Molecular Weight of Polyethylene Glycols by Vapor Pressure Osmometry: An Alternative Data Treatment

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ABSTRACT: In this work, we determined the number average molecular weight of some polyethylene glycols (PEGs) using vapor pressure osmometry. In general, this technique works with a plot of $\Delta r_p/c_p$ versus c_p (concentration) and the molecular weight is determined by the calibration constant obtained from the curve intercept. We demonstrated that this method induces a high dispersion of the data, which can be minimized using a plot of Δr_p versus c_p. Therefore, more precise values of molecular weight can be obtained and the number average molecular weight, M_n, of several PEGs is directly determined from the ratio between the curve slopes obtained for a standard and the polymer sample. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 595–600, 1997

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INTRODUCTION

Vapor pressure osmometry (VPO) is a very common technique used to determine the molecular weight of organic molecules and the number average molecular weight, M_n, of polymers.[1–3] This technique is described by ANSI/ASTM D 3592-77, which has established a "standard recommended practice for determining molecular weight by vapour pressure osmometry."[4] This standard defines that the technique is applicable to all polymers that dissolve completely without reaction or degradation, within a practical weight range between 10,000 and a lower limit that is determined by the requirement that the solute have negligible vapor pressure. For higher molecular weight solutes, the precision with which M_n can be determined is critically dependent on the ideality of the solute-solvent system.

As is well known, this method is based on the colligative properties of a solution, which presents a lower vapor pressure than the pure solvent, and the principles of this technique have been described elsewhere.[4] The chemical potential of the pure solvent, μ_A^*, is lowered by the presence of the

solute according to $\mu_A = \mu_A^* + RT \ln a_A$, and consequently, the solvent vapor pressure in the solution is also lowered. Therefore, in order to maintain constant the vapor pressure in the instrument vessel, the solvent should be transferred toward the solution by condensation. Then, this technique is called osmometry because there is a solvent transfer from a diluted system toward a more concentrated one. The solvent condensation causes a temperature rise of the junction containing the solution, and this effect induces an electrical output that can be detected by a Wheatstone bridge arrangement.[1–4]

At steady state, the temperature difference, $(\Delta T)_i$, between both thermistors is given by

$$(\Delta T)_i = K_i[c/M_n + A_2 c^2 + A_3 c^3 + \cdots] \quad (1)$$

where K_i is a calibration constant at the steady state; c is the solution concentration and depends on the units that one is using; M_n is the number average molecular weight of the polymer; and A_2 and A_3 are the second and third virial coefficients of the polymer, respectively.[3]

On the other hand, this difference of temperature is proportional to the difference of the electrical resistance, Δr, between both thermistors, and in order to establish this proportionality, we

should consider the experimental parameters characteristic of both, the instrument and the system. These parameters are included in a calibration constant, K_i, that can be determined, in the limit of infinite dilution for a low-molecular-weight standard (s), by the equation

$$(\Delta r_s/m_s)_{m_s \to 0} = K_s \qquad (2)$$

where m_s is the molality of the standard, and K_s may be determined by regression analysis as the intercept of the curve $\Delta r_s/m_s$ versus m_s.[1-4]

In a similar way, we can determine the difference of the electrical resistance, Δr_p, for polymer solutions of different concentrations, c_p (in g/kg) (a polymer/solvent mass ratio), and another constant, K_p, can be obtained by regression analysis of the plot $\Delta r_p/c_p$ versus c_p, where p represents the polymer. The ratio of polymer mass by solvent mass is usually considered as the unit for polymer concentration, in a polymer solution of unknown molecular weight. Therefore, M_n values can be determined from a simple ratio between two calibration constants, K_s and K_p, [eq. (3)] that represent the ratio between two intercepts of the experimental curves $(\Delta r_i/m_i)_{m_i \to 0} = K_i$, where i should be considered the standard, s, or the polymer, p, and m_i is the concentration (molality or polymer/solvent mass ratio):

$$M_n = K_s/K_p \text{ (g/mol)} \qquad (3)$$

Collins et al.[2] reported that, in general, the plot of $\Delta r_p/c_p$ versus c_p exhibits a significant scattering of the points and may yield a straight line which does not pass through the origin or even may not be linear. Therefore, the regression analysis to obtain the curve intercept is, in some cases, very difficult or imprecise. In order to minimize this problem, some correction factors must be introduced. These experimental results were not theoretically explained and should be attributed to solvent effects.

