On the Reliability of Molecular Weight Determination by Vapor Pressure Osmometry

L. MRKVIČAKOVÁ and S. POKORNY, *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia*

Synopsis

A study is reported of the calibration of vapor pressure osmometry using seven types of polymers having a number average molecular weight up to 35,000 as standards, and chloroform, methyl-*tert*-butyl ether, and benzene as solvents. The effect of the chemical structure of standards is demonstrated in terms of calibration relation for different combinations of solvent–polymer series.

INTRODUCTION

Vapor pressure osmometry (VPO) still remains an irreplaceable method of determination of the number average molecular weight M_n of oligomers and polymers in the range $1-3 \times 10^4$. For this range of M_n values, there is sufficient reported experimental evidence now of the noncolligative behavior of the polymer in solution in the case of the VPO method.[1-5] That is recalculation of experimental data of high molecular standards by means of a classical equation gives lower $\overline{M}_n$ values than the real ones

$$\overline{M}_n = K \left(\frac{\Delta V}{c} \right)^{-1}_{c=0} \tag{1}$$

$(\overline{M}_{VPO} < \overline{M}_n)$. Here, K is the calibration constant obtained by means of a low-molecular weight compound, ΔV is the difference between potentials corresponding to the difference between the temperatures of solution and solvent, and c is concentration. For this reason, many authors have demonstrated[2-6] that a calibration function must each time be determined, for the given solvent, operational temperature, and type of commercial apparatus, valid within the whole experimentally accessible range of molecular weights. It has not been proved, however, that these calibration dependences are universal, i.e., independent of the primary chemical structure of the polymeric compound. This aspect is dealt with in the present study.

EXPERIMENTAL

Properties of the substances and solvents used are summarized in Tables I and II.

Osmometric measurements were performed with a Hitachi Perkin-Elmer,

CCC 0021-8995/85/031211-08$04.00

TABLE I
Substances Used in This Study

Substance	Origin	$\overline{M}_n{}^a$	$\overline{M}_n{}^b$	$\overline{M}_w{}^b$
Benzyl	Hitachi Perkin-Elmer	210		
Polystyrene	(PS)			
PS 1	Chrompack	570		
PS 2	Chrompack	955	1060[c]	
PS 3	Waters Assoc.	2100		
PS 4	Waters Assoc.	3100		
PS 5	Waters Assoc.	9700		
PS 6	Waters Assoc.	15,000		17,000[c]
PS 7	Waters Assoc.	20,000		
PS 8	Waters Assoc.	36,000		
Polybutadiene	(PB) Prepared by anionic "liv-			
PB 1	ing" polymerization (1,4-dili-		1100[c]	1210[c]
PB 2	thium butane in methyl-*tert*-		1500[c]	1650[c]
PB 3	butyl ether)[7]		1970[c]	2130[c]
PB 4			2950[c]	3130[c]
PB 5			5150[c]	5510[c]
PB 6			6140[c]	6660[c]
Polyisobutylene	(PIB) Prepared by cationic po-			
PIB 1	lymerization (diethylalumi-		5840[c]	22,700[e]
PIB 2	nium chloride and water)		9160[c]	31,700[e]
PIB 3			23,200[d]	69,000[e]
Polyisoprene	(PIP)			
PIP 1	Chrompack	970		
PIP 2	Chrompack	3350		
PIP 3	Chrompack	10,500		
PIP 4	Chrompack	30,400	31,400[d]	
Polyoxyethylene	(POE)			
POE 1	Fluka AG	600		
POE 2	Koch-Light	1000		
POE 3	Fluka AG	2400		
POE 4	Koch-Light	4000	4100[f]	7070[e]
POE 5	Koch-Light	6000	6240[f]	8300[e]
POE 6	Merck	10,000		15,700[e]
Poly(methyl methacry-late)	(PMMA)			
PMMA 1	Prepared by anionic polymeri-		13,000[c]	46,000[c]
PMMA 2	zation[8]		18,500[c]	40,000[c]
PMMA 3			35,000[c]	73,000[c]
Polydimethylsiloxane	(PDMSi)			
PDMSi 1	SF 96 Hewlett Packard		3830[f]	
PDMSi 2	Lukooil M 500, Lachema		7100[f]	37,700[e]
PDMSi 3	DC 200, Hewlett-Packard		26,800[d]	86,200[c]

[a] Given by supplier.
[b] Measured values.
[c] Determined by size exclusion chromatography.
[d] Determined by membrane osmometry.
[e] Determined by light scattering.
[f] Determined by ebulliometry.

