

# Osmotic Virial Coefficients of Aqueous Poly(ethylene glycol) from Laser-Light Scattering and Isopiestic Measurements

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**ABSTRACT:** Second and third osmotic virial coefficients ( $A_{22}$  and  $A_{222}$ ) of poly(ethylene glycol) (PEG) in aqueous solution were determined from a simultaneous evaluation of laser-light scattering data (diluted solutions) and isopiestic data (concentrated solutions). In contradiction to literature data, it is found that neither  $A_{22}$  nor  $A_{222}$  depends on the molecular mass of PEG. The reasons for the lacking accuracy of previously reported data are discussed. With virial coefficients independent of molecular mass, the osmotic virial equation describes well the available reliable experimental data, which cover PEG 200 to PEG 40000 at temperatures between 278 and 333 K, up to polymer concentrations of about  $0.6 \text{ g cm}^{-3}$ . An extrapolation indicates that at about 376 K, both  $A_{22}$  and  $A_{222}$  are zero.

## Introduction

Water-soluble polymers—both synthetic and natural—are widely used in many fields.<sup>1–3</sup> The number of applications is increasing and it is expected that water-soluble polymers will be one of the major product groups of the next century.<sup>4</sup> Understanding properties of simple synthetic polymers in aqueous solution is a key to progress in our knowledge of the more complex biopolymers in their native environment.

There is a wealth of methods for studying thermodynamic properties of aqueous polymer solutions. Among the most widely used are vapor-pressure measurements, osmometry, laser-light scattering, and the isopiestic method. Comprehensive discussions of these methods have been given in the literature (e.g., Elias,<sup>5</sup> Schröder et al.,<sup>6</sup> and Slade<sup>7</sup>). Most of these methods have been known for a long time, and it could be concluded that plenty of reliable thermodynamic data on aqueous polymer solutions are available. However, this is not the case.

There is an enormous difference in the number of experimental studies of thermodynamic properties of organic compared to aqueous polymer solutions. In a survey on second osmotic virial coefficients, Lechner and Steinmeier<sup>8</sup> quote more than 600 sources for data on organic polymer solutions, but less than 20 for aqueous solutions. Even though that survey is not complete, the ratio of both numbers is probably a good estimate. Furthermore, big discrepancies are common in the literature data on thermodynamic properties of aqueous polymer solutions. For example, numbers reported for the second osmotic virial coefficient  $A_{22}$  of aqueous PEG 6000 at room temperature differ between  $2.6 \times 10^{-3}$  and  $4.5 \times 10^{-3} \text{ mol cm}^3 \text{ g}^{-2}$ .

There are several reasons for that situation: Due to the specific properties of water, experimental studies of aqueous polymer solutions are usually more difficult than those of polymers in organic solutions. Furthermore, many authors report results of the correlation of their data, e.g., with the osmotic virial equation, but do not thoroughly compare that correlation with data from other sources. This situation stands in contrast to the increasing number of applications where accurate data on thermodynamic properties of aqueous polymer solu-

tions are needed, like, for example, in modeling aqueous two-phase systems, which are used in extraction processes in biotechnology.<sup>9</sup>

The aim of the present work is to contribute to the development of procedures for the reliable determination of thermodynamic data on aqueous polymer solutions. The simplest water-soluble polymer, poly(ethylene glycol) (PEG,  $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$ ) was chosen for the basic studies. Poly(ethylene oxide) (PEO) is not discussed here. The monomer unit in PEO is identical with that in PEG, but its molecular mass is about 2 orders of magnitude larger. For recent work on properties of aqueous PEO, see, e.g., Devanand and Selser.<sup>10,11</sup>

PEG is a widely used polymer and its preparation, properties, and applications have been discussed by Bailey and Koleske,<sup>12</sup> Meltzer,<sup>1</sup> and Molyneux.<sup>3</sup> Thermodynamic properties of aqueous PEG have probably been studied by more authors than those of any other water-soluble polymer. A comprehensive survey of the literature data is given in Appendix A. The most important methods used to study aqueous PEG solutions are conventional vapor-pressure measurements,<sup>13–15</sup> differential vapor-pressure measurements,<sup>16–18</sup> vapor-pressure osmometry,<sup>15,19–27</sup> membrane osmometry,<sup>28–30</sup> laser-light scattering,<sup>15,31–33</sup> and isopiestic investigations.<sup>34–37</sup> With most methods the activity of water is measured. However, at low polymer concentration the activity of water in the polymer solution hardly differs from that of pure water, so that it is usually difficult to get reliable data at polymer concentrations below about  $0.05 \text{ g cm}^{-3}$ . The concentration range below about  $0.05 \text{ g cm}^{-3}$  can be covered mainly with membrane osmometry and laser-light scattering. These two methods are, however, difficult to apply for small PEGs.

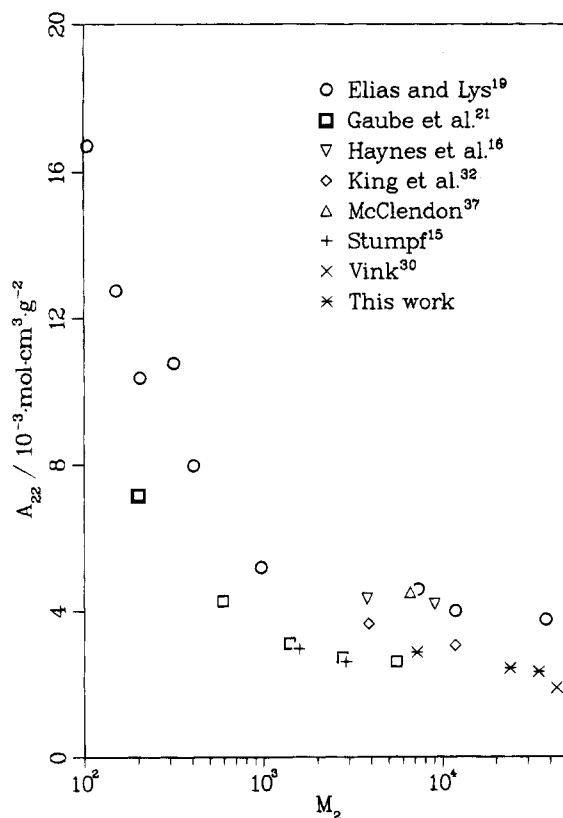
It is common practice to correlate thermodynamic data of aqueous polymer solutions with the osmotic virial equation:

$$\ln a_1 = -\frac{c_2}{\varrho_1} \left( \frac{1}{M_2} + A_{22}c_2 + A_{222}c_2^2 + \dots \right) \quad (1)$$

where  $a_1$  is the activity of the solvent (water),  $c_2$  is the concentration of the polymer in mass/volume,  $\varrho_1$  is the molar density of pure water,  $M_2$  is the molecular mass of the polymer, and  $A_{22}$  and  $A_{222}$  are the second and third osmotic virial coefficients of the polymer in the

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**Figure 1.** Second osmotic virial coefficients of PEG in aqueous solution at about 298 K. Literature data were obtained with different methods (cf. Table 4). Data from this work are from laser-light scattering using  $A_{22}c_2^2 = 0$ .

solvent, respectively. If the experimental data are plotted as reduced solvent activity ( $\rho_1 \ln a_1/c_2$ ) (also called "apparent inverse molecular mass") over  $c_2$ , the numbers for  $M_2$ ,  $A_{22}$ , and  $A_{222}$  can be evaluated at  $c_2 = 0$ . The function value at  $c_2 = 0$  is  $1/M_2$ ,  $A_{22}$  is related to the slope (first derivative), and  $A_{222}$  is related to the curvature (second derivative).

In most studies, besides the molecular mass only second osmotic virial coefficients  $A_{22}$  are reported. The literature data on  $A_{22}$  of aqueous PEG scatter considerably so that it is difficult to assess which source to rely on. A typical example is given in Figure 1. As PEG is always narrowly distributed, actual differences in the samples are not likely to explain the discrepancies in the literature data. Therefore, they have to be largely attributed to experimental problems and/or errors in the evaluation of the primary data. Despite the considerably scattering data, a marked increase in  $A_{22}$  with decreasing molecular mass  $M_2$  is commonly accepted in the literature.<sup>15,19,21</sup> For instance, Stumpf<sup>15</sup> reports a variation of  $A_{22}$  proportional to  $M_2^{-0.82}$ . Only few scattering data on the third osmotic virial coefficient  $A_{222}$  of aqueous PEG are available.<sup>15,21,30</sup>

One reason for the large discrepancies in the literature data on  $A_{22}$  and  $A_{222}$  of aqueous PEG is revealed by a simple discussion of eq 1. A reliable determination of  $A_{22}$  and  $A_{222}$  requires accurate experimental data from low to intermediate polymer concentration  $c_2$ , i.e., in a range where  $A_{22}$  and  $A_{222}$  influence the experimental results beyond the unavoidable scattering. However, quantifying "low" and "intermediate" is far from being easy, as it depends on the polymer-solvent system, the conditions, and the experimental technique. Usually no single experimental technique allows one to cover the entire concentration range in which data should be

**Table 1.** Experimental Data on the Mass- and Number-Averaged Molecular Mass of the PEGs Used in the Present Work

	$M_2^{(w)}$		$M_2^{(n)}$		$M_2^{(w)}/M_2^{(n)}$
	this work	supplier	this work	supplier	this work
PEG 6000	6950 <sup>a</sup>	c	6700 <sup>a</sup>	6340 <sup>b</sup>	1.04
PEG 23000	20500 <sup>a</sup>	22500 <sup>a</sup>	20000 <sup>a</sup>	21200 <sup>a</sup> 20300 <sup>b</sup>	1.03
PEG 35000	35700 <sup>a</sup>	c	34400 <sup>a</sup>	39000 <sup>b</sup>	1.04

<sup>a</sup> Gel permeation chromatography. <sup>b</sup> End group analysis. <sup>c</sup> Not available.

available. However, the majority of the previous studies of thermodynamic properties of aqueous PEG were carried out using only a single experimental method. Therefore, in the present work primary data for aqueous PEG measured with two different experimental methods, laser-light scattering and isopiestic investigations, were simultaneously evaluated. When used alone, neither of these two techniques is sufficient to reliably determine  $A_{22}$  and  $A_{222}$ , but, as the concentration ranges of laser-light scattering and the isopiestic method complement each other, the simultaneous evaluation of experimental data from both methods allows an accurate determination of the osmotic virial coefficients.

