Some Aspects of the Estimation of $\overline{M}_n$ by Vapor Pressure Osmometry

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Synopsis

The constants a, b of the equation $\log \overline{M}_n = a - b \log [\lim (\Delta R/c)]$ in benzene and chloroform were obtained at 25, 37, and 45°C for the Knauer vapor osmometer and compared with those published by Brzeziński et al. for the Mechrolab 302. It was found that the constant b in the above solvents had identical values, depending on the temperature used. The value of a depends on the resistance of the thermistors. The procedure used for obtaining $\lim (\Delta R/c)$ from the concentration dependence is discussed. Comparison of the limiting slope dependence and the gradient dependence reveals the error of the zero point, which cannot always be eliminated by employing a procedure by Glover.

INTRODUCTION

The vapor osmometry method (VPO) utilizes the dependence of the decrease in vapor tension of a solvent in solution on the molality of solution in the determination of the number-average molecular weights ($\overline{M}_n$) of the solute. The method is based on a precise determination of the temperature difference between a drop of solution and a drop of solvent hanging on temperature-recording thermistors. The resulting temperature of the thermistor which is surrounded by the drop solution is given by the temperature and concentration changes which occur in approaching the steady state. A number-average molecular weight $\overline{M}_n$ can be calculated from the experimentally determined temperature or resistance difference, ΔT or ΔR, using the calibration constant. The calibration constant K is not, in fact, simply the operating constant of the apparatus, but depends on the solute molecular weight. The variation of K with solute is not negligible when comparing very low molecular weight calibration standards with high polymers, and therefore, the calibration with low molecular weight standards, in general, is unjustified. In practice, $\overline{M}_n$ is determined by assessing the dependence of the calibration constant on molecular weight by means of a set of standards of molecular weights or by operating the instrument in such a manner that the solute dependence of the calibration constant will be eliminated and the correct value of $\overline{M}_n$ obtained.

In this paper both procedures are commented on, and the concentration dependence of the resistance difference is discussed.

EFFECT OF MOLECULAR WEIGHT ON THE CALIBRATION CONSTANT

The calibration constant K depends on experimental conditions, i.e., tem-

perature and solvent.[1,2] By using the molecular weight standards, it was also possible to prove the dependence of the calibration constant K on the molecular weight of the solute. The requirement put forward by some author,[3] namely, that a standard with the same molecular weight as the sample under investigation be used in the measurement, appeared to be very strict. Figure 1 shows the dependence of K on $\overline{M}_n$ for two different commercial models, Mechrolab 302 and Knauer. The calibration constant increases very rapidly with molecular weight. If chloroform is used as a solvent in the measurements, the calibration constant for $\overline{M}_n = 4000$ is some 1.5 times higher than for $\overline{M}_n = 200$ at 37°C.

The temperature conditions in a drop of solution are the result of the temperature contribution of solvent condensation and of thermal losses from the drop due to conductivity and radiation.[4,5] In the case of commercial equipment, there is also a thermal contribution due to the heating of the thermistors. The relationship between heat supply due to solvent condensation, on the one hand, and self-heating of the thermistors, on the other, plays a decisive role in the evaporation of the solvent in the drop of solution and in the change of the concentration conditions in the drop.[6] With increasing molecular weight of the solute, this seems to lead to a rise in temperature in the drop of solvent, and thus to a higher temperature difference ΔT or resistance difference ΔR between the thermistor of the solvent and the thermistor of the solution, than would correspond to the molality of solution. ΔT with respect to ΔR exhibits a solute dependence which is attributed to the rate-controlling factor of the diffusion of solute through the solution drop.[6]

Recently, the VPO apparatus was calibrated for a given solvent, temperature, and thermistor assembly by measurements with a substance of known molecular weight at a number of solution concentrations. The calibration constant was then calculated from the expression

$$K = M_n \lim_{c=0} (\Delta R/c) \tag{1}$$

where K is an apparatus constant for a given solvent, temperature, and thermistor assembly and ΔR is the bridge imbalance for a concentration c. Equation (1) is not fulfilled within a broad range of molecular weights due to nonideal conditions in the drop of solution.
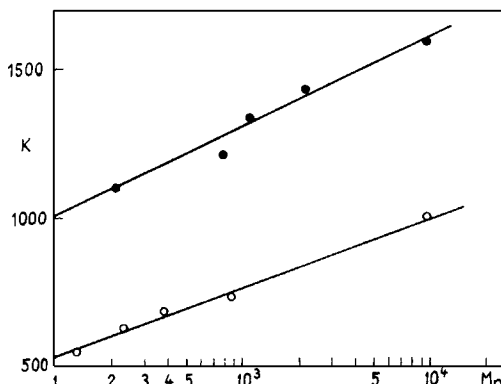

Fig. 1. Dependence of the calibration constant on the molecular weight of the standards as determined in ref. 7 (O, $CHCl_3$, 37°C) and in the present work (●, C_6H_6, 45°C).

