm{s}} = \sum_{i=2}^{N} c_i \tag{8}$$

c_{s} is the total concentration of the polymer. A_2^{osm} and A_3^{osm} are the second and third osmotic virial coefficients of the polydisperse polymer in the solvent, respectively. The mixed virial coefficients A_{ij} and A_{ijk} ($i \neq j \neq k$) are directly related to the partial derivatives in eqs 2 and 3:

$$A_{ij} = \frac{a_{ij}}{2M_{\mathrm{n},i}} \tag{9}$$

$$A_{ijk} = \frac{a_{ijk}}{3M_{\mathrm{n},i}} \tag{10}$$

M_{n} is the number-average molecular mass of the polydis-

Table 5. Experimental Results for the Excess Rayleigh Ratio at 293.15 K

$100c_s$/	$10^4(Kc_s/R^E_\Theta)$/mol·g^{-1}											
g·cm^{-3}	$\Theta = 36.2°$	$\Theta = 44.5°$	$\Theta = 54.0°$	$\Theta = 64.9°$	$\Theta = 77.1°$	$\Theta = 90.0°$	$\Theta = 102.9°$	$\Theta = 115.1°$	$\Theta = 126.0°$	$\Theta = 135.5°$	$\Theta = 143.8°$	$\Theta = 151.3°$
PVP 10												
0.304	1.1839	1.1320	1.1270	1.1029		1.1173	1.1124	1.1077	1.0754	1.1029		
0.611	1.2063	1.1709	1.1579	1.1502		1.1579	1.1527	1.1527	1.1131	1.1502		
0.611	0.6728	0.9787	1.0151	1.1037		1.1228	1.1179	1.1228	1.0852	1.0608		
0.899	1.2330	1.2095	1.2019	1.2000		1.2076	1.2038	1.2019	1.1925	1.2038		
0.899	0.8000	1.0648	1.0985	1.1622		1.1801	1.1711	1.1783	1.1379	1.1362		
1.20	1.2687	1.2454	1.2409	1.2409		1.2485	1.2454	1.2439	1.2319	1.2470		
1.20	0.8937	1.1383	1.1577	1.2186		1.2319	1.2186	1.2304	1.1750	1.1915		
1.50	1.3251	1.3101	1.3074	1.3034		1.3088	1.3034	1.3048	1.2928	1.3048		
1.50	0.9773	1.2082	1.2257	1.2773		1.2902	1.2811	1.2902	1.2621	1.2559		
PVP 50												
0.404		2.2434	2.2465	2.1357		2.2572	2.2388	2.2697	2.2373	2.2728	2.2886	
0.617		2.4931	2.5006	2.4003		2.5144	2.4993	2.5257	2.4981	2.5207	2.5295	
0.809		2.7154	2.7232	2.7368		2.7459	2.7459	2.7551	2.7402	2.7459	2.7551	
0.809		2.7482	2.7505	2.6552		2.7655	2.7471	2.7737	2.7448	2.7784	2.7621	
1.01		3.0017	3.0061	3.0171		3.0249	3.0271	3.0360	3.0160	3.0338	3.0484	
1.01		3.0260	3.0304	2.9353		3.0461	3.0293	3.0552	3.0260	3.0586	3.0405	
1.51		3.6961	3.7129	3.7219		3.7365	3.7434	3.7491	3.7365	3.7434	3.7537	
1.51		3.7860	3.7709	3.6784		3.7883	3.7582	3.7977	3.7525	3.8130	3.7698	
2.02		4.6340	4.6236	4.5145		4.6379	4.6054	4.6471	4.5964	4.6642	4.6158	
2.02		4.5331	4.5658	4.5646		4.5862	4.5964	4.5977	4.5926	4.5952	4.6171	
PVP 1000												
0.0149		1.0428	1.0955	1.1527	1.2736	1.3265	1.3968	1.4857	1.5306	1.5804	1.5521	
0.0284		1.0933	1.1436	1.2012	1.3228	1.3730	1.4423	1.5311	1.5749	1.6235	1.6022	
0.0546		1.2031	1.2529	1.3155	1.4399	1.4821	1.5481	1.6358	1.6778	1.7246	1.7015	
0.0546		1.2129	1.2636	1.3214	1.4488	1.4941	1.5601	1.6504	1.6918	1.7408	1.7186	
0.0837		1.3588	1.4064	1.4673	1.6017	1.6359	1.7012	1.7872	1.8280	1.8752	1.8513	
0.0837		1.3518	1.3986	1.4569	1.5920	1.6288	1.6944	1.7826	1.8221	1.8727	1.8453	
0.112		1.5009	1.5480	1.6088	1.7505	1.7778	1.8428	1.9293	1.9667	2.0181	1.9851	
0.112		1.5105	1.5580	1.6148	1.7573	1.7879	1.8507	1.9392	1.9770	2.0311	1.9977	
0.140		1.6540	1.7486	1.7567	1.9062	1.9274	1.9900	2.0777	2.1131	2.1657	2.1289	
0.140		1.6555	1.7546	1.7638	1.9126	1.9327	1.9949	2.0811	2.1159	2.1682	2.1246	
PVP 1000FL												
0.0201		1.0786		1.1780	1.2471	1.3226	1.3818		1.4912	1.5175	1.5374	1.5729
0.0401		1.1721		1.2696	1.3432	1.4147	1.4734		1.5811	1.6052	1.6252	1.6573
0.0600		1.2815		1.3757	1.4491	1.5174	1.5757		1.6825	1.7060	1.7259	1.7601
0.0600		1.2883		1.3795	1.4538	1.5226	1.5787		1.6895	1.7036	1.7320	1.7690
0.0800		1.4109		1.5006	1.5772	1.6424	1.7002		1.8088	1.8239	1.8514	1.8873
0.0800		1.4015		1.4927	1.5700	1.6354	1.6936		1.7998	1.8229	1.8420	1.8754
0.0999		1.5194		1.6058	1.6828	1.7452	1.8008		1.9081	1.9243	1.9488	1.9854
0.0999		1.5110		1.5717	1.6773	1.7396	1.7965		1.9005	1.9239	1.9427	1.9757
0.149		1.8030		1.8441	1.9625	2.0166	2.0702		2.1686	2.1905	2.2065	2.2390
0.149		1.8162		1.8942	1.9717	2.0257	2.0770		2.1787	2.1969	2.2174	2.2557

