Molecular Weight Determination of High Polymers by Means of Vapor Pressure Osmometry and the Solute Dependence of the Constant of Calibration

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Synopsis

Data are presented to show that the calibration constant of the vapor pressure osmometer is in fact not a constant, but rather depends on the nature of the solute. It is shown that the assumption of the constancy of the calibration constant is particularly severe when comparing low molecular weight standards and polymeric materials. A model is presented which visualizes either condensation or evaporation taking place at the solution drop surface, depending on the relative magnitudes of the concentration and Thermistor self-heating. In terms of this model, the solute dependence of the calibration constant is attributed to the formation of a diffusion-controlled surface concentration of the solution drop that differs from the concentration of the drop as a whole. Experimental evidence consistent with a diffusion-controlled surface layer is given. A method based on this model is given for operating the instrument so that the solute dependence of the calibration constant disappears. When the instrument is run in this manner, $\bar{M}_n$ determinations from vapor pressure and membrane osmometry are in significantly better agreement than when the instrument is operated as recommended by the manufacturer.

INTRODUCTION

Vapor pressure osmometry, hereafter referred to as VPO, is a commonly used method to measure the number-average molecular weight $\bar{M}_n$ of polymers up to molecular weights of approximately 10,000.[1] One commercially available version of the VPO that is capable of operating at 130°C is the Hewlett-Packard design. High-temperature operation is often needed since no room temperature solvents are known for many polymers such as polyethylene.

Although the exact operating principles for the VPO are not completely understood, the basic principle and operating procedure are straightforward. A known weight of polymer is dissolved in a solvent, and a drop of this solution and a drop of the solvent are suspended from separate Thermistors in a closed cell saturated with the solvent vapor. The Thermistors are connected to form the "legs" of a Wheatstone bridge circuit so that, at a constant applied voltage (0.50 V is specified), the difference between the solution activities of the two drops results in a differential mass transfer be-

tween them and therefore in a small temperature difference. The small temperature difference between the Thermistors causes the bridge to become unbalanced, and a resistance difference, ΔR, is measured. After a short period of time, typically 2 to 3 min is recommended,[1] the approximate steady-state value of ΔR is measured and then used along with a calibration constant to determine the $\bar{M}_n$ of the polymer. Such instructions assume that calibration with low molecular weight materials is valid and that the approximately constant value of ΔR that is reached after a relatively short time accurately mirrors the steady state, assuming one exists.

The VPO has two major shortcomings. The first is that the method becomes less accurate as molecular weight is increased, being most accurate below 10,000 molecular weight.[1] This drawback has reportedly been overcome by Wachter and Simon[2] at low temperature by the construction of a very sensitive version of the VPO. Unfortunately, no instrument similar to that of Wachter and Simon that is capable of operation to 130°C is commercially available at this time.

The second major problem associated with the VPO concerns the use of calibration, which relegates VPO to something less than an "absolute" method for the determination of $\bar{M}_n$. No rigorous justification is usually given for applying calibration constants obtained with low molecular weight standards, except that various standards yield approximately the same constant, and results obtained for polymers roughly agree with those obtained by the membrane osmometer.[3] The only commonly used method to determine $\bar{M}_n$ without the use of calibration is membrane osmometry. However, membrane osmometry has the problem of permeation through the membrane, which limits its utility to molecular weights greater than 25,000 for narrow fractions[4] and is generally unsuitable for most broad molecular weight distribution whole polymers.

Two excellent attempts to develop a theoretical model to describe the VPO operation have been put forth,[5,6] but both make the simplifying assumptions that (1) the effect of Thermistor self-heating is negligible, (2) the process is not diffusion controlled within the drop, and (3) the drop itself is of uniform temperature (no conduction problems). Simon et al.[5] have concluded that diffusion of solvent through the cell atmosphere is the rate-controlling factor. Assumptions (2) and (3) were considered valid assumptions since (2) would lead to solute-dependent behavior and (3) would lead to a strong dependence on drop size; neither dependence was observed experimentally. The first of the above assumptions may well be valid at the very high ΔR values obtained for low molecular weight materials where the heat due to condensation on the solution drop is much greater than the Thermistor self-heating. However, the determination of $\bar{M}_n$ for high molecular weight materials restricts the experimentalist to the low ΔR values obtained for workable weight concentrations, and, therefore, Thermistor self-heating is expected to be of greater importance.

As a consequence of the questionable validity of calibration and the need to extend the molecular weight range of the VPO at high temperatures

into that of the membrane osmometer so as to plug the gap that exists where neither method is considered accurate, I have undertaken a study to define and clarify the major processes in VPO and to show how they relate to the calibration constant, and therefore to the final value of $\bar{M}_n$ obtained. My experiments involve polymers of known $\bar{M}_n$ ranging from about 3,500 to 80,000. Drop size, bridge voltage, type and concentration of polymer, and degree of saturation of the cell atmosphere were evaluated.

The results show that the behavior of high polymers is quite different from that of low molecular weight materials in the VPO. Bridge voltage is found to be a significant variable whose effect is related to the type and concentration of the polymer. The calibration constant clearly depends on the nature of the solute, and, therefore, the operating procedures involving a constant obtained with low molecular weight materials are not valid for high polymers. With high polymers, diffusion through the solution drop apparently becomes a significant rate-controlling process. It is possible, however, to operate the osmometer in such a way that the solute dependence of the calibration constant is eliminated—bridge voltage is varied according to the ΔR reading for the polymer, and a longer time than the manufacturer advocates is allowed for ΔR to reach a steady state.

