

## Aspects of Vapor Pressure Osmometry\*

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### Synopsis

Three aspects of vapor pressure osmometry were examined: drop size, solute volatility, and the constancy of the calibration factor. It was shown that there is a drop size effect which is dependent on the solute concentration. Solutes having vapor pressures as low as 0.3 mm Hg under the operating conditions were found to give unsatisfactory results. The calibration factor was determined using eight compounds in the molecular weight range of 128 to 883 in chloroform, toluene, and methyl ethyl ketone at several temperatures; a small but significant dependence of the calibration factor on molecular weight was demonstrated. The results fitted, with a high degree of accuracy, the relation  $\log \bar{M}_n = a + b \log (\Delta V/C)_{C=0}$ , where  $a$  and  $b$  are constants for a given solvent/temperature combination. However, measurements with standard polystyrene samples, using extrapolations of this relationship to higher molecular weights, revealed considerable discrepancies in results for the one compound under different solvent/temperature combinations.

### INTRODUCTION

The technique of vapor pressure osmometry as a means of determining the number-average molecular weight of polymeric compounds has been widely accepted for some years and commercial equipment for this purpose, for molecular weights up to about 20,000, has been available for more than a decade. The operating principle of such instruments is as follows: Two thermistor beads, which form two arms of a bridge circuit, are suspended in a thermostatted chamber saturated with solvent vapor. By means of guided syringes, a drop of solvent is placed on one thermistor (the reference bead) and a drop of solution on the other (the measuring bead). Considered in very simple terms, solvent condenses on the measuring bead, because of the lower vapor pressure of the solution, thereby warming the measuring bead and the difference in temperature between the two beads results in a bridge imbalance. In practice, other factors also affect the temperature difference, as discussed below.

At steady state, the temperature difference  $(\Delta T)_s$  is given by

$$(\Delta T)_s = K_s \left( \frac{C}{\bar{M}_n} + A_2 C^2 + A_3 C^3 + \dots \right) \quad (1)$$

where  $K_s$  is a calibration constant at the steady state,  $C$  is the solution concentration,  $\bar{M}_n$  is the number-average molecular weight of the solute, and  $A_2$  and  $A_3$  are the second and third virial coefficients of the solute, respectively. Several

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attempts have been made to analyze the heat transfer processes taking place in the thermal chamber.<sup>1,2</sup> However, it has been found that processes such as heat conduction from the solution drop surface to the ambient vapor and from the solution drop to the thermistor lead wire can occur,<sup>3,4</sup> so that true thermodynamic equilibrium between the solution drop and the solvent vapor may not be attained. Furthermore, the thermodynamic efficiencies of the heat transfer processes may be less than unity,<sup>5</sup> and uncertainty exists as to the contribution, if any, of certain diffusion-controlled processes within the solution drop to the overall heat transfer mechanism.<sup>1,2,3,6,8</sup> Thus, attempts at calculating the value of  $K_s$  have been unsuccessful.<sup>3,4</sup>

In practice, the apparatus is calibrated for a given solvent, temperature, and thermistor probe by measurements with a substance of known molecular weight at a number of solution concentrations. The results are then calculated from the expression

$$\bar{M}_n = \frac{k}{(\Delta V/C)_{C=0}} \quad (2)$$

where  $k$  is an apparatus constant for a given solvent, temperature, and thermistor assembly; and  $\Delta V$  is the bridge imbalance for a concentration  $C$ .

Certain operating variables, chiefly the size of the drop on the thermistor beads and the reading time interval, have been examined and conflicting results reported as to the importance of these factors. Thus, it has been claimed that the drop size does not affect the results,<sup>3,9</sup> whereas other workers have demonstrated a significant drop size effect.<sup>5,6,10</sup> Inversion of the thermistor beads, as an aid to achieving reproducible drop sizes, has been advocated.<sup>10</sup> Similarly, conflicting views have been advanced as to the time interval after replacement of the solution drop at which the reading should be taken.<sup>3,5,11</sup>

Recently, the question has been raised as to whether the calibration factor  $k$  is in fact simply an apparatus/operating conditions constant. Earlier studies indicated that the value of  $k$  was independent of the solute molecular weight,<sup>3</sup> and, indeed, this premise is the basis of the normal operating procedure. However, it has recently been suggested<sup>6-8</sup> that the contribution of diffusion-controlled (and hence molecular weight-dependent) processes in the solution drop and thermistor self-heating effects may not be negligible, as was assumed previously.<sup>1,2</sup>

This seemingly straightforward point is actually difficult to resolve as only a very small proportion of the molecular weight range of the instrument is accessible for calibration purposes because of the need for compounds having very high purity and accurately known number-average molecular weight. Polymers are in general excluded from this application because of the lack of an independent method of measurement of number-average molecular weight to sufficient accuracy. The length of the extrapolation from the calibration range, which greatly magnifies the effect of even a small molecular weight dependence, leads to the possibility of significant errors in the molecular weight of polymers determined by this method. In those instances where the molecular weight of a relatively high molecular weight compound could be determined by another method, it has frequently been observed that vapor pressure osmometry gave a low result.<sup>6,7</sup>

In the present work, the constancy of the calibration factor has been closely

examined using carefully purified calibrating compounds and a variety of solvents. Some other factors, chiefly drop size and solute volatility, have also been examined with a view to establishing more firmly the effect of these on vapor pressure osmometry measurements.

