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Fits to Osmotic Pressure Data

Cohen and Highsmith have provided alternative, polynomial fits to empirically measured osmotic pressures of solutions, particularly those available for general use in osmotic stress experiments (Parsegian et al., 1995). There are several ways such data can be fit. We (Reid and Rand, 1997) have suggested another alternative to what was published earlier (Parsegian et al., 1995), based on the original idea of Haldane (1928) and recently used by Fullerton et al. (1992). According to that simple idea, nonideal osmotic pressure results because of the “binding” of water to solute, effectively removing it from activity, or equivalently, because of the exclusion of neighboring solute molecules from each solute molecule’s local “hydration shell.” Such mutual exclusion, or preferential hydration, is the basis behind the use of “osmotic stress” to probe aqueous compartments.

In addition to such “binding” or exclusion, it is observed (see Table 1 and Fig. 1) that osmotic pressures of equivalent weight concentrations of larger solutes become independent of molecular weight. The osmotic pressures of polyethylene glycols (PEGs) become practically independent of their nominal osmolality, as determined from their nominal or number average, or “vendor MW” (MW_{vendor}). The larger molecules behave osmotically as if they have a considerably smaller ideal or effective molecular weight (MW_{eff}), or equivalently, they behave colligatively, as if the osmotic unit were a fraction of a molecule. This is consistent with the idea that for very large polymers, as with persistence lengths, some effective mass acts osmotically independently of distant parts of the molecule.

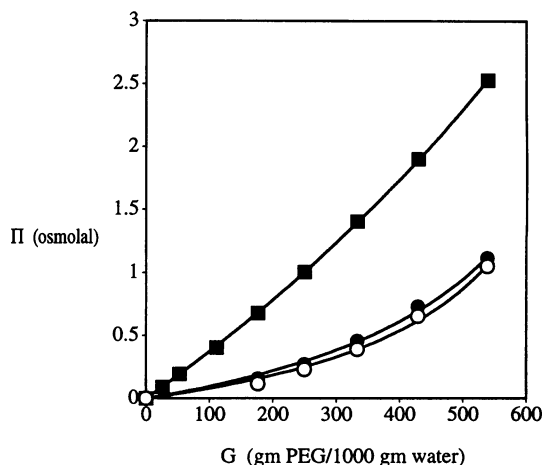


FIGURE 1 Plot of the empirical data, Π versus G , as shown in Table 1, for PEGs of MW_{vendor} 300 (■), 3000 (●), and 8000 (○). Osmotic pressure is nearly independent of MW_{vendor} for higher MWs. The fitted lines are to $\Pi = (G/MW_{\text{eff}})/1000 - m^*(G)$; the fitting parameters MW_{eff} and m are provided in Table 1.

The table provides our complete set of new experimental data for 10 different PEGs. These data are entirely consistent with our older data, used by Cohen and Highsmith. These data will be integrated with the older data, and the alternative fits discussed in these letters will be made available at the websites <http://aqueous.labs.brocku.ca/osfile.html> and <http://www.mgsl.dcrn.nih.gov/docs/OsmoticStress.html>.

Our fits to nonideal osmotic pressure were made on the following basis: 1) that m grams of water per gram of PEG are effectively removed by PEG from being active, or exclude other PEG molecules (following Haldane, 1928);

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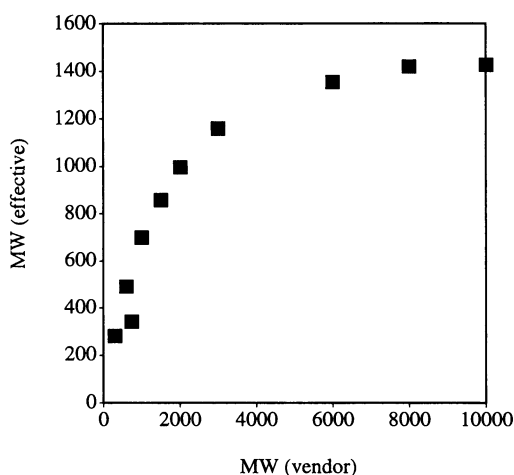


FIGURE 2 Plot of MW_{eff} versus MW_{vendor} for all PEGs measured. MW_{eff} is determined as described in the text and provided in Table 1.

and 2) that PEG molecules act with some effective or ideal molecular weight MW_{eff} . Derivation of MW_{eff} precludes the need to know the actual MW of the osmotically active species.