EXPERIMENTAL

All experiments were run on a Hewlett-Packard vapor pressure osmometer, Model 302, operated at 130°C with distilled o-dichlorobenzene as the solvent. Drop size was measured with a cathetometer through a viewing mirror.

The Wheatstone bridge circuit of the instrument was modified as shown in Figure 1 such that the bridge voltage could be varied.

Calibration standards were: (1) tristearin, chromatography grade, Supelco, Inc., and (2) dotriacontane, Eastman "white label." Both were used as received. Accurate molecular weights for these materials were obtained by mass spectrometry.

Calibration was accomplished with both tristearin and dotriacontane, and values for K of 655 and 658 were obtained, respectively. An average
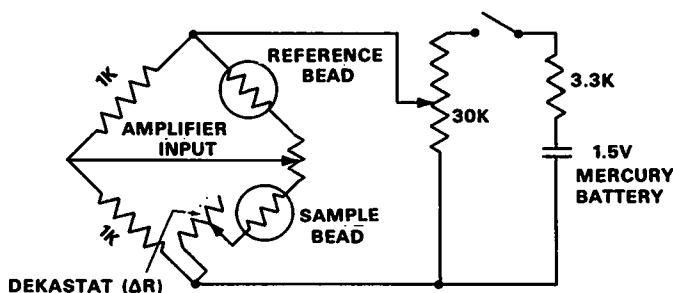

Fig. 1. Diagram of modified Wheatstone bridge circuit for the Hewlett-Packard Model 302 vapor pressure osmometer.

value for K of 656 was used in the later determination of $\bar{M}_n$ for the polymeric samples.

The high polymers were: (1) seven polystyrene standards of $\bar{M}_n$ 3,525, 10,300, 20,000, 51,000, 97,000, 160,000, and 400,000, obtained from ArRo Laboratories, where the $\bar{M}_n$ of all but the 3,525 standard had been determined by membrane osmometry; (2) hydrogenated polybutadiene, 108MH, of $\bar{M}_n$ 82,000, which had been obtained from Phillips and then extracted with carbon disulfide to remove the approximately 0.05% Ionol that was said to be present; and (3) NBS 1475 polyethylene standard of $\bar{M}_n$ 18,300.

Two operating procedures were used in the molecular weight determinations: (1) 2-min readings of ΔR according to the procedure outlined in the instruction manual,[1] and (2) steady-state readings taken after 20 min.   Procedure (2) was used in this paper unless otherwise indicated.

RESULTS AND DISCUSSION

Effect of Drop Size on ΔR

Meeks and Goldfarb[7] have shown that drop size has a significant effect on VPO readings.   They attributed such effects to conduction within the drop resulting from the net processes of condensation (or evaporation) and Thermistor self-heating.   However, because their data were obtained at only one bridge voltage, they could give no quantitative support for the importance of Thermistor self-heating.

With drop length l taken as a measure of drop size, Figure 2 is a plot of ΔR versus drop length at a bridge voltage of 0.5 volts.   The slopes of the lines vary with ΔR; as ΔR is increased, the slope first goes to zero and then becomes negative.   A similar plot was reported by Meeks and Goldfarb.[7]

Figure 3 gives plots of $\delta(\Delta R)/\delta l$ (the slope of ΔR versus drop length as given in Fig. 2) versus ΔR at a constant drop length of 0.25 cm and at two different bridge voltages for various materials ranging from polymers to low molecular weight calibration materials.   Since a trend for the dependence of ΔR on drop length (i.e., $\delta(\Delta R)/\delta l$ on the ΔR range at a given bridge voltage) is apparent from Figure 3, the nature of the solute is assumed to play little role in the observed drop size effects.   From Figure 3, an approximate proportionality between V^2, the square of the bridge voltage, and ΔR, when the effect of drop size is negligible ($\delta(\Delta R)/\delta l = 0$), appears to hold.   The ratio of V^2 is 0.09:0.25 for the two V^2 values represented in Figure 3, and for ΔR, when $\delta(\Delta R)/\delta l = 0$, the ratio is approximately 1.1:3.0 ohms.

