Second Virial Coefficients of Poly(ethylene glycol) in Aqueous Solutions at Freezing Point

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ABSTRACT: The second virial coefficients B_{ij} (nm^3) of poly(ethylene glycol) with molecular weight $M = 600-10^4$ in water are measured by freezing point depression. B_{12} represents the virial cross coefficient for two PEG solutes with different molecular weights M_1 and M_2. B_{11} can be well described by the scaling law $M^{3\nu}$ with $\nu \simeq 0.60$. That is, the good solvent behavior is observed even for such low molecular weight. In terms of the hard-sphere model, the effective diameter of PEG ranges from 1.3 to 7.9 nm. Since the second virial coefficient is generally increased with decreasing temperature, our results at freezing point provide an upper bound. The virial cross coefficient is found to follow $B_{12} = B_{11}[1 + (M_2/M_1)^\nu]^3/8$. This result indicates that the effective hard-sphere picture is also reasonable for dilute solutions of different polymer molecules in good solvents.

Introduction

Poly(ethylene glycol) (PEG) is a linear, water-soluble polymer with rather interesting features. Its amphiphilic nature is demonstrated in the fact that it is also soluble in a large number of organic solvents. The solubility of PEO decreases with rising temperature, in contrast to normal polymer behavior. Moreover, it exhibits both lower and upper critical solution temperature in aqueous solutions (LCST and UCST).[1−5] Poly(ethylene glycol) of low molecular weight, in the range 200−20 000 g/mol, exhibits lubricity, good stability, and low toxicity and is therefore used in lubricants, electronics, cosmetics, and pharmaceuticals. Note that while PEO chains were "uncapped", their behavior is believed to be the same as that of PEG chains for dilute solutions. "PEG" and "PEO" are hence used interchangeably for lower molar masses.

The second virial coefficient of polymers in solution is a measure of solvent quality. It varies in accordance with the nature of solvent−polymer interaction and is sensitive to the molecular weight. Numerous articles have reported the second virial coefficients for PEG in water at room temperature. It is found that the second virial coefficient is positive over the temperature range 20−90 °C and is generally increased with decreasing temperature.[3,5] This fact indicates that water is a good solvent for PEG, and the degree of association between PEG and water decreases with increasing temperature.

The osmotic second virial coefficient B_2 is also a measure for the interaction between a pair of macromolecules. The osmotic pressure Π can be written in the form of a virial equation,

$$\frac{\Pi}{ckT} = 1 + B_2 c + ... \tag{1}$$

where k is the Boltzmann constant. Note that c is the number density of the polymer (number per unit volume). The osmotic second virial coefficient is related to the potential of mean force between a pair of polymer W by[6]

$$B_2 = 2\pi \int_0^\infty \left(1 - \exp\left[-\frac{W(r)}{kT}\right]\right) r^2 \, \mathrm{d}r \tag{2}$$

where r is the center-of-mass separation between polymers. Evidently, B has a unit of volume and can be considered as a characteristic volume associated with a polymer chain in a good solvent. Recast in terms of the mass density ρ (mass per unit volume), the virial equation becomes the well-known form for polymer solutions

$$\frac{\Pi}{\rho RT} = \frac{1}{M} + A_2\rho + ... \tag{3}$$

where R is the gas constant and M the molecular weight. By comparing eqs 1 and 3, A_2 is related to B_2 by

$$A_2 = \frac{B_2 N_\mathrm{a}}{M^2} \tag{4}$$

Here N_a is Avogadro's number.