Equation (1) shows that the temperature difference between the thermistors is proportional to both the sample concentration and the difference between their electrical resistance. In this work, we are demonstrating that the dispersion of the data in those plots can be minimized if we use plots of Δr_s versus m_s, instead of $\Delta r_s/m_s$ versus m_s, and Δr_p versus m_p, instead of $\Delta r_p/m_p$ versus m_p, for the standard and the polymer, respectively. Consequently, more precise molecular weight values are obtained, and the number average molecular weight, M_n, of polymers is directly determined from the ratio between the plot slopes for both standard, Θ_s, and polymer sample, Θ_p:

$$M_n = \Theta_s/\Theta_p \text{ (g/mol)} \qquad (4)$$

It is important to point out that this equation is valid for an ideal and diluted solution, for which the osmotic effect is proportional to the concentration. In order to test this alternative method, we choose a series of polyethylene glycols (PEGs), since it is well known that they represent a class of linear polymers with low-molecular-weight polydispersities.[5,6]

EXPERIMENTAL

Polyethylene glycols (PEGs) 200, 300, and 400 were supplied by Merck, and PEG-600, -1000, and -6000 were supplied by Riedel de Haen; these numbers specified the nominal number average molecular weight. These polymers are known to be very hygroscopic, and they must be carefully dried before using. PEG-200, -300, -400, -600, and -1000 were dried by adding 4 Å molecular sieves to the polymer in the liquid state (40°C in the case of PEG-1000). The drying process can be evaluated by infrared spectroscopy, following the band at 3500 cm^{-1} to constant intensity. PEG-6000 was used as received.

VPO measurements were performed at 55°C in a Kanuer instrument with a universal probe. Benzil (M_s = 210.23 g/mol) was used as a standard, and the solvent was toluene. The concentration range was from 2 to 16 g kg, depending on the polymer molecular weight. It is important to point out that this concentration range is lower than that suggested in the apparatus manual[7] but is within the concentration range indicated by the ASTM regulation.[4] We used only one standard since the polymer molecular weight range is lower than 5,000, except for PEG-6000.[4]

The Δr values were chosen as those maxima which remained constant over a certain period of time. The drop sizes were kept constant throughout the whole procedure, and the measurements for each polymer were repeated three times, beginning with the most dilute solution. Measurements of the calibration curve were repeated several times.

Table I   Simulated Values for the Calibration Constant K_i for the Two Different Methods

$\Delta(\Delta r_i)$ (%)	K_i (1)	ΔK_i (1) (%)	K_i (2)	ΔK_i (2) (%)
0	1,000[a]	0	1,000	0
+5 (1 or 3)	985	−1.5	1,050	+5.0
−5 (1 or 3)	1,015	+1.5	950	−5.0
+5 (1 and 3)	1,000	0.0	1,050	+5.0
+5 (1), −5 (3)	970	−3.0	1,050	+5.0
−5 (1), +5 (3)	1,030	−3.0	950	−5.0
−5 (1 and 3)	1,000	0.0	950	−5.0
$\Sigma(|\Delta 1,000|)/9$		1.3		3.3

K_i (1) values were obtained with the slope of the plot Δr_i versus m_i; K_i (2) values were obtained from the intercept of the plot $\Delta r_i/m_i$ versus m_i.

[a] Expected values considering $\Delta r_i = 1,000\ m_i$ in absence of experimental errors. (i) points where the maximum error of 5% has been considered.