The results in Figure 3 are interpreted in terms of the following model. The Thermistor beads for both the solution and pure solvent drops have a heat capacity C_s and resistance R_0, and generate heat at the rate equal to the square of the bridge voltage, V^2, divided by R_0.   As shown in Figure 4, a schematic diagram for the transport process, heat will be gained or lost to the surroundings by the Thermistor through a liquid drop on the
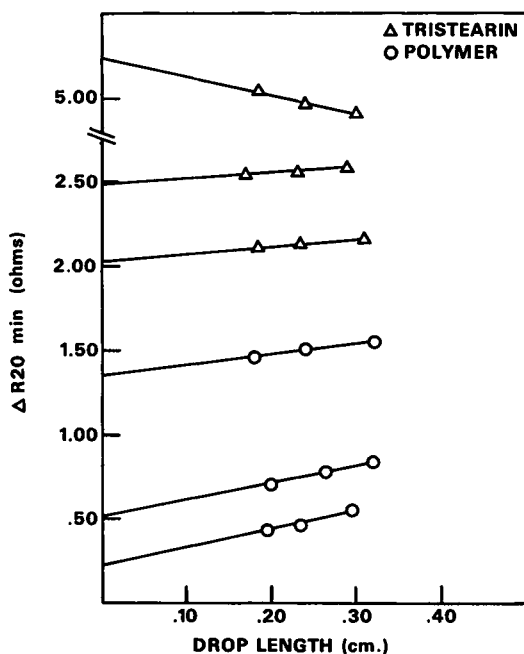
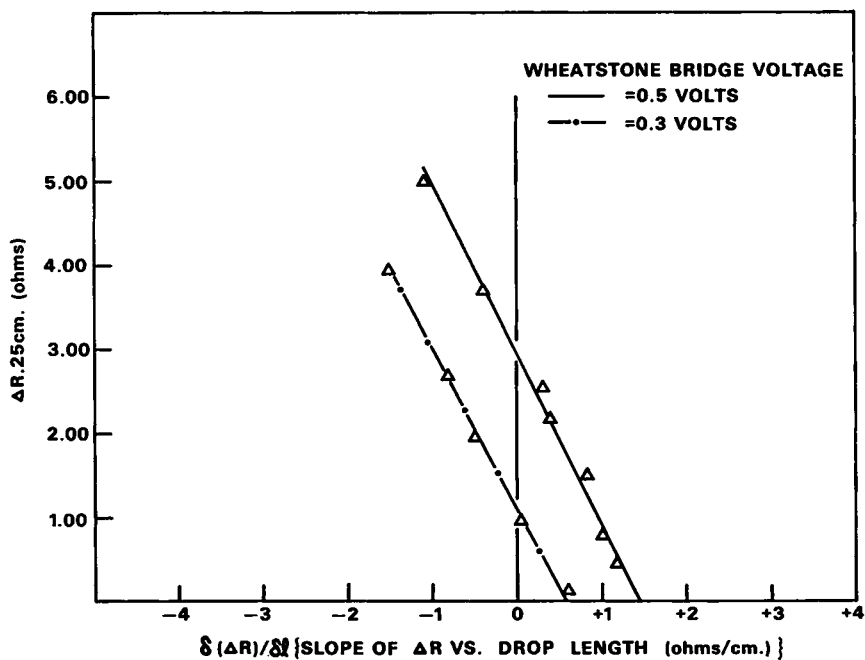Fig. 2. Plot of ΔR taken after 20 min for a fixed bridge voltage of 0.50 volts vs. solution drop length.

Fig. 3. Dependence of $\delta(\Delta R)/\delta l$ (the slope of ΔR vs. drop length as illustrated in Fig. 2) on ΔR at a constant drop length of 0.25 cm.
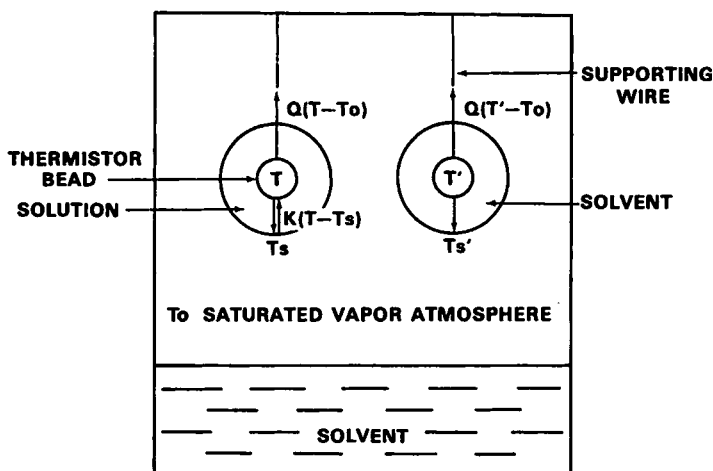
Fig. 4. Schematic diagram of the VPO cell depicting the net heat flow from the Thermistor beads.

bead according to $-K(T - T_s)$, where K is the net liquid and glass thermal conductivity, T is the Thermistor temperature, and T_s is the temperature of the drop surface. T_s depends on the Thermistor self-heating, heat losses at the drop surface, and the rate of solvent condensation (or evaporation, depending on the net heat flow through the drop). Heat will be lost through the wire supporting the Thermistor according to $Q(T - T_0)$, where Q is the thermal conductivity of the wire and T_0 is the cell temperature. Therefore, the differential equation for the change of thermistor temperature with time is

$$C_v \frac{dT}{dt} = \frac{V^2}{R_0} - K(T - T_s) - Q(T - T_0) \tag{1}$$

or for an approximate steady-state,

$$0 = \frac{V^2}{R_0} - K(T - T_s) - Q(T - T_0). \tag{2}$$

At a point of zero drop size effects, the term containing K must be zero, because it is the only term which varies with drop size. Thus, at the point of zero drop size effects, $T - T_0 = V^2/R_0Q$ and $T = T_s$. Assuming a steady-state temperature T' for the pure solvent Thermistor, $T - T' \equiv \Delta T = V^2/R_0Q + (T_0 - T')$; or since $\Delta R \simeq a\Delta T$, where a is a constant involving temperature, the thermistor constant, and R_0,

