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A novel analytical method to estimate molar mass and virial coefficients of polymers from osmometry

Krishna S. Amur, Sujata F. Harlapur and Tejraj M. Aminabhavi*
Chemistry Department, Karnatak University, Dharwad 580 003, India
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In the routine analysis of osmometric data for polymer–solvent systems, a graphical method has been used to estimate the virial coefficients and number average molar mass. However, it is realized that the graphical method has the disadvantage due to inaccuracies involved in the estimation of the intercept and slope. The least-squares method is certainly a better alternative, but it also has certain limitations. A new analytical method is suggested which is no less effective than the least-squares method, but also provides valuable information about the behaviour of the observed points in the experimental data. A comparative study of the different methods is presented here to indicate the advantages of the new method over the conventional treatments. © 1997 Elsevier Science Ltd.

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Introduction

Osmometry is one of the classical methods, used routinely in most polymer characterization laboratories, to estimate molar mass and virial coefficients of polymers in solution[2]. In an osmotic experiment, solvent flow across a semi-permeable membrane is prevented by osmotic pressure, π, which is a difference in pressure across the membrane. However, in the theoretical development of osmometry, an equation analogous to ideal gas law, i.e. $\pi V = RT$ (where V is volume of the solution containing a mole of the solute) is used. This equation is applicable to low concentrations, i.e. at sufficiently low mole fraction of the solute, n_2, so that

$$\pi V = n_2 RT \text{ or } \pi = \frac{cRT}{M} \tag{1}$$

where $c(= n_2 M/V)$ is the concentration in mass per unit volume and M is the molar mass of the polymer.

For a polymer solution over the range of concentrations it becomes necessary to consider higher virial coefficients, so that non-ideality can be studied:

$$\frac{\pi}{RTc} = \frac{1}{\bar{M}_n} + Ac + Bc^2 \tag{2}$$

where A and B are, respectively, the second and third virial coefficients, $\bar{M}_n = \sum n_i M_i / \sum n_i$ is the number average molar mass of the polymer, n_i being the number of molecules of molar mass, M_i, per gram of the dry polymer. In essence, osmometry indicates the number of polymer particles per unit volume.

However, to understand the interactions between polymer and solvent molecules, accurate values of A and B are required. The majority of research papers[2–5] including some standard textbooks[6–8] deal with the calculation of A by a graphical method, i.e. from a plot of π/cRT *versus* c and by ignoring B, $\bar{M}_n$ and A are determined from the intercept and slope, respectively. When the third virial coefficient, B, is taken into account, it is usually estimated using the following equation:

$$\sqrt{\frac{\pi}{c}} = \sqrt{\frac{RT}{\bar{M}_n}}(1 + B'c) \tag{3}$$

when the third virial coefficient is assumed to be related to the second virial coefficient by the following equations:

$$A = \frac{2B'}{\bar{M}_n} \text{ and } B = \frac{1}{4}A^2\bar{M}_n \tag{4}$$

Thus, from the graph of $\sqrt{(\pi/c)}$ *versus* c, the intercept on the ordinate axis and slope of the line give a fairly good estimate of the parameters. Alternatively, one can apply the least-squares method to equation (2) or equation (3) to estimate A, B and $\bar{M}_n$.

The graphical method has a disadvantage due to inaccuracies involved in the estimate of the intercept and slope. Also, both in the graphical method and the least-squares method, it is not clear as to how different observation points influence the ultimate estimation of $\bar{M}_n$, A and B. For this reason, we suggest the use of a simple analytical method which provides valuable information about the behaviour of the observed points in the data, besides being as effective as the least-squares method.

Analytical approach

In this paper, we carry out a comparative study of the different methods with the help of an example and show that the information provided by the analytical method draws our attention to some observed points that lead to erratic results and help us to ignore them in the final analysis.