## EXPERIMENTAL

The compounds used were (a) naphthalene, (b) benzil, (c) methyl stearate, (d) cholesterol, (e) cholesteryl caproate, (f) cholesteryl stearate, (g) dicholesteryl adipate, (h) pentaerythrityl tetracaproate, (i) pentaerythrityl tetrastearate, (j) tripalmitin, (k) 1,2-dichlorobenzene, (l) squalane, and (m) polystyrene. The source and method of purification of these compounds were as follows: (a) BDH OAS grade, zone refined, approximately 100 passes; (b) BDH technical grade, recrystallized twice from toluene; (c) BDH chromatographically pure, zone refined, approximately 100 passes; (d) BDH technical grade, recrystallized twice from hexane and extracted several times with hot ethanol; (e)–(g) prepared from cholesterol and the appropriate acid, recrystallized from chloroform, extracted several times with hot ethanol; (h) U.S. National Research Laboratories reference material, code 6170; (i) Pressure Chemical Co., standard reference material; (j) BDH chromatographic grade, purified by TLC and recrystallized from acetone; (k) Fluka puriss. grade; (l) Eastman special grade, and (m) Pressure Chemical Co. narrow molecular weight standard materials batches 12b and 8b.

Compound purity was assessed from the shape of the melting curve using a du Pont Model 900 differential thermal analyzer equipped with its DSC cell and using a heating rate of 5°C/min. Extractions and recrystallizations were repeated until the sharpness of the melting point indicated high-purity material, that is, a melting range of no more than 0.5°C between the extrapolated onset of melting and the maximum of the melting peak. For example, the liquid crystal transitions of the cholesterol esters, which are only discernible with samples of high purity,<sup>12</sup> were clearly seen. Exceptions to this procedure were compounds (h)–(m), which were used in their as-received state. DTA indicated that (k) contained a small amount of 1,3-dichlorobenzene; while unidentified impurities were present in (h) and (i) (small amounts) and in (l) (larger amount).

The methyl ethyl ketone was BDH special grade for chromatography, while all other solvents used were BDH AR grade.

The vapor pressure osmometer used in these studies was a modified Hewlett-Packard Model 302B. Modifications to the electronics were made to reduce sources of thermal emf's and to enable the equipment to be operated simultaneously in the recorder and null-method modes. The thermal chamber was not altered. Details of the modifications and the instrument performance are given elsewhere.<sup>13</sup> The routine operating procedure was to record the bridge imbalance–time curve, but to determine the equilibrium reading by the null method. The time to reach the equilibrium value depended on the drop size, solvent, and operating temperature, as detailed below, but was generally in the range of 2–6 min. Three readings were taken at each concentration. The concentration range used was 2–10 g/kg, except for naphthalene, 1,2-dichlorobenzene, and tripalmitin, where more dilute solutions were employed (0.2–5 g/kg).

In investigations of the constancy of the calibration factor  $k$ , at least eight solutions were measured for each compound, and the straight line of best fit to

the plot of  $\Delta V$  versus concentration was calculated by linear regression analysis. The correlation coefficient was in each case at least 0.99, unless otherwise stated. No evidence was seen of a contribution of the higher terms in eq. (1), and hence no corrections were required.<sup>14</sup>

## RESULTS AND DISCUSSION

### Drop Size Effects

Drop sizes, assessed by measuring the length of the thermistor bead and solution drop with a traveling microscope,<sup>5</sup> ranged from about 1.4 mm to about 3.0 mm in length. All investigations reported in this section used solutions of squalane in toluene at an operating temperature of 50°C.

It was apparent that there is a drop size effect which is related to the concentration of the solution. This effect is shown partly by the shape of the bridge imbalance-versus-time curve and partly by the actual magnitude of the reading.

For dilute solutions (less than about 6 g/kg, or  $1.5 \times 10^{-2} M$ ) the shape of the bridge imbalance-time curve was the same for all drop sizes. More concentrated solutions (6–12 g/kg) showed a downward curvature in the  $\Delta V-t$  curve with small drops ( $\sim 1.4$ – $1.5$  mm in length), but not with larger drops; while with solutions of greater than 12 g/kg concentration, a downward slant was apparent with drops up to about 1.8 mm in length. The slope of this trace for a given drop size increased with increasing concentration. Representative curves are shown in Figures 1 and 2.

