

## Vapor Pressure Osmometry: A Model Accounting for the Solute Dependence of the Calibration Constant

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### Synopsis

A model describing the operation of the vapor pressure osmometer has been developed to account for the solute dependence of the calibration constant. This model envisions the existence of a diffusion-controlled surface concentration that differs from the concentration of the drop as a whole. Three limiting cases approximated for the surface concentration depend on the relative magnitudes of thermistor self-heating and solution concentration. Quantitative predictions of the dependence of  $d(\Delta R)/d(V^2)$  (the variation of thermistor resistance difference with thermistor self-heating) on both solute molecular weight and solution concentration are in good agreement with experimental data.

### INTRODUCTION

Vapor pressure osmometry, VPO, is frequently used to determine the number-average molecular weight of nonvolatile materials, particularly of polymeric materials whose molecular weight is under 10,000. In practice, the temperature difference between two thermistors, one supporting a solution drop and the other a drop of pure solvent, is measured as a resistance difference  $\Delta R$ . This difference in turn is usually assumed to be related to the weight concentration  $C_0$  of the solution, such that

$$\Delta R = \frac{a}{\bar{M}_n} C_0 + bC_0^2 + \dots$$

where  $\bar{M}_n$  is the number-average molecular weight of the sample and  $a$  is a constant that is assumed to be independent of solute and is often referred to as the calibration constant. However, in a previous paper,<sup>1</sup> I demonstrated that the common practice of applying calibration constants obtained with low molecular weight standards to materials of considerably higher molecular weight is generally unjustified. I concluded that the calibration constant varies with the molecular weight of the solute and that the assumption of the constancy of the calibration constant is particularly poor when low molecular weight standards are compared with high molec-

ular weight polymers. This behavior was ascribed to the tendency for a diffusion-controlled surface concentration to form on the solution drop. I also showed that operating the vapor osmometer so as to eliminate the solute dependence of the calibration constant yields molecular weights in good agreement with those determined by membrane osmometry.

Both Van Dam<sup>2</sup> and Tomlinson et al.<sup>3</sup> have developed excellent models to account for the effects of instrument design variables on the observed instrument response. But up to now there has been no theoretical model to account for the solute dependence of the calibration constant. I have therefore attempted to provide such a model and to quantitatively compare it with some experimental results obtained with dotriacontane, tristearin, and standard polystyrene materials of known molecular weights. It clearly accounts for the solute dependence of the calibration constant by taking into consideration the effects of thermistor self-heating and the limitation of solute diffusion within the drop.

### EXPERIMENTAL

The detailed procedures and conditions for operating the Hewlett-Packard vapor pressure osmometer have been described.<sup>1</sup>

Accurate molecular weights for dotriacontane and tristearin were obtained by mass spectrometry. The polystyrene materials were obtained from ArRo Laboratories.

Diffusion coefficients were obtained in *o*-dichlorobenzene at 25°C using a Beckman Model E ultracentrifuge. Such measurements were considered adequate because the temperature dependence of the diffusion constant is, to a good approximation, independent of solute.<sup>4</sup> Moreover, the ratio of diffusion constants for dotriacontane and tristearin was desired. The diffusion constants were obtained from plots of the square of the second moment<sup>5</sup> versus time.

### THEORETICAL MODEL

Because many of the expressions used in the development were somewhat unwieldy and had been derived elsewhere,<sup>2,3</sup> they were left in their most general terms. Further, it was assumed that the observed resistance differences of the thermistors,  $\Delta R$ , were always directly proportional to their temperature difference and that steady-state conditions (i.e.,  $d(\Delta R)/dt = 0$ ) were in effect. By contrast with the assumptions made in previous models,<sup>2,3</sup> however, the drop was not assumed to be uniform in concentration or temperature, and the effect of thermistor self-heating was not considered negligible.

The heat flows from the various heat sinks and sources in the model are shown schematically in Figure 1. Specifically, the symbols are:  $T_0$ , temperature of solvent vapor;  $T$ , temperature of thermistor;  $T_s$ , temperature of drop surface;  $k$ , overall thermal conductivity of glass bead and liquid drop;  $h$ , convective heat transfer coefficient;  $U$ , overall coefficient