$$\Delta R = a \left\{ \frac{V^2}{R_0Q} - (T_1 - T') \right\}. \tag{3}$$

If we make the approximation that $T_0 - T'$ is proportional to V^2/R_0, then agreement is obtained with the experimental results (namely, that at the point of zero drop size effects, $\Delta R \propto V^2$). This approximation is presum-

ably a good one because Thermistor self-heating is the only source of heat for the pure solvent drop. Since our simple model describing the heat flow within the drop appears to be able to account for the observed dependence of ΔR on V^2 at the point of zero drop size effects, drop size effects will be assumed to be the result of the net heat flow within the drop due to the resultant of Thermistor self-heating and heat losses of the supporting wires, and the resultant of condensation (or evaporation) and heat losses at the drop surface. Further, at the point of zero drop size effects for the solution drop, no net heat flow within the solution drop occurs.

Solute Dependence of the Calibration Constant

The complex relationships among ΔR, bridge voltage, and type and concentration of polymer are summarized in Figures 5–8. Figure 5 gives plots of ΔR versus V^2 for various solutes. Immediately apparent from Figure 5 is the increase in ΔR with bridge voltage. In order to check whether this increase with V^2 resulted from a pair of badly mismatched Thermistors with different resistances, the resistances of the Thermistors were carefully checked and found to be the same within our ability to measure ($\pm 5\ \Omega$, approximately $\pm 0.1\%$ of the measured value). Although it may be argued that differential Thermistor self-heating could give rise to the variation of ΔR with V^2, this explanation is unable to account for the strong solute dependence of the variation of ΔR with V^2. The dependence of the variation of ΔR with V^2 on the nature of the solute indi-
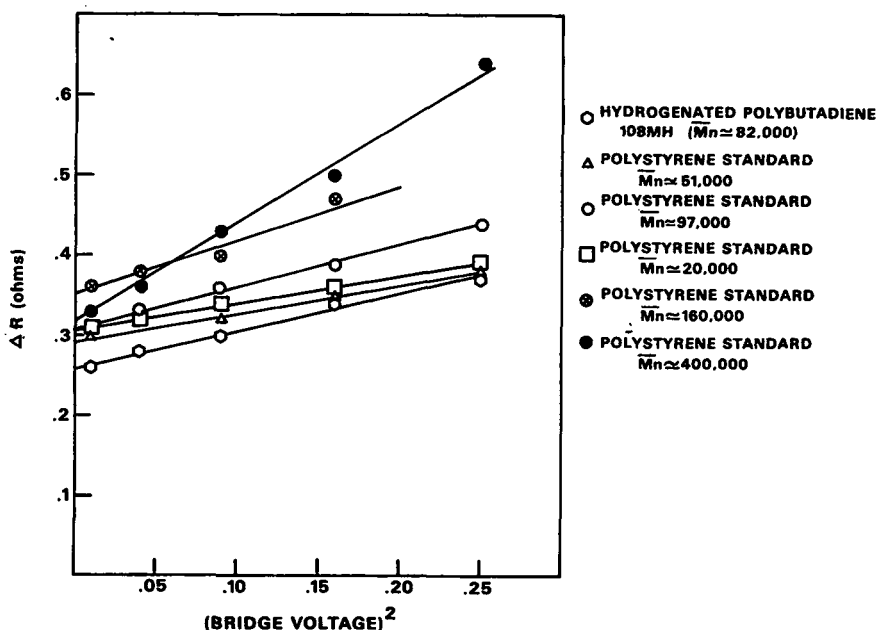

Fig. 5. Variation of ΔR with the square of the bridge voltage, V^2, for various solutes.
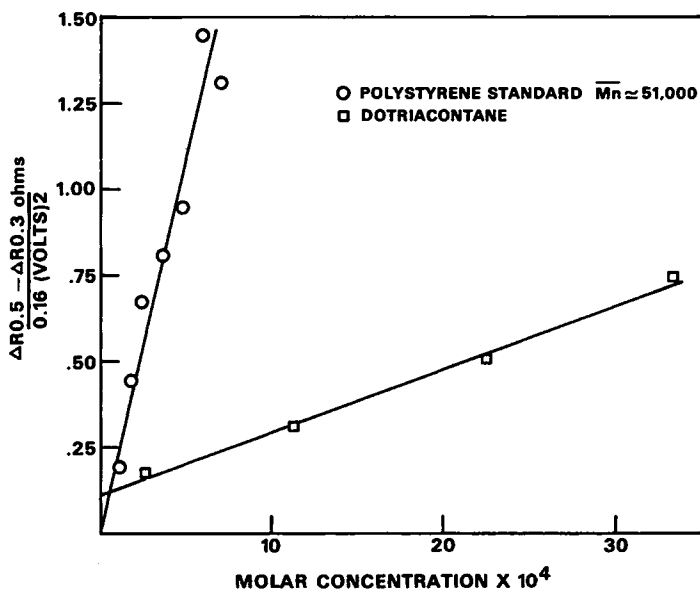
Fig. 6. Effect of molar concentration on the slope of the variation of ΔR with the square of the bridge voltage, $\delta(\Delta R)/\delta V^2$. The value of ΔR at 0.5 volts bridge voltage, $\Delta R_{0.5}$, minus ΔR at 0.3 volts bridge voltage, $\Delta R_{0.3}$, divided by (0.5 volts)^2–(0.3 volts)^2 has been taken as a measure of $\delta(\Delta R)/\delta V^2$ at a particular concentration.