## Experimental Section

**Materials.** Aqueous solutions of three different PEGs, designated here as PEG 6000, PEG 23000, and PEG 35000, were studied in the present work. PEG 6000 and PEG 35000 were supplied by Hoechst, Frankfurt, Germany (lot numbers 664762 and E06373013), and PEG 23000 was supplied by Polymer Standard Service, Mainz, Germany (lot number peg230-mw22500). The PEGs contained less than 0.005 g g<sup>-1</sup> water.

All PEGs were characterized by gel-permeation chromatography (GPC). The eluent was water containing both sodium sulfate and sodium azide (0.007 and 0.002 g g<sup>-1</sup>, respectively). A constant flow rate of 1 cm<sup>3</sup> min<sup>-1</sup> was maintained by a HPLC pump (Spectra Physics, San Jose, CA, Type P 1000). The eluent was degassed in-line (degasser from ERMA, Tokyo, Japan, Type ERC-3512). About 100  $\mu$ L of the polymer solution ( $c_2 \approx 6$  mg cm<sup>-3</sup>) was injected in the eluent using a Rheodyne valve. Prior to injection, the sample was filtered with 0.45  $\mu$ m filters (Sartorius, Göttingen, Germany). Three separation columns (Polymer Standard Service, Mainz, Germany, Types HEMA-Bio 40, 100, and 1000) were mounted in-line. Detectors were a multiangle laser-light scattering photometer (Wyatt Technology, Santa Barbara, CA, Type DAWN F) and an interferometric refractometer (Wyatt Technology, Santa Barbara, CA, Type Optilab 903). The volume shift between these detectors was measured using a rectangular concentration profile. Details on the calibration of the detectors are given in Appendix B.

The results for the number-averaged molecular mass  $M_2^{(n)}$  and the mass-averaged molecular mass  $M_2^{(w)}$  determined in these GPC experiments are compared to supplier's data in Table 1. Relative deviations between the independent measurements range between 1.5 and 13%. The polydispersity ratio  $M_2^{(w)}/M_2^{(n)}$  of the PEGs is about 1.04, so that it does not have to be taken into account in the interpretation of the thermodynamic measurements. With laser-light scattering, numbers of  $M_2^{(w)}$  are determined; the isopiestic method and other methods with which the activity of the solvent is measured yield numbers for  $M_2^{(n)}$ . Also the averages for the virial coefficients obtained with these methods differ.<sup>5</sup> As these differences are small for PEG, generally no superscripts are used here with  $M_2$ ,  $A_{22}$ , or  $A_{222}$ .

**Preparation of Solutions.** For the preparation of the solutions, HPLC water of Merck, Darmstadt, Germany (purity better than 0.9995 g g<sup>-1</sup>), was used. About 30 g of a stock solution with  $c_2 \approx 0.05$  g cm<sup>-3</sup> was prepared using an analytical

balance with a resolution of 0.1 mg (Mettler, Giessen, Germany, type AE 240). Care was taken to dissolve all PEG by thoroughly stirring. Other samples were obtained from a dilution series.

**Densimetric Data.** For the conversion of polymer mass fractions  $\xi_2 = m_2/(m_1 + m_2)$  determined gravimetrically into concentrations  $c_2 = m_2/V$ , the specific density  $\rho^* = (m_1 + m_2)/V$  of the PEG solution has to be known:

$$c_2 = \rho^* \xi_2 \quad (2)$$

Several authors have measured the specific density of aqueous PEG solutions.<sup>9,38,39</sup> However, these literature data only cover PEG concentrations up to about 0.2 g cm<sup>-3</sup> at temperatures between 293 and 333 K. Therefore, in the present work complementary measurements were carried out which extend the temperature and concentration range (278 ≤  $T/K$  ≤ 333,  $c_2$  up to 0.6 g cm<sup>-3</sup>). The results are given in Appendix C together with a correlation which was also used for the conversion of  $\xi_2$  in  $c_2$  (cf. eq 2).

**Laser-Light Scattering.** The laser-light scattering photometer used for the thermodynamic studies of the present work was the same as in the GPC measurements. In both cases, it was applied in a flow mode, but in the thermodynamic experiments, only polymer solution (and no eluent) was pumped through the optical cell of the MALLS photometer at a low flow rate (about 0.5 cm<sup>3</sup> min<sup>-1</sup>) using a syringe pump (Infors, Basel, Switzerland, Type Predicor) with 5 cm<sup>3</sup> syringes. Filters (0.2 μm; Sartorius, Göttingen, Germany) were inserted in the line between the syringe and the optical flow cell of the MALLS photometer. The optical cell was thermostated by built-in Peltier elements. To ensure that the sample reached the cell temperature, the line leading to the cell was thermostated. The overall accuracy of the temperature measurement is about 0.2 K.

Derivations of the basic equation for the evaluation of laser-light scattering data are given in many textbooks (e.g., Elias,<sup>5</sup> and Tanford<sup>40</sup>). Following that derivation, one finds an expression relating data measured in the laser-light scattering experiment to the concentration dependence of the chemical potential of the solvent  $\mu_1$ :

$$\frac{Kc_2}{R_E} = - \frac{\rho_1}{RT} \frac{\partial \mu_1}{\partial c_2} \quad (3)$$

The terms on the left side of eq 3 are experimental quantities. The constant  $K$  is determined as described in Appendix B. The excess Rayleigh ratio  $R_E$  accounts primarily for the difference between the intensity of light scattered from the polymer solution to that scattered from the pure solvent. Equation 3 only holds when  $R_E$  does not depend on the angle  $\Theta$  under which the light is scattered. That requirement is fulfilled for small molecules, like the PEGs studied in the present work. Experimental results for  $R_E$  measured under different angles  $\Theta$  (here 16 angles between 22 and 158°) show no systematic dependence on  $\Theta$ . This also excludes the presence of large aggregates.

**Isopiestic Method.** Isopiestic data on concentrated PEG solutions ( $c_2$  between about 0.1 and 0.6 g cm<sup>-3</sup>) were taken from a recent study of Grossmann et al.<sup>35</sup> The isopiestic method is therefore only very briefly described here: An aqueous polymer solution (sample) is placed in a closed thermostated vessel together with an aqueous solution of another nonvolatile substance (reference, typically a salt), of which the water activity is known as a function of composition. In the vessel, mass transfer of water between the sample and the reference solution takes place through the vapor phase, until the activity of water in the sample is the same as that in the reference solution. The experiment is stopped when equilibrium is reached. From gravimetric analysis of the sample and reference solution before and after the experiment, the water activity in the equilibrated sample is determined.

## Experimental Data and Evaluation

**Laser-Light Scattering.** For each PEG, between six and eight samples with concentrations  $c_2$  between about

**Table 2. Results from the Evaluation of Laser-Light Scattering Data of Aqueous PEG Solutions Using  $A_{222} = 0$**

	$T$ (K)	$M_2$	$A_{22}$ (10 <sup>-3</sup> (mol cm <sup>3</sup> )/g <sup>2</sup> )
PEG 6000	278.2	14150	4.65
	298.2	7204	2.89
	313.2	9392	2.67
PEG 23000	298.2	23952	2.43
	313.2	27256	1.96
PEG 35000	278.2	40807	3.18
	298.2	34654	2.32
	313.2	38465	1.95

0.001 and 0.05 g cm<sup>-3</sup> were studied with laser-light scattering at 278, 298, and 313 K. The results are given in Tables 6–8 in Appendix D. The evaluation is based on eq 3. Using the osmotic virial equation 1 in which the activity of the solvent is normalized according to Raoult's law

$$\frac{\mu_1}{RT} = \frac{\mu_{1,\text{pure}}}{RT} + \ln a_1 \quad (4)$$

results in

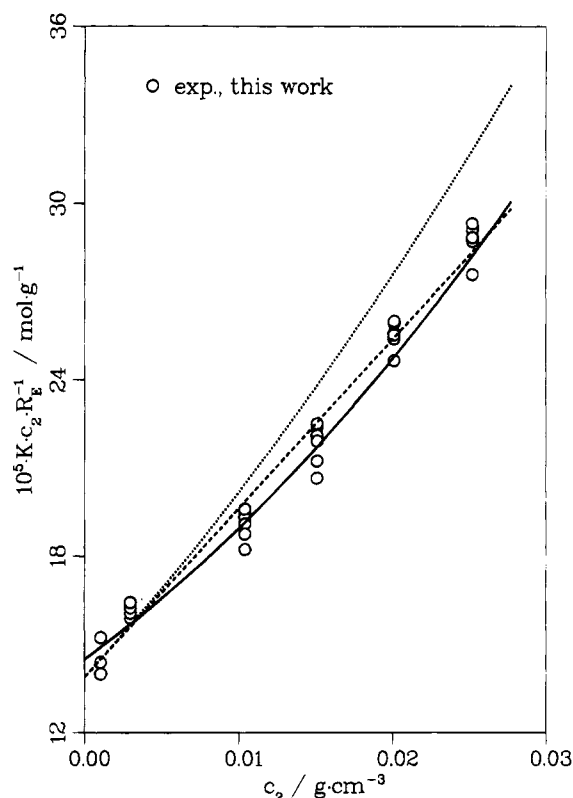
$$\frac{Kc_2}{R_E} = \frac{1}{M_2} + 2A_{22}c_2 + 3A_{222}c_2^2 + \dots \quad (5)$$

Equation 5 is commonly used for the evaluation of laser-light scattering data of small polymers. It is common practice (e.g., in commercial laser-light scattering software) to assume that, due to the low polymer concentrations, the contribution from the third osmotic virial coefficient can be neglected:

$$A_{222}c_2^2 \approx 0 \quad (6)$$

Therefore, in a first step,  $M_2$  and  $A_{22}$  were fitted to the laser-light scattering data neglecting higher osmotic virial coefficients. The results are given in Table 2. A comparison of the results obtained at 298 K with results from other methods (cf. Table 1 for  $M_2$  and Figure 1 for  $A_{22}$ ) shows reasonable agreement. In some cases, the numbers obtained for  $M_2$  at other temperatures seem to be somewhat too high (for a discussion, see next section).