RESULTS AND DISCUSSION

Numerical Simulation

We have performed and compared the errors for the calibration constant values obtained from a
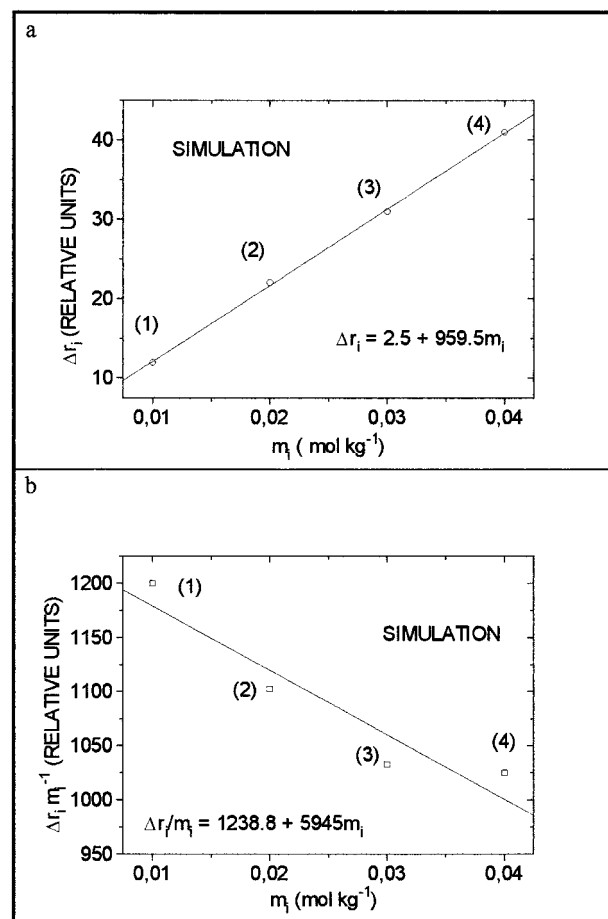

Figure 1   Simulated plots. (a) Δr_i versus m_i and (b) $\Delta r_i/m_i$ versus m_i, using the hypothetical equation $\Delta r_i = 1.0 + 1,000\ m_i$, considering an error of +5% in the point (2).

numerical simulation, based on the two different procedures and a same hypothetical data base. In the first case, we determined the calibration constant value from intercept of the plots $\Delta r_i/m_i$ versus m_i; and in the second one, we determined the value from the slopes of the plots Δr_i versus m_i. For this numerical simulation, we have considered two hypothetical situations, as follows.

Linear Plot with Intercept Equal to Zero

In this case, experimental data should be represented by a hypothetical linear equation $\Delta r_i = K_i m_i$, and the plot $\Delta r_i/m_i$ versus m_i should be linear with an intercept equal to zero. Assuming, by hypothesis, that $K_i = 1,000$ and four solutions with different concentrations, 0.01, 0.02, 0.03, and 0.04 mol/kg, we calculated the hypothetical experimental data Δr_i using the linear equation. In Table I, we showed typical errors obtained for the calibration constant value using both plot types, supposing that 1. there is a maximum error of ±5% in only one Δr_i value (point 1 or point 3); and 2. the same maximum error is attributed to both points 1 and 3, simultaneously. The influence of these simulations on the value of the calibration constant is shown in Table I for both cases, and one can see that the plot $\Delta r_i/m_i$ versus m_i induces, always, a higher average deviation from the expected value for the calibration constant defined as $K_i = 1,000$.