Meeks and Goldfarb reported<sup>5</sup> an approximately linear decrease in the bridge imbalance with time, the slope being steepest with small drops and still discernible with large drops. They advocated that the bridge imbalance (a resistance in their case) should be extrapolated to  $t = 0$  and found a linear relationship between this quantity ( $\Delta R_{t=0}$ ) and drop length and a linear dependence of the slope of this line on the actual bridge imbalance. Similar results were obtained by Bersted for the bridge imbalance at equilibrium.<sup>6</sup> These findings contrast with those of other workers who reported there was no dependence on drop size.<sup>3,9</sup> It has been generally agreed that nonuniform temperature in the drop would lead to a dependence on drop size, that is, thermal conduction effects are significant.<sup>6,9</sup>

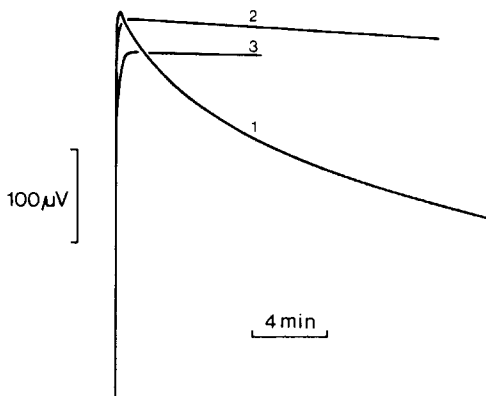


Fig. 1. Effect of drop size on  $\Delta V$ -time curves. Drop lengths: (1) 1.41 mm; (2) 1.76 mm; (3) 2.61 mm. Solution, 14.61 g/kg squalane in toluene at 50°C.

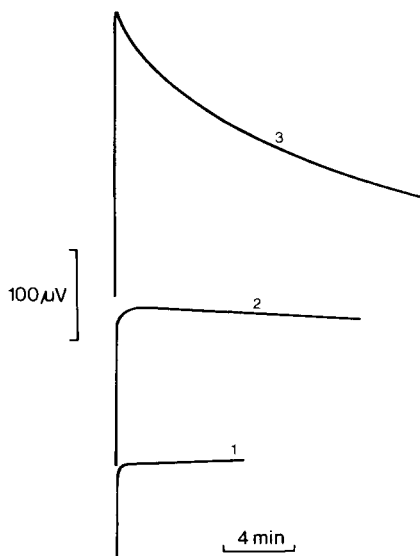


Fig. 2. Effect of concentration on  $\Delta V$ -time curves for small drops: (1) drop length 1.36 mm, concentration 1.78 g/kg; (2) drop length 1.37 mm, concentration 6.77 g/kg; (3) drop length 1.41 mm, concentration 14.61 g/kg. All solutions, squalane in toluene at 50°C.

The present work confirms the existence of a drop size dependence. Figure 3 shows  $\Delta V_{t=0}$  versus drop length for a number of concentrations (the curved traces relating to small drop sizes were not used for this purpose because of the uncertainty in their extrapolation), and Figure 4 gives the slope of these lines,  $\delta(\Delta V)/\delta l$ , versus the bridge imbalance at a drop length of 2.0 mm. Thus, it seems that in any calculations on the thermal equilibrium in the chamber, thermal conduction effects within the drop should be taken into account.

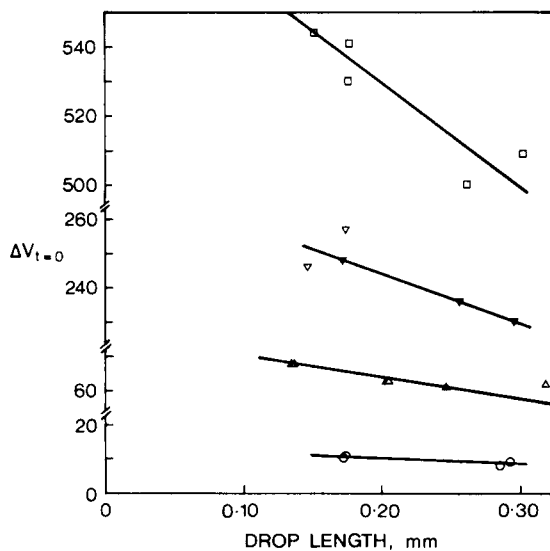


Fig. 3. Dependence of  $\Delta V_{t=0}$  on drop length for different values of  $\Delta V$ .