For accurate molecular weight determinations, the dependence of the calibration constant on molecular weight, under the particular operating conditions and over the appropriate molecular weight range, was determined. These results show that the independence of K on the solute molecular weight can be obtained if new calibration constant K_s is calculated from the expression

$$K_s = \overline{M}_n \left[\lim_{c=0} (\Delta R/c) \right]^b \qquad (2)$$

where b is a constant for the given solvent and temperature. By taking the log of eq. (2), one obtains an equation in a form suitable for calculating $\overline{M}_n$ and formally identical with that proposed by Brzeziński et al.[7]:

$$\log \overline{M}_n = a - b \log \left[\lim_{c=0} (\Delta R/c) \right] \qquad (3)$$

By measuring a set of standard molecular weights, it is possible to determine the constants by eq. (3). In this way, all complicating influences of temperature and concentration conditions in the drop of solution are ruled out, independent of their type or origin. A commercial apparatus can be used in the measurements without any additional modifications and within a comparatively broad range of molecular weights.

The constants of eq. (3) were determined for benzene and chloroform at several temperatures. The standards used are characterized in Table I. At least four solutions were measured for each compound, and the straight line of the best fit to the plot of ΔR versus concentration was calculated. The individual standards were repeatedly measured during several years with different thermistor assemblies and with both the original and a new type of insulation of the solvent-vapor chamber of the Knauer model. The values of the determined constants a,b are given in Table II, together with those of Brzeziński et al.,[7] determined using the Mechrolab 302.

The agreement between the constants a and b obtained with two commercial models can be evaluated only under the same experimental conditions used, namely, benzene at 25°C and chloroform at 37°C. The $a = \log K_s$ values are lower with Mechrolab 302. The difference between the values obtained with these two models is given by the different resistance of the thermistors used. For

TABLE I
Standards Used

Standard	$\overline{M}_n{}^a$	Supplier
Benzil	210.2	Lachema Brno
Poly(propyleneglycol) (PPG)	790	Waters Assoc.
Tristearine	891	Lachema Brno
PPG	1220	Waters Assoc.
	2020	Waters Assoc.
	3100	Waters Assoc.
	3900	Waters Assoc.
Polystyrene	3540	Knauer
	9430	Waters Assoc.
	19,250	Pressure Chem.
	34,900	Knauer

[a] Values given by supplier.

TABLE II
Constants of Calibration, Eq. (3), for Benzene and Chloroform[a]

Solvent	Temp. (°C)	a	b
Mechrolab 302 (Ref. 7)			
$CHCl_3$	25	2.730	1.079
	37	2.862	1.168
C_6H_6	25	2.393	1.111
Knauer model (this work)			
$CHCl_3$	37	3.432	1.160
	45	3.406	1.037
C_6H_6	25	3.001	1.111
	37	3.110	1.086
	45	3.115	1.066

[a] Concentration, c (g solute/1000 g solution); bridge imbalance, ΔR (ohms).

benzene, b is the same for both (1.111); for chloroform, b differs by 0.7%. For these solvents the constant b is the same for both types of apparatus.

Table II also shows that b decreases with increasing temperature of measurement. From this one can conclude that the calibration constant dependency on the molecular weight of the solute decreases with increasing temperature of measurement. In Figure 2, b is plotted versus the reciprocal difference between the boiling point and the temperature of measurement, $1/\Delta T$. The number of experimental points which can be used in the determination of the precise temperature dependence of b is small. If a straight line is drawn through these points at a temperature of measurement situated at the same distance from the boiling point of the given solvent, the b observed for chloroform is higher than that found for benzene. We believe that this is due to the lower heat of evaporation[8] of chloroform, 279.3 J/kg (20°C), compared to benzene, 433.8 J/kg (25°C). In a more detailed verification of the dependence of the constant b on temperature, there is the possibility of ascertaining a temperature at which $b = 1$, i.e., the calibration constant will be independent of the molecular weight of the solute.