In osmometry, π is calculated from the height, h of the liquid column using $\pi = h\rho g$, where ρ is density of the polymer solution and g, the gravitational acceleration. A set of h_i values are obtained corresponding to concentrations, c_i so that the experimental data consist of a set of observation points:

$$(c_i, h_i) \text{ where } i = 1, 2, ..., p \tag{5}$$

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* To whom correspondence should be addressed

Since equation (2) is non-linear, an expeditious method of finding $\bar{M}_n$ and A is to consider its linearized form given below:

$$\frac{h}{c} = \left(\frac{\lambda}{\bar{M}_n}\right) + \lambda A c \tag{6}$$

where $\lambda = RT/\rho g$, R is the molar gas constant and T, the Kelvin temperature. According to equation (6), a plot of h_i/c_i *versus* c_i is a straight line whose intercept on the ordinate axis is $\lambda/\bar{M}_n$ and the slope is λA. From this information, we obtain $\bar{M}_n$ and A.

By inserting the values of (c_i, h_i), $i = 1, 2$ in equation (6), two simultaneous equations emerge which can be solved to give:

$$\bar{M}_n = \frac{\lambda(c_1 - c_2)}{(H_2 c_1 - H_1 c_2)} \text{ and } A = \frac{(H_1 - H_2)}{(c_1 - c_2)\lambda} \tag{7}$$

where $H_i = h_i/c_i$, $i = 1, 2$, etc. If the set given by equation (5) consists of more than two observation points, i.e. if $p > 2$, then denoting by $\bar{M}_{n(i,j)}$ and $A_{(i,j)}$ the values determined by the points (c_i, h_i) and (c_j, h_j), $1 \le i < j \le p$, we take their average:

$$\overline{M}_n = [(p-2)!2/p!][M_{n(1,2)} + M_{n(1,3)} + \dots + M_{n(p-1,p)}] \tag{8}$$

$$A = [(p-2)!2!/p!][A_{(1,2)} + A_{(1,3)} + \dots\dots\dots + A_{(p-1,p)}] \tag{9}$$

To calculate B, we need to consider the following three simultaneous equations:

$$\left(\frac{1}{\lambda}\right)\left(\frac{h_i}{c_i}\right) = \frac{1}{\bar{M}_n} + Ac_i + Bc_i^2 \quad i = 1,\ 2,\ 3 \tag{10}$$

Solving these, we get the following set of relations:

$$A = -(1/\lambda z)[(c_2^2 - c_3^2)H_1 + (c_3^2 - c_1^2)H_2 + (c_1^2 - c_2^2)H_3] \tag{11}$$

$$B = (1/\lambda z)[(c_2 - c_3)H_1 + (c_3 - c_1)H_2 + (c_1 - c_2)H_3] \tag{12}$$

$$\bar{M}_n = \lambda z[(c_1 - c_2)c_1c_2H_3 + (c_2 - c_3)c_2c_3H_1 + (c_3 - c_1)c_1c_3H_2]^{-1} \tag{13}$$

where

$$z = c_1c_2(c_1 - c_2) + c_2c_3(c_2 - c_3) + c_3c_1(c_3 - c_1) \tag{14}$$

The symbols λ and H_i have the same meanings as assigned above.

Let us now consider p observation points with $p > 3$ and denote by $A_{(i,j,k)}$, $B_{(i,j,k)}$ and $\bar{M}_{n(i,j,k)}$, the corresponding values determined by the points (c_i,h_i), (c_j,h_j) and (c_k,h_k) where $1 \le i < j < k \le p$. In this case, there are $p!/(p-3)!3!$ number of values of each of A, B and $\bar{M}_n$. Taking an average over these values in the final step, we obtain

$$\overline{M}_n = [(p-3)!3!/p!]\sum \bar{M}_{n(i,j,k)}, \quad i < j < k \tag{15}$$

$$A = [(p-3)!3!/p!]\sum A_{(i,j,k)}, \quad i < j < k \tag{16}$$

$$B = [(p-3)!3!/p!]\sum B_{(i,j,k)}, \quad i < j < k \tag{17}$$

Illustration

Consider the data taken from osmotic pressure measurements[6] on a solution of polystyrene in toluene at 25°C with density, $\rho = 0.8618$ g cm^{-3} in *Table 1*.

