Generalization of a Double-Point Method to Determine the Intrinsic Viscosity in a Polymer-Solvent Mixture

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A double-point method proposed in literature for the determination of the Intrinsic Viscosity of a polymer-solvent solution and based on the Ram-Moham-Rao single point equation, have been extended to all single-point expressions available in literature. To assess the validity of the method, Intrinsic Viscosity values of several rubber-solvent mixtures, calculated following the classical procedure of looking for the common intercept of Huggins and Kraemer plots, have been compared with the ones calculated by means of the double-point methods. The deviations between the results obtained by both methodologies allows assuring that double-point equations are a reliable alternative of Huggins and Kraemer plots to determine Intrinsic Viscosity values.

1. Introduction

In the last decades, the importance of polymer-type materials is growing exponentially, as a consequence of their almost infinite range of applications. Because most of them are obtained by means of dissolution processes (Miller-Chou and Koenig, 2003), the rheology of the polymer-solvent systems is really important (Kraguljac et al., 2009). Besides, the intrinsic viscosity technique is one of the most employed methodologies with the aim of obtaining thermodynamic parameters of such mixtures (Mehrdad et al., 2011), such as Infinite Dilution coefficients.

The Intrinsic Viscosity ($[\eta]$) is the viscosity of and infinite diluted polymer solution. It is usually calculated from flow time measurements which are extrapolated to infinite dilution by means of Huggins (1942), Kraemer (1938) or Schulz-Blaschkle (1941) expressions (Eqs 1, 2 and 3).

$$\frac{\eta_{sp}}{c} = [\eta] + K_H [\eta]^2 c \tag{1}$$

$$\frac{\ln(\eta_r)}{c} = [\eta] + K_K [\eta]^2 c \tag{2}$$

$$\frac{\eta_{sp}}{c} = [\eta] + K_{SB} [\eta] \eta_i \tag{3}$$

In these equations, c is the concentration of polymer solution, K_H is the Huggins constant, K_K is the Kramer constant and K_{SB} is the Schulz-Blaschkle constant. Relative viscosity (η_r) is obtained as the relation between the flow time of the polymer solution through a capillary tube of known diameter and length and the flow time of the pure solvent through the same capillary tube. Specific viscosity (η_{sp}) is defined as relative viscosity minus one, and represents the viscosity increasing due to the polymer. The intrinsic

viscosity ([η]) is usually obtained from intercept of the Kraemer, Huggins or Schulz-Blaschkle relationships, using η_r and η_{sp} experimentally determined for different polymer solutions; theoretically, $K_K + K_H = 0.5$. However, single-point equations have been proposed with the aim of determining the intrinsic viscosity by a single flow-time measurement. The most important expressions are the Solomon-Ciuta (1963) one, Eq 4 the Deb-Chatterjee (1968) one, Eq 5, the Ram-Mohan-Rao (1986) one, Eq 6, the Kuwahara (1963) one, Eq 7 and the Palit and Kar (1967) one, Eq 8.

$$[\eta] = \frac{1}{c}\sqrt{2\eta_{sp} - 2\ln(\eta_r)} \tag{4}$$

$$[\eta] = \frac{1}{2c}\sqrt[3]{3\ln(\eta_r) + \frac{3}{2}(\eta_{sp})^2 - 3\eta_{sp}} \tag{5}$$

$$[\eta] = \frac{1}{2c}\left[\eta_{sp} + \ln(\eta_r)\right] \tag{6}$$

$$[\eta] = \frac{1}{4c}\left[\eta_{sp} + 3\ln(\eta_r)\right] \tag{7}$$

$$[\eta] = \frac{1}{c}\sqrt[4]{4\eta_{sp} - 2\eta_{sp}^2 + \frac{4}{3}\eta_{sp}^3 - 4\ln(\eta_r)} \tag{8}$$

The former expressions are based on assuming $K_K + K_H = 0.5$ and have the advantage of being capable of extrapolating to infinite dilution by means of a single experimental measurement, while for applying Huggins or Kraemer plots, at least five measurements should be desirable. However, the main drawback of employing these expressions is that the final Intrinsic Viscosity result can be different depending on the polymer concentration in the solution employed to perform the single-point measurement.