**Influence of  $A_{222}$  on Laser-Light Scattering Data.** The example in Figure 2 shows that, using the results given in Table 2, laser-light scattering data are generally correlated well. It is furthermore possible to accurately correlate isopiestic data for aqueous PEG up to polymer concentrations of about 0.6 g cm<sup>-3</sup> using the results for  $M_2$  and  $A_{22}$  given in Table 2 when additionally the third osmotic virial coefficient  $A_{222}$  is fitted to the isopiestic data. However, this procedure introduces an inconsistency regarding the evaluation of the laser-light scattering data. The correlation with nonzero  $A_{222}$  does not describe the laser-light scattering data well (cf. Figure 2). More importantly, the correlation with  $A_{222}$  determined from the isopiestic data clearly shows that the influence of the term  $A_{222}c_2^2$  is important in the concentration range where laser-light scattering data are taken. Hence, it must be concluded that it is wrong to use eq 6 in the evaluation of the laser-light scattering data. This holds for all PEGs and temperatures studied in the present work. The easiest way out of this problem would be to fit both  $A_{22}$  and  $A_{222}$  to laser-light scattering data. However, due to the scattering of the primary data, this generally does not yield unambiguous



**Figure 2.** Correlation of laser-light scattering data of aqueous PEG 6000 at 298 K with different methods: (---)  $M_2$  and  $A_{22}$  from laser-light scattering alone ( $A_{222} = 0$ , method I); (···)  $M_2$  and  $A_{22}$  from method I,  $A_{222}$  from isopiestic data; (—) simultaneous correlation of laser-light scattering and isopiestic data.

results. Therefore, other ways to reliably determine both  $A_{22}$  and  $A_{222}$  must be looked for.

**Simultaneous Evaluation of Laser-Light Scattering and Isopiestic Data.** The isopiestic method provides a simple but reliable means to measure the activity of water in concentrated PEG solutions. Experimental data on PEG 6000 and PEG 35000 are available for temperatures between 278 and 333 K at polymer concentrations  $c_2$  between about 0.1 and 0.6 g cm<sup>-3</sup> (Grossmann et al.<sup>35</sup>). Those results were used for a simultaneous evaluation with the laser-light scattering data from the present work. For each polymer and temperature, the molecular mass and the second and third osmotic virial coefficients were determined from a simultaneous least squares fit of experimental data from both sources. The objective function of that fit was

$$\text{SSQ} = \frac{1}{N_{\text{LS}}} \sum_i \left( \frac{Y_{\text{LS}i}^{\text{calc}} - Y_{\text{LS}i}^{\text{exp}}}{Y_{\text{LS}i}^{\text{exp}}} \right)^2 + \frac{1}{N_{\text{ISO}}} \sum_i \left( \frac{Y_{\text{ISO}i}^{\text{calc}} - Y_{\text{ISO}i}^{\text{exp}}}{Y_{\text{ISO}i}^{\text{exp}}} \right)^2 \quad (7)$$

$$Y_{\text{LS}i} = \frac{Kc_{2i}}{R_{\text{E}i}} \quad (8)$$

$$Y_{\text{ISO}i} = \ln a_{1i} \quad (9)$$

To cover all polymers and temperatures studied with laser-light scattering, the isopiestic data had to be interpolated. For that interpolation, the model of Grossmann et al.<sup>35</sup> was used. The uncertainty intro-

**Table 3.** Results from the Simultaneous Evaluation of Laser-Light Scattering and Isopiestic Data of Aqueous PEG Solutions

	$T$ (K)	$M_2$	$A_{22}$ ( $10^{-3}(\text{mol cm}^3/\text{g}^2)$ )	$A_{222}$ ( $10^{-2}(\text{mol cm}^6/\text{g}^3)$ )
PEG 6000	278.2	9116	2.48	2.79
	298.2	6902	1.90	2.18
	313.2	7298	1.24	1.61
PEG 23000	298.2	20729	1.67	1.96
	313.2	18711	0.97	1.59
PEG 35000	278.2	37055	2.57	2.63
	298.2	32483	1.80	2.24
	313.2	35020	1.44	1.45

duced by that procedure is smaller than the experimental error of the isopiestic measurements.

**Membrane Osmometry.** Membrane osmometry provides a means to collect thermodynamic data on aqueous PEG solutions at low polymer concentrations and could—at least in principle—substitute laser-light scattering studies. Therefore, also some measurements with membrane osmometry were carried out in the present work. They are described and discussed in Appendix E.

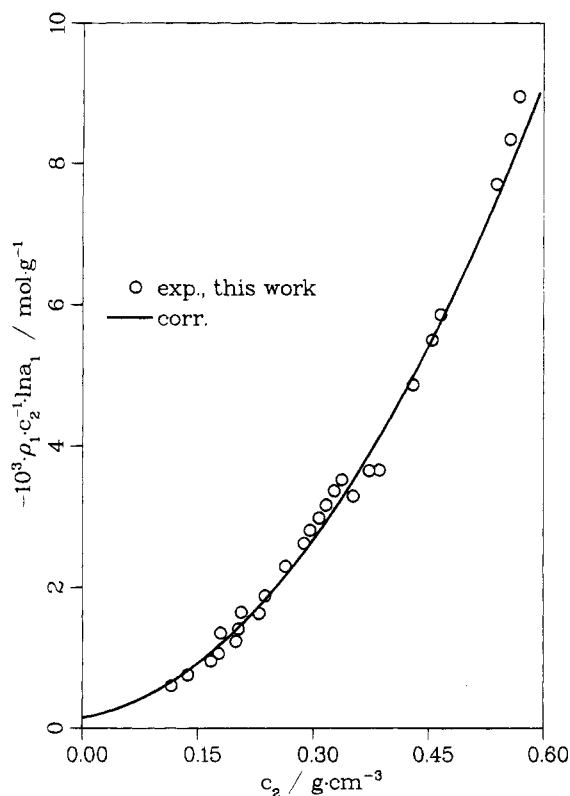
### Results from the Simultaneous Evaluation of Laser-Light Scattering and Isopiestic Data

The results for the molecular mass and the osmotic virial coefficients of PEG 6000, PEG 23000, and PEG 35000 obtained in the present work from the simultaneous correlation of laser-light scattering and isopiestic data are given in Table 3. From the example in Figure 2 it can be seen that the simultaneous correlation yields a good fit of laser-light scattering data. The result of the simultaneous correlation is more satisfactory than that from the conventional evaluation (laser-light scattering data alone,  $A_{222} = 0$ ).

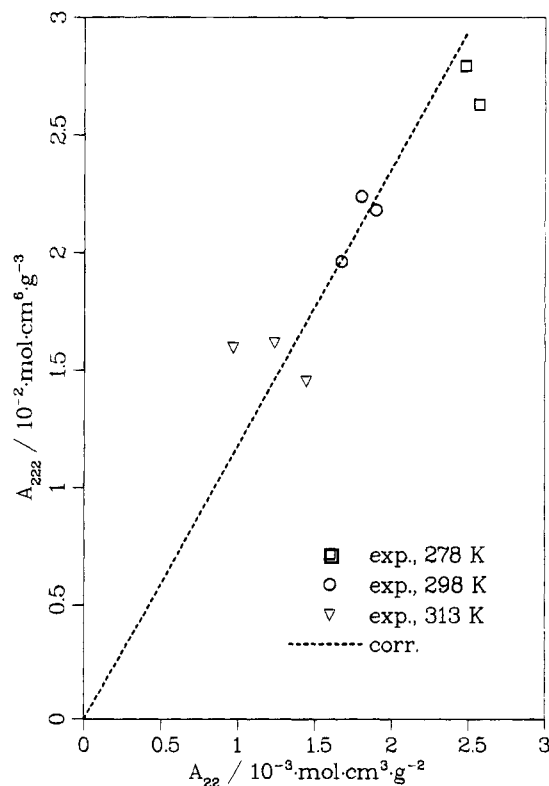
For all correlations, the function value at  $c_2 = 0$  is  $1/M_2$ . Figure 2 therefore also indicates that the numbers for  $M_2$  obtained from the simultaneous correlation appear to be more reasonable than those obtained with the conventional evaluation. The numbers for  $M_2$  obtained at 298 K also compare favorably with those determined with independent methods (cf. Table 1). As for the conventional evaluation (Table 2), in some cases  $M_2$  obtained at other temperatures deviate significantly from those obtained at 298 K. It should, however, be noted that  $A_{22}$  and  $A_{222}$  from the experiments, where the result for  $M_2$  is conspicuous, do not show any extraordinary trend.