Linear Plot with a Nonzero Linear Coefficient

Collins et al.[2] and others[1] reported that the plot $\Delta r_i/m_i$ versus m_i should exhibit a nonzero linear coefficient. To consider this situation, we have been assumed a linear equation $\Delta r_i = 1.0 + 1,000\ m_i$ as another hypothetical example, where m_i values were chosen as the same concentration val-
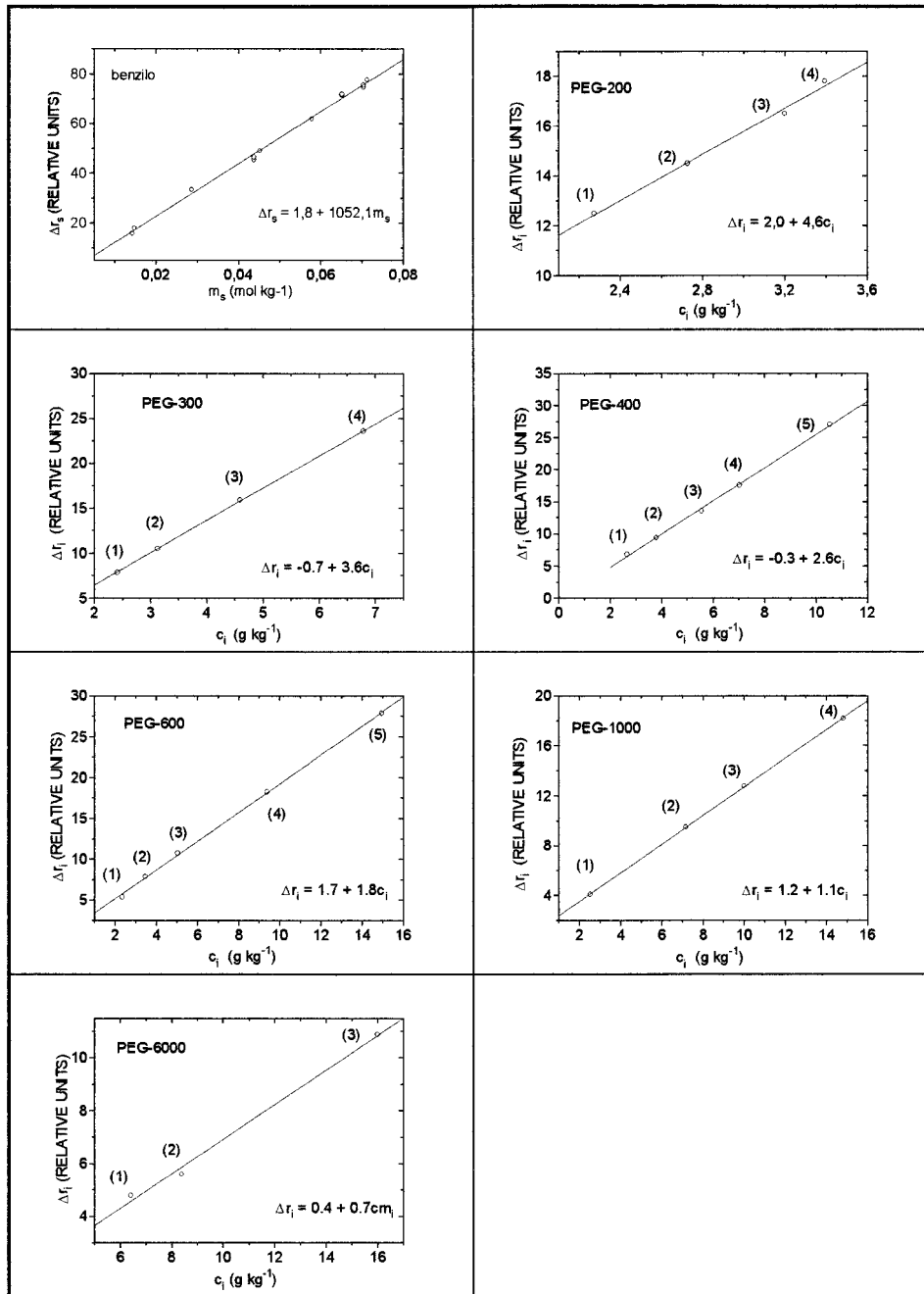
Figure 2 Plots for Δr_i versus concentration m_i (molality) for Benzil and c_i (g/kg) for different PEGs.

ues. The intercept of this linear equation is 0.1% of the hypothetical K_i value. The Δr_i values were calculated with this hypothetical equation, and the calibration constants were obtained from either the slope of the plots Δr_i versus m_i or the intercept of the plot $\Delta r_i/m_i$ versus m_i. These calculated values were K_i = 1,000 and 1,112.5, respectively, and the second value corresponds to +10.1% of the expected one. The higher difference

of this last value compared with the hypothetical one is explained considering that the function $\Delta r_i/m_i$ is not the derived from the function when the plot exhibits a nonzero linear coefficient.

