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ORIGINAL CONTRIBUTION

Determination of intrinsic viscosities of macromolecules and nanoparticles. Comparison of single-point and dilution procedures

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Abstract The determination of the intrinsic viscosity by single-point determinations, like that based on the Solomon–Ciuta equation, have been proposed as efficient alternatives to dilution procedures. With a basis on theoretical analysis and computer simulation, we evaluate the systematic and global bias of the Solomon–Ciuta result and show how it depends on the strength of the concentration dependence of the solution viscosity (represented by the intrinsic viscosity and the Huggins constant) and the concentration of the single measured solution. We propose that an estimated Huggins constant can be employed in a corrected Solomon–Ciuta procedure, which may yield results for the intrinsic viscosity that are even more accurate than those from the Huggins extrapolation. This gives support and utility to the use of the single-point procedure when the intrinsic viscosity has to be determined for a unique concentration. We also pinpoint specific circumstances where the dilution–extrapolation procedures should be preferred.

Keywords Error calculation · Intrinsic viscosity · Huggins · Solomon–Ciuta

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Introduction

As it is widely known, one of the most salient features of macromolecules is the intense increment in viscosity that they produce when, even in minute amounts, they are dissolved in ordinary solvents. The viscosity intensifying effect, characterized by the intrinsic viscosity, $[\eta]$, is extensively used for analysis or characterization of synthetic polymers [1–3], biological macromolecules [4, 5], nanoparticles, and colloids [6]. Indeed, $[\eta]$ provides information about fundamental properties of the solute and its interaction with the solvent [7–9] and, thanks to theoretical or computational tools, it can be precisely related to the conformation of flexible (linear and nonlinear) chains [10–13], wormlike macromolecules and micelles [14–16], and rigid particles of arbitrary shape [17, 18].

The increment in the solution viscosity, η, with respect to that of the pure solvent, η_0, the relative viscosity, is the ratio $\eta_r = \eta/\eta_0$. The specific viscosity of a solution of concentration c is

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_r - 1 \tag{1}$$

and the intrinsic viscosity is defined as:

$$[\eta] = \lim_{c\to 0} \frac{\eta_{sp}}{c} = \lim_{c\to 0} \frac{\eta_r - 1}{c} \tag{2}$$

A classical procedure for its determination, based on Eq. 2, consists of the determination of viscosities of solutions of various concentrations, followed by extrapolation of η_{sp}/c to zero concentration. In a range of

moderate concentrations, the dependence is linear and can be written as the Huggins equation [19]:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \tag{3}$$

where k_H is the (dimensionless) Huggins constant. Thus, $[\eta]$ can be obtained as the intercept in a linear least-squares fit [20]. The measurements are usually made with inexpensive glass capillary viscometers that, like the Ubbelohde design, allow for in situ dilution, and it is noteworthy that microfluidic, microchip-based dilution viscometers are emerging [21].

The Huggins extrapolation procedure follows from the first principles of the concentration-dependence of the solution viscosity. However, other combinations of solution viscosity and concentration can be formulated so that, in the limit of zero-concentration, they also give $[\eta]$. One of such cases is that of the Solomon–Ciuta [22, 23] equation,

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

In some instances – but not always, as it will be shown hereafter – such alternative combinations may present a rather weak concentration dependence, so that the value resulting from the measurement for a single concentration may provide a good approximation to $[\eta]$. This gives rise to the so-called single-point procedures that avoid multiple measurements and extrapolation. In addition to saving work and reagents, such methods are the only choice when multiple dilutions are not feasible or practical. This is the case when measurements have to be done online, as in the viscosity detectors used in gel permeation or size exclusion chromatography (SEC) and flow field fractionation (FFF). The development of the pressure imbalance differential viscometer (a fluid analogue of the electric Wheatstone bridge) [24–26] that directly measures η_r has made possible multiple-detection SEC instrumentation that is a powerful technique for the characterization of complex, polydisperse materials.

The concepts underlying the various procedures for the determination of the intrinsic viscosity are sometimes overlooked because they are either simple or classical. In particular, one aspect that, as far as we know, has not been adequately described in the literature, is that concerning the error or uncertainty in the intrinsic viscosity; the instrumental errors will propagate [27] to the final result for $[\eta]$ in a manner that will obviously depend on the procedure (choice of equation, extrapolation or single point, etc.) chosen for data-handling. Such aspects are the topics considered in the present paper.