Figure 3 shows isopiestic data for PEG 6000 at 293 K together with results of the simultaneous correlation of these data with the laser-light scattering data. The agreement is very satisfactory. (The small difference in the temperature between the laser-light scattering and the isopiestic data set was accounted for but is not important in the resolution used in Figure 3.)

Probably the most important result from the present work is that neither  $A_{22}$  nor  $A_{222}$  determined from a simultaneous fit of laser-light scattering and isopiestic data shows a systematic influence of the molecular mass of PEG (cf. Table 3). This can also be seen from Figure 4 in which  $A_{222}$  are plotted as a function of  $A_{22}$ . The data can be correlated well by a straight line. That straight line hits the origin ( $A_{22} = A_{222} = 0$ ) within the experimental uncertainty. The linear relation between  $A_{22}$  and  $A_{222}$  indicates that both properties depend in the same simple way on temperature. Therefore, for



**Figure 3.** Comparison of isopiestic data for PEG 6000 with the result from a simultaneous correlation of those data with laser-light scattering data.



**Figure 4.** Results from the simultaneous evaluation of laser-light scattering and isopiestic data for different PEGs and temperatures.

correlating both  $A_{22}(T)$  and  $A_{222}(T)$

$$A_j = \alpha_j + \frac{\beta_j}{T} \quad j = 22 \text{ or } 222 \quad (10)$$

was chosen. Figure 4 furthermore indicates that both  $A_{22}$  and  $A_{222}$  of aqueous PEG are zero at the same temperature, i.e., the  $\Theta$ -temperature ( $T_\Theta$ ). That finding allows us to eliminate one of the four parameters of the correlations for  $A_{22}$  and  $A_{222}$  according to eq 10, finally resulting in

$$\frac{A_{22}}{\text{mol cm}^3 \text{ g}^{-2}} = 2.49 \left( \frac{1}{T/K} - \frac{1}{T_\Theta/K} \right) \quad (11)$$

$$\frac{A_{222}}{\text{mol cm}^6 \text{ g}^{-3}} = 29.3 \left( \frac{1}{T/K} - \frac{1}{T_\Theta/K} \right) \quad (12)$$

with

$$T_\Theta = 375.7 \text{ K}$$

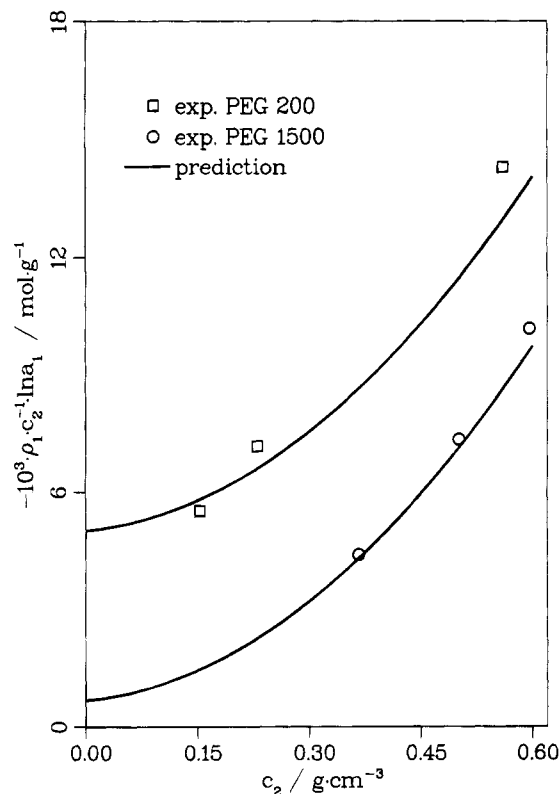
Virtually the same result for  $T_\Theta$  (375.2 K) was obtained earlier by Polik and Burchard<sup>33</sup> from laser-light scattering studies. The result for  $T_\Theta$  is also in reasonable agreement with data obtained from cloud point (liquid-liquid equilibrium) measurements of Boucher and Hines<sup>41</sup> ( $T_\Theta = 369 \pm 3 \text{ K}$ ).

### Comparison with Literature Data

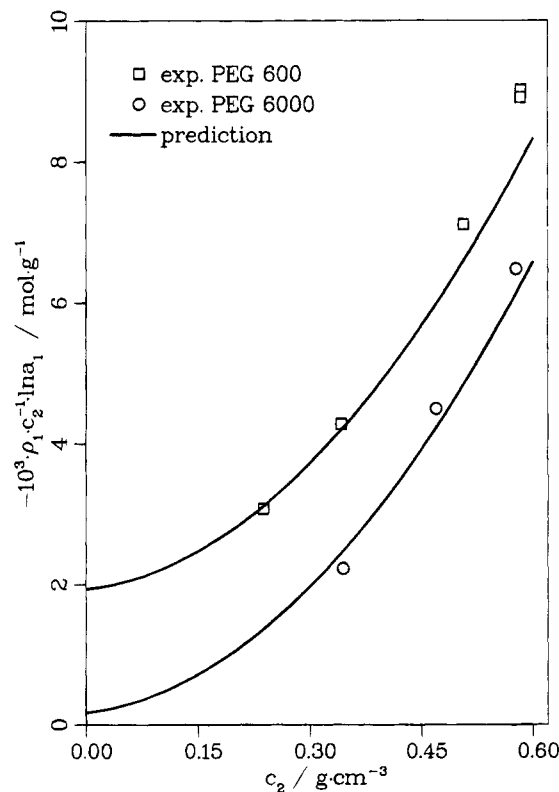
In this section, results from the simultaneous correlation of the laser-light scattering and isopiestic data are compared to literature data on thermodynamic properties of aqueous PEG. The osmotic virial coefficients  $A_{22}$  and  $A_{222}$  were taken from the correlations given in eqs 11 and 12; for the molecular mass  $M_2$  the numbers reported in the literature were used, so that the calculated results for the water activity are strict predictions. As the osmotic virial expansion truncated after the third term cannot give reliable results for highly concentrated solutions, no data for polymer concentrations above about  $0.6 \text{ g cm}^{-3}$  were included in the comparison.

The smallest PEG for which data were included in the data base used to determine  $A_{22}$  and  $A_{222}$  was PEG 6000. It is therefore interesting to compare the results from the correlation to experimental results for PEG 200. Figure 5 shows that, with osmotic virial coefficients which are independent of molecular mass, the prediction of the thermodynamic properties of PEG 200 is very satisfactory. This unexpected result does not change essentially, if the parameters of the osmotic virial equation are determined using data on PEG 35000 alone. The success of predicting activities of PEG 200 from data of a PEG with a molecular mass more than 2 orders of magnitude larger impressively demonstrates the benefits which can be drawn from the simultaneous evaluation of laser-light scattering and isopiestic data. It stands in sharp contrast to previous attempts to correlate thermodynamic data of aqueous PEG solutions, in which  $A_{22}$  for PEG 200 was reported to be several times higher than that of large PEGs (cf. Figure 1).

Further examples in which the osmotic virial equation with  $A_{22}$  and  $A_{222}$  independent of molecular mass are compared to experimental data from different sources are shown in Figures 6 and 7. At concentrations up to about  $0.6 \text{ g cm}^{-3}$ , the correlation represents reliable experimental data (which are available for PEG 200 to PEG 40000 at temperatures between 278 and 333 K) generally well. Regarding discrepancies that are observed at the highest temperatures for the smallest PEGs, it should be considered that the data base used

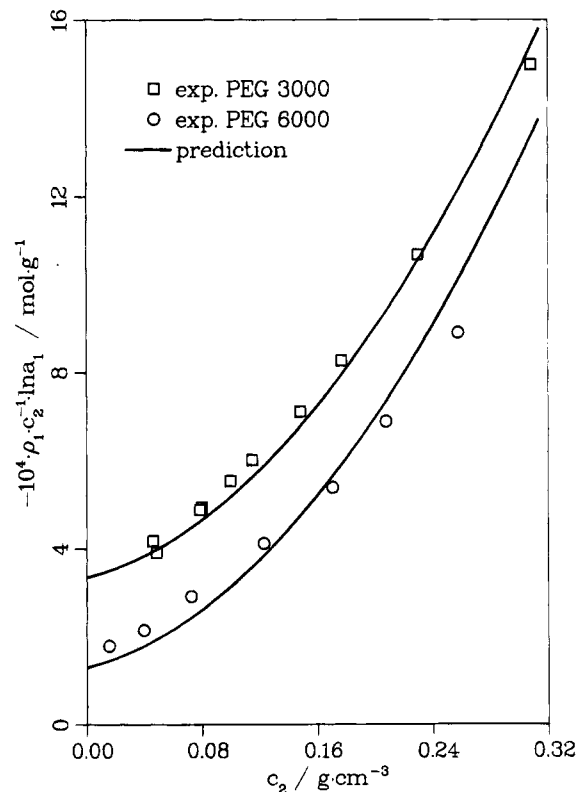


**Figure 5.** Comparison of isopiestic data<sup>36</sup> of aqueous PEG 200 and PEG 1500 at 293 K with predictions (original osmotic virial equation).



**Figure 6.** Comparison of isopiestic data<sup>36</sup> of aqueous PEG 600 and PEG 6000 at 313 K with predictions (original osmotic virial equation).

to determine the parameters of the correlation was narrow, so that a very simple way of describing the temperature dependence of the osmotic virial coefficients had to be chosen.



**Figure 7.** Comparison of vapor-pressure osmometric data<sup>21</sup> of aqueous PEG 3000 and PEG 6000 at 333 K with predictions (original osmotic virial equation).