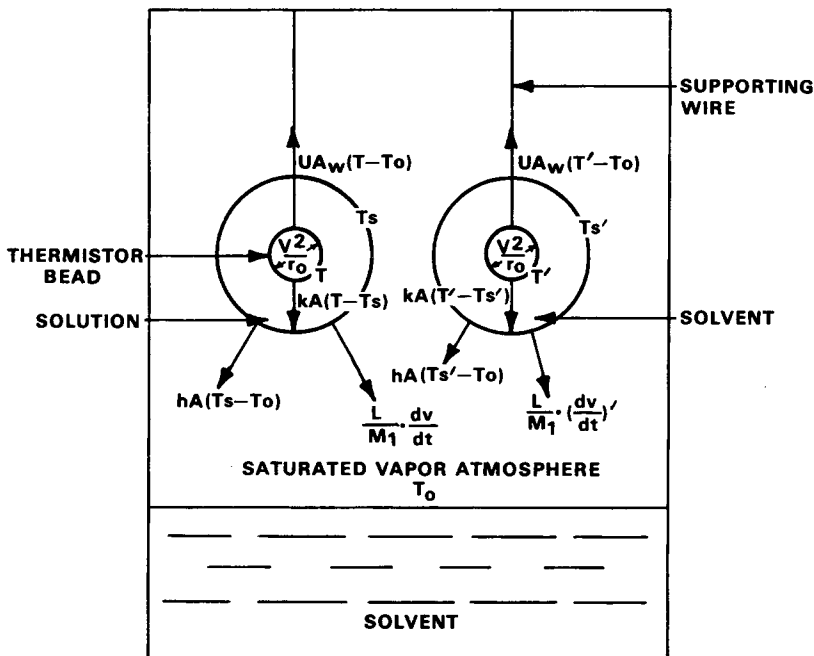


Fig. 1. Schematic diagram depicting the various heat factors involved in the model.

for heat transfer between the source of heat in the thermistor and the vapor via the thermistor connecting wires and the more massive support structure;  $A$ , outside area of drop;  $A_w$ , cross sectional area of connecting wires;  $V$ , Wheatstone bridge voltage applied to thermistors;  $r_0$ , resistance of thermistors;  $L$ , molar heat of vaporization of solvent;  $M_1$ , molecular weight of solvent;  $dv/dt$ , mass transfer of solvent to drop (g solvent/sec). The primes refer to the reference (solvent) drop.

Thus, the various expressions are:  $kA(T_s - T)$ , heat flow from drop surface to thermistor;  $hA(T_s - T_0)$ , heat loss by convection;  $UA_w(T - T_0)$ , heat loss through thermistor connecting wire;  $V^2/r_0$ , heat generated by thermistor self-heating;  $L/M_1 \cdot dv/dt$ , heat transfer due to mass transfer of the solvent to the surface of the drop from the cell atmosphere.

From a heat balance at the drop surface,

$$L/M_1 \cdot dv/dt = hA(T_s - T_0) + kA(T_s - T). \quad (1)$$

From a heat balance at the thermistor,

$$kA(T_s - T) = UA_w(T - T_0) - V^2/r_0. \quad (2)$$

For the case of mass transfer by diffusion from an atmosphere containing solvent vapor at temperature  $T_0$ , surface drop temperature  $T_s$ , and a drop of nonideal solution of weight concentration  $C_0$ ,  $dv/dt$  can be represented<sup>2</sup> as

$$dv/dt = (\alpha_0 C_0 / \bar{M}_n + \beta_0 C_0^2 + \dots) - \gamma_0 (T_s - T_0) \quad (3)$$

where  $\alpha_0$ ,  $\beta_0$ , and  $\gamma_0$  are complex functions of the drop size and shape, the thermal conductivity of the vapor-air mixture, the diffusion coefficient of the solvent through air, the vapor pressure of the solvent at  $T_0$ , and the latent heat of vaporization of the solvent. In addition,  $\beta_0$  is a function of the second virial coefficient of the solution. Because the drop is not necessarily of uniform concentration,  $C_0$  in eq. (3) is replaced by an effective surface concentration,  $C$ .

Combining eqs. (1), (2), and (3) so as to eliminate  $T_s$  gives

$$T - T_0 = (\alpha C / \bar{M}_n + \beta C^2 + \dots) + \gamma(V^2/r_0) \quad (4)$$

where

$$\alpha = \frac{\alpha_0 L}{M_1 \left[ hA + \frac{L\gamma_0}{M_1} + UA_w \left( 1 + \frac{h}{k} + \frac{L\gamma_0}{M_1 k A} \right) \right]}$$

$$\beta = \frac{\beta_0 L}{M_1 \left[ hA + \frac{L\gamma_0}{M_1} + UA_w \left( 1 + \frac{h}{k} + \frac{L\gamma_0}{M_1 k A} \right) \right]}$$

$$\gamma = \frac{\left( 1 + \frac{h}{k} + \frac{L\gamma_0}{M_1 k A} \right)}{\left[ \frac{L\gamma_0}{M_1} hA + UA_w \left( 1 + \frac{h}{k} + \frac{L\gamma_0}{M_1 k A} \right) \right]}$$