perse polymer, and ξ_i is the mass fraction of (monodisperse) component i of the polydisperse polymer.

A similar derivation with fixed temperature and fixed chemical potential μ_1 of the solvent (instead of a fixed or neglected pressure) leads to an expression for the osmotic pressure π^* of a solution of a polydisperse polymer (cf. Kurata[6]):

$$\frac{\pi^*}{RT} = c_s\left(\frac{1}{M_n} + A_2^{osm}c_s + A_3^{osm}{c_s}^2 + ...\right) \tag{11}$$

The basic equation for the evaluation of laser-light-scattering data in multicomponent systems is (cf. Stockmayer;[7] Kirkwood and Goldberg;[8] Kurata[6])

$$\frac{Kc_s}{R^E_\Theta} = \frac{1}{M_w P_\Theta} + 2A_2^{LS}c_s + 3A_3^{LS}{c_s}^2 + ... \tag{12}$$

K is the optical constant:

$$K = \frac{4\pi^4 {n_1}^2\left(\frac{\partial n}{\partial c_s}\right)^2}{N_A \lambda^4} \tag{13}$$

R^E_Θ is the excess Rayleigh ratio, which accounts primarily for the difference between the intensity of light scattered at an angle θ from the polymer solution and the intensity of that scattered from the pure solvent, and M_w is the mass-average molecular mass of the polymer. The particle scattering function P_θ describes the angular dependence of the Rayleigh ratio. P_θ is the ratio of the excess Rayleigh ratios at the angle of observation θ, that is, R^E_Θ, and at $\theta = 0$, that is, $R^E_{\Theta=0}$ (cf. Kratochvil[9]):

$$P_\theta = \frac{R^E_\Theta}{R^E_{\Theta=0}} \tag{14}$$

As discussed before by Kany et al.,[2] P_θ was approximated by

$$P_\theta = 1 + \Lambda_1 \sin^4(\Theta/2) \tag{15}$$

where Λ_1 was considered to be an adjustable parameter characterizing each polydisperse polymer sample. However, eq 15 was only used to extrapolate the experimental laser-light-scattering results to $\theta = 0$. Therefore, the parameters Λ_1 are not given here; they are available elsewhere.[4] M_w, A_2^{LS}, and A_3^{LS} were determined from the experimental (i.e. extrapolated) numbers for $R^E_{\Theta=0}$ using eq 12. A_2^{LS} and A_3^{LS} are the light-scattering second and third virial coefficients, respectively. These virial coefficients are related to A_{ij} and