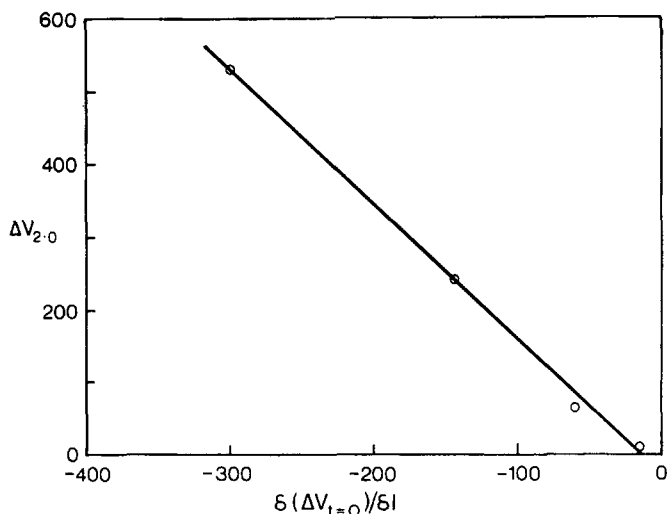


Fig. 4. Dependence of  $\Delta V_{2,0}$  on the slope of  $\Delta V_{t=0}$ -vs.-drop length curves.

To minimize drop size effects, the remainder of the work reported here employed medium size drops (1.8–1.9 mm in length) and solution concentrations generally in the range of 2–10 g/kg.

### Rate of Approach to Equilibrium

For a given drop size, the shape of the  $\Delta V$ - $t$  curve was found to differ with different solute/solvent/temperature combinations, the distinguishing features being the number of changes of direction which occurred on replacement of the solution drop, the direction of final approach to the equilibrium value, and the

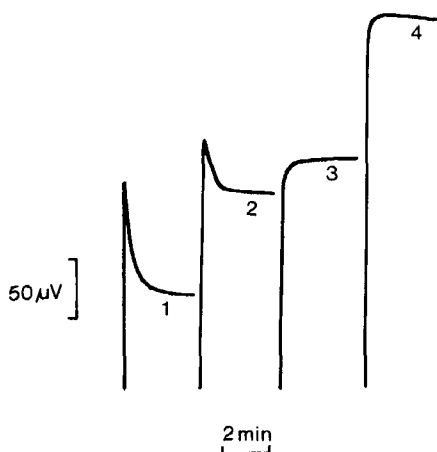


Fig. 5. Representative  $\Delta V$ -time curves showing differences in approach to equilibrium position. System, cholesterol/toluene/40°C. Solution concentrations: (1) 2.99 g/kg; (2) 5.57 g/kg; (3) 6.56 g/kg; (4) 10.03 g/kg.

rate of approach to the equilibrium reading. No clear pattern could be identified linking the type of curve with the particular solute, solvent, or temperature. A mixture of curve types is shown in Figure 5. Because of the variation in the direction and rate of approach to the equilibrium value, the taking of readings after a fixed time interval without waiting for the attainment of equilibrium<sup>11</sup> could lead to erroneous results.

The time to reach the equilibrium value with chloroform gradually increased over a period of several days, particularly if the instrument previously contained toluene at a higher temperature. Replacement of the solvent in the reservoir restored this time to its original value. Gas chromatography showed that the chloroform contained about 1.5% ethanol and 0.01% toluene, whereas chloroform from the reservoir after operation at 37°C, when the previous solvent was toluene at 60°C, had a toluene content of 0.05%. Chloroform which was washed with water and dried over molecular sieves (ethanol content then about 150 ppm) still displayed this trend. This illustrates the pronounced effect which certain impurities can have on instrument performance.

### Solute Volatility Effects

The lower limit of the usable molecular weight range is set by the volatility of the solute under the operating conditions. For example, with 1,2-dichlorobenzene in toluene at 40°C (vapor pressure 3.5 mm Hg), after the usual rapid changes of bridge imbalance on replacing the solution drop, a steady downward drift occurred and no equilibrium value was reached in the normal reading time interval (up to 7 min). Furthermore, the drift rate increased with increasing solute concentration in the range examined (0.4–2.1 g/kg). With the solvent on both thermistor beads, a steady value was reached in about 1 min (Fig. 6). Similar traces were obtained for naphthalene in toluene at 60°C (vapor pressure 1.8 mm Hg), while at 40°C (naphthalene vapor pressure 0.3 mm Hg) equilibrium was reached within 2 min with dilute solutions (up to 1.3 g/kg), but a downward drift was apparent at higher concentrations.