In good solvents, the polymer molecule is often regarded as a random coil, and two coils tend to repel each other. Its second virial coefficient B_2 can then be estimated by approximating the potential of mean force as interactions between two hard spheres with a radius comparable to their radius of gyration R_g[7,8]

$$B_2 \sim {R_\mathrm{g}}^3 \tag{5}$$

Since $R_\mathrm{g} \sim N^\nu \sim M^\nu$ in a good solvent with $\nu \simeq 0.6$, one has the following scaling relation:

$$B_2 \propto M^{3\nu} \tag{6}$$

In terms of the second virial coefficient used in the typical Zimm plot, the dependence of A_2 on molecular

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weight is given by

$$A_2 \sim M^{3\nu-2} \qquad (7)$$

The scaling relations 6 and 7 have been confirmed by experiments. Devanand and Selser[1] reported the scaling relation for PEO with molecular weight range 10^5-10^6 at 30 °C

$$B_2(\mathrm{nm}^3) = 3.06 \times 10^{-5} M^{1.8} \qquad (8)$$

where the unit of M is g mol^{-1}. Kawaguchi et al. also obtained B with $M \approx 10^4-10^6$ at 25 °C

$$B_2(\mathrm{nm}^3) = 6.18 \times 10^{-6} M^{1.81} \qquad (9)$$

It should be noted that B_2 obtained from eq 9 is about 1 order of magnitude smaller than that from eq 8 despite the fact that both equations follow the same scaling relation.

Static light scattering and membrane osmometry are commonly adopted to determine the second virial coefficient of polymers with molecular weight more than 10^4. On the basis of Zimm plot method, the former approach is capable of obtaining both the radius of gyration and the osmotic second virial coefficient. However, because of the ability to detect small values of the intensity of scattered radiation, the lower limit of M by light scattering measurements is typically 2×10^4 g mol^{-1}. The latter approach calculates both the molecular weight and the second virial coefficient according to the plot of $\Pi/\rho RT$ vs ρ with an intercept M^{-1}. The lower limit of this method is determined by the extent to which the membrane is permeated by polymer molecules. Most membranes are cellulose-based and have a typical molecular-weight cutoff of 10^4 g mol^{-1} or more.[7] Consequently, the second virial coefficients of PEO with $M < 10^4$ cannot be easily determined by these two approaches.

In this paper we study the second virial coefficients of PEO with $M = 600-10^4$ in water by the method of freezing point depression. Since B_2 of PEO rises with deceasing temperature, one anticipates that the second virial coefficient at its freezing point is close to the maximum value. Furthermore, we investigate the second virial cross coefficient B_{12} of a PEO mixture of molecular weights M_1 and M_2. In addition to furnishing information on overall interactions between polymers of different molecular weight in dilute solutions, the results of PEO cross coefficients also provide insights concerning microscopic interactions between the different polymer molecules. After the second virial coefficients B_{11} are undoubtedly determined, the cross coefficients B_{12} can be experimentally obtained.

Background Theory

The depression of solvent freezing point caused by a solute is commonly used to evaluate the molar mass of the solute in a dilute solution. In the limit of infinite dilution, the freezing point depression is determined by the number of moles of polymer molecules per unit volume of solution. However, as the polymer concentration is high enough, part of the freezing point depression is contributed by the interaction between two polymers. In this section we derive the relationship between the freezing point depression and the osmotic pressure, which is then related to the virial coefficients by the virial expansion. This resultant equation provides a way to determining the second virial coefficients of dilute polymer solutions at their freezing points.

For a dilute solution of solute B in solvent A at solid−liquid equilibrium, the chemical potential of A in the two phases are equal, $\mu^*_{\mathrm{A(s)}} = \mu^*_{\mathrm{A(l)}} + kT \ln a_{\mathrm{A}}$. For pure A, the activity is $a_{\mathrm{A}} = 1$. The chemical potential μ^*_{A} of a pure substance equals its molar Gibbs free energy G_{A}. Therefore, one has

$$RT_{\mathrm{f}} \ln a_{\mathrm{A}} = -(\Delta H_{\mathrm{A}} - T_{\mathrm{f}}\Delta S_{\mathrm{A}}) \qquad (10)$$

where ΔH_{A} is the molar enthalpy of fusion of pure A at temperature T_{f}, $\Delta H_{\mathrm{A}} = H^*_{\mathrm{A(l)}} - H^*_{\mathrm{A(s)}}$. Differentiation of eq 10 gives

$$\left(\frac{\partial \ln a_{\mathrm{A}}}{\partial T_{\mathrm{f}}}\right)_P = \frac{\Delta H_{\mathrm{A}}}{RT_{\mathrm{f}}^{2}} \qquad (11)$$