cated in Figure 5 is not particularly serious with regard to the calibration of the instrument if the slopes are independent of solute concentration. This situation would only have the effect of displacing the curves obtained (at one chosen bridge voltage) in a plot of ΔR versus C for differing solutes along the ΔR axis (a zero point displacement). This is shown in the Appendix. This displacement would be dependent on solute, but it would not affect the calculation of $\bar{M}_n$ since only the initial slope is used and the calibration constant would be unaffected. It should be noted that concentration independence does not guarantee the validity of calibration, but rather implies that the results in Figure 5 would not contradict the procedure of calibration.

Unfortunately, the situation is not this simple, as can be seen from Figure 6. The value of $\Delta R_{0.5}$ (the ΔR value at 0.5 volts bridge voltage) minus $\Delta R_{0.3}$ has been taken as a measure of the slope of the plot of ΔR versus V^2 at a particular concentration (or ΔR range) as in Figure 5. From Figure 6 it is evident that the magnitude of the solute-dependent variation of ΔR with V^2 increases with molar concentration (or ΔR range). This important result means that *the calibration constant does vary with solute.* This is proved in Appendix I.

A Proposed Model

Any model proposed to explain the solute dependence of the calibration constant must contain as important variables the bridge voltage and the
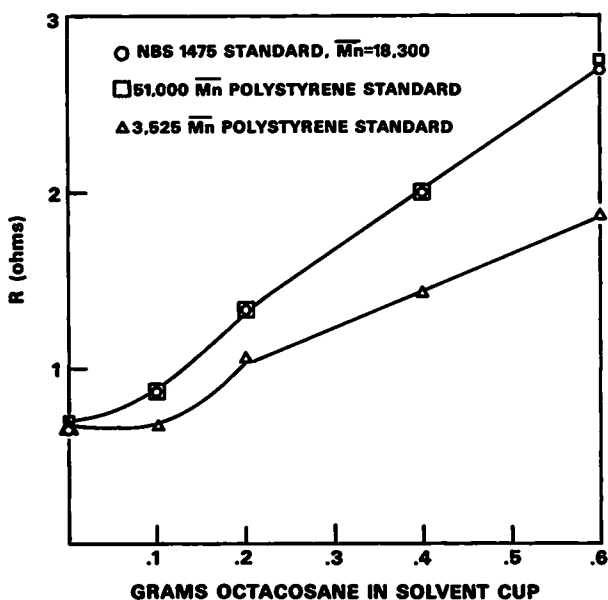
Fig. 7. ΔR as a function of the saturation of the cell atmosphere in which the number of grams of octacosane in the solvent cup regulate the cell atmosphere.
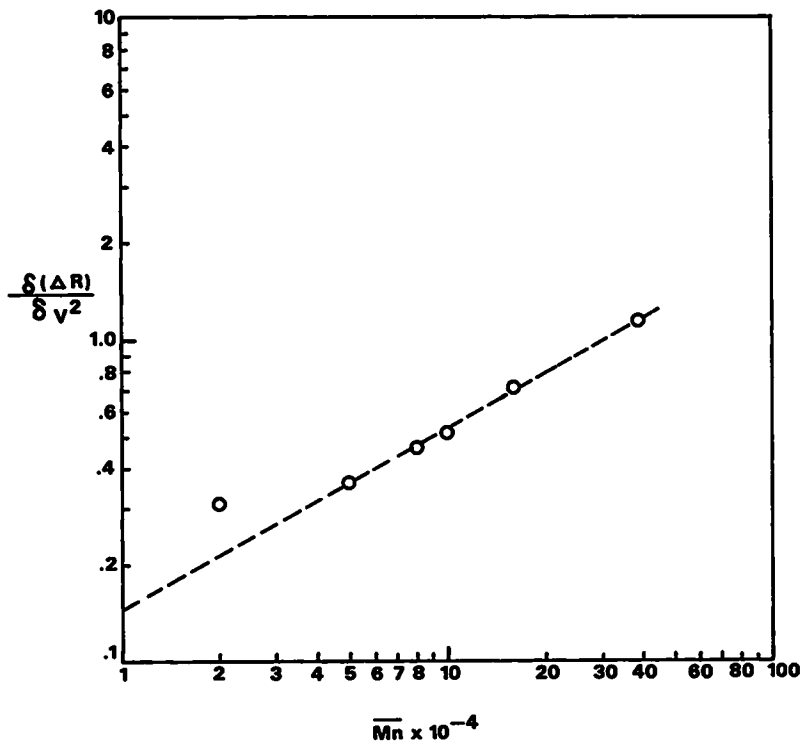

Fig. 8. Plot of the slopes $\delta(\Delta R/\delta V^2$ of the lines in Fig. 5 vs. molecular weight $\bar{M}_n$.

nature of the solute.   Therefore, this model cannot contain as an assumption the negligible effect of Thermistor self-heating (due to electrical heating by the finite bridge voltage).   Other questionable assumptions that could lead to a dependence on the nature of the solute are the uniform concentration of the solution drop and the lack of heat conduction problems within the drop.