If both thermistors and drops are identical except for the presence of solute in one drop, the temperature difference for the two drops can be represented as

$$\Delta T \equiv T - T' = \frac{\alpha C}{\bar{M}_n} + \beta C^2 + \dots \quad (5)$$

For the case where a diffusion-controlled surface concentration is formed,  $C$  can be approximated by considering the kinetics of solvent mass transfer and solute diffusion. For a steady-state condition where  $d(\Delta R)/dt \approx 0$ , the rate of diffusion must be such that the rate of mass transfer of solvent to the drop surface gives rise to the condition that  $dC/dt \approx 0$ . Consequently,

$$\frac{dw}{dt} = C \cdot \frac{dv}{dt} \quad (6)$$

where  $w$  and  $v$  are the weights of the solute and solvent (approximating the solution weight for dilute solutions), respectively. Equation (6) gives the relation between the rate of solvent mass transfer at the drop surface and the rate of solute transfer needed to keep the concentration constant.

Rather than the development of an exact analytical solution, the approximate, but completely general, method of the "equiaccessible surface"<sup>6</sup> was employed to solve the problem. In this method, the rate of mass transfer of solute to the surface is equal to  $D_0(C_0 - C)/\delta$  under steady-state conditions, where  $D_0$  is the diffusion coefficient of the solute,  $C_0$  is the concentration of the drop as a whole, and  $\delta$  is the effective film thickness,<sup>6</sup> which

is a fictitious layer that is independent of solute and dependent only on the geometric shape of the surface. Therefore, equating the rates gives

$$\frac{D_0(C_0 - C)}{\delta} = C \left( \frac{dv}{dt} \right) \quad (7)$$

or

$$C = \frac{C_0}{1 + \left( \frac{dv}{dt} \right) \frac{\delta}{D_0}} \quad (8)$$

If the approximation is made that the surface concentration does not differ substantially from that of the solution as a whole (i.e.,  $(C - C_0)/C \ll 1$ ), then  $(dv/dt)(\delta/D_0) \ll 1$ . Expanding  $C_0/[1 + (dv/dt)\delta/D_0]$  in terms of  $(dv/dt)(\delta/D_0)$ , neglecting terms in  $dv/dt$  higher than the first power in  $(dv/dt)(\delta/D_0)$  (since  $(dv/dt)(\delta/D_0) \ll 1$ ), substituting from eqs. (1) and (2) for  $dv/dt$ , and rearranging gives

$$C = C_0 \left[ 1 + \frac{\delta M_1 \left( \frac{V^2}{r_0} - UA_w(T - T_0) - hA(T_s - T_0) \right)}{LD_0} \right] \quad (9)$$

To further elaborate on the theory, the following three limiting cases were analyzed: I, no condensation on or evaporation from the solution drop; II, evaporation predominates at the solution drop surface; III, condensation predominates at the solution drop surface.

**Case I.** For the case where no mass transfer of solvent takes place on the surface of the solution drop,  $V^2/r_0 - UA_w(T - T_0) - hA(T_s - T_0)$  is equal to zero and  $C = C_0$  from eq. (9). Therefore, as pointed out elsewhere,<sup>1</sup> calibration of the VPO is entirely valid. An approximation to this state can be made by operating the VPO so that the size of the solution drop has no effect, and by using low concentrations so that heat losses at the solution drop surface [i.e.,  $hA(T_s - T_0)$ ] are small enough that  $[\delta h A M_1 (T_s - T_0)]/LD_0 \ll 1$ . It has been shown that  $V^2/r_0 - UA_w(T - T_0) = 0$  for the case of zero drop size effects.<sup>1</sup> Consequently, from eq. (9),  $C \simeq C_0$ . I have already shown that  $\bar{M}_n$  determinations from vapor pressure and membrane osmometry are in significantly better agreement when the instrument is operated in the manner suggested for this case than when it is operated as recommended by the manufacturer.<sup>1</sup>

**Case II.** If heat losses from the thermistor supporting wire are kept small compared to  $V^2/r_0$  by the reduction of the supporting wire diameter and the solution concentration is small enough so that the tendency for evaporation (due to thermistor self-heating) is large compared with the tendency for condensation, then evaporation of solvent represents the major mode of heat loss and  $V^2/r_0 \gg UA_w(T - T_0) + hA(T_s - T_0)$ . For this case, eq. (9) reduces to

$$C \approx C_0 \left[ 1 + \frac{M_1 \cdot \delta \cdot V^2}{L \cdot D_0 \cdot r_0} \right] \quad (10)$$