Integration of eq 11 from state 1 (pure A) to state 2 (solution) at constant pressure yields

$$\ln a_{\mathrm{A},2} = \int_{T^*_{\mathrm{f}}}^{T_{\mathrm{f}}} \frac{\Delta H_{\mathrm{A}}}{RT^2}\,\mathrm{d}T = \frac{\Delta H_{\mathrm{A}}}{R}\frac{\Delta T_{\mathrm{f}}}{T^*_{\mathrm{f}}T_{\mathrm{f}}} \qquad (12)$$

where T^*_{f} is the freezing point of pure A and the freezing-point depression is $\Delta T_{\mathrm{f}} = T_{\mathrm{f}} - T^*_{\mathrm{f}}$. In a dilute solution, ΔH_{A} can be reasonably approximated as a constant.

According to the Gibbs−Duhem equation, one has $\mathrm{d}\mu_{\mathrm{A}} = V_{\mathrm{A}}\,\mathrm{d}P - S_{\mathrm{A}}\,\mathrm{d}T$. At constant temperature, the chemical potential change from state 1 (pure A) to state 2 (solution) is then given by

$$\ln a_{\mathrm{A},2} = -\frac{1}{RT}\int_P^{P+\Pi} V_{\mathrm{A}}\,\mathrm{d}P = -\frac{V_{\mathrm{A}}\Pi}{RT} \qquad (13)$$

Here we assume that the molar volume of the solvent V_{A} is unaffected by the pressure. Since T_{f} is close to T^*_{f}, we approximate T_{f} by T^*_{f}. Equating eq 12 with eq 13 yields

$$\Delta T_{\mathrm{f}} = -\frac{T^*_{\mathrm{f}}V_{\mathrm{A}}}{\Delta H_{\mathrm{A}}}\Pi \qquad (14)$$

Using eq 1 for the osmotic pressure and expressing the equation in terms of the solute molality $m \cong cV_{\mathrm{A}}/M_{\mathrm{A}}N_{\mathrm{a}}$, one obtains

$$-\frac{\Delta T_{\mathrm{f}}}{m} = K_{\mathrm{f}}(1 + N_{\mathrm{a}}\rho_{\mathrm{A}}B_2 m + \ldots) \qquad (15)$$

where ρ_{A} is the solvent density, and the solvent's molal freezing point depression constant K_{f} is defined as

$$K_{\mathrm{f}} = \frac{M_{\mathrm{A}}RT^{*2}_{\mathrm{f}}}{\Delta H_{\mathrm{A}}}$$

For water at 0 °C, the value of K_{f} is 1.860 K kg/mol. If one plots $-\Delta T_{\mathrm{f}}/m$ against m, eq 15 indicates that a straight line of the slope $K_{\mathrm{f}}N_{\mathrm{a}}\rho_{\mathrm{A}}B_2$ can be observed with the intercept K_f in the dilute limit. When $N_a\rho_A B_2 m \ll 1$, one recovers the well-known result $-\Delta T_f = K_f m$.

Experimental Section

Materials. Poly(ethylene glycol) with vendor average molecular weights of 1000 and 2000 g/mol were purchased from Riedel-deHaen, 600, 3000, 4000, and 6000 g/mol from Fluka, 8000 g/mol from Aldrich, and 10 000 g/mol from Merck. PEG sample solutions were prepared under magnetic stirring for at least 12 h at room temperature. The water used in the preparation of the solutions was obtained first from distillation, which was then fed into the reverse osmosis system, Millipore Milli-Q Plus. The concentrations are given in molarity. In the experiments for measuring the second virial cross coefficients, the molar ratio of the two polymers with different molecular weights in the solution is kept at 1:1.

Freezing-Point Depression. The depression of water freezing point was measured by use of Advanced Micro Osmometer, model 3300 (USA). It operates based on the principle of freezing-point osmometry. The volume of the sample is 20 μL. The calibration was performed by using the standard solution of 50 and 850 mOsm. The resolution is 1 mOsm, which is equivalent to 0.001 K freezing-point depression.