So, for all the reasons stated above, recently Curvale and Cesco (2009) proposed an intermediate strategy named as double-point equation, based on the Ram-Mohan-Rao expression, which is represented in Equation 9. In this equation, c_1 and c_2 are concentrations of the two polymer solutions (being $c_2 > c_1$), $\eta_{r,1}$ and $\eta_{r,2}$ are the relative viscosities, and $\eta_{sp,1}$ and $\eta_{sp,2}$ are the specific viscosities.

$$[\eta] = \frac{1}{2}\frac{c_2}{c_2 - c_1}\left[\frac{\eta_{sp,1}}{c_1} + \frac{\ln(\eta_{r,1})}{c_1}\right] - \frac{1}{2}\frac{c_1}{c_2 - c_1}\left[\frac{\eta_{sp,2}}{c_2} + \frac{\ln(\eta_{r,2})}{c_2}\right] \tag{9}$$

So the final aim of this paper is to generalize the double-point method by extending it not only to Ram-Mohan-Rao expression but also to any single-point equation, and analysing its validity by comparing the obtained results with previously calculated ones by means of the classical procedure of seeking the common intercept of Huggins and Kraemer equations.

2. Theoretical background

Assuming two polymer-solvent solutions of compositions c_1 and c_2 (being $c_2 > c_1$), their Intrinsic Viscosities determined by any of the single-point equations will be $[\eta]_1$ and $[\eta]_2$, respectively. These values should be equal because the Intrinsic Viscosity is defined as an extrapolation of the viscosity to infinite dilution conditions; however, due to all single point methods make this extrapolation from only one concentration point, the final Intrinsic Viscosity value is not the same in both cases. So, a reasonable approximation could be considering that the true Intrinsic Viscosity value is in between the points (c_1, $[\eta]_1$) and (c_2, $[\eta]_2$). Assuming a linear relationship, the slope (m) of the straight line joining the points (c_1, $[\eta]_1$) and (c_2, $[\eta]_2$) will be (Eq 10):

$$m = \frac{[\eta]_2 - [\eta]_1}{c_2 - c_1} \tag{10}$$

If we now consider a generic point i (whose concentration is c_i) belonging to the previous straight line, its Intrinsic Viscosity ($[\eta]_i$) will be able to be calculated with Eq (11), taking into account that the slope of the line is described by means of Eq 10.

$$[\eta]_i = m(c_i - c_1) + [\eta]_1 = \left(\frac{[\eta]_2 - [\eta]_1}{c_2 - c_1}\right)(c_i - c_1) + [\eta]_1 \tag{11}$$

If we now consider the case when c_i tends to 0 (because the Intrinsic Viscosity is the viscosity of an infinite polymer solution), the Eq 11 is transformed into Eq 12.

$$[\eta]_{c \to 0} = \left(\frac{c_2}{c_2 - c_1}\right)[\eta]_1 - \left(\frac{c_1}{c_2 - c_1}\right)[\eta]_2 \tag{12}$$

In this last expression, the terms $[\eta]_1$ and $[\eta]_2$ can be replaced by any of the Eqs 4 to 8.
The final result is that the Intrinsic Viscosity of whatever polymer-solvent mixture can be determined with Eq 12, by simply two flow-time measurements at two different compositions, c_1 and c_2, and calculating the relative and specific viscosities (which appear in $[\eta]_1$ and $[\eta]_2$ terms) by any Eq from 4 to 8.

3. Results and discussion

To assess the reliability of the generalized double-point proposed here, we have compared the results that we have previously determined for different poly (styrene-butadiene) rubber-cyclohexane mixtures at 30 ºC, following the classical procedure of finding the common intercept of Huggins and Kraemer plots, with the obtained values with the Eq 12 combined with all the Eqs 4 to 8.
The studied polymers employed as examples were, on one hand a poly (styrene-b-butene/ethylene-b-styrene) triblock copolymer (SEBS) (Ovejero et al., 2007) and, on the other hand, three poly (styrene – butadiene – styrene) triblock copolymers (SBSs) with different structure and styrene content, named C411, C500 and C501 respectively (Ovejero et al., 2010). The main characteristics of these materials are summarized in Table 1. The Table also shows the Intrinsic Viscosity values ($[\eta]$) of each cyclohexane-polymer mixtures, obtained from the common intercept of Huggins and Kraemer plots (values named as $[\eta]_{real}$).

Table 1. Main characteristics of the employed polymers

POLYMER	Mw (kg/kmol)	ρ (kg/m^3)	$[\eta]_{real}$ at 30 ºC
SEBS	86000	960	0.938
C411	237000	908	1.250
C500	78000	931	0.709
C501	113000	929	0.952

On the other hand, Tables 2 to 5 show the Intrinsic Viscosity values determined for each cyclohexane-polymer-binary mixture at different compositions with any single-point (subscript 1) or double point (subscript 2) method (values named as $[\eta]_{calc}$).