On this basis, therefore, where G grams of PEG are added to 1000 grams of water, mG grams of water are effectively removed from activity, leaving $1000 - mG$ grams of active

water. G/MW_{eff} is the ideal molality of the solution. Π , as reported by osmotic or vapor pressure or other measuring devices of colligative properties, is the equivalent ideal osmolality of the solution. Therefore,

$$\Pi = (G/MW_{\text{eff}})/(1000 - mG)$$

was fit to empirical plots of Π versus G (Table 1), evaluating m and MW_{eff} (Reid, 1995).

Fig. 1 shows, as examples, the measured osmotic pressure for PEGs of MW_{vendor} 's 300, 3000, and 8000 and fits to that data. The 3000 and 8000 MW data clearly show the independence of osmotic pressure and molality.

Fig. 2 shows how MW_{eff} of PEG plateaus at ~ 1400 . On the basis of our model, that maximum molecular mass appears to act osmotically as independent particles, or conversely, PEG of molecular weight 10,000, for example, acts as $10,000/1400 = 7$ independent ideal solute molecules.

Fig. 3 shows that PEG, with increasing size, appears to act osmotically, as if it "binds" or excludes from other PEGs up to 120% of its own weight in water. Importantly, this exclusion is not trivial, and extends to even smaller solute molecules. Bezrukov and Vodyanoy (1993) showed, using salt activity measurements, that PEG binds water to ~ 110 – 120% of its own weight. The enhanced osmotic activity of glucose in PEG solutions shows that glucose to the same extent, does not have access to all of the solution water, (Reid and Rand, 1997; Reid, 1995).

TABLE 1 Measured osmotic pressures for solutions of PEG from MW 300 to 10,000, and fits to those data

