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HEINEMANN

Polymer Vol. 36 No. 10, pp. 1975–1978, 1995

0032-3861/95/$10.00+0.00

Neglected turbidity correction in light scattering experiments—a source of erroneous values of the second virial coefficient*

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(Received 10 June 1994; revised 11 October 1994)

Neglecting turbidity leads to an overestimation of the second virial coefficient in light scattering experiments. Although this effect is totally negligible for polymers in good solvents, it is dominant for systems consisting of large compact particles and for polymers at theta conditions. The turbidity correction is proportional to the characteristic constant of light scatterning K and thus inversely proportional to λ^4. The true virial coefficient can be obtained by extrapolation of Kc/R to vanishing value of K. Light scattering of a well characterized sample of polystyrene in cyclohexane at three different wavelengths and several temperatures has been used to demonstrate the correction for turbidity. The true second virial coefficient for polystyrene in cyclohexane at various temperatures was obtained. Theta temperature and the entropic factor ψ were found to be 35.4°C and 0.21, respectively. Alternative procedures for evaluating the correction using light scattering data measured at a single wavelength were also offered.

(Keywords: turbidity correction; light scattering; second virial coefficient)

INTRODUCTION AND THEORY

Light scattering of polymer solutions is routinely analysed using the equation[1-6]:

$$Kc/R_\theta = 1/MP(\theta) + 2A_2c + \ldots \qquad (1)$$

where c is the polymer concentration (in mass per volume units), M is the molecular weight of the polymer, R_θ is the excess of the Rayleigh ratio over that of the solvent, both measured at angle θ with respect to the primary beam, A_2 is the second virial coefficient and K is a characteristic constant for the polymer–solvent system defined as:

$$K = 2\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c)^2/\lambda_0^4 N_\mathrm{A} \qquad (2)$$

with n being the refractive index of the solvent, $\mathrm{d}n/\mathrm{d}c$ the refractive increment of the polymer, λ_0 the wavelength of light in vacuum and N_A the Avogadro number.

$P(\theta)$ is the scattering factor characterizing the scattering envelope. Its value is equal to unity at $\theta = 0°$ for all particles; it does not change significantly for any angle provided that the maximum dimension of the particles is less than $\lambda/20$.

The Rayleigh ratio is the ratio of the light intensities of the primary beam entering a small volume element and the scattered beam leaving that element. However, in a real experiment, we do not measure the ratio of these intensities. We measure the ratio of intensities of the primary beam entering the cell and the scattered beam reaching the detector. The primary beam, before reaching the scattering element, travels a distance L_p through the scattering solution and is weakened by the turbidity τ of the solution by a factor $\exp(-L_\mathrm{p}\tau)$. Similarly, the scattered beam travels a distance L_s before reaching the wall of the cell and is weakened by a factor $\exp(-L_\mathrm{s}\tau)$. Consequently, instead of measuring R_θ, we are measuring R_θ^*, which is related to R_θ as:

$$R_\theta^* = R_\theta \exp[-(L_\mathrm{p} + L_\mathrm{s})\tau] \qquad (3)$$

The turbidity of a non-absorbing liquid is related to its Rayleigh ratio at 0°, R_0, as:

$$\tau = \int_0^{2\pi}\int_0^{\pi} R_\theta \sin\theta \,\mathrm{d}\theta\,\mathrm{d}\phi = xR_0 \qquad (4)$$

where $x = 16\pi/3$ for particles smaller than $\lambda/20$; it slowly decreases for larger particles. Making appropriate substitutions, we find that the actually measured quantity Kc/R_θ^* must be interpreted as:

$$Kc/R_\theta^* = (Kc/R_\theta)\exp[(L_\mathrm{p} + L_\mathrm{s})xR_0] \qquad (5)$$

For dilute solutions the argument of the exponential is small compared to unity and we may write:

$$Kc/R_\theta^* = (Kc/R_\theta)[1 + (L_\mathrm{p} + L_\mathrm{s})xR_0 + \ldots] \qquad (6)$$

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* Dedicated to Professor Pavel Kratochvil on the occasion of his 65th birthday

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Substituting equation (1) for Kc/R_θ, we obtain finally:

$$\begin{aligned} Kc/R_\theta^* &= 1/MP(\theta) + 2A_2c + Kc(L_p + L_s)xR_0/R_\theta + \cdots \\ &= 1/MP(\theta) + [2A_2 + K(L_p + L_s)xR_0/R_\theta]c + \cdots \\ &= 1/MP(\theta) + (2A_2 + A_T)c + \cdots \end{aligned} \tag{7}$$

where

$$A_T = K(L_p + L_s)xR_0/R_\theta \tag{8}$$

Thus, the molecular weight M and the function $P(\theta)$ that are evaluated by extrapolation to vanishing concentration are obtained correctly. However, the term usually interpreted as $2A_2$ is actually a sum of two terms.