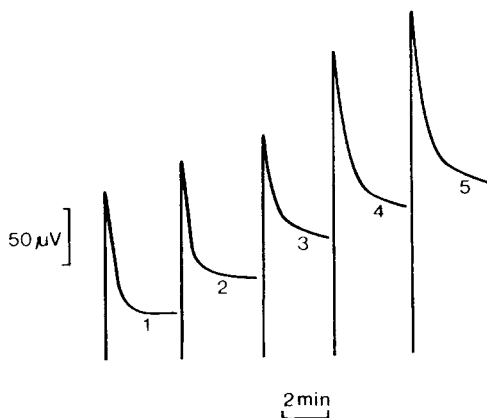


Fig. 6. Effect of solute volatility. Representative  $\Delta V$ -time curves for the system 1,2-dichlorobenzene/toluene/40°C. Solution concentrations: (1) 0; (2) 0.44 g/kg; (3) 1.11 g/kg; (4) 1.77 g/kg; (5) 2.11 g/kg.

Higuchi et al.<sup>15</sup> suggested, from results with very simple apparatus, that the value of a volatility ratio,

$$r = \frac{P_2}{X_2 P_1} \quad (3)$$

should not exceed 0.03, where  $P_2$  and  $P_1$  are the vapor pressure of solute and solvent, respectively, and  $X_2$  is the solute mole fraction. In the naphthalene/toluene/40°C case cited above,  $r = 6$  for a solution concentration of 1.3 g/kg. For comparison, benzil at 40°C and a concentration of 5 g/kg, which gave quite satisfactory performance judging by the shape of the bridge imbalance-time curves, has an  $r$  value of 0.04. For a given solute, solvent, and temperature combination, eq. (3) indicates that the higher the solute concentration, the lower the value of  $r$ . The present work shows that the higher the concentration, the less satisfactory the results become, within the time scale used, and that solute volatility effects are more complex than eq. (3) would indicate. Thus, the use of a compound for calibration purposes whose vapor pressure under the operating conditions is more than about 0.2 mm Hg should be avoided.

### The Constancy of the Calibration Factor

To investigate whether the calibration factor  $k$  depended on the nature of the solute, especially its molecular weight,  $k$  was determined with a number of solutes in the molecular weight range of 128–883 under a variety of solvent/temperature conditions. The values of  $k$  were calculated from the slope of the line of best fit of the plot bridge imbalance versus concentration (Table I). These values are plotted against the solute molecular weight (Fig. 7), the error bars denoting

TABLE I  
Values of the Calibration Factor  $k$  for Various Solute, Solvent,  
Temperature Combinations

Solute	Mol. wt.	Chloroform	Toluene		MEK	
		37°C	60°C	40°C	37°C	25°C
Naphthalene	128.2	29420	—	—	13840	11910
Benzil	210.2	30040	16040	11570	14510	12330
Methyl stearate	298.5	29730	16410	11920	14300	11760
Cholesterol	386.6	29490	16470	12120	13980	11420
Cholesteryl caproate	484.8	29960	16510	11890	14520	11500
Cholesteryl stearate	653.1	30340	16490	11910	—	—
Tripalmitin	807.3	—	16590 <sup>a</sup>	12340 <sup>a</sup>	—	—
Dicholesteryl adipate	883.3	30810	16680	12200	—	—
Pentaerythrityl tetracaproate <sup>b</sup>	528.2	31570	16950	12580	14470	11890
Pentaerythrityl tetrastearate <sup>b</sup>	1202.0	34020	18920	—	—	—

<sup>a</sup> Four points only.

<sup>b</sup> DTA indicates these compounds are less pure than the others.



the 95% confidence limits. All lines were calculated by unweighted linear regression analysis. The shape of the bridge imbalance-time curve in each system given in Table I showed no sign of any volatility effects; results for systems which did so, for example, using naphthalene at higher temperatures, were discarded. The reason for the opposite sign of the MEK/25°C case is not clear.

DTA indicated that the pentaerythryl tetracaproate and tetrastearate samples were less pure than the other compounds used in this investigation, and a GPC trace of the tetrastearate showed the presence of a small amount of a lower molecular weight compound. Both these materials gave high values of  $k$  com-