Substituting eq. (10) into eq. (5) and neglecting terms in  $[(\delta \cdot V^2 \cdot M_1)/D_0 \cdot r_0 \cdot L]^2$  gives

$$T - T' \simeq \frac{\alpha C_0 \left(1 + \frac{M_1 \cdot \delta \cdot V^2}{L \cdot D_0 \cdot r_0}\right)}{\bar{M}_n} + \beta C_0^2 \left(1 + \frac{2M_1 \cdot \delta \cdot V^2}{L \cdot D_0 \cdot r_0}\right). \quad (11)$$

Terms in  $[(M_1 \cdot \delta \cdot V^2)/(L \cdot D_0 \cdot r_0)]^2$  are neglected since the assumption that  $C - C_0/C \ll 1$  implies that  $[(M_1 \cdot \delta \cdot V^2)/(L \cdot D_0 \cdot r_0)] \ll 1$ , from eq. (10).

**Case III.** Condensation will predominate at the solution drop surface when the effect of heat transfer to the drop surface from condensation is much greater than that due to thermistor self-heating. This case occurs at high concentrations and low bridge voltages such that  $hA(T_s - T_0) \gg (V^2/r_0) - UA_w(T - T_0)$  and  $T_s \approx T$ . The approximation of  $T_s$  by  $T$  for this case can be justified from the following argument. Since for a drop of uniform temperature the heat losses through the thermistor supporting wires have been calculated<sup>3</sup> to be significantly less than the heat losses at the drop surface due to conduction through the vapor, and since at sufficiently high solution concentrations, the heat generated by condensation at the drop surface is large compared to the thermistor self-heating, then this case closely approximates that where the major heat sinks and sources are at the drop surface, and consequently  $T_s \approx T$ . Equation (9) thus becomes

$$C = C_0 \left[1 + \frac{\delta h A M_1 (T_s - T_0)}{L \cdot D_0}\right]. \quad (12)$$

Combining this expression with eq. (5) and neglecting terms in  $[M_1 h A \delta / (L \cdot D_0)]^2$  gives

$$T - T' \simeq \frac{\left(\frac{\alpha}{\bar{M}_n} C_0 + \beta C_0^2\right)}{\left[1 - \frac{C_0 \delta h A M_1}{L \cdot D_0} - \frac{2\beta C_0^2 \delta h A M_1}{L \cdot D_0}\right]}. \quad (13)$$

The neglect of higher-order terms in the above expansion arises out of the assumption that  $(C - C_0)$  is small compared to  $C_0$ .

### COMPARISON OF THEORY WITH EXPERIMENTAL DATA

I have previously shown that the measured value of  $\Delta R$  varies linearly with the square of the bridge voltage,  $V^2$ , that the slope of the line formed for a plot of  $\Delta R$  versus  $V^2$  varies linearly with molar concentration, and that the logarithm of this slope varies linearly with the logarithm of the molecular weight.<sup>1</sup> According to the present model, these experimental studies are assumed to belong under case II, where  $V^2/r_0 \gg UA_w(T - T_0) + hA(T_s - T_0)$ , since the bridge voltage used was significantly higher and the solution concentration significantly lower than that needed for the condition of zero drop size effects ( $\sim$  case I). Now, however, the theoretical