Basic theory

In general, the concentration dependence of the solution viscosity can be expressed as a Taylor expansion:

$$\eta = A_0 + A_1 c + A_2 c^2 + \ldots \tag{5}$$

where $A_0 = \eta_0$ and $A_1 = \eta_0[\eta]$. The Huggins equation holds where the cubic and following terms in Eq. 5 can be neglected, and then $A_2 = \eta_0 k_H[\eta]^2$. In other words, the Huggins equation is practically exact for a range of concentration such that cubic and further terms can be safely neglected. The dependence of η or η_r on c is quadratic in this range. For η_r, we have

$$\eta_r = 1 + [\eta]c + k_H[\eta]^2 c^2 \tag{6}$$

Over a certain range of concentrations, and within a given tolerance in the $[\eta]$ value, the Huggins equation must hold. We shall refer to a solution in this range as a "Huggins solution," and it will be used as the primary reference for the analysis reported in this work.

Alternatively, $[\eta]$ can be obtained by linear extrapolation of the so-called inherent viscosity, $\eta_{inh} = (\ln \eta_r)/c$ according to the Kraemer equation [28]

$$\frac{\ln \eta_r}{c} = [\eta] - k_K[\eta]^2 c \tag{7}$$

where k_K is the Kraemer constant. In the Kraemer plot, $(\ln \eta_r)/c$ vs c, $[\eta]$ is the intercept, and the slope should be $-k_K[\eta]^2$. It is frequent to display the $[\eta]$ determination in a dual Huggins–Kraemer plot, and a simple computer program (`VISFIT`) for the dual linear least-squares fit with a common intercept has been developed [29].

It should be remarked that, for a Huggins solution, the Kraemer equation may not be valid for the whole range where the Huggins equation holds; one can see a slightly curved Kramer plot where the Huggins plot is linear. The Kramer plot is linear only at sufficiently low concentrations. Then, the following relationship holds between the dimensionless constants k_H and k_K,

$$k_H + k_K = 1/2 \tag{8}$$

We also remark that the validity of this relationship is not conditioned by the nature of the polymer/system solvent; instead, it is a merely mathematical consequence, valid regardless of the physical conditions of the solution.

On the assumption that the linear Huggins and Kraemer equations would both be valid, Eqs. 3 and 7 can be combined in the following way:

$$\frac{\eta_{sp}}{c} - \frac{\ln \eta_r}{c} = (k_H + k_K)[\eta]^2 c \tag{9}$$

and recalling the relation between the Huggins and Kramer constant, Eq. 8, one immediately obtains the Solomon–Ciuta expression, Eq. 4. This expression eliminates the concentration dependence of the Huggins and Kraemer expression and is therefore an excellent candidate for single-point measurements. The Solomon–Ciuta is strictly correct only when the linear Huggins and Kraemer equations are both valid.

In general, the Solomon–Ciuta value will be deviated somehow from the reference value, and this systematic deviation will depend on the concentration dependence for a particular solute/solvent system. Of course, the global deviation or uncertainty will depend on the propagation of random, experimental errors. The former, systematic part can be treated separately in a simple manner, as described next.

Systematic differences among the various procedures

Mathematical aspects are simplified by the introduction of reduced, dimensionless quantities. First, we use a reduced concentration, C (capital) as:

$$C = [\eta]c \tag{10}$$

and we define the Huggins, Kraemer, and Solomon–Ciuta functions, H, K, and S, as:

$$H = \eta_{sp}/([\eta]c) = \eta_{sp}/C \tag{11}$$

$$K = \ln \eta_r/([\eta]c) = \ln \eta_r/C \tag{12}$$

and

$$S = [2(\eta_r - 1 - \ln \eta_r)]^{1/2}/([\eta]c) = [2(\eta_r - 1 - \ln \eta_r)]^{1/2}/C \tag{13}$$

The two latter are related to the former through

$$K = \ln(1 + HC)/C \tag{14}$$

and

$$S = \left[2(HC - \ln(1 + HC))\right]^{1/2}/C \tag{15}$$

We note that, at zero concentration, the three functions are $H = K = S = 1$.