Model 115 apparatus.[9] The reference values of the solvent potential V_0, read before and after each measurement of the concentration series, were carefully maintained identical within the limits of experimental error, to guarantee stable conditions in the measuring cell. The V values were read off 3–5 min after the sample had been added dropwise. The time needed to

TABLE II
Solvents Used in This Study

Solvent	Boiling point (°C)	Heat of vaporization at measuring temp (J·g⁻¹)	Measuring temp (°C)
Methyl-*tert*-butyl ether (MTBE)	56	300.3	28
Chloroform (CH)	61.2	264.6	37
Benzene (B)	80.2	424.6	40

attain a stationary state for the individual solvents was determined each time by means of an attached Hitachi, Model 165-0023 recorder. The polymer concentrations were chosen so as to make the final potential difference values, $V - V_0 = \Delta V$, lie, if possible, in the range 30–200 μV. In such a case, however, usually with high-molecular-weight polymers, the dependence of V and ΔV values on concentration c was not linear. To eliminate the zero-error ΔV_0 (if any), the experimental dependence was assumed to be[10]

$$V = V_0 + \Delta V_0 + Ac + Bc^2 \tag{2}$$

where $A = (\Delta V/c)_{c=0}$. Parameters of this equation were calculated by employing the method of quadratic regression.

RESULTS AND DISCUSSION

The VPO behavior of a number of polymer–solvent pairs was investigated. For the measured dependences of limiting values of "potential differences" $(\Delta V/c)_{c=0}$ on molecular weight M, the parameters of calibration functions were determined within the experimentally available range of molecular weights.

Calibration Independent of the Calibration Compound Used

The experimental dependences for combinations polystyrene–methyl-tert-butyl ether (Ps–MTBE) and polyoxyethylene–chloroform (POE–CH) (Fig. 1) satisfied, within the limits of experimental error, the generally used relation of molecular weight determination ($M_n \leq 2000$) given by eq. (1). As this result is at variance with the reported findings,[1-4] we regarded it as necessary to check whether the cause of the dependence thus obtained should not be seen in a tendency towards aggregation with increasing molecular weight. Association behavior of some polymers in solution may be expected for solvents with a low "solvent power," or for θ-solvents. In this case, recalculation of the experimental $(\Delta V/c)_{c=0}$ values using relation (1) may give also M_n values higher than the real ones, which would lead to a phenomenon quite opposite to the one described in the Introduction.[1-4] The behavior of PS 8 in MTBE and of polyisobutylene in chloroform (PIB in CH) was therefore studied by means of the classical light scattering, a highly sensitive method of determination and characterization of association processes. In the same concentration range as that of VPO measurements, no
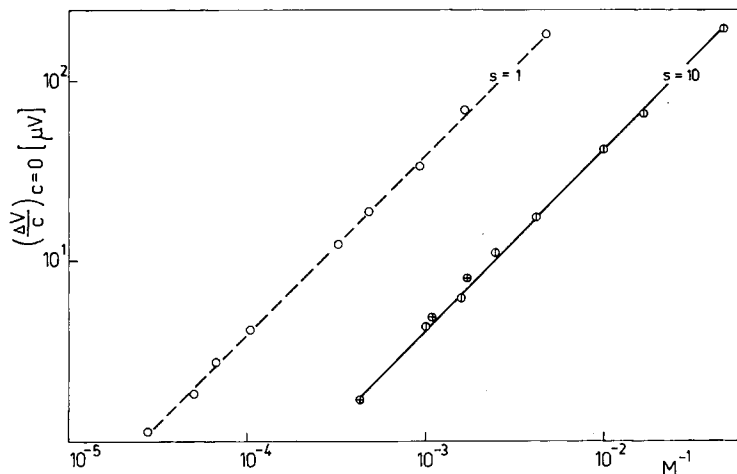
Fig. 1.   Dependence given by Eq. (1) for (○) PS in MTBE and for (◐) POE or for (⊕) PIB in CH; s = scaling factor.