The theoretical aspects of the heat and mass transfer within the solution drop were excellently described by Bersted.[6] He suggested restricting the variation of the bridge voltage such that all thermal losses from the drop would be balanced by the self-heating effect. Such a procedure is exceedingly difficult but gives correct values for $\overline{M}_n$.
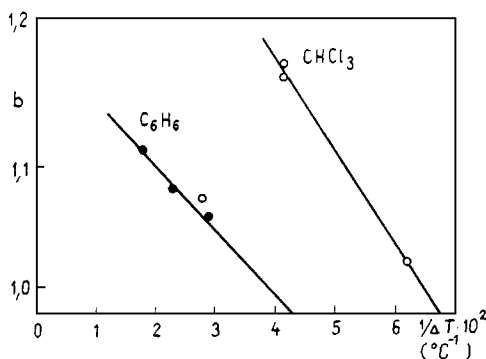

Fig. 2. Dependence of the constant b on the reciprocal difference between the boiling point and the temperature of measurement, $1/\Delta T$.

As there is a constant decrease in b with increasing temperature, a similar effect can be expected by increasing the temperature of measurement with a constant bridge voltage. The following operating conditions should be used: a cell atmosphere of a constant degree of saturation, low solution concentrations, and a drop size as small as possible. Higher measurement temperatures will diminish the self-heating effect, the diffusion coefficient of the solute will increase, and a decreased tendency for the formation of surface concentrations can be expected. The higher the temperature of measurement, the higher the diffusion coefficient of the solute, which implies a smaller difference between the inner and outer concentration of the drop.

Thus to obtain better approximations of the correct values of $\overline{M}_n$ by VPO, increasing the temperature of measurement is suggested as experimentally easy; and this procedure is in agreement with the theoretical model of Bersted.[6]

ELIMINATION OF THE DEPENDENCE OF THE CALIBRATION CONSTANT ON MOLECULAR WEIGHT

In order to eliminate the dependence of the calibration constant on molecular weight, some authors modify the conditions of measurement[9] or adjust the Wheatstone bridge.[6,10] Using a large amount of experimental material, Kamide et al.[10] have shown that the dependence of K_s on $\overline{M}_n$ can be eliminated, although at the expense of reducing apparatus efficiency, and the limit of utilizability of VPO can be shifted to $\overline{M}_n = 10^5$ while preserving good accuracy of measurement. The modification suggested by them consists in introducing compensating resistances into the Wheatstone bridge so as to allow an additional improvement of the identity of the thermistor characteristics. They have also partly modified the solvent-vapor chamber and thermistor assembly proposed by Dohner et al.[9] In this way they seem to have succeeded in reducing the inputs of undesired heat sources.

We found that the agreement between the measured data and those given by the manufacturers was even better than indicated by the authors, because the molecular weights of the PS standards of Pressure Chemical as given by Kamide[10] were not number- but weight-average molecular weights. This is evident from the data supplied by manufacturers of the above standards, the majority of which is available in our laboratory. If one bears in mind the polydispersity of standards as given by the manufacturer, then the fit between $\overline{M}_n$ values determined with an adjusted VPO apparatus and those given by the standards is excellent (Table III).

The finding described in ref. 10 that standards 1a and 11a exhibit $\overline{M}_n$ values differing from those given by the manufacturer has been confirmed by our own measurements with standard 1a. Its molecular weight was repeatedly determined using a fast-membrane Knauer osmometer. We determined an $\overline{M}_n$ of 196,000 ± 3% in toluene at 37°C from 15 concentrations. With standard 11a Adams et al.[11] found an $\overline{M}_n$ of 3700, also at variance with the $\overline{M}_n$ given by the manufacturer but in good agreement with the M_n determined by Kamide et al.[10]

The relative error of measurement given in Table III has been considerably reduced with respect to values given by Kamide et al. Within the given range, the error is independent of molecular weight, and it may be expected that even

TABLE III
Molecular Weights of PS Standards Given by the Manufacturer and Determined by
Kamide et al.[a]

Designation	Manufacturer		$\overline{M}_n \times 10^{-4}$, Kamide et al.	Relative error, %
	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n \times 10^{-4}$		
12a	1.10	0.205	0.194	5.4
11a	1.10	0.440	0.361 (0.370)[b]	2.4
8a	1.06	1.030	1.018	1.2
2b	1.06	1.930	1.90	1.6
4a	1.06	9.170	9.03	1.5
1a	1.06	15.100	21.50 (19.60)[c]	−8.8
3a	1.06	38.800	37.30	3.9

[a] Ref. 10; conditions: benzene at 40°C.
[b] Value in parentheses from ref. 11.
[c] Value in parentheses from present work.

without any further technical improvements, the VPO apparatus thus adjusted would provide results with an error less than ±10% over a broader $\overline{M}_n$ range than that so far described in the literature.