Results and Discussion

The nonideal behavior of a dilute polymer solution is displayed through the second virial coefficient due to the interaction between two polymer molecules. In addition to the contribution associated with polymer concentrations, the depression of water freezing point due to polymer solutes is also related to the interaction between two polymer molecules, that is, the second virial coefficient. For poly(ethylene oxide) in a salt-free aqueous solution, the second virial coefficient increases with decreasing temperature. On the basis of freezing point depression, the second virial coefficient, which is close to its maximum value, is then determined for molecular weight range $600-10^4$ in this study.

For dilute solutions of small solute molecules such as ethylene glycol, one has $-\Delta T_f = K_f m$, and hence a horizontal line is obtained in the figure of $-\Delta T_f/m$ vs m.[10] It is the so-called colligative properties, which vary linearly with the number concentration of the solute. However, the deviation from the horizontal line can be evidently observed as the concentration is increased. This is caused by the intermolecular interaction. Moreover, under the condition that the solute molecule prefers to be with solvent rather than with its own kind, the deviation is dominated by the excluded volume. Consequently, one can readily anticipate that the deviation is positive and more significant when a solute possesses a larger size at the same number concentration. It is worth noting that even at the freezing point PEG is so well solvated by water, most probably due to hydrogen bonds, that precipitation/phase separation would not take place.

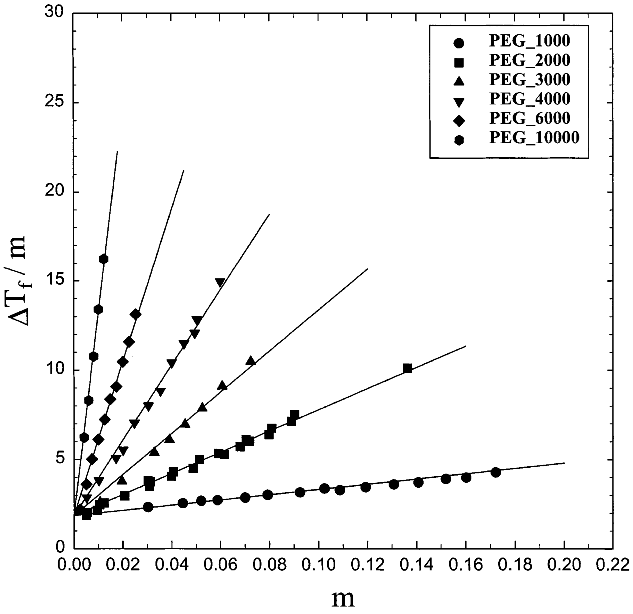

Figure 1. Variation of freezing point depression $-\Delta T_f/m$ with the polymer concentration m for various molecular weights.

Figure 1 shows a plot of freezing point depression $-\Delta T_f/m$ vs the polymer concentration m for different molecular weights. The PEG solutions are in the range of 0.3−25 wt %. The experimental data points at low enough concentrations can be well fitted by straight lines with a fixed intercept $K_f = 1.860$ K kg/mol, which is consistent with the prediction by eq 15. The deviation from the ideal behavior, $\Pi = mkT$, is reflected through the slope. In other words, the slope represents the intermolecular interaction between two polymers and is linearly related to the second virial coefficient, which is positive. When two coils are forced to overlap strongly, many contacts must take place between them. Each contact gives rise an energy of order kT. The potential of mean force, which can be estimated from the overall overlap energy, is then many times of kT. Consequently, the corresponding Boltzmann exponential in eq 2 is very small, and the coils refuse to penetrate each other.[8] In a good solvent, the second virial coefficient of a polymer is therefore proportional to its excluded volume, which can be characterized by the size of the polymer, e.g., radius of gyration. Because $R_g \sim M^\nu$, one expects that the slope grows with the molecular weight, as depicted in Figure 1.