anomalies were detected in the scattering behavior of these polymers (angular dependences of the intensities of scattered light were symmetrical with respect to ∠ 90°), and the calculated molecular weights M_w were in satisfactory agreement with the values determined in other solvents. The second virial coefficient was positive in both cases (for PS 8 in MTBE, $A_2 = 4 \times 10^{-4}$, and for PIB in CH, $A_2 = 1 \times 10^{-3}$), having values corresponding to a comparatively good "solvent power." Also for POE ($M_n \leq 10^4$), for which chloroform is, however, a θ-solvent at 25°C (cf. Ref. 11), aggregation was regarded as not too probable at the operational temperature 37°C. Another factor which reduces the experimental $(\Delta V/c)_{c=0}$ value consists of polydispersity of the measured substance.[12] The M_{VPO} value calculated using eq. (1) is then higher than the real M_n value. The narrow molecular weight distributions of PS (preparation by the anionic polymerization—Waters) and of POE (Table I) cannot virtually affect the course of experimental dependences in Figure 1, and thus can be regarded as real.

Calibration Depending on Molecular Weight of the Calibration Compound

The experimental data reported so far[2-4] satisfy the calibration function in the form

$$\left(\frac{\Delta V}{c}\right)_{c=0} = K_1 M^{-a} \tag{3}$$

for the exponent $a < 1$. An alternative analytical description of the calibration dependence ensued from Bernstedt's interpretation of the role of diffusion in a drop of solution on the thermistor[5]

$$\left(\frac{\Delta V}{c}\right)_{c=0} = K_2 \frac{1 + \beta M^{0.5}}{M} \tag{4}$$

In eqs. (3) and (4), K_1 and K_2 are constants. The deviation of the exponent a from unity and of the parameter β from zero are a measure of the non-colligative behavior in the VPO method. Equations (3) and (4) assume the form (1) for $a = 1$ or $\beta = 0$.

The trend of deviation of the experimental $(\Delta V/c)_{c=0}$ values from an ideal dependence (1) can be seen in Figure 2. For these polymer–solvent systems, it was necessary to determine parameters of calibration functions valid over the whole range of molecular weights of the samples under investigation (calibration compounds). Parameters K_1 and a occurring in the logarithmic form of eq. (3) were evaluated by the linear regression method. The same method was used to calculate K_2 and β: for this purpose, eq. (4) was rearranged to $M(\Delta V/c)_{c=0} = K_2 + K_2 \beta M^{0.5}$. The correlation coefficients, i.e., probabilities with which the given point of the set under investigation lies on the regression straight line, were generally very high (> 0.995), and for each pair of dependences (3) and (4) (cf. Fig. 3) almost identical. Hence, both suggested calibration functions are of equal value as regards accuracy of the description of experimental dependences $(\Delta V/c)_{c=0}$ vs. M, but the correction to polydispersity is simpler for the calibration function given by eq. (3) (cf. Refs. 6 and 12).