As it can be observed, the double-point methods perform, in many cases, better estimations than the single-point methods, especially when working with the most diluted compositions; this is especially noticeable in the case of the mixtures with C411 and C500 rubbers. To further reinforce what previously said, Figures 1and 2 show the deviations of the $[\eta]_{calc}$ values with respect to the $[\eta]_{real}$ values. The deviations have been calculated according to Eq 13.

$$\text{Deviation} = \text{abs}\left(\frac{[\eta]_{real} - [\eta]_{calc}}{[\eta]_{real}} 100\right) \tag{13}$$

Table 2. *[η] Values obtained by single and double point methods when comparing with Table 1 values, for cyclohexane – SEBS mixtures*

	COMPOSITIONS (g/dL)				
	0.401	0.322	0.233	0.128	0.078
PROCEDURE	$[\eta]_{calc}$ at 30 °C				
(Solomon-Ciuta)$_1$	0.924	0.901	0.944	0.938	0.935
(Deb-Chatterjee)$_1$	0.952	0.923	0.961	0.947	0.941
(Ram-Mohan-Rao)$_1$	0.955	0.925	0.963	0.948	0.941
(Kuwahara)$_1$	0.913	0.892	0.937	0.934	0.932
(Palit and Kar)$_1$	0.969	0.936	0.972	0.953	0.944
(Solomon-Ciuta)$_2$		0.810	1.056	0.930	0.931
(Deb-Chatterjee)$_2$		0.804	1.062	0.930	0.930
(Ram-Mohan-Rao)$_2$		0.801	1.061	0.929	0.930
(Kuwahara)$_2$		0.809	1.053	0.930	0.930
(Palit and Kar)$_2$		0.801	1.065	0.930	0.930

Table 3. *[η] Values obtained by single and double point method when comparing with Table 1 values, for cyclohexane – C411 mixtures*

	COMPOSITIONS (g/dL)				
	0.416	0.333	0.249	0.167	0.083
PROCEDURE	$[\eta]_{calc}$ at 30 °C				
(Solomon-Ciuta)$_1$	1.292	1.296	1.286	1.267	1.261
(Deb-Chatterjee)$_1$	1.350	1.342	1.320	1.289	1.273
(Ram-Mohan-Rao)$_1$	1.360	1.348	1.324	1.291	1.273
(Kuwahara)$_1$	1.273	1.279	1.273	1.258	1.256
(Palit and Kar)$_1$	1.385	1.370	1.341	1.303	1.279
(Solomon-Ciuta)$_2$		1.308	1.259	1.229	1.256
(Deb-Chatterjee)$_2$		1.309	1.257	1.227	1.256
(Ram-Mohan-Rao)$_2$		1.302	1.252	1.224	1.255
(Kuwahara)$_2$		1.300	1.255	1.227	1.255
(Palit and Kar)$_2$		1.309	1.255	1.225	1.255

Table 4. *[η] Values obtained by single and double point method when comparing with Table 1 values, for cyclohexane – C500 mixtures*

	COMPOSITIONS (g/dL)				
	0.392	0.313	0.235	0.157	0.078
PROCEDURE	$[\eta]_{calc}$ at 30 °C				
(Solomon-Ciuta)$_1$	0.719	0.723	0.715	0.712	0.713
(Deb-Chatterjee)$_1$	0.736	0.736	0.725	0.719	0.717
(Ram-Mohan-Rao)$_1$	0.738	0.737	0.726	0.719	0.717
(Kuwahara)$_1$	0.713	0.717	0.711	0.709	0.712
(Palit and Kar)$_1$	0.747	0.745	0.731	0.723	0.719
(Solomon-Ciuta)$_2$		0.736	0.692	0.706	0.714
(Deb-Chatterjee)$_2$		0.737	0.691	0.706	0.714
(Ram-Mohan-Rao)$_2$		0.736	0.690	0.706	0.714
(Kuwahara)$_2$		0.735	0.691	0.706	0.714
(Palit and Kar)$_2$		0.737	0.690	0.706	0.714

Table 5. [η] Values obtained by single and double point method when comparing with Table 1 values, for cyclohexane – C501 mixtures