I believe that a model based on the ideas proposed earlier to describe drop size effects is consistent with my experimental data.   This simple model visualizes the pure solvent drop as continually evaporating due to Thermistor self-heating.   The rate of evaporation varies directly with V^2, and so does the temperature of the drop.   The behavior of the solution drop, is, however, not so simple.   Whether condensation or evaporation takes place at the surface of the solution drop depends on the resultant of the tendency for condensation, heat losses at the drop surface, heat losses from the Thermistor supporting wires, and thermistor self-heating.   At low molar concentrations, with little tendency for condensation, and relatively high bridge voltages (high Thermistor self-heating), evaporation takes place and the net heat flow within the drop is from Thermistor bead to drop surface.   However, for high concentrations and low bridge voltages, condensation takes place with the net heat flow from drop surface to Thermistor bead.   The evaporation (or condensation) at the drop surface tends to produce a diffusion-controlled surface concentration that differs from the rest of the solution drop as a whole.   For the case of evaporation, the presence of the excess surface concentration formed will tend to lower the rate of evaporation of the solution drop, and therefore the temperature will rise, resulting in a higher ΔR reading than the original concentration would have produced.   The temperature of this drop will continue to rise with time until a point is reached such that diffusion, rate of evaporation, Thermistor self-heating, and heat losses lead to a quasi-steady state.   A similar argument applies for the case of high concentrations and low bridge voltages.

The variation of ΔR with V^2 and the variation of $\delta(\Delta R)/\delta V^2$ with molecular weight can qualitatively be accounted for by the above model as follows.   If the tendency for condensation is so low (due to the low concentrations used) and the bridge voltage relatively high (as is the case for the majority of samples represented in Fig. 5), such that heat flow within the solution drop is from Thermistor bead to drop surface, then an excess surface concentration will tend to be formed to an extent which monotonically increases with V^2.   The variation of ΔR with V^2 for lower molecular weight materials may not involve a diffusion layer, but rather be a direct result of increased drop temperature due to self-heating.

Because of the inverse relationship of the diffusion coefficient to molecular weight, an increased tendency for the formation of surface concentrations with molecular weight is predicted by my model.   This prediction is consistent with the data in Figure 7.

In much the same way that increasing the bridge voltage increases the rate of evaporation and therefore presumably the surface concentration, incomplete saturation of the cell atmosphere would be expected to have a similar effect.   Figure 8 gives ΔR as a function of the number of grams of vapor pressure-lowering solute, octacosane, in the solvent cup containing approximately 25 ml of o-dichlorobenzene.   Each addition to the solvent cup was accompanied by a wait of one day for the cell atmosphere to reach equilibrium.   Contrary to the findings of Kamide,[8] in which he states that, for all practical purposes, unsaturation of the cell atmosphere has no measurable effect on ΔR, unsaturation of the cell vapor does appear to have a tremendous effect on ΔR, as would be expected by the existence of a diffusion controlled surface layer.

Alternate Models

A couple of other mechanisms to account for the observed solute dependence deserve closer examination.   Other ways in which the solute could affect the ΔR readings in the manner exhibited in Figures 5–8 are (1) the presence of an excess surface concentration due to the lowering of the surface tension of the solution relative to that of the pure solvent,[9] and (2) the effect of solute on the thermal conduction process of the drop by means of either dramatically changing the thermal conduction of the solution relative to the pure solvent or else by changing the drop shape or size (surface tension, viscosity, etc.).

In order to check for the possibility of an excess surface concentration due to the lowering of the surface tension of the solution relative to that of the pure solvent, the surface tensions for the pure solvent, o-dichlorobenzene, and solutions in the middle of our normal concentration ranges for the 3,525 and 51,000 molecular weight polystyrene standards were measured by the capillary rise method at 23°C and found to be the same as the pure solvent within ±1%.   Room temperature measurement of the surface tension was considered adequate since the molecular weight dependence on surface absorption and therefore surface tension is reported to be smaller the further from the θ-temperature.[10]   It therefore appears unlikely that any surface activity on the part of the solutes used accounts for the apparent solute dependences discussed earlier.

The second alternate mechanism is that the presence of the solute affects the drop size, shape, and/or thermal conduction coefficient and is therefore the origin of the solute dependence.   The major variables affecting drop shape are the surface tension and the drop size.   Since the surface tension was eliminated earlier as a variable depending on the nature of the solute, only drop size need be considered as an important solute dependent variable affecting drop shape.   The drop sizes obtained for tristearin, 3,525 and 51,000 molecular weight polystyrene standards, were measured, and the drop lengths were found to be the same within ±0.01 cm with no systematic trends dependent on the solute.   From Figure 3, it is seen that

any systematic error that was not detected in our experiment could lead to an error of at most 0.03Ω for the extreme case of approximately zero concentration and 0.5 volts bridge voltage. The argument that the presence of approximately 1% polymer changes the thermal conduction coefficient to the extent so as to produce as much as a 25% change in ΔR as the bridge voltage is changed seems somewhat unlikely if the additivity rule[11] for nonelectrolytes is assumed because the thermal conduction coefficients for polystyrene,[12] polyethylene,[13] and o-dichlorobenzene[14] are of the same order of magnitude. Finally, the independence of the drop size effects from the nature of the solute is inconsistent with this explanation.