On the basis of eq 15, the second virial coefficients were extracted from the figure of $-\Delta T_f/m$ vs m for PEG of different molecular weights. B_2 increases with rising the molecular weight. It varies from 4.27 to 1012.2 nm^3, corresponding to M from 600 to 10^4. In terms of the hard-sphere model, the second virial coefficient is related to the effective radius by $B_2 = 16\pi R_b^3/3$.[1,13] Consequently, the effective radius R_b changes from 0.64 to 3.93 nm. The validity of this result can be examined by comparing it with the literature value of radius of gyration for PEG. For $M = 10^4$, the R_g value extrapolated from the power law determined by static light scattering from PEO of higher molecular weight is 4.22 nm (25 °C)[2] or 4.62 nm (30 °C).[1] The typical ratio of effective radius to radius of gyration is $R_b/R_g \approx 0.6-0.7$.[11] Since the radius of gyration, like the second virial coefficient, is expected to rise with decreasing temperature, the fact that the ratio of R_b at freezing point to R_g at room temperature is greater than 0.85 is reasonable.

In good solvents, it is expected that the second virial coefficient follows the scaling law, eq 6. To inspect experimental results further, we plot ln B_2 against ln M. As shown in Figure 2, the data points can be well represented by a straight line with a slope equal to $3\nu = 1.8$,

$$B_2\,(\mathrm{nm}^3) = 5.72 \times 10^{-5} M^{1.8} \qquad (16)$$

The exponent 3ν supports the effective hard-sphere picture for intermolecular interactions between PEG

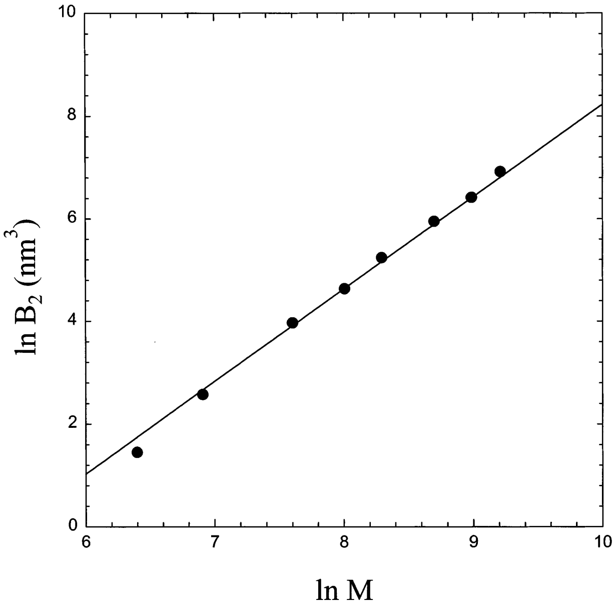

Figure 2. Plot of ln B_2 against ln M. The slope is $3\nu \simeq 1.8$.

molecules. The value obtained from eq 16 is greater than those extrapolated from eqs 8 and 9 for a given molecular weight. This is not surprising because the second virial coefficient is expected to be maximum at the freezing point.

Although second virial coefficients of dissolved single polymers B_{ii} have been reported extensively, only few reports have appeared for two-solute systems by membrane osmometry.[12] In the present work, we employ the method of freezing point depression to obtain the cross coefficient B_{ij} for pairs of polymers that are chemically similar. In a two-solute system, second virial coefficients can be derived in an analogous manner by replacing the osmotic pressure equation for the single-solute system with that for two-solute system.[13]

$$\frac{\Pi}{mkT} = 1 + (B_{11}x_1^{\,2} + 2B_{12}x_1x_2 + B_{22}x_2^{\,2})m + \ldots \tag{17}$$

where x_i is the mole fraction of the solute i with molecular weight M_i. The potential of mean force in eq 2 for B_{12} is simply the cross potential between molecules 1 and 2, W_{12}.

For a solution of two PEG solutes with different molecular weights, the osmotic second virial cross coefficient is obtained by performing a series of experiments for different concentrations m with a fixed mole fraction. A simple choice for the solution of two PEG solutes is $x_1 = x_2 = {}^1/_2$. Once second virial coefficients B_{ii} are determined, the cross coefficient B_{ij} is related to the second virial coefficient associated with the two-solute system B_2 by

$$B_{12} = 2B_2 - \frac{1}{2}(B_{11} + B_{22}) \tag{18}$$

Figure 3 demonstrates the variation of the freezing point depression $-\Delta T_f/m$ with the concentration m for two-solute systems with $x_1 = {}^1/_2$. Again, the data points can be well represented by a straight line with the intercept K_f. In Figure 3a,b, one can clearly see that the slope of the two-solute system is within those associated with the single polymers. In other words, B_2 is higher than B_{11} but smaller than B_{22} when $M_1 < M_2$. On the basis of eq 18, second virial cross coefficients B_{ij} can then be calculated and are listed in Table 1.