Table 6. Experimental Results for the Excess Rayleigh Ratio at 333.15 K

$100c_s$/ $g \cdot cm^{-3}$	$10^4(Kc_s/R_\Theta^E)$/mol·g^{-1}											
	$\Theta = 44.5°$	$\Theta = 54.0°$	$\Theta = 64.9°$	$\Theta = 77.1°$	$\Theta = 90.0°$	$\Theta = 102.9°$	$\Theta = 115.1°$	$\Theta = 126.0°$	$\Theta = 135.5°$	$\Theta = 143.8°$	$\Theta = 151.3°$	$\Theta = 158.2°$
PVP 10												
0.378	1.0312	1.0276	1.0383	1.0529	1.0312	1.0276	1.0206	1.0312	1.0103	0.9741	1.0069	0.9145
0.727	1.0592	1.0572	1.0670	1.0852	1.0651	1.0592	1.0514	1.0651	1.0438	1.0161	1.0592	0.9043
1.44	1.2437	1.2263	1.2356	1.2423	1.2276	1.2119	1.2106	1.2171	1.2042	1.1684	1.2289	1.1212
2.16	1.3054	1.2829	1.2896	1.2965	1.2829	1.2639	1.2639	1.2686	1.2602	1.2197	1.2781	1.1891
3.62	1.5201	1.4931	1.5002	1.5065	1.4923	1.4679	1.4709	1.4731	1.4664	1.4212	1.4854	1.3709
4.35	1.6426	1.6119	1.6179	1.6263	1.6111	1.5844	1.5866	1.5895	1.5837	1.5363	1.6043	1.5100
4.83	1.7204	1.6900	1.6952	1.7051	1.6870	1.6599	1.6620	1.6664	1.6584	1.6122	1.6811	1.6021
PVP 50												
0.206	2.0712	2.0414	2.0022	2.0256	1.9920	2.0177		2.0203	2.0203	2.1450		2.2565
0.397	2.1759	2.2224	2.2290	2.2676	2.2778	2.2917		2.2727	2.2917	2.2143		1.9037
0.397	2.3599	2.2987	2.2761	2.2813	2.2625	2.2727		2.2830	2.3110	2.4186		2.8592
0.611	2.5911	2.5248	2.4949	2.4989	2.4723	2.4829		2.4909	2.5179	2.6383		2.9411
0.611	2.4069	2.4347	2.4424	2.4697	2.4922	2.4922		2.4816	2.5221	2.4194		2.0486
0.812	2.7480	2.6683	2.6398	2.6409	2.6196	2.6263		2.6364	2.6776	2.7803		3.0865
0.812	2.5481	2.5672	2.5822	2.6063	2.6409	2.6352		2.6319	2.6823	2.5651		2.1803
1.02	3.0459	2.9564	2.9152	2.9163	2.8762	2.8880		2.9010	2.9552	3.0921		3.1968
1.02	2.8645	2.8709	2.8773	2.8837	2.9196	2.9010		2.8891	2.9575	2.8155		2.3729
2.03	3.8835	3.8747	3.9081	3.8913	3.9573	3.9200		3.9061	4.0087	3.8048		3.1910
PVP 1000												
0.0322	1.0897	1.1085	1.1395	1.2264	1.2632	1.3349		1.4628	1.4950	1.6113		1.6482
0.0322	1.0586	1.0878	1.1306	1.2240	1.2764	1.3408		1.4584	1.5051	1.5628		1.6018
0.0458	1.1698	1.1910	1.2229	1.3129	1.3538	1.4156		1.5262	1.5746	1.6392		1.6619
0.0458	1.1730	1.1890	1.2190	1.3085	1.3439	1.4167		1.5452	1.5824	1.6976		1.7383
0.0644	1.2632	1.2831	1.3148	1.4117	1.4510	1.5182		1.6372	1.6898	1.7667		1.8200
0.0816	1.3480	1.3584	1.3829	1.4752	1.5064	1.5697		1.6860	1.7429	1.8207		1.8573
0.0816	1.3608	1.3668	1.3907	1.4819	1.5089	1.5785		1.7040	1.7473	1.8612		1.8902
0.122	1.5753	1.5755	1.5937	1.6906	1.7083	1.7768		1.9024	1.9480	2.0662		2.1076
0.122	1.5681	1.5691	1.5879	1.6826	1.7049	1.7650		1.8819	1.9452	2.0278		2.0502
PVP 1000FL												
0.0165	1.1921	1.2053	1.2467	1.2937	1.4051	1.4376	1.5321	1.5651	1.6296	1.5880		1.5429
0.0328	1.2858	1.3020	1.3543	1.4064	1.5121	1.5400	1.6381	1.6666	1.7264	1.6795		1.6433
0.0328	1.2910	1.3192	1.3810	1.4569	1.5409	1.5822	1.6741	1.7128	1.7568	1.7150		1.6817
0.0489	1.3349	1.3626	1.4249	1.5023	1.5867	1.6268	1.7193	1.7584	1.8018	1.7584		1.7371
0.0489	1.3895	1.4026	1.4576	1.5123	1.6186	1.6455	1.7434	1.7745	1.8325	1.7819		1.7576
0.0654	1.4352	1.4497	1.5045	1.5621	1.6641	1.6913	1.7896	1.8211	1.8773	1.8276		1.8122
0.0654	1.4040	1.4312	1.4936	1.5712	1.6551	1.6936	1.7872	1.8256	1.8698	1.8237		1.8040
0.0825	1.5011	1.5125	1.5681	1.6264	1.7266	1.7526	1.8510	1.8809	1.9390	1.8847		1.8717
0.0825	1.4630	1.4898	1.5517	1.6308	1.7139	1.7507	1.8452	1.8825	1.9287	1.8787		1.8717
0.123	1.6381	1.6611	1.7216	1.8040	1.8839	1.9166	2.0134	2.0485	2.0962	2.0404		2.0238

Table 7. Osmotic Pressure π^* at 303.15 K from Membrane Osmometry

PVP 50		PVP 1000		PVP 1000FL	
$100\xi_s$/g·g^{-1}	π^*/Pa	$100\xi_s$/g·g^{-1}	π^*/Pa	$100\xi_s$/g·g^{-1}	π^*/Pa
0.524	601^{+11}_{-13}	1.955	684^{+12}_{-12}	0.478	107^a
0.894	1052^{+16}_{-15}	2.076	818^{+16}_{-17}	0.969	198^{+3}_{-4}
2.116	2873^{+4}_{-5}	2.912	1536^{+16}_{-17}	0.982	272^a
2.801	4244^{+49}_{-44}	2.955	1637^a	1.076	302^{+10}_{-8}
		4.001	3296^{+25}_{-26}	1.918	799^a
				1.966	817^{+17}_{-25}
				2.070	893^{+17}_{-25}
				2.943	1792^a
				3.116	1897^a
				3.915	3027^a

[a] Only a single data point.

Table 8. Osmotic Pressure π^* at 333.15 K from Membrane Osmometry

PVP 1000		PVP 1000FL	
$100\xi_s$/g·g^{-1}	π^*/Pa	$100\xi_s$/g·g^{-1}	π^*/Pa
0.626	127^{+3}_{-4}	0.582	154^{+10}_{-17}
1.027	250^{+2}_{-1}	0.948	264^{+7}_{-6}
2.076	723^{+11}_{-11}	2.088	819^{+32}_{-33}
		2.961	1567^{+47}_{-47}

A_{ijk} of eqs 9 and 10 through

$$A_2^{\mathrm{LS}} = \frac{1}{{M_\mathrm{w}}^2}\sum_{i=2}^{N}\sum_{j=2}^{N}\xi_i\xi_j\,M_iM_j\,A_{ij} \tag{16}$$

and

$$A_3^{\mathrm{LS}} = \frac{1}{{M_\mathrm{w}}^2}\sum_{i=2}^{N}\sum_{j=2}^{N}\sum_{k=2}^{N}\xi_i\xi_j\,\xi_kM_iM_j\,A_{ijk} - \frac{4}{3{M_\mathrm{w}}^3}\sum_{i=2}^{N}\sum_{j=2}^{N}\sum_{k=2}^{N}\sum_{l=2}^{N}\xi_i\xi_j\,\xi_k\xi_lM_iM_j\,M_kM_l(A_{ij}A_{jk} - A_{ik}A_{jl}) \tag{17}$$

Light-scattering virial coefficients A_2^{LS} and A_3^{LS} differ from osmotic virial coefficients A_2^{osm} and A_3^{osm} only for polydisperse polymers, whereas there is no such difference for monodisperse polymers.