A Method to Operate the VPO to Eliminate the Solute Dependence of K

A couple of earlier observations must be considered in defining a method to operate the VPO in order to sidestep earlier difficulties. In view of the tremendous dependence of ΔR on impurities in the solvent cup, from which the cell atmosphere is presumably saturated, the cup should be drained and washed at least every day.

Data given earlier suggested that ΔR, instead of being a sole function of the solution activity as is usually assumed, is rather a function of the solution activity (approximately mirrored by ΔR), as well as the Wheatstone bridge voltage and the nature of the solute. Based on my model, the ideal operating point would be where no evaporation or condensation takes place at the solution drop surface. This would entail the variation of the bridge voltage such that all thermal losses from the drop would be balanced by the self-heating effect. However, knowing the bridge voltage that would lead to this ideal case for a given concentration of an unknown sample is exceedingly difficult, if not impossible. Consequently, an approximation to this state must be used.

A reasonable starting point for approximating the postulated ideal state is to consider the point of zero drop size effects. At this point, heat losses from the drop surface can be replenished only by condensation. Whether or not this approximation is good enough, such that the diffusion is not a limiting process, depends on the relative rates of condensation and solute diffusion within the drop. Consequently, the higher the molecular weight of the solute, the smaller the rate of condensation that can be tolerated. It follows that, in order to extend the use of the instrument to high molecular weights, concentrations and ΔR values should be kept as low as possible.

In order to test whether or not taking the bridge voltage into account gives better agreement for standard high polymer samples with the $\bar{M}_n$ values obtained by membrane osmometry, a number of standard samples were run under controlled conditions. This better agreement, or the lack thereof, will be taken as a measure of the validity of my explanation of the solute dependence of K.

The procedure, taking into account the interplay between bridge voltage and ΔR, is given as follows. First, each sample was run using 2-min ΔR readings at 0.5 volts bridge voltage in the manner recommended by the

manufacturer so that the approximate ΔR range for each concentration would be known.   Then all samples were run again in the following manner: The bridge voltage was set to a value for each concentration based on the straight-line relationship between ΔR at zero drop-size effects and V^2 with zero intercept as taken from Figure 3.   The approximate ΔR reading obtained earlier in the conventional manner was used to set V^2 such that the new operating point was where the effect of drop size vanished.   Readings of ΔR were taken at 20 min, at which time the ΔR reading had stabilized and an approximate steady state reached.   During the 20-min period, the zero adjust was checked every 4 min.

The method of data treatment consisted of fitting the experimental data to a polynomial of degree 2 by means of a least-squares best fit on the IBM 360 computer.   The molecular weight was taken as $\bar{M}_n = K/a_1$, where a_1 is the first-order coefficient and, presumably, the initial slope of a ΔR-versus-C curve where the solution behavior is ideal.   The results of the analysis are summarized in Table I.

From Table I it may be seen that the results for $\bar{M}_n$ for the majority of samples run by the proposed method are in significantly better agreement with those obtained using the membrane osmometer than are the values for $\bar{M}_n$ obtained by operating the instrument in the manner suggested by the manufacturer (constant bridge voltage).   Further, it is evident that the disparity between the $\bar{M}_n$ values as obtained by membrane osmometry and those obtained by VPO at constant bridge voltage generally increases as the molecular weight increases.   This disparity has been attributed by Wachter and Simon[2] to discrimination by the membrane osmometer in regard to the low molecular weight species assumed present.   Our results, however, indicate that not all the disparity between the membrane osmometry and VPO (at constant bridge voltage) values for $\bar{M}_n$ can be attributed to membrane deficiencies.

It can be seen from the results in Table I that the 95% confidence limits are "tighter" for the results obtained using the manufacturer's operating procedure than the variable bridge voltage method.   The residuals from the analysis of variance appeared to be normally distributed and random with respect to concentration in the case of both operating procedures. This essentially rules out systematic errors in the two methods accounting for the greater variability of the variable bridge voltage procedure.   It is therefore deemed probable that the additional random variability is related to the varying of the bridge voltage.   It should be remembered that in our procedure for taking the bridge voltage into account, we guessed an approximate bridge voltage and then used a 2-min reading based on this bridge voltage to determine the final operating point.   Since in this method of successive approximations, no *a priori* knowledge of the "correct" bridge voltage was at hand, a further degree of random error was no doubt introduced.