The molecular weight standards are an absolutely necessary aid in measurements with vapor osmometers. In the range of molecular weights greater than 1000, there is a lack of nonpolymeric compounds whose high purity would guarantee an exact value. So far it does not seem that these compounds would be available in the near future. For this reason polymeric standards are used in the calibration of vapor osmometers, although in some cases they are not correctly characterized by their molecular properties. It seems that the only way to improve the characterization of standards is by raising the precision of independent methods of determining molecular weights. To save time spent in measurements with vapor osmometers, I would like to indicate some other standards exhibiting characteristics other than those given by the manufacturer. By measuring 36 different concentrations of solutions of the poly(propylene-glycol) standard Waters No. 41983, $\overline{M}_n = 3900$, it was determined that $\overline{M}_n = 2660 \pm 3\%$. The measurements were performed in chloroform, benzene, and methyl ethyl ketone. A polystyrene standard of the same firm, No. 25169, with the given $\overline{M}_n = 3100$ and $\overline{M}_w = 4000$ gives, by repeated measurements in the same solvents, $\overline{M}_n = 3770 \pm 2.5\%$ from 10 concentrations.

CONCENTRATION DEPENDENCE OF THE RESISTANCE DIFFERENCE

If polymer solutions were ideal and the vapor osmometer worked until real thermodynamical equilibrium had been established, $\overline{M}_n$ could be determined from a measurement at a single concentration. Under real conditions, however, the concentration dependence of the temperature or resistance difference, ΔT or ΔR, respectively, is evaluated in order to obtain the respective values of $\lim_{c=0}$ ($\Delta T/c$) or $\lim_{c=0}$ ($\Delta R/c$). The evaluation of the concentration dependence is not always unambiguous and contains an inherent information about the nonideal character of solution under investigation and about the possible anomalies in the behavior of the vapor osmometer.

In some papers[12] and prospects[13] one finds a discussion of the dependence of

the measured resistance difference on solution concentration, or directly some exemplary dependences valid for some standards or compounds. Sometimes for the same types of polymers in the given solvent authors find different slopes of concentration dependence, from which it may even be deduced that the second virial coefficient A_2 is negative. Such findings are rather unusual and have no analogy in other measurements of colligative properties, e.g., in membrane osmometry. Kamide et al.[10] give a virial series expansion of the concentration dependence of the temperature difference for VPO and of the osmotic pressure for membrane osmometry:

$$T = K_s' \, (c/\overline{M}_n + A_{2,v}c^2 + A_{3,v}c^3 + \cdots \tag{4}$$

$$\pi = RT(c/\overline{M}_n + A_{2,0}c^2 + A_{3,0}c^3 + \cdots \tag{5}$$

The above series are graphically represented by a straight line or a curve passing through the origin; the second virial coefficient is either positive or zero,[14] if the temperature of measurement does not approach the theta temperature.

A more common procedure is that in which the molecular weight is obtained from the concentration dependence by using the method of limiting slope[15]: here $\Delta T/c$ or $\Delta R/c$ is plotted against concentration c and extrapolated to concentration $c = 0$. Both modes of extrapolation are shown in Figures 3–5. The figures show experimentally obtained concentration dependences without the zero-point error and with this error for commercial low-molecular-weight polybutadienes.

With various polymer-solvent systems, one obtains straight lines with $A_{2,v} = 0$ or with $A_{2,v}$ greater than zero. The gradient dependences (Fig. 4) of the limiting slope dependence, where $A_{2,v} = 0$, are straight lines, without the zero-point error. If the second virial coefficient $A_{2,v}$ is larger than zero, two cases may arise, namely, that the gradient dependence is a curve (Fig. 3) or that the gradient dependence exhibits a zero-point error (Fig. 4). The limiting slope dependence does not reveal the zero-point error and leads to the wrong value for the molecular
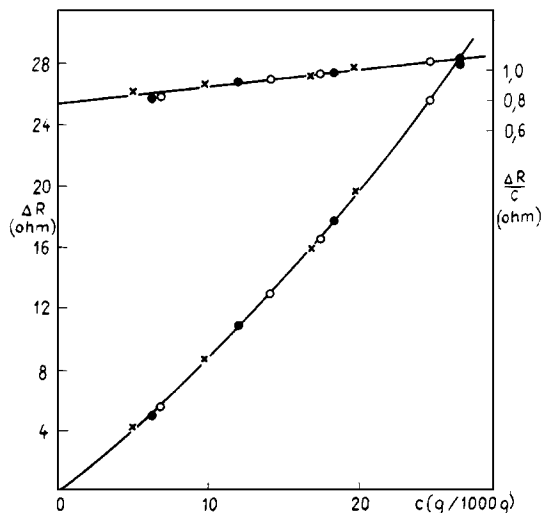