Let us consider now a simulation when an error of +5% is supposed to occur in the second point. In this case, the theoretical value of Δr_i is 22.5 instead of 21.0, which has been considered before. With this new value, the best fit of each
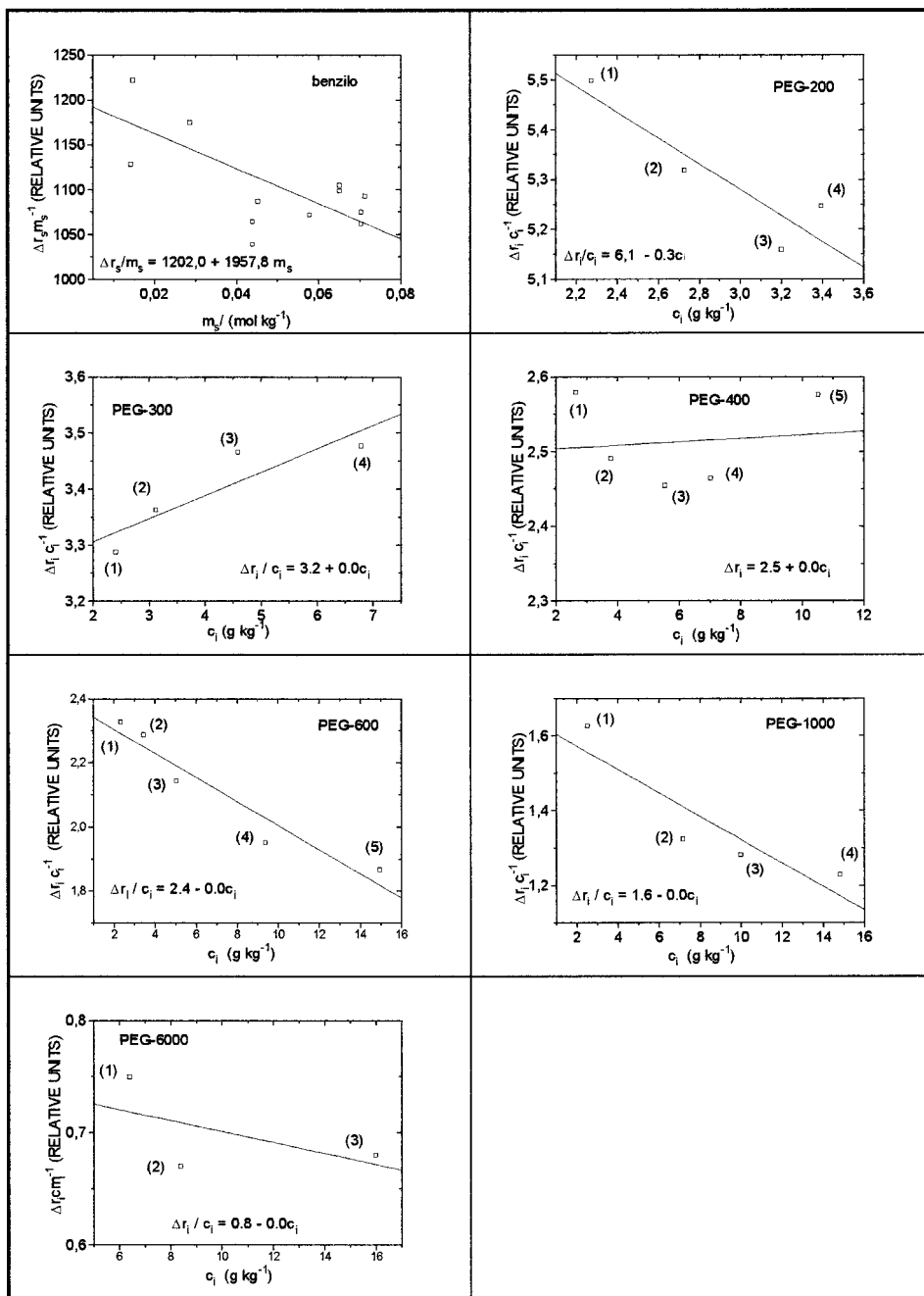
Figure 3 Plots for $\Delta r_i / m_i$ versus concentration m_i (molality) for Benzil and c_i (g/kg) for several PEGs.

plot gives the following values for K_i: 959.5 for the plot a (a difference of 4.1% from the theoretical value) [Fig. 1(a)] and 1,238.8 for the plot b (a difference of 19.3% from the expected value) [Fig. 1(b)].