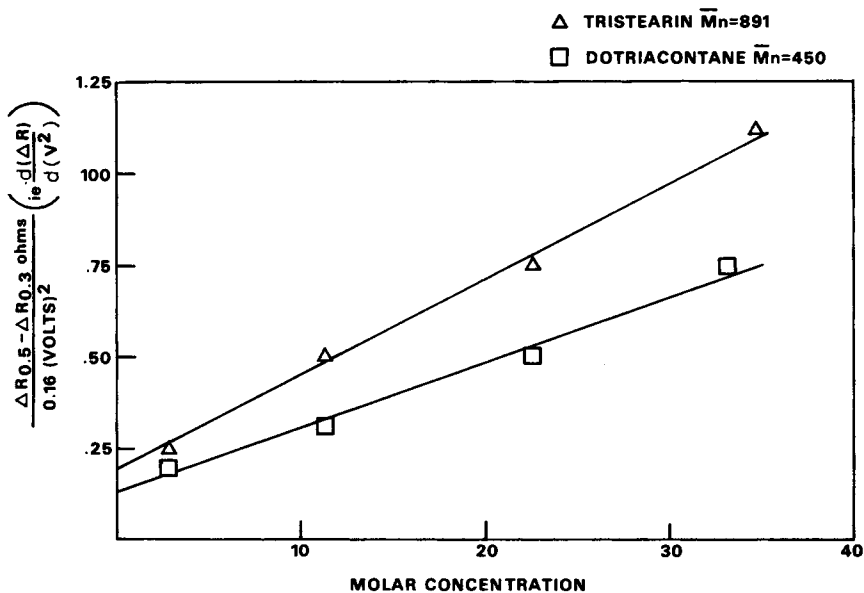


Fig. 2. Effect of molar concentration on the slope of the variation of  $\Delta R$  with the square of the bridge voltage,  $d(\Delta R)/d(V^2)$ .

equations relating to case II must be modified to account for such experimental observations.

The variation of  $d(\Delta R)/d(V^2)$  with molar concentration is shown for dotriacontane and tristearin in Figure 2. The origin of this variation is of great importance because the solute dependence of the calibration constant is directly related to the solute dependence of the variation of  $\Delta R$  with  $V^2$  (i.e., to the variation of  $d(\Delta R)/d(V^2)$  with respect to molar concentration and solute).<sup>1</sup>

In order to compare theoretical predictions with the experimental data, a proportionality between  $T - T'$  and  $\Delta R$  (the observed resistance difference between the two thermistors) is assumed. At low molecular weights where the second term of eq. (11) becomes negligible, taking the derivative of eq. (11) with respect to  $V^2$  permits the ratio of the variation of  $d\Delta T/dV^2$  with molar concentration for two materials to be given by

$$\frac{\frac{d}{dC_m} \left( \frac{d\Delta T}{dV^2} \right)_1}{\frac{d}{dC_m} \left( \frac{d\Delta T}{dV^2} \right)_2} = \frac{D_1}{D_2} \quad (14)$$

As measured in our laboratory, the diffusion constants for dotriacontane and tristearin at 25°C in *o*-dichlorobenzene are  $(3.1 \pm 0.2) \times 10^6$  cm<sup>2</sup>/sec and  $(2.0 \pm 0.3) \times 10^6$  cm<sup>2</sup>/sec, respectively. The calculated ratio of  $1.55 \pm 0.19$  is in reasonable agreement with the value of 1.46 as determined from Figure 2 and eq. (14). However, because the poor precision in the mea-

surement of the diffusion constants makes the apparent agreement inconclusive, further agreement between theory and experiment is necessary to demonstrate the applicability of the theory.

In order to compare the theoretical and experimental variation of  $d(\Delta T)/d(V^2)$  with molecular weight, the logarithm of  $d(\Delta T)/d(V^2)$  must be calculated. From eq. (11),

$$\log \frac{d(\Delta T)}{dV^2} = \log \frac{1}{D_0} + \log \left[ \frac{\alpha}{M_n} C_0 + 2\beta C_0^2 \right] + \log \left( \frac{\delta \cdot M_1}{L} \right). \quad (15)$$

Substituting the relation<sup>4</sup>

$$\frac{1}{D_0} = \frac{M^{\left[ \frac{1}{2} + \frac{(a-1/2)}{3} \right]}}{KT}$$

where  $a$  is the exponent in the empirical viscosity relation,  $M$  is the molecular weight, and  $K$  is the Boltzman constant, for  $1/D_0$  gives

$$\begin{aligned} \log \frac{d(\Delta T)}{dV^2} = & \left[ \frac{1}{2} + \left( a - \frac{1}{2} \right) / 3 \right] \log M \\ & + \log \left[ \frac{\alpha}{M_n} C_0 + 2\beta C_0^2 \right] + \log \left[ \frac{\delta \cdot M_1}{L \cdot KT} \right]. \quad (16) \end{aligned}$$

The molecular weight dependence of the first term will dominate for sufficiently high molecular weights, and the second and third terms may be considered approximately independent of molecular weight. Therefore, using the experimentally determined value of  $a$  of 0.74 for polystyrene permits eq. (16) to be represented as follows:

$$\log \frac{d(\Delta T)}{dV^2} \simeq 0.58 \log M + \text{constant}. \quad (17)$$

Comparing the predicted slope of 0.58 with the slope of 0.57 which was calculated from experimental results obtained with polystyrene standards (from a plot of  $\delta(\Delta R)/\delta V^2$  in Figure 7 of my earlier paper<sup>1</sup>) shows satisfactory agreement. Thus the model appears to adequately account for the solute dependence of the calibration constant. By contrast, the calibration constant can be considered solute independent only if no evaporation or condensation takes place at the solution drop surface.

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