### Modified Osmotic Virial Equation

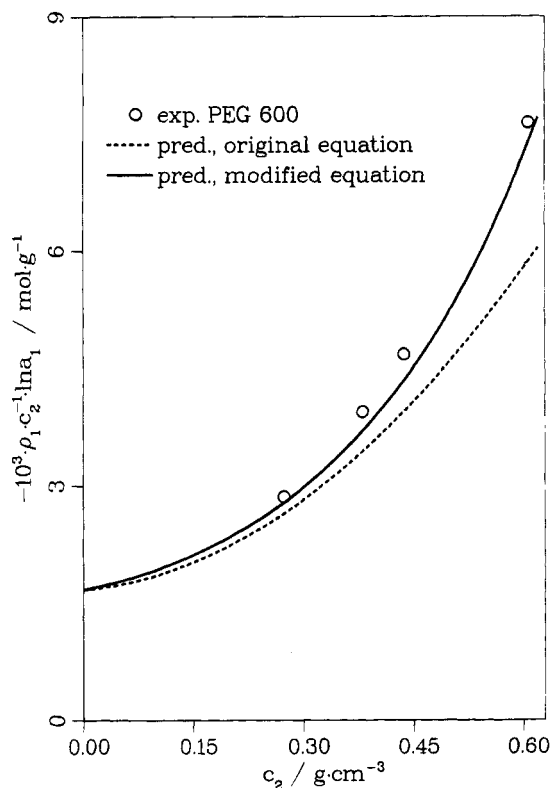
In the present work also a modified form of the osmotic virial equation was developed. The result of the derivation given in Appendix F is

$$\ln a_1 = -M_1 \left( \ln \left( \frac{\varrho^*}{\varrho^* - c_2} \right) \left( \frac{1}{M_2} + 2A_{22}^* \varrho^* + 3A_{222}^* \varrho^{*2} + \dots \right) - c_2 \left( 2A_{22}^* + 3A_{222}^* \left( \varrho^* + \frac{c_2}{2} \right) + \dots \right) + \dots \right) \quad (13)$$

where  $M_1$  and  $M_2$  stand for the molecular mass of the solvent and solute (polymer), respectively,  $\varrho^*$  is a specific density (usual choice:  $\varrho^* = \varrho_{\text{pure},1}^*$ ), and  $A_{22}^*$  and  $A_{222}^*$  are the osmotic virial coefficients of the modified equation.

The parameters for the modified equation were determined using essentially the same procedure as for the original equation. In particular, it was again found that  $A_{22}^*$  and  $A_{222}^*$  do not depend on the molecular mass of the solvent when they are simultaneously fitted to laser-light scattering and isopiestic data and that extrapolations over the entire range of PEG molecular mass from about 35000 down to 200 are successful. This shows that this important finding is not due to a fortuitous choice of the thermodynamic model but rather a result of the appropriate choice of the experimental data, which are used to determine the model parameters.

The parameters obtained in the present work to describe the thermodynamic properties of aqueous PEG with the modified osmotic virial equation 13 are



**Figure 8.** Comparison of isopiestic data<sup>36</sup> of aqueous PEG 600 at 333 K with predictions from the original and the modified osmotic virial equation.

$$\frac{A_{22}^*}{\text{mol cm}^3 \text{ g}^{-2}} = 3.46 \left( \frac{1}{T/K} - \frac{1}{T_\Theta/K} \right) \quad (14)$$

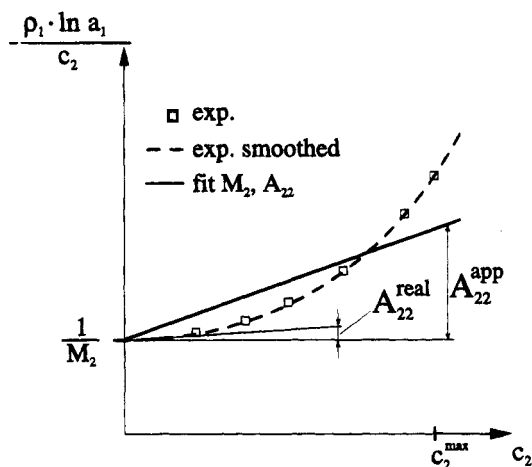
$$\frac{A_{222}^*}{\text{mol cm}^6 \text{ g}^{-3}} = 16.93 \left( \frac{1}{T/K} - \frac{1}{T_\Theta/K} \right) \quad (15)$$

$$T_\Theta = 370.1 \text{ K}$$

Using these parameters, the results from eq 13 are similar to those from the original osmotic virial equation when the polymer concentration is below about 0.4 g cm<sup>-3</sup>. At higher concentrations, in many cases the modified osmotic virial equation gives a somewhat better agreement with experimental results than the original one, especially at high temperatures (cf. Figure 8). However, the uncertainty of the experimental data makes it difficult to decide whether this is a major improvement. The modified osmotic virial equation will therefore not be discussed in more detail in the present paper, but as that equation is as simple to handle as the original one, it can easily be tested with other systems.

#### Discussion of Discrepancies in Literature Data for $A_{22}$ and $A_{222}$

There are important discrepancies between the results for the osmotic virial coefficients found in the present work and those reported in the literature. For instance, the data reported in the literature for  $A_{22}$  of aqueous PEG at about 298 K range between about  $3 \times 10^{-3} \text{ mol cm}^3 \text{ g}^{-2}$  for PEG 6000 and  $10^{-2} \text{ mol cm}^3 \text{ g}^{-2}$  for PEG 200 (cf. Figure 1), whereas the number from the present investigation is  $A_{22} = 1.7 \times 10^{-3} \text{ mol cm}^3 \text{ g}^{-2}$  for all PEGs. This shows that it is worthwhile to discuss possible sources of error in the determination



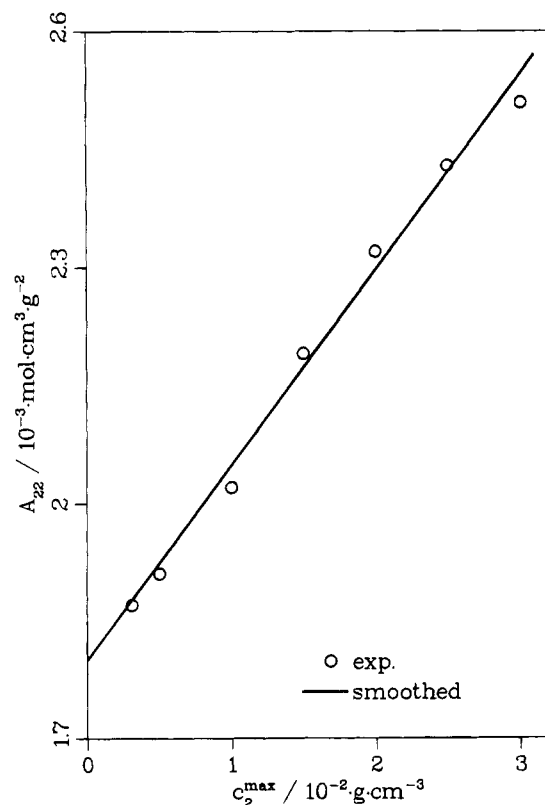
**Figure 9.** Error in the conventional evaluation of thermodynamic data of diluted PEG solutions. Due to the wrong assumption  $A_{222} = 0$ , the resulting number for  $A_{22}$  is too high.

of osmotic virial coefficients from thermodynamic data of polymer solutions. For this purpose, reduced solvent activity  $(\rho_1 \ln a_1)/c_2$  as a function of the polymer concentration  $c_2$  is discussed.

If only thermodynamic data for concentrated solutions but not for dilute solutions are used, the extrapolation to  $c_2 = 0$  is uncertain and numbers obtained for  $M_2$ ,  $A_{22}$ , and  $A_{222}$  are likely to be wrong. For instance, when the isopiestic data for PEG 6000 at 293 K of Grossmann et al.<sup>35</sup> are used (lowest  $c_2 = 0.12 \text{ g cm}^{-3}$ ) and  $M_2$ ,  $A_{22}$ , and  $A_{222}$  are fitted to those data, the resulting  $M_2$  is above  $10^6$ , which simply shows that the extrapolation to  $c_2 = 0$  completely fails. Therefore, several authors have taken data for  $M_2$ , which were determined with independent methods like gel-permeation chromatography, and fitted only  $A_{22}$  and  $A_{222}$  to thermodynamic data. There are two problems with that procedure: If the intercept  $1/M_2$  with the y-axis is fixed but does not fit together with the extrapolation of the thermodynamic data, there is little chance that the numbers for  $A_{22}$  and  $A_{222}$  will be reasonable. But even if that is excluded, a second, more severe problem remains: Without data in the dilute region, it is difficult to separate contributions from  $A_{22}$  and  $A_{222}$  and there are different sets of parameters giving similar fits. The solution found in the present work from the simultaneous evaluation of laser-light scattering and isopiestic data is simply hidden behind a multitude of other possibilities.

If only data on dilute solutions are used, the curvature in the plot of the reduced solvent activity  $(\rho_1 \ln a_1)/c_2$  over  $c_2$  is not easily recognized, especially as these data often scatter considerably. Because of this, it is common to use a linear fit ( $A_{222} = 0$ ). But fitting data showing an upward curvature linearly leads to a slope at  $c_2 = 0$  that is too steep. The second virial coefficient  $A_{22}$  is overestimated (cf. Figure 9). This explains why  $A_{22}$  determined in the present work by the simultaneous evaluation of laser-light scattering and isopiestic data are distinctly lower than those reported in the literature.