All parameters of calibration dependences calculated using our measurements are summarized in Table III. Only experimental data on polymers of low polydispersity ($M_w/M_n \leq 2$), the number of which in the accessible range of M_n was sufficient, were included in the calculation. For the other polymers, only a qualitative characterization of their behavior in the VPO method was carried out. The experimental $(\Delta V/c)_{c=0}$ values of polymers with a higher polydispersity, PIB, and polydimethylsiloxane (PDMSi) were not corrected, and it should therefore be borne in mind that their deviations from an ideal behavior do not correspond to the parameters in Table III, even if the experimental points roughly obey the calculated dependences (Fig. 3).
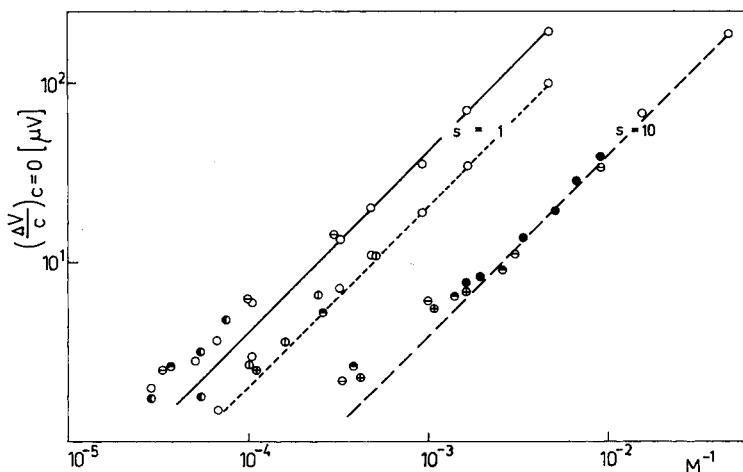

Fig. 2. Experimentally determined $(\Delta V/c)_{c=0}$ values as a function of M [eq. (1)]: (———) CH; (— — —) MTBE; (– – –) B; (○) PS; (●) PB; (⊕)PIB; (⊖IP; (○) POE; (○) PMMA; (○) PDMSi; $s =$ scaling factor.
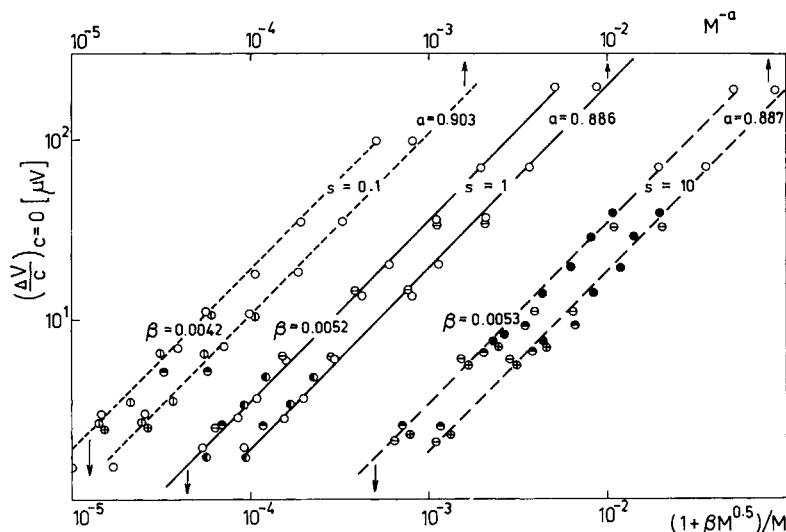
Fig. 3.   Experimentally determined $(\Delta V/c)_{c=0}$ values as a function M^{-a} [eq. (3)] or function $(1 + \beta M^{0.5})/M$ [eq. (4)]. Specification of calculated dependences and meaning of notation of experimental points are given in Figure 2.

CONCLUSIONS

We have shown that the measure of noncolligative behavior of high-molecular weight compounds in solution in their evaluation with commercial VPO apparatuses need not be the same if these compounds are not chemically identical. Parameters of calibration functions may be different not only for the same polymer in different solvents,[4,6] but also for different polymers in the same solvent. As an example, let us mention the ideal calibration (independent of molecular weight of the calibration compound) of PS, which is most often used for this purpose: This calibration cannot be used in MTBE in the analysis of polybutadiene (PB), PIB, polyisoprene (PIP), and PDMSi. Similarly, parameters of calibration functions [eqs. (3) and (4)] determined by means of a series of PS in CH cannot be applied to POE or PIB.