Table 1 Experimental osmometric data of polystyrene in toluene[6]

Concentration (g l^{-1})	h (cm) toluene	$H = h/c$	$\sqrt{H}$
$c_1 = 2.56$	$h_1 = 0.325$	$H_1 = 0.1270$	$\sqrt{H_1} = 0.3563$
$c_2 = 3.80$	$h_2 = 0.545$	$H_2 = 0.1434$	$\sqrt{H_2} = 0.3787$
$c_3 = 5.38$	$h_3 = 0.893$	$H_3 = 0.1660$	$\sqrt{H_3} = 0.4074$
$c_4 = 7.80$	$h_4 = 1.578$	$H_4 = 0.2823$	$\sqrt{H_4} = 0.4498$
$c_5 = 8.68$	$h_5 = 1.856$	$H_5 = 0.2138$	$\sqrt{H_5} = 0.4624$

Table 2 Calculated values of the parameters from equations (3), (6) and (7) and *Table 1*

(i,j)	$\lambda/M_{n(i,j)}$	$\lambda A_{(i,j)}$	$[\sqrt{(\lambda/\bar{M}_n)}]_{(i,j)}$	$[\sqrt{(\lambda/\bar{M}_n)}B']_{(i,j)}$
(1,2)	0.0926	0.0133	0.3100	0.0181
(1,3)	0.0915	0.0138	0.3099	0.0181
(1,4)	0.0901	0.0144	0.3106	0.0172
(1,5)	0.0906	0.0142	0.3119	0.0173
(2,3)	0.0891	0.0130	0.3097	0.0182
(2,4)	0.0875	0.0147	0.3118	0.0171
(2,5)	0.0886	0.0144	0.3135	0.0172
(3,4)	0.0852	0.0150	0.3132	0.0175
(3,5)	0.0880	0.0145	0.3169	0.0167
(4,5)	0.1002	0.0131	0.3379	0.0144

Table 3 Values calculated from *Table 1* and equations (11)–(14)

(i,j,k)	$\lambda/\bar{M}_{n(i,j,k)}$	$\lambda A_{(i,j,k)}$	$\lambda B_{(i,j,k)} \times 10^4$
(1,2,3)	0.0964	0.0111	3.548
(1,2,4)	0.0956	0.0115	2.750
(1,2,5)	0.0948	0.0121	1.873
(1,3,4)	0.0974	0.0106	2.229
(1,3,5)	0.0978	0.0106	1.072
(1,4,5)	0.0859	0.0166	-2.113
(2,3,4)	0.0929	0.0126	1.821
(2,3,5)	0.0901	0.0138	0.442
(2,4,5)	0.0821	0.0186	-3.348
(3,4,5)	0.0608	0.0227	-5.823

Table 4 Values of $\lambda/\bar{M}_n$ and λA calculated from equation (6) by different methods[a]

Method	$\lambda/\bar{M}_n$	λA	No. of observation points used from *Table 1*
Graphical	0.0890	0.0145	All five
Least-squares	0.0892	0.0144	All five
Analytical	0.0902	0.0141	All five

[a] *Table 2* is used for the analytical method

Table 5 Values of $\lambda/\bar{M}_n$, λA and λB from equation (2) by different methods[a]

Method	$\lambda/\bar{M}_n$	λA	$\lambda B \times 10^4$	No. of observation points used from *Table 1*
Analytical	0.0964	0.0111	3.5476	First three
Least-squares	0.0966	0.0109	3.6441	First three
Analytical	0.0955	0.0115	2.5870	First four
Least-squares	0.0948	0.0120	2.3638	First four
Analytical	0.0889	0.0138	-3.0128	All five
Least-squares	0.0921	0.0132	0.9971	All five

[a] *Table 3* is used in the analytical method.