We assume that the solution is in the concentration range where the concentration dependence of the viscosity is adequately represented by a quadratic form, thus obeying the Huggins linear relationship that, in terms of the reduced quantities, reads, simply:

$$H = 1 + k_H C \tag{16}$$

In these terms, the linear Kraemer relationship is written as:

$$K = 1 - k_K C \tag{17}$$

However, if Eq. 16 is valid, Eq. 17 will be generally invalid, and, as a consequence, S would not be concentration-independent. Actually, the concentration dependence of K is governed by

$$K = \ln(1 + C + k_H C^2)/C \tag{18}$$

and would only be linear, with the form of Eq. 17, under the special situation when $d^2K/dC^2 = 0$. This situation will depend, of course, on the k_H value (we have already mentioned that $k_K = 1/2 - k_H$ in any case). It has been reported [7, 8, 30] that such condition occurs for a special case, when $k_H = 1/3$.

The concentration dependence of K and S in the a range where H is linear can be investigated easily by plotting Eqs. 14 and 15. Such a range reaches at least $\eta_r \approx 3$, which corresponds to $C \approx 2$. Plots of H, K, and S vs C, for various values of k_H are presented in Fig. 1.

As indicated above, our reference is a "Huggins solution," i.e., any solution at a moderately low concentration so that η is accurately described by Eq. 3 or Eq. 5. Let us use the notation $[\eta]_{\mathrm{SCsp}}$ for the outcome of a single-point measurement expressed by the Solomon–Ciuta equation (Eq. 4), while $[\eta]_{\mathrm{ref}}$ would be the exact or reference (Huggins) value. From Eqs. 4 and 13, it follows that

$$[\eta]_{\mathrm{SCsp}}/[\eta]_{\mathrm{ref}} = S \tag{19}$$

so that the systematic error or bias introduced by the single-point Solomon–Ciuta method is determined by the S function that has been introduced in the preceding section where we have computed S in terms of the reduced quantities H, C, etc. We now return to the quantities in physical units and note that S is a function of k_H and $[\eta]c$. The relative deviation of $[\eta]_{\mathrm{SCsp}}$ from the exact value, denoted as $\delta([\eta]_{\mathrm{SCsp}})$, is given by

$$\delta([\eta]_{\mathrm{SCsp}}) = ([\eta]_{\mathrm{SCsp}} - [\eta]_{\mathrm{ref}})/[\eta]_{\mathrm{ref}} = S - 1 \tag{20}$$

Its value in a percentage manner $(100(S - 1))$ is plotted in Fig. 2a as a function of the two variables k_H

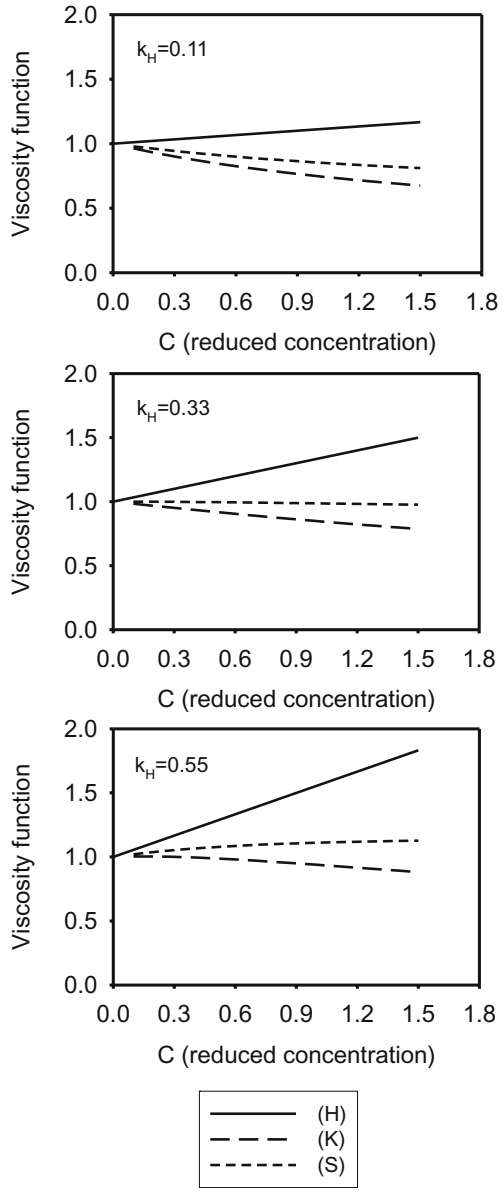

Fig. 1 Plots of Huggins (H), Kraemer (K), and Solomon–Ciuta (S) functions vs reduced concentration C, for Huggins solutions with the indicated value of k_H