Let us evaluate the second term for a typical polymer solution: low-molecular-weight polystyrene in cyclohexane. Let us assume that the measurement was done using green Hg light, $\lambda_0 = 546$ nm, and using a cell with 2 cm diameter. Then $L_p = L_s = 1$ cm. For low-molecular-weight polymers, $R_0 = R_\theta$ and $x = 16\pi/3$. The refractive increment of polystyrene in cyclohexane is 0.169 (refs. 7, 8). Consequently $K = 2.15 \times 10^{-7}$ g^{-2} cm^2 mol and the value of the second term is 7.20×10^{-6} g^2 cm^3 mol.

For polymers in good solvents, A_2 is typically of the order of 1×10^{-4} g^{-2} cm^3 mol (refs. 1, 2) and the above correction is not significant. However, in two types of systems, the turbidity term becomes important:

(1) For large compact particles (e.g. latexes), the product A_2M is expected to be of order 0.1 or even less[9]. The molecular weight of latexes is of the order 10^8–10^9. Thus A_2 is expected to be of the order 10^{-8}–10^{-10}. Obviously, this value is totally overshadowed by the turbidity term: light scattering cannot be used for measuring the virial coefficient in this case.

(2) For many theoretical studies, accurate knowledge of the theta temperature is required. Quite often it is found by measuring by light scattering the temperature dependence of the second virial coefficient and interpolating for its zero value[4–6,10–12]. Owing to the turbidity effect, the virial coefficient obtained is too high and, consequently, the estimated theta temperature is too low. For verification of the turbidity effect, we utilized the fact that the A_T value is proportional to the light scattering constant K. The latter is inversely proportional to λ_0^4 and, consequently, steeply increases with decreasing wavelength. We have measured a solution of a well defined sample of polystyrene in cyclohexane as a function of temperature using different wavelengths of the primary light and evaluated the apparent second virial coefficient.

EXPERIMENTAL

Materials

Polystyrene sample lot 4b from Pressure Chemical Co. was used for all measurements. For this sample, manufacturer's value of M_w is 110 000. Our older measurements using the sedimentation equilibrium technique[13–15] and various solvents yielded values 114 000–117 000. Manufacturer's value of M_w/M_n was less than 1.06; our value of M_z/M_w was 1.015. Anhydrous cyclohexane was purchased from Fisher Scientific Co. and used without further purification.

Polystyrene solutions were prepared from a stock solution by dilution. All samples were filtered before performing light scattering measurements.

Light scattering

This was measured using a modified Fica 50 photometer equipped with a mercury lamp, a polarizer providing vertically polarized light, and interference filters for 366, 436 and 546 nm. The temperature of the solution in the scattering cells was kept constant within 0.1°C. The scattered light was registered by a laboratory photometer (Pacific Instruments model 110) and its output was measured by a Hewlett–Packard multimeter (model 3478A), which was interfaced to a computer. All measurements were performed at angle 90°. The inner diameter of the scattering cells was 2.0 cm.

For evaluation of the intensity of scattered light, we used a glass working standard throughout all our measurements. We calibrated our glass standard using the known values of Rayleigh ratio of benzene at 20°C for 546 and 436 nm ($R_u = 16.3 \times 10^{-7}$ cm^{-1} at 546 nm, and 47.4×10^{-7} at 436 nm, respectively[2]). Because fluorescence from impurities always present in benzene adversely affects the measurement of benzene at 366 nm, we used carbon tetrachloride ($R_u = 28.9 \times 10^{-7}$ cm^{-1} at 20°C and 366 nm (ref. 1)) for calibration of our glass standard at 366 nm. Unlike volatile organic solvents, the Rayleigh ratio of the glass standard does not change appreciably with the change of temperature[2].

RESULTS AND DISCUSSION

For our measurement at 19.2°C and 21.6°C and $\lambda_0 = 546$ nm we used the literature values[7,8] for polystyrene of similar molecular weight in cyclohexane, dn/dc = 0.169 ml g^{-1}. The refractive index of cyclohexane was 1.428. These values led to $K = 2.15 \times 10^{-7}$ cm^2 mol g^{-2}. Using this value of K, we obtained from the intercept of Kc/R_{90} vs. c the values of $M_w = 112\,800$ and 111 600, respectively. This is in a good agreement with previously measured values[13–15]. For calculation of K at other temperatures and wavelengths, the dn/dc values are not known with sufficient accuracy. For evaluation of K we have therefore utilized the fact that the molecular weight of the polystyrene sample does not depend on temperature or wavelength. Thus, for each temperature and wavelength we have adjusted the K value to yield the correct molecular weight (110 000). The adjusted values of K are assembled in *Table 1* together with dn/dc values calculated from them using equation (2) and the known dependence of refractive index of cyclohexane on temperature. The refractive index increments obtained for 546 nm and 436 nm are very close to the literature values for polystyrene of similar molecular weight[8,12]. The slight increase of dn/dc with increasing temperature is obvious (especially at 366 nm) despite the experimental error of our measurements.