PROCEDURE	COMPOSITIONS (g/dL)				
	0.395	0.316	0.237	0.158	0.079
	$[\eta]_{calc}$ at 30 ºC				
(Solomon-Ciuta)$_1$	0.939	0.932	0.941	0.957	0.944
(Deb-Chatterjee)$_1$	0.968	0.955	0.958	0.969	0.950
(Ram-Mohan-Rao)$_1$	0.971	0.957	0.960	0.969	0.950
(Kuwahara)$_1$	0.928	0.923	0.933	0.951	0.941
(Palit and Kar)$_1$	0.986	0.969	0.969	0.976	0.953
(Solomon-Ciuta)$_2$		0.905	0.966	0.989	0.931
(Deb-Chatterjee)$_2$		0.904	0.967	0.990	0.931
(Ram-Mohan-Rao)$_2$		0.901	0.966	0.989	0.930
(Kuwahara)$_2$		0.903	0.964	0.988	0.931
(Palit and Kar)$_2$		0.903	0.968	0.991	0.931

a)   b)
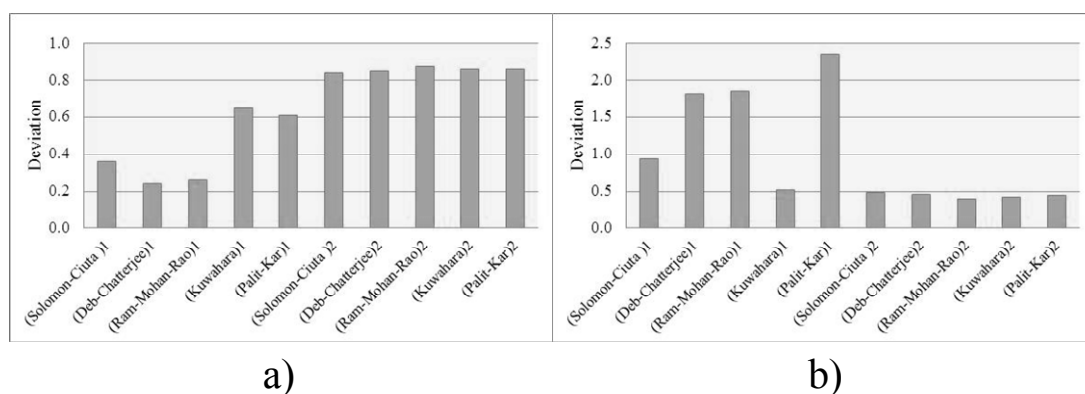
Figure 1. Deviations of the $[\eta]_{calc}$ values with respect to the $[\eta]_{real}$ values, for a) cyclohexane – SEBS mixture and b) cyclohexane – C411 mixture

a)   b)
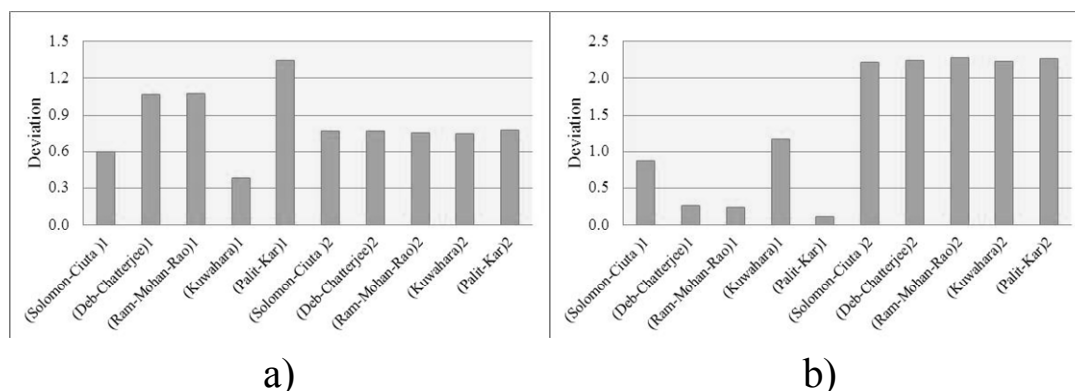
Figure 2. Deviations of the $[\eta]_{calc}$ values with respect to the $[\eta]_{real}$ values, for a) cyclohexane – C500 mixture and b) cyclohexane – C501 mixture

Another important point is that both single-point and double-point methods approximate better to the "real" Intrinsic Viscosity value (being the "real" value the one obtained by getting the common slope of Huggins and Kraemer plots) whenever the compositions are as low as possible. This seems to be logical, taking into account that Intrinsic Viscosity is defined as the viscosity of an infinite diluted polymer-solvent solution. As a final remark simply comment that double-point methods have demonstrated to be a reliable alternative to obtain accurate values on Intrinsic Viscosity. With them, it is possible to achieve a reasonable time saving because one two experimental points are needed, while to draw a proper straight line are necessary at least five points.

4. Conclusion

A generalized double-point method to determine the Intrinsic Viscosity of a polymer-solvent mixture is proposed here. The assessment of this method was done by comparing the Intrinsic Viscosity values obtained by this method, with the ones obtained following the traditional procedure (common intercept of Huggins and Kraemer plots). In all cases a good agreement between both methodologies was reached, especially when applying the low composition values to the double-point method.

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