Pseudocomponents. The molecular mass distribution of each PVP sample was approximated by eight pseudocomponents. The molecular mass and the mass fraction of each pseudocomponent were determined applying the same method as in previous investigations on DEX.[2] The results are given in Table 11.

Simultaneous Evaluation of Laser-Light-Scattering, Membrane Osmometric, and Isopiestic Data. Experimental data from laser-light-scattering experiments,

Table 9. Activity of Water a_1 from Isopiestic Investigations

278.15 K			293.15 K			333.15 K		
	ξ_s/g·g^{-1}			ξ_s/g·g^{-1}			ξ_s/g·g^{-1}	
a_1	PVP 10	PVP 50	a_1	PVP 10	PVP 50	a_1	PVP 10	PVP 50
0.9825	0.3506		0.9942	0.2489	0.2639	0.9829	0.4435	0.4498
0.9813	0.3736	0.3826	0.9888	0.3363	0.3464	0.9811		0.4505
0.9789	0.3998	0.3989	0.9884	0.3500		0.9791		0.4670
0.9774	0.4000		0.9883	0.3356	0.3362	0.9783		0.4961
0.9797		0.4017	0.9874		0.3466	0.9772	0.4934	0.4931
0.9769		0.4237	0.9868	0.3526	0.3577	0.9753	0.5029	
0.9735	0.4098	0.4146	0.9865		0.3579	0.9751		0.5170
0.9731	0.4202	0.4233	0.9823	0.3917	0.3990	0.9716	0.5398	
			0.9818		0.3874			

Table 10. Density of Aqueous Solutions of Poly(pyrrolidone)

		ρ^*/g·cm^{-3}		
	ξ_a/g·g^{-1}	278.15 K	293.15 K	333.15 K
PVP 10	0.0052	1.0011		
	0.0103	1.0022		
	0.0124		1.0005	0.9865
	0.0252	1.0055		
	0.0288		1.0044	0.9945
	0.0484	1.0107		
	0.0563		1.0106	0.9946
	0.0918	1.0205		
	0.0940		1.0187	1.0025
	0.1884		1.0399	1.0223
	0.1957	1.0446		
	0.2979	1.0705		
	0.3728		1.0859	1.0652
PVP 50	0.0010		1.004	0.9854
	0.0061	1.0013		
	0.0128	1.0028		
	0.0200	1.0044		
	0.0295		1.0047	0.9895
	0.0436		1.0081	0.9926
	0.0491	1.0109		
	0.0993		1.0208	1.0047
	0.1034	1.0234		
	0.1886	1.0441		
	0.1975		1.0432	1.0261
	0.2899	1.0701		
	0.3890		1.0919	1.0734
PVP 1000	0.0051	1.0012		
	0.0061		0.9996	
	0.0100	1.0023		
	0.0113		1.0007	0.9557
	0.0201	1.0041		
	0.0263		1.0040	0.9889
	0.0483	1.0113		
	0.0513		1.0084	0.9947
	0.0945		1.0204	1.0044
	0.2000		1.0453	

membrane osmometry (both at low polymer concentrations), and isopiestic measurements (at high polymer concentrations) were simultaneously evaluated to determine the number- and weight-average molecular masses as well as the second and third virial coefficients of PVP in aqueous solution. In a procedure similar to that described before for DEX,[2] the pure component virial coefficients A_{ii} and A_{iii} were expressed by two-parametric empirical expressions:

$$A_{ii} = \alpha_2 M_i^{\beta_2} \tag{18}$$

and

$$A_{iii} = \alpha_3 M_i^{\beta_3} \tag{19}$$

where α_j and β_j ($j = 2$ or 3) are constants. Thus, it is possible to describe solutions of polydisperse polymers either in the common way (i.e. neglecting the influence of polydispersity by setting $\beta_2 = \beta_3 = 0$) or by taking that influence into account. When the influence of polydispersity is taken into account, mixed virial coefficients (between polymers differing only in molecular weight) are required. These mixed virial coefficients were approximated using geometric mixing rules:

$$A_{ij} = (A_{ii}A_{jj})^{1/2} \tag{20}$$

$$A_{ijk} = (A_{iii}A_{jjj}A_{kkk})^{1/3} \tag{21}$$

The experimental results were evaluated using two different methods. Method I assumes that A_{ii} and A_{iii} depend on the molecular mass of PVP, whereas method II assumes that A_{ii} and A_{iii} do not depend on the molecular mass of PVP. As shown before,[1,2] in an evaluation with method II, the number-average and weight-average molecular masses of each polymer sample should not be taken from the GPC experiments (cf. Figure 2) but have to be treated as unknown adjustable parameters. In an evaluation according to method I, the molecular mass distribution has to be known a priori. In such evaluations the pseudocomponent mass fractions were taken from Table 11 and used in eqs 6 and 7 as well as in eqs 16 and 17. The influence of temperature on A_{ii} and A_{iii} was expressed by the following empirical equation for α_2 and α_3:

$$\alpha_j = \alpha_j(T) = \alpha_j^{(0)}\left(\frac{1}{T} - \frac{1}{T_\Theta}\right) \quad (j = 2, 3) \tag{22}$$

where T_Θ is the temperature where all osmotic virial coefficients are zero.