The dependence of the apparent virial coefficient on the wavelength is most obvious from plots of $(Kc/R_{90})/\lim_{c\to 0}(Kc/R_{90}) \equiv KcM/R_{90}$ vs. c (*Figure 1*). In this plot all dependences have intercept equal to unity, and their slope is $2A_{app}M_w$. Using the known value of M_w, A_{app} is easily evaluated. The A_{app} values are also included in *Table 1*. They are plotted in a Zimm-like fashion against the (wavelength-dependent) value of K and temperature in *Figure 2*. Extrapolating to vanishing value of K we obtained the true value of the virial coefficient A_2 at each temperature. From the slope of these dependences we

Table 1 Characteristic constant K, refractive index increment and apparent second virial coefficient for polystyrene–cyclohexane system at various temperatures and three wavelengths

	546 nm			436 nm			366 nm		
T(°C)	$K \times 10^7$ ($cm^2 mol g^{-2}$)	dn/dc ($ml g^{-1}$)	$A_{app} \times 10^5$ ($cm^3 mol g^{-2}$)	$K \times 10^7$ ($cm^2 mol g^{-2}$)	dn/dc ($ml g^{-1}$)	$A_{app} \times 10^5$ ($cm^3 mol g^{-2}$)	$K \times 10^7$ ($cm^2 mol g^{-2}$)	dn/dc ($ml g^{-1}$)	$A_{app} \times 10^5$ ($cm^3 mol g^{-2}$)
19.2	2.20	0.170	−17.8	5.92	0.179	−17.8	13.2	0.187	−16.6
21.5	2.18	0.170	−13.9	5.92	0.179	−13.4	13.3	0.187	−12.4
25.8	2.10	0.168	−9.14	5.98	0.180	−7.12	13.6	0.190	−5.51
28.1	2.09	0.168	−6.23	5.91	0.179	−5.45	13.4	0.189	−3.95
30.4	2.13	0.169	−3.39	5.90	0.179	−2.59	13.5	0.190	−0.98
31.6	2.08	0.167	−2.87	5.94	0.180	−1.89	13.6	0.191	0.55
33.8	2.15	0.170	−1.07	6.02	0.182	−0.67	13.9	0.192	1.16
34.8	2.13	0.169	−0.23	5.95	0.180	−0.04	13.7	0.192	1.29
36.0	2.14	0.170	0.65	6.01	0.182	1.27	13.9	0.193	2.48
37.8	2.15	0.170	2.60	6.02	0.182	3.00	14.1	0.194	4.97

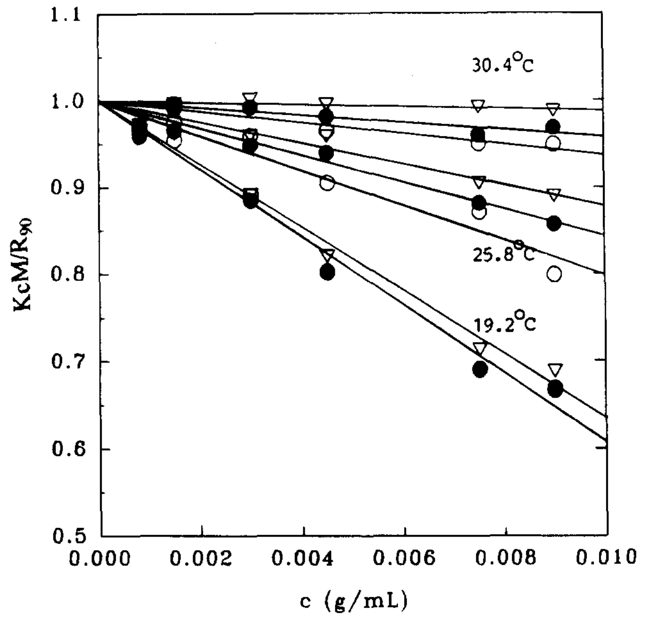

Figure 1 Plot of KcM/R_{90} as a function of concentration at several temperatures and wavelengths: (○) 546 nm; (●) 436 nm; (▽) 366 nm