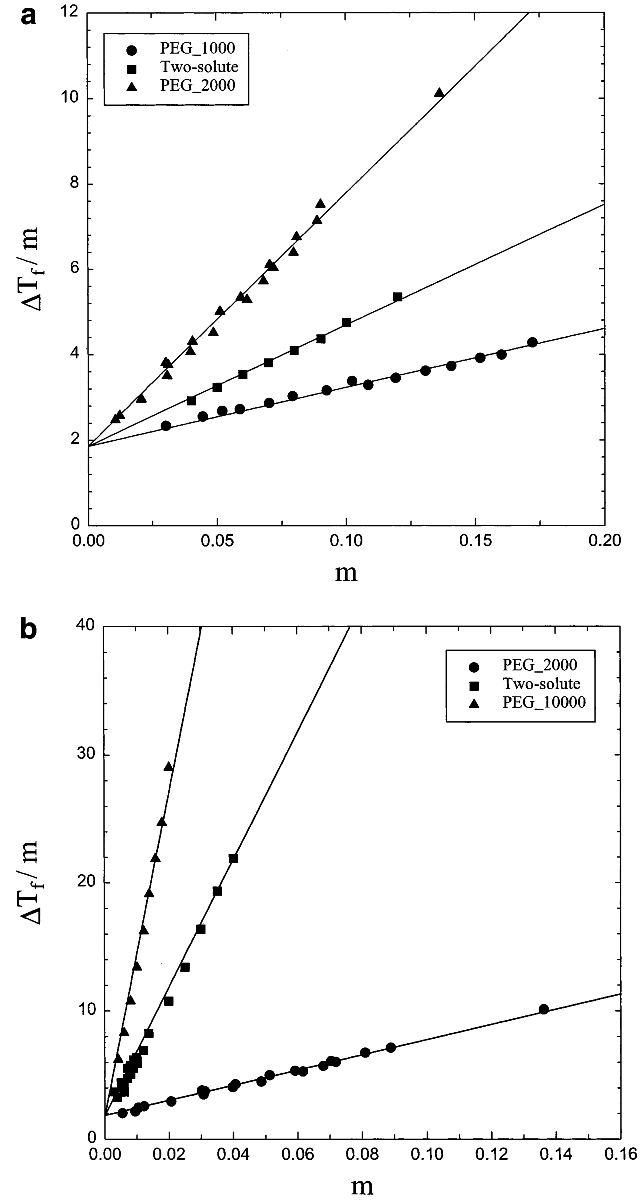

Figure 3. Plot of $-\Delta T_f/m$ vs m gives the second virial cross coefficient for PEG solutions of different molecular weights. (a) $M_1 = 1000$ and $M_2 = 2000$; (b) $M_1 = 2000$ and $M_2 = 10\,000$.

Table 1. Second Virial Coefficients Including B_{11} and B_{12} (nm^3)

M	1000	2000	3000	4000	6000	8000	10000
1000	13.1	23.3	37.3	72.2	124	146	276
2000	23.3	52.9		107	192	245	406
3000	37.3		103	140	247	348	436
4000	72.2	107	140	189			627
6000	124	192	247		384		831
8000	146	245	348			613	958
10000	276	406	436	627	831	958	1010