If that explanation for the overestimation of  $A_{22}$  by assuming  $A_{222} = 0$  holds, the numbers for  $A_{22}$  should depend on the concentration range of the data used for the fit. The expected tendency is: The higher the maximal concentration  $c_2^{\text{max}}$ , the higher the resulting number of  $A_{22}$ . To check this hypothesis, different sets of laser-light scattering data for PEG 35000 at 298 K were evaluated using  $A_{222} = 0$ . Starting from the data set given in Table 8 in Appendix D ( $c_2^{\text{max}} = 0.03 \text{ g cm}^{-3}$ ),



**Figure 10.** Second osmotic virial coefficients of PEG 35000 at 298 K determined using different sets of laser-light scattering data. Starting from a complete set ( $c_2^{\max} = 0.03 \text{ g cm}^{-3}$ ), step by step the data point with the highest  $c_2$  is removed.

step by step the data point with the highest polymer concentration was eliminated until  $c_2^{\max}$  was only  $0.003 \text{ g cm}^{-3}$ . The results for  $A_{22}$  obtained from these data sets are given in Figure 10. Not only is the expected tendency observed, but from an extrapolation to  $c_2 = 0$  a number for  $A_{22}$  is found ( $1.8 \times 10^{-3} \text{ mol cm}^3 \text{ g}^{-2}$ ) which agrees favorably with the result from the simultaneous evaluation of laser-light scattering and isopiestic data ( $A_{22} = 1.7 \times 10^{-3} \text{ mol cm}^3 \text{ g}^{-2}$ ). This shows that  $A_{22}$  for aqueous PEG which are determined conventionally (using  $A_{222} = 0$ ) depend on the concentration range of the data used for the fit. This finding explains at least some of the scattering of the literature data on  $A_{22}$  of PEG (cf. Figure 1).

It can be assumed that PEG is not the only polymer where the influence of  $A_{222}$  in the dilute region is important, and it must be concluded that generally, even at low polymer concentration, the assumption  $A_{222} = 0$  should not be used for the evaluation of thermodynamic data of polymer solutions without verification.

It must be emphasized that none of the above-mentioned problems would occur if the primary data were free of scattering. Any curvature could then easily be recognized in the plot of the reduced solvent activity ( $q_1 \ln a_1/c_2$ ) over  $c_2$ , and it would be possible either to determine  $A_{22}$  and  $A_{222}$  from a simultaneous fit or to use an extrapolation technique like that shown in Figure 10. For instance, the laser-light scattering data for PEG 35000 taken in the present work at 298 K show only little scattering and can successfully be evaluated as shown in Figure 10. If, however, the same procedure is applied to the data taken at the same temperature for PEG 6000, which scatter considerably more (cf. Figure 2), no useful information is obtained. Unfortu-

nately, experience shows that in many cases the scattering of the thermodynamic data for diluted aqueous polymer solutions is prohibitively large for a reliable determination of both  $A_{22}$  and  $A_{222}$ , so that other ways must be taken.

Combining thermodynamic data on dilute and concentrated polymer solutions is obviously a good solution. One of the major advantages of that method is that even with scattering primary data reliable information on  $A_{22}$  and  $A_{222}$  can be obtained. In the case of PEG, using that method was the key to obtaining a simple but nevertheless accurate and predictive correlation.

## Conclusions

An improved method for the determination of thermodynamic properties of aqueous polymer solutions is presented. It consists of a simultaneous evaluation of data for dilute and concentrated solutions, e.g., measured with laser-light scattering and the isopiestic method. The simultaneous evaluation of laser-light scattering and isopiestic data has considerable advantages over the common procedure to separately evaluate the corresponding data sets taken with different experimental methods. Erroneous assumptions, like neglecting the influence of the third osmotic virial coefficient  $A_{222}$  in the evaluation of the laser-light scattering data, are avoided. Furthermore, an unambiguous separation of contributions from the second ( $A_{22}$ ) and third ( $A_{222}$ ) osmotic virial coefficients is achieved. Using the new method, it is found that neither  $A_{22}$  nor  $A_{222}$  depends on the molecular mass of the PEG. For instance,  $A_{22}$  and  $A_{222}$  determined from data for PEG 35000 can be used to reliably predict the thermodynamic properties of PEG 200. Such predictions are far beyond the scope of results of the conventional evaluation of thermodynamic data of aqueous PEG, which usually result in  $A_{22}$  and  $A_{222}$  that depend on molecular mass.

A very simple correlation for the temperature dependence of the osmotic virial coefficients is reported in which only three parameters are used to describe both  $A_{22}(T)$  and  $A_{222}(T)$  for all PEGs. With osmotic virial coefficients from that correlation, thermodynamic data on aqueous PEG solutions are well described in the whole range where reliable data exist (PEG 200 to PEG 40000,  $278 \leq T/\text{K} \leq 333$ ) at concentrations up to about  $0.6 \text{ g cm}^{-3}$ .

## Appendix A: Survey of Literature Data on Thermodynamic Properties of Aqueous PEG

Table 4 gives a survey of literature data on the thermodynamic properties of aqueous PEG. It is comprehensive for direct measurements of the activity of water (i.e., by vapor-pressure measurements, osmometry, and the isopiestic method) as well as for laser-light scattering and calorimetric studies. Furthermore, two sources reporting work on the properties of solutions of small amounts of water in liquid PEG were included as well as two sedimentation studies which report numbers for  $A_{22}$ .

At elevated temperatures, the system PEG–water (PEO–water) shows an interesting phase behavior with a closed liquid–liquid immiscibility region. This phenomenon has been studied by Boucher and Hines<sup>41</sup> and Saeki et al.<sup>48</sup> (not quoted in Table 4).

## Appendix B: Calibration of the MALLS Photometer and the Refractometer

**MALLS Photometer.** To calculate Rayleigh ratios, the detectors of the MALLS photometer have to be



Table 4. Survey of Experimental Data on Thermodynamic Properties of Aqueous PEG Solutions

method	PEG	T (K)	source
vapor-pressure	280, 410, 550	293, 303 <sup>a</sup>	Elworthy and Florence <sup>13</sup>
	400	298 <sup>a</sup>	Medved et al. <sup>14</sup>
	200, 3000	293 <sup>a</sup>	Stumpf <sup>15</sup>
differential vapor-pressure	3350, 8000	298 <sup>a</sup>	Haynes et al. <sup>16</sup>
	340, 650, 1460, 4150	298, 308 <sup>a</sup>	Lakhanpal et al. <sup>17</sup>
	300, 3000, 5000	303, 323, 328, 333, 338 <sup>a</sup>	Malcolm and Rowlinson <sup>18</sup>
vapor-pressure osmometry	60, 100, 150, 200, 300, 400, 1000	298	Elias and Lys <sup>19</sup>
	4000	298 <sup>a</sup>	Franks <sup>20</sup>
	200, 600, 1550, 3000, 6000	293, 313, 333 <sup>a</sup>	Gaube et al. <sup>21</sup>
	20000	293	Lagerwerff et al. <sup>22</sup>
	200, 1000, 1500, 4000, 20000	298	Lawlor <sup>23</sup>
	6000	288, 298, 308, 318, 328, 338	Michel and Kaufmann <sup>24</sup>
	20000	293	Painter <sup>25</sup>
	600, 1000, 1500, 3000, 8000	308, 318, 343	Rogers and Tam <sup>26</sup>
	200, 600, 1550, 3000, 6000	293, 313, 333, 343 <sup>a</sup>	Stumpf <sup>15</sup>
	6000	298	Zur <sup>27</sup>
	1540, 4000, 6000	300 <sup>a</sup>	Heyer et al. <sup>28</sup>
	23200, 39300, 88500	298 <sup>a</sup>	Schulz <sup>29</sup>
membrane osmometry	43500	298 <sup>a</sup>	Vink <sup>30</sup>
	6000	298	Alexandrowicz <sup>31</sup>
	3350, 8000	298	King et al. <sup>32</sup>
light scattering	20000	293–363 <sup>b</sup>	Polik and Burchard <sup>33</sup>
	1550, 3000	293 <sup>a</sup>	Stumpf <sup>15</sup>
	200, 400, 1000, 1500, 3000, 6000, 12000, 20000	298	Adamcová <sup>34</sup>
isopiestic method	400, 1000, 6000, 35000	293, 333 <sup>a</sup>	Grossmann et al. <sup>35</sup>
	200, 600, 1500, 6000	293, 313, 333 <sup>a</sup>	Herskowitz and Gottlieb <sup>36</sup>
	6000	298	McClendon <sup>37</sup>
gas-liquid chromatography	400, 600, 1000, 1500, 7500	323–413 <sup>c,d</sup>	Bestani and Shing <sup>42</sup>
	1000, 20000	343 <sup>d</sup>	Courval and Gray <sup>43</sup>
	6000, 20000	301	Edmond and Ogston <sup>44</sup>
sedimentation	6000, 10000, 37000	298	Elias and Lys <sup>19</sup>
	6000	298	Nichol et al. <sup>45</sup>
	400	278, 298, 317 <sup>a</sup>	Andersson and Olofsson <sup>46</sup>
calorimetry	400, 1000, 6000, 35000	298, 333 <sup>a</sup>	Grossmann et al. <sup>35</sup>
	300, 3000, 5000	353 <sup>a</sup>	Malcolm and Rowlinson <sup>18</sup>
	14000	298, 313	Nakayama <sup>47</sup>

<sup>a</sup> Numerical primary data available. <sup>b</sup> Eight temperatures. <sup>c</sup> Sixteen temperatures. <sup>d</sup> Limiting activity coefficient of water in PEG.

calibrated. An absolute calibration is only needed for one detector ( $\Theta = 90^\circ$ ). For the absolute calibration, toluene (Merck, Darmstadt, Germany, purity better than  $0.998 \text{ g g}^{-1}$ ) was used. It was filtered through  $0.02 \mu\text{m}$  filters (Anotop, Merck, Darmstadt, Germany). The Rayleigh ratio of toluene was taken from Kaye and McDaniel<sup>49</sup> ( $1.406 \times 10^{-5} \text{ cm}^{-1}$ ,  $296.2 \text{ K}$ ,  $\lambda = 633 \text{ nm}$ ). The other detectors were normalized with reference to the detector at  $\Theta = 90^\circ$ , using dextran samples, of which the radius of gyration was known (standards from Polymer Standard Service, Mainz, Germany). It was proved that this normalization is correct by measuring small PEGs, which scatter isotropically. The absolute calibration carried out at  $296 \text{ K}$  was used for all temperatures. The normalization was checked for each temperature showing no significant shift.