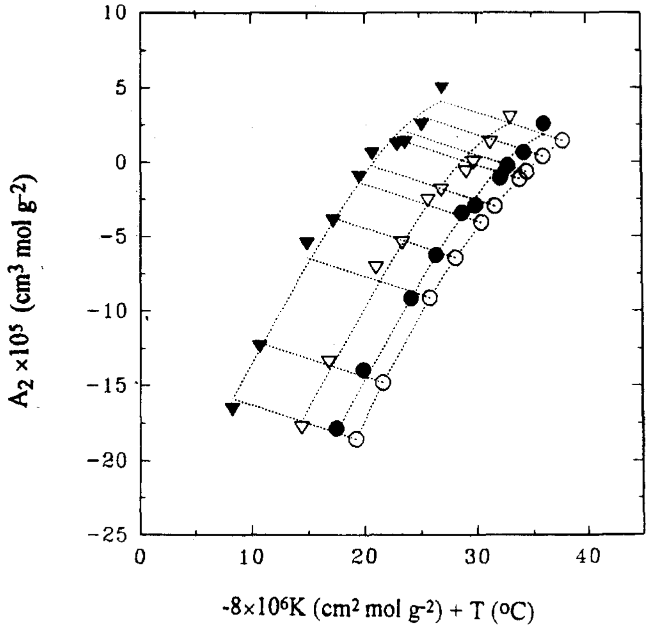

Figure 2 Plot of A_2 as a function of the light scattering constant K and temperature: (▼) $K = 13.2 \times 10^{-7}$ cm^2 mol g^{-2} ($\lambda = 366$ nm); (▽) $K = 5.95 \times 10^{-7}$ cm^2 mol g^{-2} ($\lambda = 436$ nm); (●) $K = 2.15 \times 10^{-7}$ cm^2 mol g^{-2} ($\lambda = 546$ nm); (○) $K = 0$

obtained the (average) value $(L_p + L_s) = 2.36$ cm, in good agreement with the expected value 2.0 cm.

Finally, we have interpolated the experimental dependence for a vanishing value of A_{app}. This provided us with the apparent and true values of the pseudo-ideal temperature Θ and the entropic parameter ψ:

$$A_2 = v_2^2 \psi (1 - \Theta/T)/V_1 \qquad (9)$$

where V_1 and v_2 are the solvent molar volume and polymer specific volume, respectively. These values are collected in *Table 2*. Values of Θ and ψ at theta temperature obtained at vanishing K are in good agreement with Krigbaum's earlier values obtained from osmotic pressure measurements[11].

The correction procedure outlined above is based on measuring the light scattering at several wavelengths, which might be inconvenient. However, it does not need knowledge of the instrumental parameters $(L_p + L_s)$ and of the particle-size-dependent parameter x. When these parameters are accessible, the correction could be evaluated from measurements at a single wavelength utilizing equations (7) and (8) directly. The quantity R_θ needed for the evaluation of the factor x in equation (4) is quite generally related to the radius of gyration R_g of the scattering particles as:

Table 2 Apparent and true Θ temperatures and entropic factors ψ

	$\lambda = 366$ nm	436 nm	546 nm	$\lambda \to \infty$
Θ(°C)	31.7	33.9	34.7	35.4
ψ	0.26	0.22	0.25	0.21

$$R_\theta = R_0(1 + \cos^2\theta)(1 - \tfrac{1}{3}q^2R_g^2 + \cdots) \qquad (10)$$

where $q = 4\pi n \sin(\theta/2)/\lambda_0$ is the scattering vector. R_g^2 is obtained routinely from the analysis of the scattering envelope at vanishing concentration (it is not affected by the turbidity in this limit). The integration yields:

$$x = \frac{16\pi}{3}\left(1 - \frac{8\pi^2 n^2 R_g^2}{3\lambda_0^2} + \cdots\right) \tag{11}$$

When the scattering particles are so large that neglect of the higher-order terms in equation (4) is not warranted, the turbidities τ may be measured directly using a spectrophotometer and their values substituted into equation (3).

It should also be mentioned that multiple scattering of light at larger turbidities may appreciably distort the scattering envelope and the concentration dependence. However, this phenomenon is eliminated by a careful extrapolation of the experimental data to vanishing concentration.

CONCLUSION

Our present results show that neglect of the turbidity correction in static light scattering experiments will lead to an overestimated second virial coefficient. The turbidity correction is proportional to K and thus inversely proportional to λ^4. The true virial coefficient can be obtained by extrapolation of Kc/R to vanishing value of K. We used a well characterized sample of polystyrene in cyclohexane at three different wavelengths and several temperatures to demonstrate the correction for turbidity. The true second virial coefficient for polystyrene in cyclohexane at various temperatures, correct theta temperature and the entropic factor ψ were found and results were comparable with those in the literature. Alternative procedures for evaluating the correction using light scattering data measured at a single wavelength were also offered.

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