

## Single-Point Determination of Intrinsic Viscosity

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### Synopsis

Limitations on the use of the equations  $[\eta] = \{2(\eta_{sp} - \ln \eta_{rel})\}^{1/2}/c$  and  $[\eta] = (\eta_{sp} + 3\ln \eta_{rel})/4c$  in determining intrinsic viscosity,  $[\eta]$ , by a single point method have been pointed out. Inclusion of higher order terms in the series expansion for  $\ln \eta_{rel}$  introduces an additional term in the above equations which is negligible when the value of Huggins' constant,  $k'$ , is in the vicinity of 0.3-0.4. More accurate values for intrinsic viscosity calculated by a single point method can be obtained using these modified equations provided  $k'$  can be estimated.

Recently there have been proposed at least two equations for obtaining the intrinsic viscosity  $[\eta]$  of polymer-solvent systems by determining the viscosity at a single concentration.

Solomon and Ciuta<sup>1</sup> and Naar et al.<sup>2</sup> have proposed the use of equation

$$[\eta] = [2(\eta_{sp} - \ln \eta_{rel})]^{1/2}/c \quad (1)$$

while Kuwahara<sup>3</sup> and a Rohm and Haas bulletin<sup>4</sup> apply the relations

$$[\eta] = 1/c \ln \eta_{rel} + 1/4(\eta_{sp}/c - 1/c \ln \eta_{rel}) \quad (2a)$$

$$= (\eta_{sp} + 3 \ln \eta_{rel})/4c \quad (2b)$$

where the symbols have the usual meaning. Although use of dilute solutions (0.2%) is recommended by Solomon and Ciuta, other limitations on the applicability of these relations exist which have not been mentioned elsewhere. These will be discussed briefly here.

### Theoretical Analysis

The series expansion

$$\ln(1+x) = x - 1/2x^2 + 1/3x^3 - 1/4x^4 \dots$$

holds only for  $-1 < x < 1$ , where  $x$  in our case is  $[\eta]c + k'[\eta]^2c^2$ . Therefore, in cases where  $[\eta]$  is too high (say,  $\geq 5$ ), use of the above equations would not be valid for concentrations of above a certain limit ( $\approx 0.2\%$ ). In practice, however, eqs. (1) and (2b) seem to give quite satisfactory values for calculated  $[\eta]$  even when the above condition is violated (Table

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TABLE I. Comparison of Intrinsic Viscosity Values Determined Graphically and Those Calculated from Eqs. (1) and (4c)

Polymer-solvent system <sup>a</sup>	Concn., g./100 ml. <sup>b</sup>	$k'_{\text{graph}}$	$[\eta]_{\text{graph}} \times 10^{-2}$ , cc./g.	$[\eta]_{\text{calc}} \times 10^{-2}$ , cc./g.		Error, %	
				Eq. (4c) <sup>c</sup>	Eq. (1)	Eq. (4c)	Eq. (1)
PMMA H3A/TCE <sup>d</sup>	0.25	0.13	1.96	1.99	1.81	+1.5	-7.5
PMMA L1A/TCE	1.0	0.31	0.97	0.97	0.95	0	-2
" "	0.25	"	"	0.98(5)	0.98	+2	+1
PMMA L3A/TCE	1.0	0.40	0.54	0.53	0.55	-2	+2
" "	0.25	"	"	0.53(5)	0.54	-1	0
PMMA H3A/AMK	1.0	1.27	0.38	0.36	0.48	-5	+26
" "	0.25	"	"	0.39	0.41	+2.5	+8
PMMA L5B/AMK	1.0	2.23	0.13	0.13	0.16	0	+23
" "	0.25	"	"	0.13(4)	0.13(8)	+3	+6
PMMA L5B/acetone	1.0	0.85	0.14	0.13(8)	0.14(8)	-1.5	+7
" "	0.25	"	"	0.15(4)	0.15(7)	+10	+12
CA/acetone <sup>e</sup>	"	0.59	1.55	1.5	1.66	-3	+7
CA/MCM	"	0.40	2.34	2.3	2.41	-1	+2.5
Wood pulp/cuene	0.1	0.64	7.85	7.3	8.96	-7	+14
EC/acetone <sup>f</sup>	0.1	0.68	1.86	1.84	1.96	-1	+5
EC/CCl <sub>4</sub>	"	0.68	2.5	2.45	2.67	-2	+7
EC/C <sub>6</sub> H <sub>6</sub>	"	1.06	2.2	2.16	2.5	-2	+13.5
EC/C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	"	0.94	2.23	2.2	2.49	-2	+11.5
CN/MA	"	0.54	3.33	3.29	3.51	-2	+5
PE B3/ <i>p</i> -xylenes	0.25	1.06	1.75	1.66	2.16	-6	+23
PE F1/ <i>p</i> -xylene	"	0.25	3.27	3.32	3.09	-1.5	-5.5
PE A2/ <i>p</i> -xylene	"	0.89	1.59	1.52	1.85	-4.5	+17
PS/C <sub>6</sub> H <sub>6</sub> <sup>g</sup>	0.18	0.42	5.9	5.6	6.1	-5	+3.5
" "	0.09	"	"	5.86	6.13	-1	+3.5
" "	0.06	"	"	5.88	6.05	0	+2.5