In a good solvent the second virial coefficient B_{ii} follows the scaling relation eq 6. This result implies that the interaction between a pair of polymers can be approximated by the two-hard-sphere interaction. To confirm this picture, one can compare the experimental results of cross coefficients with those predicted by the hard-sphere picture. We estimate the second virial cross coefficient associated with the two-solute system from eq 2 based on interactions between two hard spheres with different radii

$$B_{12} = \frac{2\pi}{3}(R_{b1} + R_{b2})^3 \tag{19}$$

where R_{bi} is the effective hard-sphere radius associated with PEG of M_i. Since $B_{ii} = 16\pi R_{bi}^3/3$, eq 19 becomes

$$B_{12} = \frac{B_{11}}{8}\left(1 + \frac{R_{b2}}{R_{b1}}\right)^3$$

According to eq 6, one has

$$\frac{B_{22}}{B_{11}} = \left(\frac{R_{b2}}{R_{b1}}\right)^3 = \left(\frac{M_2}{M_1}\right)^{3\nu}$$

Combining the two foregoing equations yields a relation between B_{12} and molecular weights for PEG solutions:

$$B_{12}\,(\mathrm{nm})^3 = \frac{B_{11}}{8}\left[1 + \left(\frac{M_2}{M_1}\right)^{\nu}\right]^3 = 7.15 \times 10^{-6} M_1^{\;3\nu}\left[1 + \left(\frac{M_2}{M_1}\right)^{\nu}\right]^3 \tag{20}$$

The second equality is obtained by using eq 16.

The second virial cross coefficients calculated by eq 20 can be compared with experimental results. Figure 4 shows a plot of $\ln[2(B_{12}/B_{11})^{1/3} - 1]$ against $\ln(M_2/M_1)$ for all data points of B_{ij} listed in Table 1. The experimental results can be reasonably fitted by a straight line, which passes through the origin and has a slope $\nu \simeq 0.6$. This result indicates that the effective hard-sphere picture is also reasonable for dilute solutions of polymers of different molecular weights in good solvents. Moreover, one would anticipate that the hard-sphere picture may be a reasonable approximation to describe the interaction between a pair of polymers that are chemically similar but have different architectures, such as interactions between linear and star poly(ethylene oxide).

On the basis of the method of freezing point depression, we have obtained second virial coefficients of poly(ethylene glycol) with molecular weight less than 10^4. Our results are larger than reported values measured at room temperature and provide an upper bound of second virial coefficients of PEG. Even for such low molecular weight, the good solvent behavior is observed, and B_{11} can be well described by the scaling law $M^{3\nu}$ with $\nu \simeq 0.6$. The second virial cross coefficient is also obtained from the solution with different PEG molecular weights. The experimental result can be reasonably explained by the hard-sphere model. That is, second virial cross coefficients can be estimated in terms of the effective hard-sphere radii and B_{12} is related to B_{11} by eq 20. Our result implies that similar concept may be applied to explain the interaction between a pair of chemically similar polymers in a good solvent.

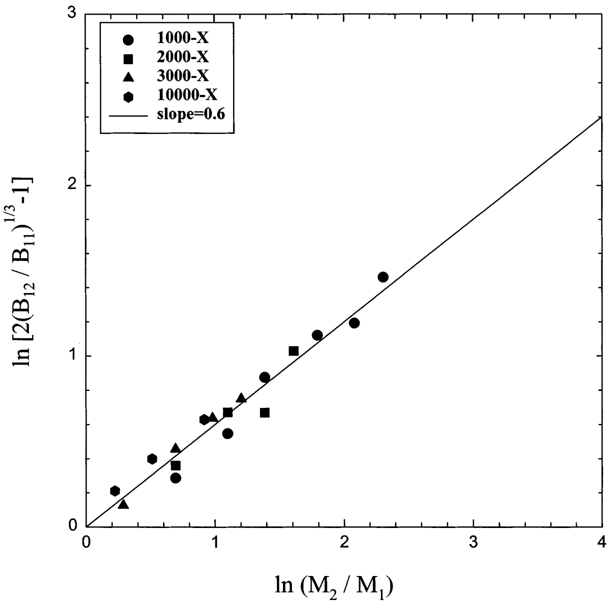

Figure 4. Plot of $\ln[2(B_{12}/B_{11})^{1/3} - 1]$ against $\ln(M_2/M_1)$ for all data points of B_{ij} listed in Table 1. The straight line is derived from eq 20, and the slope is $\nu \simeq 0.6$.

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