The remaining unknown parameters ($\alpha_2^{(0)}$, $\alpha_3^{(0)}$, β_2, β_3, T_Θ, and $\Lambda_{1,j}$ (j = PVP10, PVP 50, PVP 1000, and PVP 1000FL)) were fitted to the experimental data by minimizing an objective function as described by Kany et al.[2] The results of both evaluations confirm the previously published results for aqueous solutions of PEG[1] and of DEX.[2] Both methods allow for an equally good description of the experimental data. Typical comparisons between experimental data and both correlations are shown in Figures 3−5. Figure 3 shows a comparison for laser-light-scattering data (Rayleigh ratios Kc_s/R_Θ^E extrapolated to zero scattering angle) for PVP 10 and PVP 50. Figures 4 and 5 show similar comparisons for the reduced water activity ($-\rho_1 \ln a_1/c_s$) in aqueous solutions of PVP 50 at 293.15 K and 303.15 K from isopiestic investigations (Figure 4) and from membrane osmometry, respectively. Table 2 gives the mass-average and number-average molecular masses determined with a GPC as well as from the laser-light-scattering and (isopiestic experiments and membrane osmometry) applying both evaluation methods. The polydispersity of the samples increases with increasing molec-

Table 11. Pseudocomponents for Poly(vinylpyrrolidone) Samples

PVP 10		PVP 50		PVP 1000		PVP 1000FL	
M_i	ξ_i/g·g^{-1}	M_i	ξ_i/g·g^{-1}	M_i	ξ_i/g·g^{-1}	M_i	ξ_i/g·g^{-1}
446	0.0055	2 291	0.0137	37 120	0.0176	6 403	0.0079
748	0.0289	3 810	0.0492	61 370	0.0527	12 810	0.0248
1 582	0.1289	8 850	0.1608	137 200	0.1331	37 790	0.0734
4 041	0.3482	23 410	0.3248	362 300	0.2718	144 000	0.1890
10 180	0.3405	64 200	0.2917	999 200	0.3251	540 000	0.3280
24 740	0.1255	169 900	0.1415	2 362 000	0.1704	1 836 000	0.2949
51 550	0.0209	324 600	0.0182	5 081 000	0.0275	4 576 000	0.0767
82 350	0.0016	606 600	0.0001	8 256 000	0.0018	8 803 000	0.0052

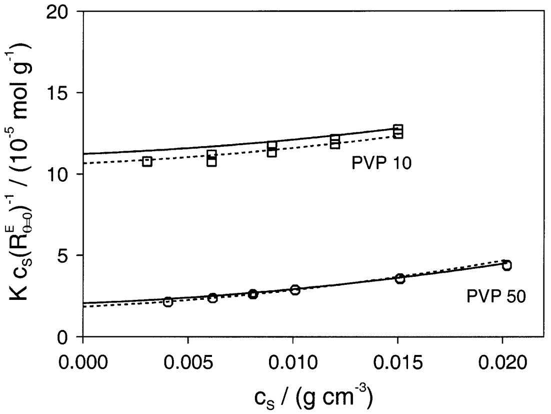

Figure 3. Experimental results of laser-light-scattering experiments of aqueous solutions of poly(vinylpyrrolidone) samples at 293.15 K: □, PVP 10; ○, PVP 50; dashed line, correlation by "method I"; full line, correlation by "method II". Both correlations give nearly the same results.

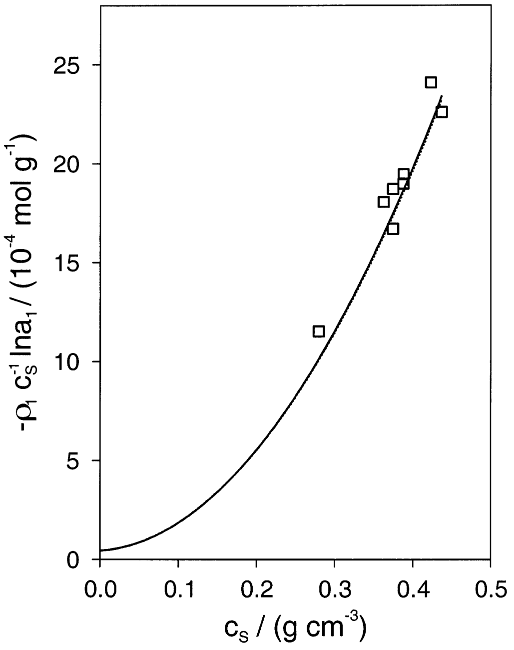

Figure 4. Reduced activity of water in aqueous solutions of PVP 50 at 293.15 K: □, from isopiestic investigations; dashed line, correlation by "method I"; full line, correlation by "method II". Both correlations give nearly the same results.