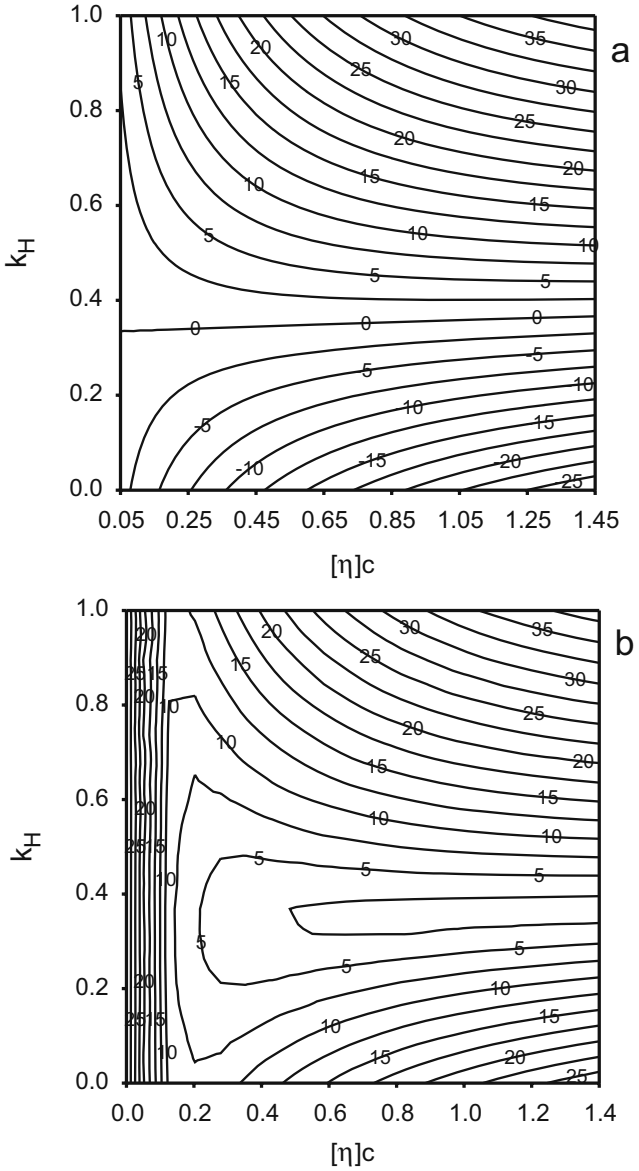

Fig. 2 **a** Systematic relative (percent) error of the single-point Solomon–Ciuta method, as a function of k_H and the reduced concentration. **b** Relative global error of the single-point Solomon–Ciuta method, for $\delta\eta_r = 0.01$

and $[\eta]c$. The contour plots indicate clearly the deviation introduced by the Solomon–Ciuta expression; for instance, a single-point Solomon–Ciuta determination with a concentration $c \approx 1/[\eta]$ such that $[\eta]c \approx 1$, for a polymer/system having a Huggins constant $k_H = 0.6$, would overestimate $[\eta]$ by about 10%. The systematic error can be lowered by measuring at lower concentrations, albeit at the cost of an increase in accidental random errors, as will be discussed below. However, for a given concentration, the deviation is determined by the Huggins constant. Remarkably, the single-point Solomon–Ciuta procedure is exact ($\delta([\eta]_{\mathrm{SCsp}}) = 0$) when $k_H = 1/3$, due to the mathematical reasons indicated in the previous section, but the discrepancy may be quite large in other cases. It is therefore pertinent to gather information on the values of Huggins constant for diverse systems.

Minireview on the Huggins constant

Experimental data for the Huggins constant, k_H, are abundant. However, this quantity is usually considered as a secondary result in the determination of $[\eta]$, and

we have not found an adequate and extensive compilation of k_H values for a variety of systems (to the best of our knowledge, the most extensive collection is that in the *Polymer Handbook* [31], where most data pertain to flexible-chain, synthetic polymers). Then, we have proceeded making such a collection of literature data (see Table 1), which is just intended to provide examples of values that one could expect, to be used for the evaluation of the procedures for the determination of $[\eta]$.