<sup>a</sup> PMMA = poly(methyl methacrylate); CA = cellulose acetate; EC = ethyl cellulose; CN = cellulose nitrate; PE = polyethylene; PS = polystyrene; TCE = Tetrachloroethane; AMK = amyl methyl ketone; MCM = methylene chloride-methanol mixture; cuene = cupriethylenediamine.

<sup>b</sup> Huggins relation [eq. (3)] is obeyed for all the examples cited above at least up to the concentration selected in the second column. <sup>c</sup> The value used for Huggins constant,  $k'$ , is the one determined graphically. <sup>d</sup> Data of Moore and Fort.<sup>7</sup> <sup>e</sup> Data of Genung and Gage.<sup>8</sup> <sup>f</sup> Data of Moore et al.<sup>9</sup> <sup>g</sup> Data of Trementozzi.<sup>10</sup> <sup>h</sup> Present study.

I, polystyrene in benzene). The reasons for this are not immediately clear.

Moreover, in the derivation of eq. (1), terms higher in order than  $c^2$  are neglected. It will be demonstrated that this is responsible for the large errors observed for calculated  $[\eta]$  in the data summarized in Table I. Taking Huggins' equation<sup>5</sup>

$$\eta_{sp} = [\eta]c + k'[\eta]^2c^2 \quad (3)$$

as the starting point, rearrangement and expansion in power series gives an expression for  $\ln \eta_{rel}$  which, after combination, results in

$$\eta_{sp} - \ln \eta_{rel} = ([\eta]^2c^2/2) \{1 + 2[\eta](k' - 1/3)c + [\eta]^2(k'^2 - 2k' + 1/2)c^2 + \dots\} \quad (4a)$$

$$= ([\eta]^2c^2/2) \{[1 + (k' - 1/3)[\eta]c]^2 - (4/3k' - 7/18)[\eta]^2c^2 + \dots\} \quad (4b)$$

This expression is correct up to terms in  $c^4$  and may be contrasted to Solomon and Ciuta's expression which is correct up to terms in  $c^2$ . It will prove convenient to neglect the term,  $(4/3k' - 7/18)[\eta]^2c^2$  on the right-hand side of eq. (4b).<sup>\*</sup> With this, eq. (4b) after rearrangement, becomes

$$[2(\eta_{sp} - \ln \eta_{rel})]^{1/2}/c = [\eta] + (k' - 1/3)[\eta]^2c \quad (4c)$$

A similar treatment with respect to eq. (2b) leads to the equation

$$(\eta_{sp} + 3 \ln \eta_{rel})/4c = [\eta] \{1 + [\eta]c(k' - 3/8) - 3/4[\eta]^2c^2(k' - 1/3) - 3/4[\eta]^3c^3(1/2 k'^2 - k' + 1/4) + \dots\} \quad (5a)$$

Again the last two terms inside the brace on the right-hand side of eq. (5a) can be neglected,<sup>†</sup> with the result that eq. (5a) becomes

$$(\eta_{sp} + 3 \ln \eta_{sp})/4c = [\eta] \{1 + (k' - 3/8)[\eta]c\} \quad (5b)$$

Equations (4c) and (5b) are two of the several empirical viscosity functions given by Billmeyer.<sup>6</sup> The important point to observe is that eqs. (4c) and (5b) reduce to eqs. (1) and (2b) for  $k' \cong 0.3-0.4$ .