Table 6 Values of $\lambda/\bar{M}_n$, λA and λB using equations (3) and (4) [a]

Method	$\lambda/\bar{M}_n$	λA	$\lambda B \times 10^4$	No. of observation points used from *Table 1*
Analytical	0.0960	0.0112	3.283	First three
Least-squares	0.0960	0.0112	3.280	First three
Analytical	0.0966	0.0110	3.120	First four
Least-squares	0.0966	0.0111	3.176	First four
Analytical	0.0995	0.0108	2.893	All five
Least-squares	0.0976	0.0109	3.044	All five
Graphical	0.0967	0.0109	3.062	All five

[a] *Table 2* is used in the analytical method

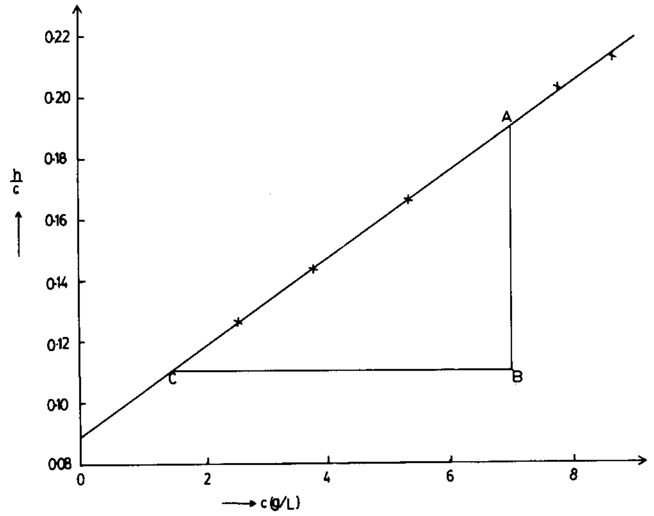

Figure 1 Plot of *h/c versus c* for polystyrene in toluene at 298.15 K with values of intercept = 0.089 and slope = 0.0145.

Note that in carrying out averaging over different sequences of observation points in the analytical method, we used equations (8) and (9) for *Tables 4, and 6* and equations (15), (16) and (17) for *Table 5*.

Comparison between the three different methods. The graphical method is applicable to equations (3) and (6) as they are linear equations. The graphs corresponding to these are given in *Figures 1 and 2*. First we consider determining the values of $\bar{M}_n$ and A only. The values of $\lambda/\bar{M}_n$ and λA obtained by a linear graph (*Figure 1*) using equation (6), the least-squares method and *Table 2* prepared by the analytical method, are listed in *Table 4*. They compare very well. In this case, since we neglect B, the variations in the results listed in *Table 2* are not very significant. However, it should be noted here that the readings obtained from graphs differ from person to person. Margerison and East[7], from whose book we have picked up the data, have listed results which when converted in our notations give

$$\frac{\lambda}{\bar{M}_n} = 0.09108 \text{ and } \lambda A = 0.0149$$

Our next attempt is to determine the third virial coefficient along with $\bar{M}_n$ and A. Here, the problem is to fit the data to a parabolic curve. First, we choose equation (10) for this purpose. Because the graphical method is not suitable in this case, the least-squares method and the analytical method are employed to list the values of $\lambda/\bar{M}_n$, λA and λB in *Table 5*, and in doing so the data in *Table 1* have been chosen in the sequence of 3, 4 and 5 observation points. This has become necessary in view of the pattern of results obtained in *Table 3* wherein we notice that, when observation points 4 and 5 dominate, the results obtained do not follow a regular pattern. This is also noticeable to some extent in *Table 2*. It is important to note here that the observation points 4 and 5 correspond to the higher side of the polymer concentration.

Next we consider equations (3) and (4). In this case, all three methods are applicable. *Table 6* exhibits the results obtained by different methods. Here, the variations do not stand out as clearly as in *Table 5*, possibly because of the assumption made with regard to the relation between second and third virial coefficients and the statistical nature of the least-squares method.

Table 7 Comparison between different methods [a]