| PEG Molecular Weight _{vendor} ($MW_{\text{Effective}} \cdot m$) | | | | | | | | | |
|--|----------------------|---------------------------|----------------------|---------------------------|----------------------|---------------------------|----------------------|-----------------------------|------------------------|
| 300 (281, $m = 0.450$) | | 400 (342, $m = 0.561$) | | 600 (491, $m = 0.753$) | | 1000 (699, $m = 0.887$) | | 1500 (857, $m = 0.956$) | |
| G (300) | Π (300) osmolal | G (400) | Π (400) osmolal | G (600) | Π (600) osmolal | G (1000) | Π (1000) osmolal | G (1500) | Π (1500) osmolal |
| 0.0 | 0.000 | 0.0 | 0.000 | 0.0 | 0.000 | 0.0 | 0.000 | 0.0 | 0.000 |
| 25.6 | 0.091 | 52.6 | 0.138 | 52.6 | 0.103 | 111.1 | 0.134 | 111.1 | 0.127 |
| 52.6 | 0.192 | 111.1 | 0.328 | 111.1 | 0.246 | 176.5 | 0.282 | 176.5 | 0.222 |
| 111.1 | 0.404 | 176.5 | 0.537 | 176.5 | 0.395 | 250.0 | 0.434 | 250.0 | 0.365 |
| 176.5 | 0.676 | 250.0 | 0.830 | 250.0 | 0.617 | 333.3 | 0.696 | 333.3 | 0.581 |
| 250.0 | 1.003 | 333.3 | 1.204 | 333.3 | 0.915 | 428.6 | 1.024 | 428.6 | 0.879 |
| 333.3 | 1.403 | 428.6 | 1.662 | 428.6 | 1.310 | 538.5 | 1.458 | 538.5 | 1.283 |
| 428.6 | 1.901 | 538.5 | 2.244 | 538.5 | 1.835 | | | | |
| 538.5 | 2.526 | | | | | | | | |
| 2000 (995, $m = 1.025$) | | 3000 (1159, $m = 1.091$) | | 6000 (1353, $m = 1.145$) | | 8000 (1419, $m = 1.193$) | | 10,000 (1426, $m = 1.196$) | |
| G (2000) | Π (2000) osmolal | G (3000) | Π (3000) osmolal | G (6000) | Π (6000) osmolal | G (8000) | Π (8000) osmolal | G (10,000) | Π (10,000) osmolal |
| 0.0 | 0.000 | 0.0 | 0.000 | 0.0 | 0.000 | 0.0 | 0.000 | 0.0 | 0.000 |
| 111.1 | 0.094 | 176.5 | 0.157 | 176.5 | 0.126 | 176.5 | 0.118 | 176.5 | 0.109 |
| 176.5 | 0.196 | 250.0 | 0.270 | 250.0 | 0.239 | 250.0 | 0.229 | 250.0 | 0.218 |
| 250.0 | 0.314 | 333.3 | 0.456 | 333.3 | 0.402 | 333.3 | 0.391 | 333.3 | 0.383 |
| 333.3 | 0.517 | 428.6 | 0.731 | 428.6 | 0.656 | 428.6 | 0.653 | | |
| 428.6 | 0.806 | 538.5 | 1.114 | 538.5 | 1.028 | 538.5 | 1.050 | | |
| 538.5 | 1.194 | | | | | | | | |

m = grams H_2O "bound" per gram of PEG.

$G(MW_{\text{vendor}})$ = grams of PEG per 1000 grams water of the PEG solutions.

$\Pi(MW_{\text{vendor}})$ = the measured osmotic pressures of the PEG solutions (ideal osmolal).

PEG Molecular Weight_{vendor} is the number average molecular weight determined by end-group titration analysis (Fluka).

$MW_{\text{Effective}}$ and m values are derived from least-squares fit to $\Pi = (G/MW_{\text{Effective}})/(1000 - m \cdot G)$.

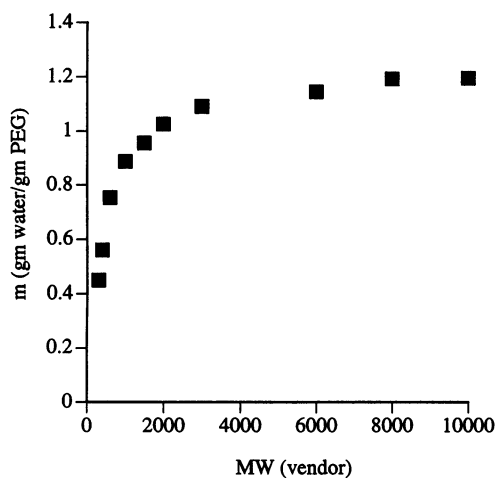


FIGURE 3 Plot of m versus MW_{vendor} . m is the number of grams of water "bound" per gram of PEG, and is determined as described in the text and provided in Table 1.

In conclusion, there are several analytical ways to fit the experimental data; three have now been proposed. The one suggested originally (Parsegian et al., 1995) was for description purposes only; the two proposed in these letters are based on different perceptions of a model mechanism lying behind the nonlinearity. Both model fits are extremely good, and although more measurements outside the data sets might be made, especially at low pressures, there appears to

be little possibility of distinguishing models. Any of the three fits can be used for the purpose of determining osmotic pressures for osmotic stress measurements, but only these latter two can be used for extrapolation. We believe there is some advantage in not needing to know or use the actual molecular weight of the solute.

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