Therefore, for both simulations, i.e., using linear equations with zero and nonzero intercepts, we could see that the plot $\Delta r_i / m_i$ versus m_i cannot be represented by a perfectly straight line parallel to the abscissa, as expected. The best fit of this plot presents a smaller slope, which induces a higher error of the calibration constant value, and thus, this error is transferred to the molecular weight value. For this reason, we decided to use the plot Δr_i versus m_i to determine the calibration constants and the number average molecular weight of the polymers.

Table II   Values of M_{ni} (g/mol) for Some PEGs Using the Plots in Figures 2 and 3

PEG	M_n (g/mol) (1)[a]	M_n (g/mol) (2)[b]
200	229 ± 10 (13%)[a]	197 ± 11 (2%)
300	292 ± 9 (3%)	376 ± 14 (20%)
400	405 ± 17 (1%)	481 ± 22 (17%)
600	585 ± 34 (3%)	501 ± 24 (17%)
1,000	956 ± 88 (4%)	751 ± 50 (25%)
6,000[d]	5,696 ± 492 (5%)	5,451 ± 621 (9%)

[a] (1) From the plots of Figure 2.
[b] (2) From the plots of Figure 3.
[c] Values in parentheses are the respective errors compared with the nominal values.
[d] For this polymer, we have used another calibration constant because we used another output range in the instrument scale.

Determination of Molecular Weight of PEG

As indicated earlier, we measured the Δr_i values for solutions of PEG-200, -300, -400, -600, -1000, and -6000 in toluene, using Benzil as a standard. Regardless, the concentration of polymer is expressed by the polymer/solvent mass ratio (g/kg), whereas the concentration unit in the case of the standard is molality, as explained earlier. The plots of Δr_i values versus concentration c_i and for $\Delta r_i/c_i$ versus c_i are shown in Figures 2 and 3, respectively. Nevertheless, the number average molecular weight of these polymers could be determined either using the plot slopes in Figure 2 [eq. (4)] or using the plot intercepts in Figure 3 [eq. (3)].

From Figure 2, we can obtain fits with better correlation coefficients than for Figure 3, and therefore, one could obtain lower errors in the calibration constants for both the standard (Benzil) and the polymer solutions. Then, these results will be reflected in a more precise value of the number average molecular weights of the polymers, as shown in Table II, with errors within the acceptable range for the molecular weight range, except for PEG-200.[4] We do not have any unquestionable answer for this exceptionally high error obtained for PEG-200, but some miscibility problem due to its lower solubility in toluene could cause the lower precision of these data.[8−10]

For this reason, we recalculated the number average molecular weight of PEG-200, using benzene as a solvent instead of toluene, either from the intercept of the curve $\Delta r_i/m_i$ versus m_i or from the slope of the curve Δr_i versus m_i; the new values are 184 ± 4 (7%) and 341 ± 73 (41%), respectively. Values in parentheses represent the errors compared with the nominal value.

CONCLUSIONS

From these results, we concluded that the VPO technique would be a more precise technique to determine the number average molecular weight of polymers if we use a direct plot of the experimental data Δr_i versus m_i instead of $\Delta r_i/m_i$ versus m_i and if we use the angular coefficient of the first plots in order to determine the calibration constants. In order to get higher precision values, we must also be concerned with the concentration limits and solubility of the samples in certain solvents and work within the concentration range indicated in the ASTM normalization.[4] It is noteworthy that the concentration limit established by the ASTM regulation is lower than that described in some instrument operation manuals.[7] Using an adequate concentration range, we avoid the aggregation of the polymer in the solutions and reduce the relative importance of the nonlinear terms describing the virial coefficients on the temperature difference [eq. (3)]. Some careful manipulation work must be also carried out when we are dealing with hygroscopic polymers, as in the case of PEGs.

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