Flexible polymer chains posses k_H values in the range 0.2–0.8, most frequently about 0.3 in good solvents. This circumstance is very fortunate for the use of the single-point, Solomon–Ciuta method, which, as described above, is exact for $k_H = 1/3$. Slightly higher values, near 0.6 are found or predicted for theta

Table 1 Values of k_H for several systems

System	k_H	References
Flexible chains		
In good solvents	0.2–0.4	[31]
In good solvents, theory	0.76	[31, 36]
In theta solvents	0.4–0.7	[31, 37]
In theta solvents, theory	0.6	[31, 36]
Denaturated proteins	0.3–0.5	[38]
Oligomeric propylene glycol $M = 130$–940 g/mol	0.9–0.5	[39]
Poly(isobutylene) $M = 5{,}000$ g/mol	1.0	[40]
Globular particles		
Spheres (uncharged) theory	0.69–0.80	[41, 42]
Silica spheres	1.0	[43]
Haemoglobin	0.81–0.93	[44]
Bovine serum albumin	0.89–1.42	[45]
Wormlike particles (from rod to coil)		
Xanthan polysaccharide	0.40–0.50	[46]
Schizophyllum commune polysaccharide	0.39–048	[47]
Poly(hexyl isocyanate)	0.39–0.59	[48]
Non-globular (multidomain) particles		
IgG antibody	0.74–0.84	[49]
Phycocianin (hexameric)	0.3	[50]
Myosin A	0.31	[51]
Fibrinogen	1.2	[52]
Aggregating, interacting macromolecules		
Folch-Pi protein	1.4, 8.4,...	[53]
IgG heteropolymer	0.6	[54]
Schizophyllan native/renaturated	0.2–0.6/1.6	[55]
Carboxymethylcellulose in acetonitrile-water-salts	2–25	[56]
Urease (polymerising)	40	[35]
Neurophysin	3	[57]
Silica rods	3.5–4.2	[58]
Chondroitin sulfates (possibly aggregating) $I = 0.15$ M	0.004–0.24	[59]
Rodlike particles		
Theoretical	0.75	[60]
Theoretical	0.4	[61]
Light meromyosin	0.64	[62]
Fd virus	1.54	[63]
Polyamide oligomers	1.0–1.7	[64]
Polyelectrolytes/Polysaccharides		
Alginate in varying ionic strength $I = 0.2$–0.005 M NaCl	0.35–0.55	[65]
Guar gum in monovalent ions/urea	0.5–0.6/0.9–1.3	[66]
Succinoglican 25/75 °C	0.34/0.44	[67]
Poly(styrene sulfonate) $M = 4.1 \times 10^5$ g/mol $I = 10^{-1} - 10^{-3}$ M	0.8–2.0	[68]
Poly(styrene sulfonate) $M = 1.1 \times 10^6$ g/mol $I = 10^{-1} - 3 \times 10^{-5}$ M	0.4–7.9	[68]
Chondroitin sulfates $I = 0.15$ M	0.004–0.24	[59]

solvents. Clearly, the value of k_H depends on the solvent quality that is related to the value of the osmotic second virial coefficient, A_2. Yamakawa gives the following expression relating both parameters [32],

$$k_H = \frac{1}{2}\left[1 - 3\left(\frac{A_2 M}{[\eta]}\right)\varphi\right], \tag{21}$$

where M is the molecular weight and φ is a complex function of the excluded volume parameter that depends on the binary cluster integral. As the prediction of k_H values from Eq. 21 seems complicated, for the purpose of the present problem, we advise choosing one of the representative values of k_H for the limiting cases of theta and good solvent conditions. These values are applicable not only to synthetic polymers, but also to biological flexible-chain macromolecules, like fully denaturated proteins or nucleic acids. It should be kept in mind that k_H presents some dependence on molecular weight, that may be irrelevant for higher polymers, but is appreciable for short chains: oligomers with M in the range 10^2–10^3 g/mol may have $k_H \geq 1$.