The optical constant  $K$  is

$$K = \frac{4\pi^2 n_1^2 \left( \frac{\partial n}{\partial c_2} \right)^2}{N_A \lambda^4} \quad (16)$$

where  $n_1$  is the refractive index of the pure solvent, which was taken from Riddick et al.<sup>50</sup>  $N_A$  is Avogadro's number, and  $\lambda$  is the laser wavelength ( $\lambda = 633 \text{ nm}$ ). The refractive index increment  $\partial n / \partial c_2$  of PEG was determined with the differential refractometer.

**Differential Refractometer.** The differential refractometer was calibrated at  $293 \text{ K}$  with aqueous solutions of sodium chloride using the refractive index increment reported by Huglin<sup>51</sup> ( $0.177 \text{ cm}^3 \text{ g}^{-1}$ ). To check the calibration, aqueous solutions of potassium

chloride were measured at  $293 \text{ K}$ . The resulting  $\partial n / \partial c_2$  of  $0.1368 \text{ cm}^3 \text{ g}^{-1}$  agrees well with the number reported by Huglin<sup>51</sup> ( $0.137 \text{ cm}^3 \text{ g}^{-1}$ ). The salts were purchased from Merck, Darmstadt, Germany (purity better than  $0.995 \text{ g g}^{-1}$ ). Using that calibration, the refractive index increments of PEG 6000 and PEG 35000 were determined at  $293 \text{ K}$ . The result ( $0.134 \text{ cm}^3 \text{ g}^{-1}$ ) is identical for both polymers within the experimental uncertainty. It agrees favorably with the number reported by Polik and Burchard<sup>33</sup> ( $0.1345 \text{ cm}^3 \text{ g}^{-1}$  at  $293 \text{ K}$ ). Therefore, for the evaluation of the experiments at  $278$  and  $313 \text{ K}$ , the results of Polik and Burchard<sup>33</sup> for those temperatures were used.

### Appendix C: Densimetric Data

The specific density of aqueous solutions of PEG 6000 and PEG 35000 was measured with a vibrating tube densimeter (Paar, Graz, Austria, Type DMA 60) at  $278$ ,  $293$ ,  $313$ , and  $333 \text{ K}$  at polymer concentrations up to  $0.6 \text{ g cm}^{-3}$ . The experimental results are given in Table 5. At each temperature, the densimeter was calibrated with bidistilled water (University of Kaiserslautern, purity better than  $0.999 \text{ g g}^{-1}$ ) and ethylene glycol (Riedel de Haen, Seelze, Germany, purity better than  $0.995 \text{ g g}^{-1}$ ). The main experimental difficulty arises from the high viscosity of the PEG solutions, especially for PEG 35000. The accuracy of the density data is estimated to be better than  $2 \times 10^{-4} \text{ g cm}^{-3}$ . The accuracy of the temperature measurement is better than  $0.5 \text{ K}$ . In agreement with the literature (e.g., Cesi et al.<sup>39</sup>), it is found that, within the experimental uncertainty, there are no differences in the specific density of the different PEGs. For each temperature the

**Table 5. Specific Density of Aqueous PEG Solutions**

	$\xi$ (g g <sup>-1</sup> )	$\rho^*$ (g cm <sup>-3</sup> )			
		278.15 K	293.15 K	313.15 K	333.15 K
PEG 6000	0.0	1.0	0.9982	0.9922	0.9832
	0.0500	1.0090	1.0066	1.0009	0.9910
	0.1004	1.0185	1.0153	1.0088	0.9984
	0.2005	1.0381	1.0331	1.0252	1.0139
	0.3003	1.0586	1.0521	1.0422	1.0307
	0.3974	1.0797	1.0709	1.0590	1.0453
	0.4965	1.0993	1.0893	1.0755	1.0608
	0.5996			1.0898	1.0733
PEG 35000	0.0493	1.0091	1.0067	1.0010	0.9910
	0.1001	1.0187	1.0155	1.0089	0.9987
	0.2021	1.0390	1.0346	1.0260	1.0148
	0.3005	1.0584	1.0523	1.0432	1.0312
	0.3995	1.0797	1.0720	1.0585	1.0444
	0.5035			1.0777	1.0645
	0.5957				1.0747

experimental data can be correlated within their experimental uncertainty using

$$\rho^* = \rho_1^* + k\xi_2 \quad (17)$$

The numbers for the specific density of pure water  $\rho_1^*$  were taken from VDI Wärmeatlas.<sup>52</sup> The results for  $k/g\text{ cm}^{-3}$  are 0.1982 (278 K), 0.1803 (293 K), 0.1656 (313 K), and 0.1539 (333 K).

The densimetric data from the present work agree well with literature data in the concentration range where literature data are available ( $c_2$  below  $0.2\text{ g cm}^{-3}$ ). At higher concentrations, the correlation proposed by Cesi et al.<sup>39</sup> deviates systematically from the experimental data from the present investigation. However, those differences are always below 1%.

#### Appendix D: Laser-Light Scattering Data

Tables 6–8 give the primary data from the laser-light scattering experiments of the present work.

#### Appendix E: Results from Membrane Osmometry

Some test measurements with membrane osmometry were carried out in the present work. An osmometer from Gonotec, Berlin, Germany, Type Osmomat 090, was used for these studies with a cellulose acetate membrane with an exclusion size of about 5000. Five samples of PEG 23000 ( $c_2$  between 0.9 and  $5\text{ mg cm}^{-3}$ ) were measured at 298 K (accuracy: about 5 Pa for the osmotic pressure and 1 K for the temperature). The results are given in Table 9.

The membrane osmometric data were evaluated using

$$\frac{\Delta p}{RTc_2} = \frac{1}{M_2} + A_{22}c_2 + A_{222}c_2^2 + \dots \quad (18)$$

They agree well with the result of the simultaneous correlation of laser-light scattering and isopiestic data from the present investigation.

Membrane osmometry has been used before to study thermodynamic properties of PEG (cf. Table 4). A remarkable result has been obtained by Vink.<sup>30</sup> Among other polymers, Vink<sup>30</sup> has studied aqueous PEG 42000 at 293 K. Using a differential technique, with PEG solutions of different concentrations on both sides of the membrane, Vink<sup>30</sup> covered the comparatively large concentration range of  $0.015 \leq c_2/g\text{ cm}^{-3} \leq 0.067$ . He reports  $A_{22} = 1.88 \times 10^{-3}\text{ mol cm}^3\text{ g}^{-2}$  and  $A_{222} = 1.93 \times 10^{-2}\text{ mol cm}^6\text{ g}^{-3}$ . This result is in excellent agreement with the findings from the present study. It has been overlooked by many authors, maybe due to the fact that  $A_{22}$  was much lower than the commonly accepted numbers.

This shows that membrane osmometry (applied to a comparatively wide range from very low to intermediate concentrations) provides an alternative to the simultaneous evaluation of laser-light scattering and isopiestic data. That procedure however strongly relies on very precise membrane osmometric data, which are sometimes difficult to obtain. Besides unavoidable scattering of the data, complications may arise from the exclusion size and inertness of the membrane. Another perhaps more attractive possibility is to use membrane osmometry as a complementary technique together with laser-light scattering and isopiestic experiments.

#### Appendix F: Modified Osmotic Virial Equation

The osmotic virial equation is often used for correlating thermodynamic data of polymer solutions. A modified version of that equation was developed in the present work. As the polydispersity of the polymers (PEG) studied here can be neglected, only the binary system solvent (water, 1)–solute (polymer, 2) is discussed.

First, a conceptually straightforward (but uncommon) way to derive the original form of the osmotic virial equation is presented. From that derivation the starting point for the modification becomes evident.