Formula	Method	$\bar{M}_n \times 10^5$	$A \times 10^4$	$B \times 10^2$	No. of observation points used
Method I	(a) Graphical	3.2950	4.9445	–	All five points
$h/c = \lambda/(\bar{M}_n) + \lambda Ac$	(b) Analytical	3.2500	4.7895	–	All five points
$\lambda = (RT)/(\rho g)$	(c) Least-squares	3.2881	4.9200	–	All five points
Method II	(a) Analytical	3.0419	3.7714	1.2097	First three points
$h/c = (\lambda/(\bar{M}_n) + \lambda Ac + \lambda Bc^2$	(b) Least-squares	3.0373	3.7327	1.2427	First three points
	(c) Analytical	3.0694	3.907	0.8822	First four points
	(d) Least-squares	3.0950	4.0744	0.8061	First four points
	(e) Analytical	3.2978	4.7185	– 1.0274	All five points
	(f) Least-squares	3.1827	4.51	0.3400	All five points
Method III	(a) Analytical	3.0534	3.8296	1.1195	First three points
$\sqrt{h/c} = \sqrt{\lambda/\bar{M}_n}(1 + B'c)$	(b) Least-squares	3.0539	3.8305	1.1185	First three points
	(c) Analytical	3.0341	3.7507	1.0639	First four points
$A = 2B'/\bar{M}_n$	(d) Least-squares	3.0344	3.7840	1.0830	First four points
	(e) Analytical	2.9465	3.6646	0.9865	All five points
$B = (B'^2)/(4\bar{M}_n)$	(f) Least-squares	3.0058	3.7205	1.0381	All five points
	(g) Graphical	3.0326	3.3712	1.0441	All five points

[a] *Tables 4–6* are used for Methods I, II and III respectively

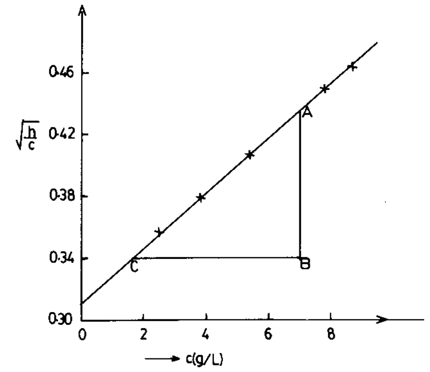

Figure 2 Plot of $\sqrt{h/c}$ *versus* c for the same system as in *Figure 1* with values of intercept = 0.311 and slope = 0.0175.

The final picture emerges clearly in *Table 7*. Here, we set $R = 8.314 \times 10^7$ ergs K^{-1} mol^{-1}, $T = 298.15$ K, $\rho = 0.8618$ g cm^{-3} and $g = 981$ cm s^{-2} so that

$$\lambda = \frac{RT}{\rho g} = 2.932528 \times 10^7 \qquad (18)$$

Since the concentrations in *Table 1* are given in the units g l^{-1}, we convert them into g cm^{-3}. Then using the results of *Tables 4–6* we arrive at the results listed in *Table 7*. In *Table 7*, the values of $\bar{M}_n$ in Method II and Method III agree very well when only the first three points of the data are taken into consideration. Since

$$\frac{\lambda}{\bar{M}_n} = \lim_{c \to 0}\left(\frac{h}{c}\right)$$

and λ is constant, all the methods should yield the same value of $\bar{M}_n$. From our computations, we notice that discrepancies occur either when the third virial coefficient is ignored or when points other than the first three in the data are included in computations.

In Method II of *Table 7*, no extra assumption is made for the third virial coefficient B. Hence, the values of $\bar{M}_n$, A and B that we can reasonably accept are obtained by taking an average of (a) and (b) in Method II. Thus,

$$\bar{M}_n = 3.0395 \times 10^5 \text{ g mol}^{-1}, \; A = 3.7520 \times 10^{-4} \text{ and}$$

$$B = 1.2262 \times 10^{-2}$$

The results obtained from *Figure 2* are given at the end of *Table 7* and the values of $\bar{M}_n$ and A agree very closely with the values given above, while the value of B differs by a margin of 13.7%. Similarly, the value obtained for B by using all the five points of the data in the least-squares method also differs from the above value of B by a margin of 14.18%. These indicate the usefulness of the analysis of the behaviour of the observation points in determining the value of B.

The present treatment shows that if B is ignored, then the results obtained from graphical, least-squares and analytical methods agree closely. On the other hand, when B is taken into account, the variation is significant and it is easy to isolate unacceptable observation points from the experimental data. It is therefore realized that such an exercise would be useful in arriving at accurate values of $\bar{M}_n$, A and B for the polymer–solvent systems from osmometric data.

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