### Discussion

The above considerations indicate that for  $k'$  values in this range (0.3-0.4), one would expect good agreement between a single-point determination [using eq. (1) or (2b)] and the graphical method. However, for a particular

<sup>\*</sup> Calculations on the examples given in Table I show that this term is quite small compared to the term  $\{1 + (k' - 1/3)[\eta]c\}^2$ , and therefore can be neglected as is actually done in getting eq. (4c). They also show that neglect of this term is generally much better than the usual neglect of all the terms other than the first term on the right-hand side of eq. (4a), as is done in deriving eq. (1). Only in the case of polystyrene in benzene ( $c = 0.18$ ) is the trend reversed.

<sup>†</sup> An identical situation exists as in the case of eq. (4c).

polymer-solvent system whose  $k'$  value is quite far from this range and especially where value of  $[\eta]$  is high, poor agreement is to be anticipated. This expectation is substantiated in Table I, where errors as large as 20% occur between the  $[\eta]$  values calculated from eq. (1) and the graphically determined  $[\eta]$  values. Notice that eq. (4c) gives better agreement in all the cases listed. A like situation exists with respect to eqs. (2b) and (5b).

Finally, to show that  $(2\eta_{sp} - \ln \eta_{rel})^{1/2}/c \rightarrow [\eta]$  as  $c \rightarrow 0$  does not necessarily justify the validity of eq. (1), since an alternate function derived by the author gives erratic values for  $[\eta]$  even though it fulfills a similar limiting condition. Such a function is

$$[\eta] = [2(\exp\eta_{sp} - \eta_{rel})]^{1/2}/c \quad (6)$$

Expanding the exponential, one gets

$$\begin{aligned} [\eta] &= 2[1 + \eta_{sp} + \eta_{sp}^2/2 + \eta_{sp}^3/6 + \dots (-1 - \eta_{sp})]^{1/2}/c \\ & \qquad \qquad \qquad \eta_{sp} < 1 \quad (6a) \\ &= (\eta_{sp}/c)[2(1/2 + \eta_{sp}/6)]^{1/2} \end{aligned}$$

Thus as  $c$  approaches zero,  $\eta_{sp}/c \rightarrow [\eta]$ .

### Conclusion

It is concluded, therefore, that eqs. (1) and (2b) are fairly accurate for single point determinations of intrinsic viscosity,  $[\eta]$ , for  $k'$  values in the vicinity of 0.3-0.4. This is generally, but not always, true for flexible polymers in good solvents.<sup>5,11,12</sup> Considerable caution should, however, be exercised in using eq. (1) or eq. (2b) for polymer-solvent systems where  $k'$  differs significantly from this range, e.g., polymers in poor solvents,<sup>11,12</sup> especially so when values of  $[\eta]$  are high. In such cases, more accurate values of  $[\eta]$  may be obtained by using eqs. (4c) or (5b) if  $k'$  for a particular polymer-solvent system can be estimated.<sup>13</sup>

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### Résumé

On a déterminé les limites d'emploi des équations  $[\eta] = \{2(\eta_{sp} - \ln \eta_{rel})\}^{1/2}/c$  et  $[\eta] = (\eta_{sp} + 3 \ln \eta_{rel})/4c$  pour déterminer la viscosité intrinsèque  $[\eta]$ , par une méthode à point unique. L'introduction de termes d'un ordre supérieur dans le développement des séries pour  $\ln \eta_{rel}$  introduit un terme supplémentaire dans les équations ci-dessus; ce terme est négligeable lorsque la valeur de la constante d'Huggins  $k'$  est proche de 0.3–0.4. Des valeurs plus précises de la viscosité intrinsèque, calculées par une méthode à point unique, peuvent être obtenues en employant ces équations modifiées, si on peut estimer  $k'$ .

### Zusammenfassung

Die begrenzte Benützbarkeit der Gleichung  $[\eta] = \{2(\eta_{sp} - \ln \eta_{rel})\}^{1/2}/c$  und  $[\eta] = (\eta_{sp} + 3 \ln \eta_{rel})/4c$  zur Bestimmung der Viskositätszahl durch eine Einpunktmethode wurde diskutiert. Berücksichtigung von Termen höherer Ordnung in der Reihenentwicklung für  $\ln \eta_{rel}$  führt einen zusätzlichen Term in die obigen Gleichungen ein, welcher bei einem Wert der Huggins-Konstanten  $k'$  in der Nähe von 0,3–0,4 vernachlässigt werden kann. Genauere Viskositätszahlwerte können nach einer Einpunktmethode unter Benützung dieser modifizierten Gleichungen berechnet werden, wenn eine Bestimmung von  $k'$  möglich ist.

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