ular mass from about 1,8 (for PVP 10) to 9.3 (for PVP 1000). The experimental results for the mass-average molecular mass scatter by about ±10%. For 293 K, the numerical evaluation by "method I" (i.e. assuming that the virial coefficients depend on molecular mass) gives for the second virial coefficient $2.33 \le (A_{22}/(10^{-4}\ \text{mol·cm}^3\text{·g}^{-2})) \le 2.97$ and for the third virial coefficient $0.51 \le (A_{222}/(10^{-2}\ \text{mol·cm·}^6\text{g}^{-3})) \le 0.74$ for $10^4 \le M \le 10^7$, where with increasing molecular mass A_{22} as well as A_{222} decreases. The influence of the molecular mass on A_{22} as well as on A_{222} is rather small. Therefore, it is not surprising that the evaluation by "method II" (i.e. assuming that the virial coefficients do not depend on molecular mass) represents the experimental data as well. Therefore, there is no need to assume that neither A_{22} nor A_{222} depend on molecular mass. These results are in accordance with previous findings for aqueous solutions of PEG[1] and DEX.[2] It is furthermore confirmed by the finding that both methods give nearly the same number for T_Θ (method I, $T_\Theta = 446$ K; method II, $T_\Theta = 442.5$ K). Neglecting the influence of molecular mass on A_{22} and A_{222} gives for temperatures between 278 and 333 K

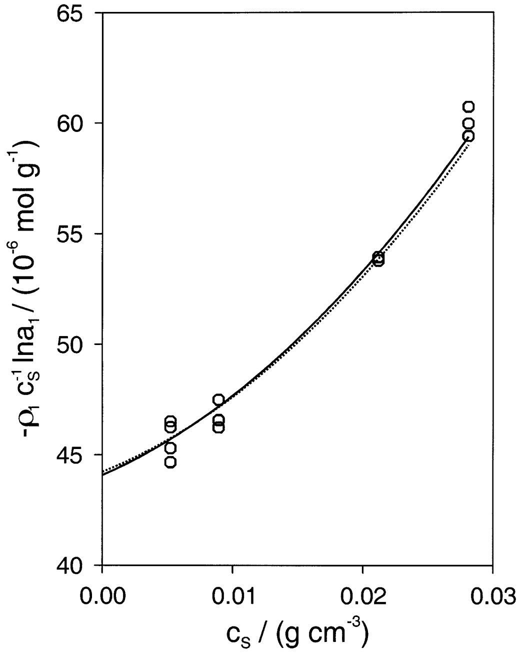

Figure 5. Reduced activity of water in aqueous solutions of PVP 50 at 303.15 K: □, from isopiestic investigations; dashed line, correlation by "method I"; full line, correlation by "method II".

$$A_2^{\text{osm}} = A_{22};\quad A_2^{\text{osm}}/\text{mol·cm}^3\text{·g}^{-2} = 0.227\left(\frac{1}{T/\text{K}} - \frac{1}{442.5}\right) \tag{23}$$

and

$$A_3^{\text{osm}} = A_{222};\quad A_3^{\text{osm}}/\text{mol·cm}^6\text{·g}^{-3} = 9.949\left(\frac{1}{T/\text{K}} - \frac{1}{442.5}\right) \tag{24}$$

resulting, for example, for 293 K in $A_2^{\text{osm}} = 2.62 \times 10^{-4}$ mol·cm^3·g^{-2} and $A_3^{\text{osm}} = 1.15 \times 10^{-2}$ mol·cm^6·g^{-3}.

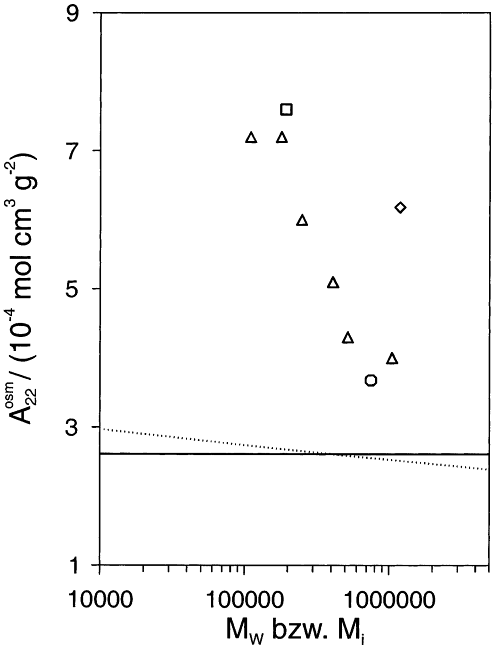

Figure 6. Second osmotic virial coefficient A_2^{osm} of poly(vinylpyrrolidone) in water at around 300 K: ◇, at 295.15 K from Edsman and Sundelöf;[11] □, at 303.15 K from Hefford;[12] △, at 298.15 K from Nakayama;[13] ○, at 293.15 K from Nordmeier;[14] dashed line, this work applying "method I"; full line, this work applying "method II. Both methods are performed at 293.15 K.

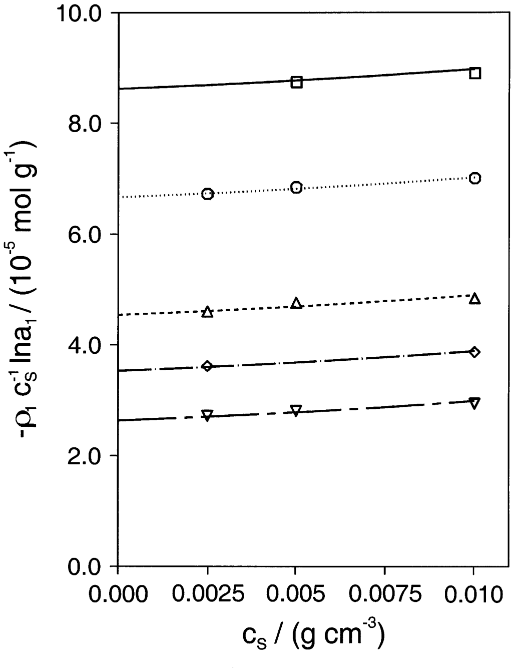

Figure 7. Reduced activity of water in aqueous solutions of poly(vinylpyrrolidone) at 298.15 K. Experimental results by Hengstenberg and Schuch[10] for PVP 12 (□), PVP 15 (○), PVP 22 (△), PVP 28 (◇), and PVP 38 (▽). Lines are predictions assuming that the osmotic virial coefficients do not depend on molecular mass.