It should be noted here that if our postulated origin of the solute dependence of the calibration constant is correct, even instruments utilizing special configurations of Thermistors to eliminate drop size variations such

TABLE I
Molecular Weights of Standards by VPO

Polymer	Accepted $\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[a]	Membrane osmometer	Determined $\bar{M}_n$		
					VPO	
				Hewlett-Packard procedure[b,d]	Amoco[c,d]	Wachter and Simon[2]
Polystyrene	3525	1.10		3,120 ± 125	3,500 ± 250	
	10,300 ± 300	1.06		9,480 ± 250	10,400 ± 870	8,800
	20,000 ± 600	1.06	19,000 ± 900	18,850 ± 800	21,500 ± 1,200	16,400
	51,000 ± 600	1.06	48,600 ± 500	38,100 ± 3,600	49,000 ± 8,000	43,900
Hydrogenated polybutadiene	82,000 ± 7,000	1.32	76,000 ± 2,400	38,000 ± 5,000	63,600 ± 10,000	
NBS Polyethylene standard	18,300 ± 1,200			12,950 ± 600	16,700 ± 1,000	

[a] Polystyrene determined by ArRo Labs; hydrogenated polybutadiene by Phillips; polyethylene by NBS.
[b] Measured at 0.5 volts.
[c] Measured at bridge voltage chosen to eliminate effect of drop size.
[d] 95% confidence limits from a regression analysis.

as the inverted arrangement of sensors[2] of Wachter and Simon and vanishingly small bridge voltages will, in the same manner as the Hewlett-Packard design, give erroneous values for $\bar{M}_n$ due to solute dependent calibration constants for higher molecular weight materials.

Finally, while the improvement in agreement with membrane osmometry results can be obtained by taking bridge voltage into account, it must be conceded that this result, or any other single observation, cannot prove the correctness of the proposed model or the existence of a diffusion-controlled surface concentration. However, I do believe a strong case has been made for the inadequacy of calibration when operating at a single bridge voltage.

CONCLUSIONS

The calibration constant exhibits a solute dependence which is attributed to the rate-controlling factor of diffusion of solute through the solution drop. The variation of K with solute is most severe when comparing very low molecular weight calibration standards with high polymers, and, therefore, the calibration with low molecular weight standards is not in general justified.

Bridge voltage and the degree of saturation of the cell atmosphere are important variables in the operation of the vapor pressure osmometer. The reduction of the bridge voltage to a vanishingly small value, as has been suggested by a number of workers, is not necessarily desirable. Our results indicate that there is no *one* ideal value for the bridge voltage, but rather the bridge voltage should be varied such that no evaporation or condensation takes place on the solution drop. This state can be approximated by operating with a cell atmosphere of constant degree of saturation, with the bridge voltage adjusted so that the operating point is very near that of zero drop size effects (for the solution drop) and with low concentrations. By operating the instrument in this manner, the solute dependence of the calibration constant can be eliminated and the correct value of $\bar{M}_n$ can be obtained.

Appendix

Proof of the Solute Dependence of the Calibration Constant

The following terms will be used in the proof:

$$\Delta R_X{}^A = \Delta R \text{ value for solute A, concentration } C^A, \text{ at bridge voltage } X$$
$$\alpha_A(C^A) = \text{slope of } \Delta R \text{ versus } V^2 \text{ for solute A at concentration } C^A$$
$$C^A = \text{molar concentration for sample A}$$
$$K_X = \text{calibration constant at } V^2 = X^2$$

Calibration is assumed to be valid at some bridge voltage X (i.e., $\Delta R_X = K_X C$ for all materials). Our assumption of solution ideality will not affect our conclusions since it is in the term linear in molar concentration that K is explicitly contained and from which $\bar{M}_n$ is calculated. Since calibration is assumed valid at X, $\Delta R_X{}^A = K_X C^A$ and $\Delta R_X{}^B = K_X C^B$ for different solutes A and B. From Figure 5 it is seen that ΔR for A and B may be represented at any other arbitrary bridge voltage y by $\Delta R_Y{}^A = K_X C^A + \alpha_A(C^A)(y^2 - x^2)$ and $\Delta R_Y{}^B = K_X C^B + \alpha_B(C^B)(y^2 - x^2)$. It should be pointed out that if α is

independent of C, then $\Delta R_Y{}^A$ and $\Delta R_Y{}^B$ will each be proportional to the molar concentration C and having the same proportionality constant, but having different intercepts. Since $\Delta R_Y{}^A$ and $\Delta R_Y{}^B$ are proportional to their respective molar concentrations, and since the proportionality constant is the same in both cases, calibration is valid for the case of α independent of C. However, the data in Figure 6 indicate that $\alpha_A(C^A)$ may be represented by $\gamma_A C^A$, where γ_A is a constant depending on solute. Therefore, ΔR for the solutes A and B at bridge voltage y can be represented by

$$\Delta R_Y{}^A = \{K_X + \gamma_A(y^2 - x^2)\}C^A$$

$$\Delta R_Y{}^B = \{K_X + \gamma_B(y^2 - x^2)\}C^B$$

where in general $\gamma_A \neq \gamma_B$, or

$$\Delta R_Y{}^A = K_Y{}^A C^A$$

$$\Delta R_Y{}^B = K_Y{}^B C^A$$

where $K_Y{}^A$ and $K_Y{}^B$ are the calibration constants at $V^2 = y^2$ for the solutes A and B, respectively, and $K_Y{}^A \neq K_Y{}^B$. Therefore, since $V^2 = y^2$ was arbitrary, it follows that calibration is a valid procedure at one value at most of V^2 (i.e., X by definition). Further, since we have no knowledge of the value of this one bridge voltage at which calibration is presumably a valid procedure (if such a single bridge voltage even exists since our data neither proves nor disproves the existence of this singular point), we will have to conclude that calibration is in general (for an arbitrary bridge voltage) not a valid procedure.

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