

A Proposed Experimental Procedure for the Vapor Pressure Osmometer to Minimize the Solute Dependence of the Calibration Constant

In two previous publications^{1,2} the operating procedure of the Hewlett-Packard Model 302 Vapor Pressure Osmometer (VPO) was critically examined. One particularly disturbing result was the demonstration of a molecular weight dependence of the calibration constant. I now propose an approximate solution to this problem.

The theoretical model² developed to explain the solute dependence of the calibration constant shows that the temperature difference (and therefore resistance difference) between the two thermistors in the VPO can be represented by

$$\Delta R = \frac{KC_0}{\bar{M}_n} (1 + \beta'/D_0) + \text{higher order terms} \quad (1)$$

where K is the calibration constant as determined using a low-molecular-weight standard, C_0 is the solution concentration, D_0 is the average diffusion coefficient for the sample in the solvent at a given temperature, and β' is a constant for a given instrument configuration and solvent system. D_0 can be shown³ to be approximated by

$$D_0 = \Phi'(K'_s)^{1/3}/(M)^{1/2} \quad (2)$$

where Φ is a universal constant, K_s the constant in the intrinsic viscosity-molecular weight relationship, and M is the molecular weight. While for a given temperature and solvent system K_s is variable for different molecular species, the variation of the cube root will be far less and consequently neglected as an approximation. Consequently, eq. (2) becomes

$$D_0 = \Phi/M^{1/2} \quad (3)$$

Ordinarily, for a polydisperse sample, M would be replaced by the viscosity-average molecular weight. However, the previous model shows that the diffusion of the smaller molecules produces the largest effects. Therefore, M is approximated by \bar{M}_n in eq. (3). Consequently, eq. (1) can be rewritten as

$$\Delta R = \frac{KC_0[1 + \beta(\bar{M}_n)^{1/2}]}{\bar{M}_n} + \text{higher terms in } C_0 \quad (4)$$

Equation (4) suggests a better calibration procedure so that the effects of the solute dependence of the calibration constant can be minimized. First, K can be determined in the usual manner using a low-molecular-weight standard by neglecting the second term in the brackets. Second, β is determined using a high-molecular-weight ($\bar{M}'_n > 20,000$) material of *known* molecular weight from

$$\beta = \frac{(S'\bar{M}'_n/K) - 1}{(\bar{M}'_n)^{1/2}} \quad (5)$$

where K is the calibration constant determined using the low-molecular-weight standard and S' , the linear coefficient determined from a polynomial regression of ΔR versus C_0 .

From a solution of eq. (4), the number-average molecular weight (\bar{M}_n) of an unknown material can be shown to be

$$\bar{M}_n = \frac{K^2}{4S^2} \left[\beta + \left(\beta^2 + \frac{4S}{K} \right)^{1/2} \right]^2 \quad (6)$$

where S is the linear coefficient in the polynomial regression of ΔR versus C_0 .

The application of the above method to polystyrene materials reported on previously¹ is given in Table I. The term β was determined by assuming $\bar{M}_n = 21,500$ to be the actual value for this sample. The data show that using a secondary standard produces dramatically better agreement with the accepted values.

For high-molecular-weight materials, the use of two calibration constants has been demonstrated to yield \bar{M}_n values that are more consistent with those obtainable using the membrane osmometer. However, it may not be clear why a high-molecular-weight standard alone cannot be used for cali-

TABLE I
Molecular Weights of Standards by VPO

Accepted \bar{M}_n ^a	Hewlett-Packard Procedure ^b	Amoco ^c	Amoco ^d
3525	3120	3500	3290
10,300	9480	10,400	10,400
20,000	18,850	21,500	21,500
51,000	38,000	49,000	46,000

^a Polystyrene determined by ArRo Labs.

^b Run as suggested in Hewlett-Packard Model 302 VPO.

^c Measured so as to eliminate drop size (Ref. 1).

^d Calculated using the 21,500 sample as the high-molecular-weight standard as suggested in this publication.

bration. This can be answered in the following way: just as a calibration constant obtained with a low-molecular-weight standard gives incorrect values for \bar{M}_n when applied to high-molecular-weight polymers, a calibration constant obtained with a high-molecular-weight standard gives increasingly erroneous results as the \bar{M}_n of the unknown decreases.

References

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