Comparison with Literature Data

Figure 6 shows a comparison between literature data for the second osmotic virial coefficient of PVP in water at temperatures around 300 K and the results of the present work (for 293 K). This comparison is very similar to that for PEG[1] and for DEX:[2] the very limited literature data scatter extremely and reveal a strong influence of the polymer molecular mass. However, and as already stated previously, the reliability of the literature data is questionable mainly for two reasons. First, second virial coefficients were determined from measurements using a single experimental procedure in a rather limited concentration range, and second, in the evaluation of the experimental data both the polydispersity of the polymer samples and the third virial coefficient were neglected. Therefore, it is more reasonable to compare direct experimental data (instead of derived properties such as the second osmotic virial coefficient) with the correlation of the present work. Such a comparison is possible with the experimental

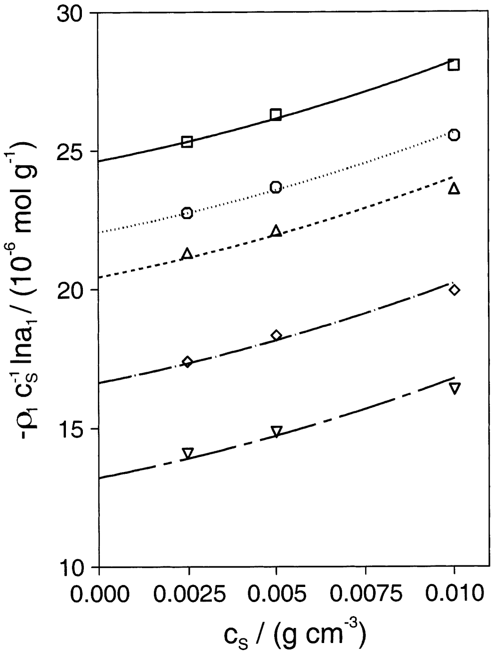

Figure 8. Reduced activity of water in aqueous solutions of poly(vinylpyrrolidone) at 298.15 K. Experimental results by Hengstenberg and Schuch[10] for PVP 41 (□), PVP 46 (○), PVP 49 (△), PVP 60 (◇), and PVP 75 (▽). Lines are predictions assuming that the osmotic virial coefficients do not depend on molecular mass.

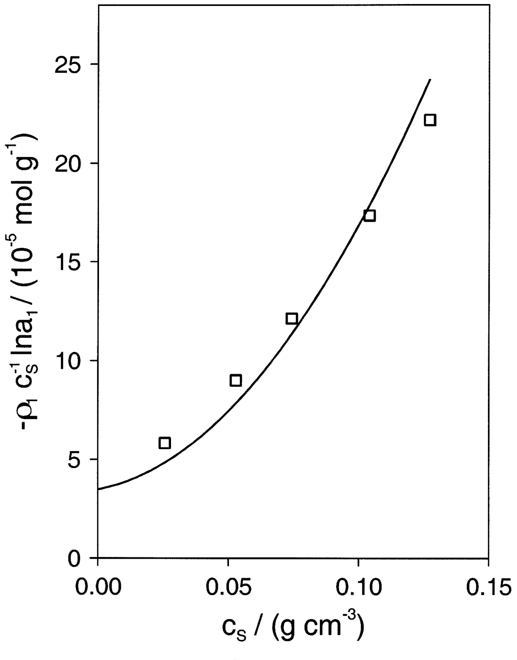

Figure 9. Reduced activity of water in aqueous solutions of PVP 90 at 298.15 K: □, experimental results by Vink;[3] line, prediction assuming that the osmotic virial coefficients do not depend on molecular mass.

results for the activity of water in aqueous solutions of several poly(vinylpyrrolidone) samples by Hengstenberg and Schuch[10] and by Vink.[3] Hengstenberg and Schuch[10] reported results of experimental investigations of ten PVP samples by membrane osmometry at 298 K at polymer mass fractions up to 0.01 g·cm^{-3}. For comparison with the correlation of the present work, the molecular mass of the polymer samples was taken from ref 10 and the activity of water was calculated with osmotic virial coefficients as given by eqs 23 and 24 (i.e., $A_2^{\mathrm{osm}} = 2.48 \times 10^{-4}$ mol·cm^3·g^{-2} and $A_3^{\mathrm{osm}} = 1.09 \times 10^{-2}$ mol·cm^6·g^{-3}). As shown in Figures 7 and 8, the predictions based on the correlation of the present work agree excellently with the experimental data. A similar comparison (cf. Figure 9) with the experimental data by Vink[3] for aqueous solutions of PVP 90 (at polymer concentrations up to nearly 0.15 g·cm^{-3}) also reveals a good agreement (adopting Vink's numerical value for the molecular mass of the PVP sample: $M_{\mathrm{n}} = 28\,600$), although the experimental data (for the reduced water activity) do not depend as strongly on the polymer concentration as the predictions.

Conclusions

The results of experimental investigation of aqueous solutions of several polydisperse PVP samples varying in the mass-average molecular mass between about 9 000 and 1 200 000 by laser-light-scattering, membrane osmometry, and isopiestic measurements at temperatures between (278 and 333) K were simultaneously evaluated to determine the second and third osmotic virial coefficients of poly(vinylpyrrolidone) in pure water. The results confirm the previous findings for aqueous solutions of the single polymers poly(ethylene glycol) and dextran, that the thermodynamic properties of such solutions can be accurately described by the osmotic virial equation neglecting the influence of the polymer molecular mass on the osmotic virial coefficients.