In the osmotic virial equation, the chemical potential  $\mu_2$  of the solute (2) is normalized according to Henry's law:

$$\frac{\mu_2}{RT} = \frac{\mu_2^\ominus}{RT} + \ln \Psi_2 + \ln \gamma_2 \quad (19)$$

where  $R$  is the universal gas constant,  $T$  is the absolute temperature, and  $\mu_2^\ominus$  is the standard state chemical potential. Different concentration units  $\Psi_2$  like  $c_2$  (mass of polymer/volume) and  $m_2$  (molality) have been used in the literature, leading to different definitions of the ideal solution. The activity coefficient  $\gamma_2$  of the polymer

**Table 6. Excess Rayleigh Ratios of PEG 6000 in Water**

278 K		298 K		313 K	
$\xi_2 \times 100$ (g g <sup>-1</sup> )	$KR_E^{-1} \times 100$ ((mol cm <sup>3</sup> )/g <sup>2</sup> )	$\xi_2 \times 100$ (g g <sup>-1</sup> )	$KR_E^{-1} \times 100$ ((mol cm <sup>3</sup> )/g <sup>2</sup> )	$\xi_2 \times 100$ (g g <sup>-1</sup> )	$KR_E^{-1} \times 100$ ((mol cm <sup>3</sup> )/g <sup>2</sup> )
0.76	1.951	0.10	13.722	0.77	1.671
1.04	1.623	0.30	5.476	1.05	1.562
1.50	1.362	1.04	1.840	1.51	1.247
1.99	1.174	1.51	1.449	2.52	0.992
2.50	1.237	2.01	1.269	2.98	0.877
2.96	1.168	2.52	1.141	4.05	0.813
4.02	1.127				
5.00	1.130				

Table 7. Excess Rayleigh Ratios of PEG 23000 in Water

298 K		313 K	
$\xi_2 \times 100$ (g g <sup>-1</sup> )	$KR_E^{-1} \times 100$ ((mol cm <sup>3</sup> )/g <sup>2</sup> )	$\xi_2 \times 100$ (g g <sup>-1</sup> )	$KR_E^{-1} \times 100$ ((mol cm <sup>3</sup> )/g <sup>2</sup> )
0.30	1.919	0.64	0.961
0.45	1.407	0.88	0.813
0.65	1.133	1.14	0.727
0.89	0.957	1.45	0.645
1.16	0.832	1.71	0.607
1.48	0.784	2.30	0.557
1.77	0.717		

accounts for differences between ideal and real solution. Only the case of polymer concentration  $c_2$  is further discussed here.

A Taylor series expansion of  $\ln \gamma_2$  around the ideal solution ( $\ln \gamma_2 = 0$  at  $c_2 = 0$ ) yields

$$\ln \gamma_2 = \left. \frac{\partial \ln \gamma_2}{\partial c_2} \right|_{c_2=0} c_2 + \frac{1}{2} \left. \frac{\partial^2 \ln \gamma_2}{\partial c_2^2} \right|_{c_2=0} c_2^2 + \dots \quad (20)$$

Introducing abbreviations for partial derivatives

$$a_{22} = \left. \frac{\partial \ln \gamma_2}{\partial c_2} \right|_{c_2=0} \quad (21)$$

$$a_{222} = \left. \frac{\partial^2 \ln \gamma_2}{\partial c_2^2} \right|_{c_2=0} \quad (22)$$

leads to

$$\ln \gamma_2 = a_{22} c_2 + \frac{1}{2} a_{222} c_2^2 \quad (23)$$

The chemical potential  $\mu_1$  of the solvent (1) is normalized according to Raoult's law:

$$\frac{\mu_1}{RT} = \frac{\mu_{1,\text{pure}}}{RT} + \ln a_1 \quad (24)$$

The activity  $a_1$  of the solvent is found by integrating the Gibbs–Duhem equation for constant temperature and pressure:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad (25)$$

$$\ln a_1 = - \int_{\text{pure}, n_1}^{\text{mix}} \frac{n_2}{n_1} d \ln(c_2 \gamma_2) \quad (26)$$

For solving the integral in eq 26, the dependence of the ratio of the mole numbers  $n_2/n_1$  on the polymer concentration  $c_2$  has to be known. As

$$n_2 = V \frac{c_2}{M_2} \quad (27)$$

an assumption on the concentration dependence of  $V/n_1$  has to be made. It is common practice to consider that term to be the molar volume of the pure solvent:

$$\frac{V}{n_1} = \frac{1}{\rho_1} = \text{const} \quad (28)$$

Solving eq 26 then leads to the well-known form of the osmotic virial equation:

$$\ln a_1 = - \frac{c_2}{\rho_1} \left( \frac{1}{M_2} + A_{22} c_2 + A_{222} c_2^2 + \dots \right) \quad (29)$$

where

$$A_{22} = \frac{a_{22}}{2M_2} \quad (30)$$

and

$$A_{222} = \frac{a_{222}}{3M_2} \quad (31)$$

are the second and third osmotic virial coefficients, respectively.

However, eq 28 is a good approximation only at low polymer concentrations, whereas, e.g., near the solubility limit of PEG in water at 293 K ( $c_2 \approx 0.6$  g cm<sup>-3</sup>), it is wrong by more than a factor of 2. A far better approximation is to assume constant specific density  $\rho^*$  of the polymer solution:

$$\rho^* = \frac{m_1 + m_2}{V} = \text{const} \quad (32)$$

For example, at 293 K the difference between the specific density of pure water  $\rho_1^*$  and that of a saturated PEG solution  $\rho_{\text{sol},\text{lim}}^*$  is less than 8%. Therefore an alternative to using eqs 27 and 28 is to use

$$\frac{n_2}{n_1} = \frac{M_1}{M_2} \frac{c_2}{\rho^* - c_2} \quad (33)$$

where  $\rho^*$  can be set equal to any specific density between  $\rho_1^*$  and  $\rho_{\text{sol},\text{lim}}^*$ . Usually, it will be most convenient to use  $\rho^* = \rho_1^*$ . This was also done in the present

Table 8. Excess Rayleigh Ratios of PEG 35000 in Water

278 K		298 K		313 K	
$\xi_2 \times 100$ (g g <sup>-1</sup> )	$KR_E^{-1} \times 100$ ((mol cm <sup>3</sup> )/g <sup>2</sup> )	$\xi_2 \times 100$ (g g <sup>-1</sup> )	$KR_E^{-1} \times 100$ ((mol cm <sup>3</sup> )/g <sup>2</sup> )	$\xi_2 \times 100$ (g g <sup>-1</sup> )	$KR_E^{-1} \times 100$ ((mol cm <sup>3</sup> )/g <sup>2</sup> )
0.10	3.042	0.11	3.345	0.10	3.163
0.34	1.370	0.31	1.393	0.31	1.215
0.51	1.100	0.50	1.005	0.52	0.842
0.80	0.932	1.00	0.717	0.77	0.723
1.06	0.877	1.50	0.662	1.02	0.638
1.53	0.805	2.00	0.644	1.51	0.541
		2.50	0.646	2.05	0.529
		3.02	0.638	2.55	0.517

**Table 9. Osmotic Pressure of PEG 23000 in Water at 298 K**

$\xi_2$ (mg g <sup>-1</sup> )	$\Delta p$ (Pa)
0.88	112.2
1.47	189.9
2.50	247.8
4.95	744.0

work. Introducing eq 33 in eq 26 and integrating yields

$$\ln a_1 = -M_1 \left( \ln \left( \frac{\varrho^*}{\varrho^* - c_2} \right) \left( \frac{1}{M_2} + 2A_{22}^* \varrho^* + 3A_{222}^* \varrho^{*2} + \dots \right) - c_2 \left( 2A_{22}^* + 3A_{222}^* \left( \varrho^* + \frac{c_2}{2} \right) + \dots \right) + \dots \right) \quad (34)$$

The original and the modified osmotic virial equation only differ in the activity  $a_1$  of the solvent, whereas they are identical for the activity  $a_2$  of the solute. The superscript asterisk with  $A_{22}$  and  $A_{222}$  indicates that the corresponding virial coefficient is to be used together with the modified equation for the solvent activity.

If the virial coefficients are defined in terms of coefficients in the power series expansion of  $\ln \gamma_2$  (eqs 20–22, 30, and 31), they are identical for both the original and the modified equation. If, however, they are defined in terms of the activity  $a_1$  of the solvent using

$$\lim_{c_2 \rightarrow 0} \frac{\partial^2 \ln a_1}{\partial c_2^2} = - \frac{2A_{22}}{\varrho_1} \quad (35)$$

$$\lim_{c_2 \rightarrow 0} \frac{\partial^3 \ln a_1}{\partial c_2^3} = - \frac{6A_{222}}{\varrho_1} \quad (36)$$

where  $A_j$  stands either for  $A_j$  or  $A_j^*$  ( $j = 22$  or  $222$ ), they are different.

## Nomenclature

### Latin

$A$	osmotic virial coefficient
$a$	activity
$a$	constant related to the osmotic virial coefficient by eqs 30 and 31
$c$	concentration in mass/volume
corr	correlated
exp	experimental
GPC	gel-permeation chromatography
$K$	optical constant
$k$	constant
$M$	molecular mass
MALLS	multiangle laser-light scattering
$m$	mass
$N$	number of data points
$N_A$	Avogadro's number
$n$	mole number
$n$	refractive index of the solution (function of $T$ and $c_2$ )
PEG	poly(ethylene glycol)
PEO	poly(ethylene oxide)
$p$	pressure
$R$	universal gas constant

$R_E$	excess Rayleigh ratio
SSQ	objective function (weighted sum of squares)
$T$	temperature
$V$	volume (of the solution)
$Y$	property

### Greek

$\alpha$	constant
$\beta$	constant
$\gamma$	activity coefficient (function of $T$ and $c_2$ )
$\Delta$	difference
$\Theta$	angle
$\lambda$	laser wavelength
$\mu$	chemical potential (function of $T$ and $c_2$ )
$\xi$	mass fraction
$\varrho$	molar density
$\varrho^*$	specific density
$\Psi$	concentration

### Subscripts

1	solvent (water), also: pure solvent at $T_{\text{mix}}$
2	solute (polymer, PEG)
22	second osmotic virial coefficient
222	third osmotic virial coefficient
E	excess
ISO	isopiestic method
$i$	data point
$j$	either 22 or 222
LS	light scattering
mix	mixture
pure	pure component (at $T_{\text{mix}}$ )
sol.lim.	solubility limit
$\Theta$	theta temperature

### Superscripts

app	apparent
calc	calculated
exp	experimental
max	maximal
(n)	number averaged
real	true
(w)	mass averaged
*	referring to modified osmotic virial equation
$\ominus$	standard state

## References and Notes

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