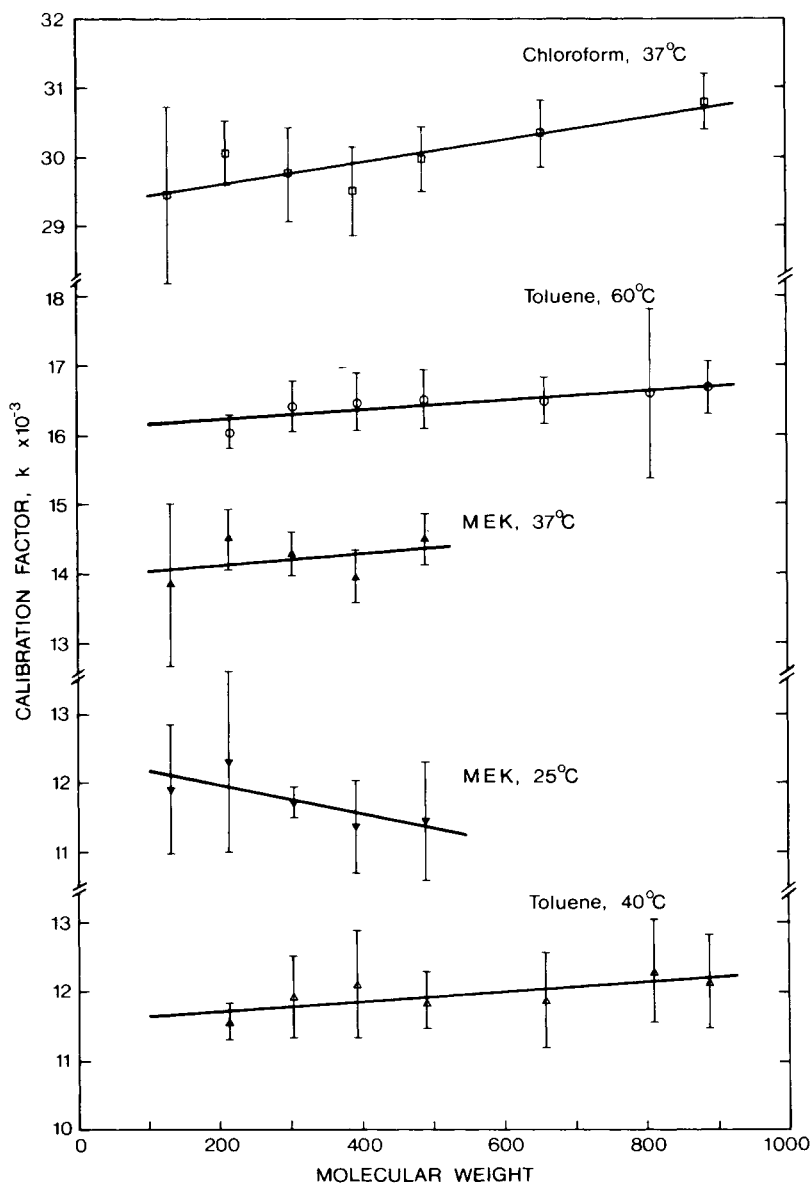


Fig. 7. Variation of the calibration factor  $k$  with molecular weight for various systems. Error bars denote 95% confidence limits.

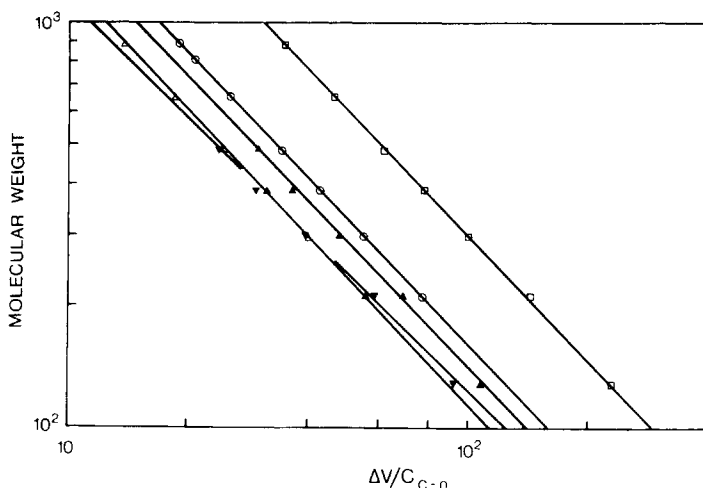


Fig. 8. Relation between  $\bar{M}_n$  and  $(\Delta V/C)_{C=0}$  for various solutes according to eq. (4): ( $\square$ ) chloroform, 37°C; ( $\circ$ ) toluene, 60°C; ( $\triangle$ ) toluene, 40°C; ( $\blacktriangle$ ) MEK, 37°C; ( $\blacktriangledown$ ) MEK, 25°C.

pared with the overall trend of results, consistent with a number-average molecular weight lower than the formula weight. These results have been omitted from Figure 7 and from the mean value of  $k$ .

The correlation coefficients for the linear relationships between  $k$  and molecular weight shown in Figure 7 range from 0.76 for the MEK/25°C case, based on only five points, to 0.86 for the chloroform/37°C system (seven points). The probability of obtaining by chance the observed correlation coefficients is less than 5% in each of the three systems with seven points and rather larger in the MEK cases.

There is, of course, no requirement that the relationship between  $k$  and molecular weight be a simple linear one. The data in Table I can also be represented, following Brzezinski et al.,<sup>7</sup> by

$$\log \bar{M}_n = a + b \log (\Delta V/C)_{C=0} \quad (4)$$

as shown in Figure 8. The calculated values of  $a$  and  $b$  (from linear regression analysis, correlation coefficient at least 0.999 in each case) are given in Table II. Thus, that  $k$  is not constant seems evident; but the form, magnitude, and even the sign of the variation is less certain.