Fig. 3. Concentration dependence of ΔR of polybutadiene rubber (Butarez HTS, Phillips Petroleum Co.) evaluated by the gradient and the limiting-slope methods at 45°C in $CHCl_3$. The different symbols represent independent measurements.
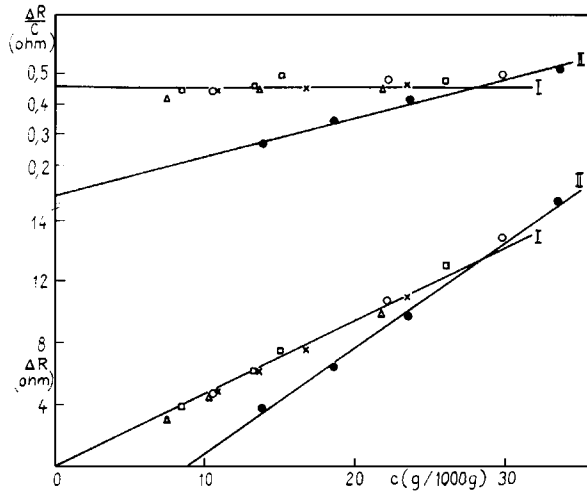
Fig. 4. Concentration dependence of ΔR of polybutadiene rubber (Butarez HTS, Phillips Petroleum Co.) evaluated by the gradient and the limiting-slope methods in 45°C in C_6H_6. Measurements were made without (I) and with (II) the zero-point error. The different symbols represent independent measurements.
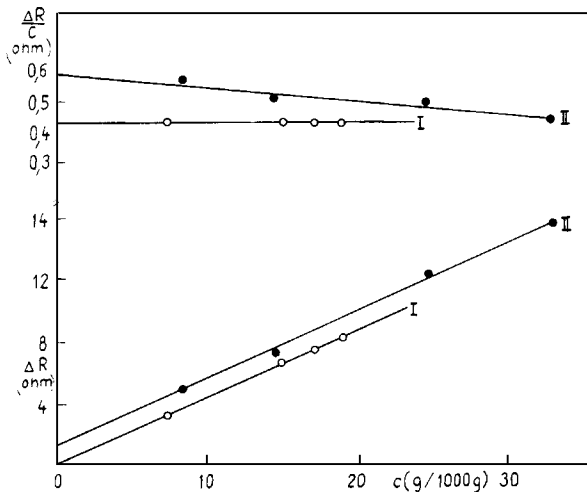

Fig. 5. Concentration dependence of ΔR of polybutadiene rubber (Butarez CTL, Phillips Petroleum Co.) evaluated by the gradient and the limiting-slope methods at 45°C in C_6H_6. Measurements were made without (I) and with (II) the zero-point error. The different symbols represent independent measurements.

weight. This negative zero-point error is quite frequent in routine measurements.

If the limiting slope dependence has its second virial coefficient $A_{2,v}$ smaller than zero, a positive zero-point error becomes operative (Fig. 5). Glover[16] assumes that from measurements subject to the zero-point error, one may obtain a correct $\overline{M}_n$ by using the equation

$$\Delta T = \Delta T_0 + K_s' \left(c/\overline{M}_n + A_{2,v}c^2 + A_{3,v}c^3 + \cdots \right) \tag{6}$$

In eq. (6) the experimental error ΔT_0, referred to as the zero-point error, is in-

volved in the calculation. The dependence in Fig. 4 demonstrates that this is not always justified, because in the majority of measurements involving the zero-point error, there is a change in the slope of the dependence of ΔT or ΔR on the concentration c. In the case of nonlinear gradient dependence, the determination of ΔT_0 also becomes rather controversial. Our measurements show that there is no dependence of the zero-point error on the molecular weight of the solute because of its sporadical existence. It is possible to obtain a plot of ΔR versus concentration without zero-point error by repeating the measurements, as shown in Figures 4 and 5. This is contrary to the conclusion of Morris,[17] who found that the origin of this plot was rarely on the calculated line and that the zero-point error varied with the solute molecular weight.

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