Nomenclature

A_{ij} = second virial coefficient for interactions between species i and j
A_{ijk} = third virial coefficient for interactions between species i, j, and k
A_2^{osm} = second osmotic virial coefficient of solute 2
A_3^{osm} = third osmotic virial coefficient of solute 2
A_2^{LS} = light-scattering second osmotic virial coefficient of solute 2
A_3^{LS} = light-scattering third osmotic virial coefficient of solute 2
a_1 = activity of water
a_{ij} = partial derivative of $\ln \gamma_i$ with respect to c_j
a_{ijk} = partial derivative of $\ln \gamma_i$ with respect to c_j and c_k
c = mass density
DEX = dextran
GPC = gel permeation chromatography
ISO = isopiestic experiment
K = optical constant
LLS = laser-light-scattering
M_{n} = number-average molecular mass
M_{w} = mass-average molecular mass
m = amount of mass
MO = membrane osmometry
N = number of components
N_{A} = Avogadro's number
n = refractive index of the solution
n_1 = refractive index of water
P = polydispersity
P_Θ = normalized Rayleigh ratio
PEG = poly(ethylene glycol)
PVP = poly(vinylpyrrolidone)
PVP(aq) = aqueous solution of poly(vinylpyrrolidone)
R = universal gas constant
R_Θ^{E} = excess Rayleigh ratio
T = absolute temperature
T_Θ = Θ-temperature ($A_2^{\mathrm{osm}} = A_3^{\mathrm{osm}} = 0$)
V = volume

Greek Letters

α_2, α_3 = parameters describing the influence of the molecular mass on the second and third virial coefficients
$\alpha_j^{(0)}$ (j = 2 or 3) = parameters describing the influence of temperature on the second and third virial coefficients
β_2, β_3 = parameters describing the influence of the molecular mass on the second and third virial coefficients
Θ = scattering angle
γ_i = activity coefficient of species i (on mass density scale)
Λ_1 = adjustable parameter
λ = laser wavelength (=633 nm)
μ_1 = chemical potential of water
π^* = osmotic pressure
ρ_1 = density of water
ρ^* = specific density of aqueous solution

Subscripts

i, j, k = components i, j, k
s = total solute (polymer)
w = water

Literature Cited

(1) Hasse, H.; Kany, H.-P.; Tintinger, R.; Maurer, G. Osmotic virial coefficients of aqueous poly(ethylene glycol) from laser-light scattering and isopiestic measurements. *Macromolecules* **1995**, *28*, 3540−3552.
(2) Kany, H.-P.; Hasse, H.; Maurer, G. Thermodynamic properties of aqueous dextran solutions from laser-light-scattering, membrane osmometry, and isopiestic measurements. *J. Chem. Eng. Data* **1999**, *44*, 230−242.
(3) Vink, H. Precision measurements of osmotic pressure in concentrated polymer solutions. *Eur. Polym. J.* **1971**, *13*, 1411−1419.
(4) Kany, H.-P. Thermodynamische Eigenschaften wässriger Polymerlösungen. Ph.D. Thesis, Universität Kaiserslautern, Kaiserslautern, 1998.
(5) Groβmann, C.; Tintinger, R.; Zhu, J.; Maurer, G. Aqueous two-phase systems of poly(ethylene glycol) and dextran−experimental results and modelling of thermodynamic properties. *Fluid Phase Equilib.* **1995**, *106*, 111−138.
(6) Kurata, M. *Thermodynamics of Polymer Solutions*; Harwood Academic Publishers: Chur, Switzerland, 1982.
(7) Stockmayer, W. H. Light scattering in multicomponent systems. *J. Chem. Phys.* **1949**, *18*, 58−61.
(8) Kirkwood, J. G.; Goldberg, R. J. Light scattering arising from composition fluctuations in multicomponent systems. *J. Chem. Phys.* **1950**, *18*, 54−57.
(9) Kratochvil, P. *Classical Light Scattering from Polymer Solutions*; Elsevier: Amsterdam, 1987.
(10) Hengstenberg, J.; Schuch, E. Molekulargewichtsbestimmung von Polyvinylpyrrolidonen (PVP) mittels des osmotischen Drucks und der Lichtstreuung ihrer Lösungen. *Makromol. Chem.* **1951**, *7*, 236−258.
(11) Edsman, K.; Sundelöf, L.-O. Interaction virial coefficients in some mixed polymer solutions. *Polymer* **1988**, *29*, 535−540.
(12) Hefford, R. J. Polymer mixing in aqueous solution. *Polymer* **1984**, *25*, 979−984.

(13) Nakayama, H. Temperature dependence of heats of solution of poly(ethylene glycol) and related compounds. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1683−1687.
(14) Nordmeier, E. Static and dynamic light-scattering solution behavior of Pullulan and Dextran in comparison. *J. Phys. Chem.* **1993**, *97*, 5770−5785.
(15) Elias, H.-G. Konstitution und Lösungseigenschaften von Makromolekülen. Ermittlung von Θ-Lösungen. *Anal. Chem.* **1961**, *33*, 1−19.
(16) Nakagaki, M.; Shimabayashi, S.; Yoshida, S.; Saito, M. Light scattering studies of aqueous solutions of poly(vinylpyrrolidone). *Yakugaku Zasshi* **1976**, *96*, 757−763.
(17) Nordmeier, E.; Lechner, M. D. Light scattering from polymer-mixed systems. 1. Selective adsorption phenomena of poly(N-vinylpyrrolidone). *Macromolecules* **1991**, *24*, 2529−2537.

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