The design of the commercial apparatus (sitting vs. hanging drops) may also have some influence on the phenomenon investigated in the VPO method. In Table IV we compare parameters of calibration dependences measured up to now using PS calibration compounds prepared by the anionic polymerization. The upper boundary of experimentally available M_{VPO} values is given by the magnitude of the K_1 or K_2 constants. From this viewpoint the latest models of commercial VPO apparatuses are virtually of equal value. In spite of this, however, the validity of the derived calibration functions relates to a narrower M_n range than in our case. As errors involved in the determination of the exponent a are comparable with each other (Table IV), it may be stated that deviations from the colligative behavior of high-molecular weight polymers in the VPO method determined in this study are still the smallest.

TABLE III
Values of Parameters[a] of Calibration Functions Given by Eqs. (3) and (4)

Solvent	Substance	$\log K_1$	α	$\log K_2$	$\beta \times 10^3$	Molecular weight range of validity
MTBE	PS	4.58419	0.999	4.58487	0.098	$\leq$ 35,999
MTBE	PB,PIP(PIB)	4.26827	0.887	4.53128	5.3	$\leq$ 30,000
CH	PS,PIP,(PMMA)	4.28105	0.995	4.61360	0.23	$\leq$ 10,000 (23,000)
B	PS,POE,(PMMA)	4.02743	0.903	4.28215	4.2	$\leq$ 15,000 (18,000)

[a] K_1 and K_2 (μV·kg·g^{-1}).

TABLE IV
Calibration Parameters[a] from Polystyrene–Chloroform System at 37°C

Apparatus	$\log K_1$	a	$\log K_2$	β	Molecular weight range of validity	Ref.
Hewlett-Packard						
Model 302	2.410	0.853	2.734	0.0099	$\leq 10{,}000$	2
	± 0.011	± 0.002				
Model 302B	∓ 4.153	∓ 0.837	5.175	0.0101	$\leq 15{,}000$	4
	± 0.056	± 0.006				
Knauer	∓ 3.091	∓ 0.862	—	—	$(35{,}000)$	3
Hitachi Perkin-Elmer,	4.346	0.908	4.542	0.0052	$\leq 15{,}000$	This
Model 115	± 0.043	± 0.005				study
	∓ 4.280	∓ 0.886	5.541	0.0052	$\leq 35{,}000$	
	∓ 0.044	∓ 0.004				

[a] K_1 and K_2 (μV·kg·g^{-1}).

The values of the parameters a and β determined so far are independent of the magnitude of evaporation heat of the solvent used.[4] A more exact interpretation of the findings reported both elsewhere and in this study requires further experimental investigation.

References

1. B. H. Bersted, *J. Appl. Polym. Sci.,* **17**, 1415 (1973).
2. J. Brzezinsky and H. Glowala, *Eur. Polym. J.,* **9**, 1251 (1973).
3. I. Kuchaříková, *J. Appl. Polym. Sci.,* **23**, 3041 (1979).
4. M. Marx-Figini and R. V. Figini, *Makromol. Chem.,* **181**, 2401 (1980).
5. B. H. Bersted, *J. Appl. Polym. Sci.,* **23**, 633 (1979).
6. R. V. Figini and M. Marx-Figini, *Makromol. Chem.,* **182**, 437 (1981).
7. V. Maroušek, F. Mikeš, A. Pleska, and O. Seyček, 5th International Microsymposium, Advances in Ionic Polymerization, Prague, 1982, Abstract 32.
8. L. Lochmann, M. Rodová, and J. Trekoval, *J. Polym. Sci., Polym. Chem. Ed.,* **12**, 2091 (1974).
9. *Instruction Manual for the Model 115 Molecular Weight Apparatus,* Hitachi Perkin-Elmer, Tokyo, 1968.
10. C. A. Glover, "Absolute Colligative Property Methods," in *Polymer Molecular Weights,* P. E. Slade, Jr., Ed. Marcel Dekker, New York, 1975, Part I, Chap. 4.
11. J. Brandrup and E. H. Immergut, *Polymer Handbook,* Wiley, New York, 1975, Chap. IV, p. 23.
12. R. V. Figini, *Makromol. Chem.,* **181**, 2409 (1980).