The compounds used as calibration standards include a wide variety of chemical classes as well as a set of related compounds. It appears that molecular

TABLE II  
Values of the Constants in the Relation  $\log \bar{M}_n = a + b \log (\Delta V)/C_{C=0}$

System	$a$	$b$
Chloroform, 37°C	4.515	-1.020
Toluene, 60°C	4.249	-1.022
Toluene, 40°C	4.123	-1.032
MEK, 37°C	4.186	-1.019
MEK, 25°C	4.004	-0.959

size rather than chemical composition determines the variation in the calibration factor.

A close examination of the data in Figure 7 shows some slight suggestion of curvature. The order of presentation of results does not correspond to their chronologic order of measurement, and some systems were remeasured two years after the initial measurement and gave excellent reproducibility. Thus, it is considered that the present results do not warrant further pursuit of this point.

The dependence of the calibration factor on molecular weight is smaller than that given by Brzezinski et al.,<sup>7</sup> who found, for example, in the case of chloroform at 37°C an increase of about 30% over the molecular weight range of 128–892 compared with an increase of only 4% in the present work over a similar molecular weight range. Both these sets of results contrast with earlier work<sup>3</sup> and with the standard operating instructions for these instruments.<sup>11</sup>

Since the variation of  $k$  with molecular weight in the present work is small, it was thought that additional measurements at a higher molecular weight would more clearly distinguish between the postulated nonconstant  $k$  and the established view of a constant value of  $k$ . Accordingly, measurements were also made with two narrow molecular weight, standard polystyrene samples, nominal molecular weight 2100 and 10,000. As their number-average molecular weights were determined by vapor pressure osmometry, these samples should not be used directly to investigate the question of the constancy of the calibration factor; but, with the two pentaerythritol derivatives, they constitute a set of fairly pure, "unknown" compounds which covers a much wider molecular weight range than that of the calibration compounds. The molecular weights of these materials have been calculated from the mean value of the calibration factor (method A)

TABLE III  
Values of the Molecular Weight Calculated from the Mean  $k$  Values and from Eq. (4) for Various Solutes

		Chloroform	Toluene		MEK	
		37°C	60°C	40°C	37°C	25°C
Mean $k$ value <sup>a</sup>		29970	16460	11990	14230	11780
Pentaerythrityl tetracaprate	$\Delta V/C$	59.79	32.11	23.82	27.40	22.52
	Corr. coeff. <sup>b</sup>	0.999	0.998	0.999	0.999	0.999
	$\bar{M}_n$ , mean $k$	501	513	503	519	523
	$\bar{M}_n$ , eq. (4)	504	513	504	526	509
Pentaerythrityl tetrastearate	$\Delta V/C$	28.30	15.73	—	—	—
	Corr. coeff. <sup>b</sup>	0.999	0.999	—	—	—
	$\bar{M}_n$ , mean $k$	1059	1046	—	—	—
	$\bar{M}_n$ , eq. (4)	1082	1064	—	—	—
Polystyrene Batch 12b	$\Delta V/C$	16.94	9.90	6.32	7.34	5.52
	Corr. coeff. <sup>b</sup>	0.999	0.983	0.999 <sup>c</sup>	0.999	0.996
	$\bar{M}_n$ , mean $k$	1770	1660	1830	1940	2130
	$\bar{M}_n$ , eq. (4)	1825	1710	1980	2010	1960
Polystyrene Batch 8b	$\Delta V/C$	4.48	2.00	1.13	1.21	1.01
	Corr. coeff. <sup>b</sup>	0.999	0.996 <sup>c</sup>	0.965	0.988	0.914 <sup>c</sup>
	$\bar{M}_n$ , mean $k$	6690	8230	10610	11760	11670
	$\bar{M}_n$ , eq. (4)	7090	8750	11700	12620	10000

<sup>a</sup> Mean of values for first eight compounds in Table I.

<sup>b</sup> Correlation coefficient from linear regression analysis.

<sup>c</sup> From 12 concentrations.

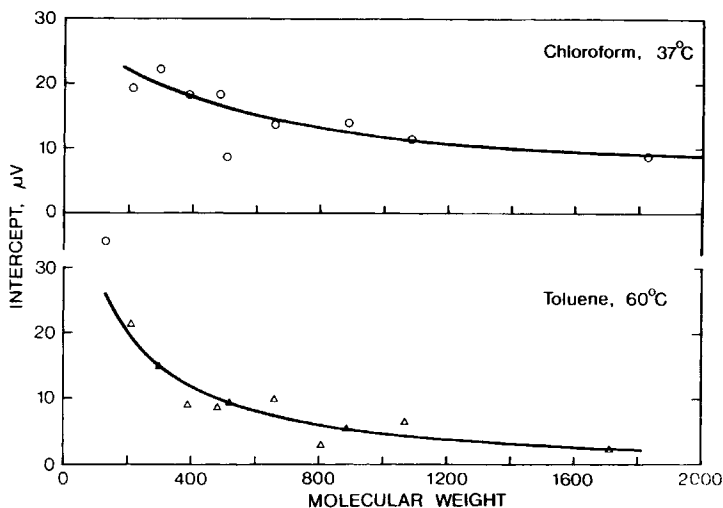


Fig. 9. Dependence of the value of the intercept in the  $\Delta V$ -vs.-concentration plots on solute molecular weight.

and from eq. (4) using the data in Table II (method B). Since method A assumes that  $k$  is independent of the solute molecular weight, this should give, for all the systems except MEK/25°C, results which are increasingly too small for compounds of molecular weight greater than about 500. The results for high molecular weight samples of low values of  $k$  are less accurate because only a few  $\mu V$  are recorded in some instances. The greater scatter thereby introduced is reflected in the lower values of the correlation coefficient. These results are given in Table III.

The outstanding feature of these results is the disparity between values of  $\bar{M}_n$  for the same compound in different systems, and this increases the higher the molecular weight of the compound. Although the values as calculated by the two methods are different, the agreement between results for the same compound in various systems is not significantly improved by the use of method B. In this method, the range in values for pentaerythrityl tetracaprate is about 4%, for polystyrene batch 12b almost 18%, and for batch 8b approaching 80%, indicating that the relationship between  $\bar{M}_n$  and  $k$  established at the lower end of the molecular weight range cannot be extrapolated to high molecular weights.

Another possibility which was considered was that  $k$  increases with molecular weight as indicated by eq. (4) up to a certain molecular weight and thereafter is constant. Calculations on this basis for the two polystyrene samples, taking various values for the transition point, showed that, since the results fall between those for methods A and B, the agreement between results for the one sample is no better than in the other methods.

On the basis of studies with an osmometer modified so that the bridge voltage could be varied, Bersted<sup>6,8</sup> stressed the importance of diffusion-controlled reactions at the drop surface and thermistor self-heating effects, both of which were previously considered to be negligible.<sup>1,2</sup> Bersted proposed that the calibration factor is independent of the solute molecular weight only if no evaporation or condensation of solvent vapor occurs, which situation pertains only under certain

(nonstandard) conditions. Otherwise, such factors as the magnitude of the heat losses from the thermistor supporting wires and the tendency for evaporation or condensation to predominate, depending on the magnitude of the thermistor self-heating effect, determine the extent to which the calibration factor varies with solute molecular weight. The present results, while confirming that the calibration factor is not a constant, also show that the dependence on molecular weight must be determined for each instrument and each solvent/temperature combination and over the appropriate molecular weight range. Not even the sign of the dependence can, at this stage, be predicted. The lack of agreement between results for the one substance under different conditions indicates that specific solvent-solute interactions may also be significant.

In calculating the line of best fit for these plots, the origin was not used as a point and, indeed, was rarely found to be on the calculated line. As the initial slope of this curve is used, an intercept on the  $\Delta V$  axis has no effect on the results. However, the magnitude of this intercept varies with solute molecular weight (Fig. 9), confirming the proposal of Bersted<sup>6</sup> and giving additional support to his model of the operating principles of vapor pressure osmometers.

These findings cast doubt on the standing of vapor pressure osmometry as an accurate method for the determination of number-average molecular weight of polymers.

## CONCLUSIONS

It has been shown that the value of the calibration factor varies with the molecular weight of the solute and that the magnitude of this effect depends on the particular instrument and its mode of operation as well as on the solvent and temperature. These results support the theoretical model of the operating principle of vapor pressure osmometry which stressed the importance of diffusion-controlled reactions at the drop surface and thermistor self-heating effects.<sup>6,8</sup>

For accurate molecular weight determinations, the dependence of the calibration factor on molecular weight, under the particular operating conditions and over the appropriate molecular weight range, should be determined using compounds of the highest purity. Extrapolation to high molecular weight of a calibration factor dependence determined over a lower molecular weight range is unsatisfactory.

The existence of drop size effects has been confirmed and the hazards of using solutes of even moderate volatility displayed. The use of a recorder to show the shape of the bridge imbalance-time trace is most desirable as an aid to the rapid recognition of nonsteady-state conditions arising from such factors as trace impurities, solute volatility, or drop size effects. Readings should be taken when the system has reached a steady state, rather than after some fixed time interval.

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