For the case of globular particles, theories predict $k_H = 0.7$–0.8 for spheres. Spherical colloids and globular proteins show values in this range or slightly higher. For rodlike particles of large aspect ratio, there is some discrepancy in theoretical predictions. Experimental data for well-characterized, nonassociating rodlike macromolecules and particles yield values in the range $k_H \approx 0.4$–0.7. Since this range is similar to that of fully flexible chains, one expects, and the experiment confirms, that wormlike chains should have such k_H over the whole range of contour to persistence length, i.e., from the coil limit to the rod limit. Flexible-chain polyelectrolytes have k_H values that increase with decreasing ionic strength, I. At high I, electrostatic interactions are shielded and values of k_H are those typical of flexible coils, but one may find $k_H > 1$ at low I, and exceedingly large values have been measured in salt-free solutions.

Rather peculiar concentration dependences of the solution viscosity, and therefore, unusual Huggins constants, can be also found in solutions where the solute molecules have a tendency to associate, either forming well-defined oligomers or aggregates. The observed k_H values will reflect not only the heterogeneity of the solute but also the possible concentration dependence of its composition. This situation may be frequent among biopolymers, including many "sticky" polysaccharides, and oligomizing proteins. Some predictions for relevant cases of heterogenous systems can be easily made on the assumption that the viscosity increases due to each component are additive. Thus, for a mixture of noninteracting components, k_H would be some sort of weighted average of those of the individual components.

However, the Huggins constant may be remarkably unusual when the composition of the heterogenous solute in not constant but concentration-dependent. This happens when the oligomerization or aggregation is reversible, governed by some chemical equilibrium. This can be shown in a simple yet relevant case, in which the solute would be in equilibrium with a dimer. This case is rather frequent among proteins, either globular like serum albumin [33] or fibrous like myosin [34]. In the limit of zero concentration, there are no dimers, and the observed intrinsic viscosity would be that of the monomer. However, the concentration dependence of the solution viscosity has a contribution from the conversion of monomers to dimers as the concentration increases, and this gives rise to a term in the observed Huggins constant $k_{H,\mathrm{obs}}$ that is related to the difference between the intrinsic viscosities of the monomer and dimer, $[\eta]_m$ and $[\eta]_d$, respectively. It can be easily shown that:

$$k_{H,\mathrm{obs}} = k_{H,m} + \frac{[\eta]_d - [\eta]_m}{[\eta]_m^2}\frac{10^{-3}K}{2M_m} \tag{22}$$

where $k_{H,m}$ and M_m are the Huggins constant and the molecular weight of the monomer and K is the dimerization equilibrium constant, expressed in liters per mole, while the intrinsic viscosities are in cubic centimeters per gram. Note that the change in Huggins constant is not related to the different values of the k_H values of monomer and dimer; it does not come from the quadratic terms in the concentration dependence of the solution viscosity but from the linear ones. Depending on the magnitude and sign of the difference $[\eta]_d - [\eta]_m$, there can be an important influence in the observed Huggins constant, which may be well beyond the usual range (say 0.2–1.0) of single species, and particularly abnormal values may appear in cases of multiple oligomerization equilibria [35].

Summarizing, there will be instances where the nature of the solution is well defined and k_H is known or can be predicted with accuracy. This suggested to us that we should propose a "corrected" single-point Solomon–Ciuta method, in which the single-point Solomon–Ciuta value $[\eta]_{\mathrm{SCsp}}$, determined from Eq. 4, is corrected with the S function, Eq. 15, evaluated with the approximate $[\eta]_{\mathrm{SCsp}}$, to give

$$[\eta]_{\mathrm{SCcorr}} = [\eta]_{\mathrm{SCsp}}/S \tag{23}$$

which would coincide with the Huggins (reference) value.

On the other hand, there may be cases where the k_H value may be abnormal or uncertain, so that a safe determination of $[\eta]$ would require successive dilutions and extrapolation to zero concentration. In this regard, we note that the Huggins extrapolation in not the only choice, and instead, we have shown that the Solomon–Ciuta value has a less pronounced concentration dependence, so that one may think of a procedure where $[\eta]$ is determined by extrapolation of various values from Eq. 4 for decreasing concentrations.

Simulation of experimental errors in the Huggins and Solomon–Ciuta methods

As noted previously, in addition to the systematic error in the single-point Solomon–Ciuta procedure, every procedure also produces experimental (accidental) errors that originate in the viscosity measurements and propagate to the values from which $[\eta]$ is calculated, either directly or from extrapolation; indeed, the extrapolation itself will introduce further experimental error.

We have devised a simple computer simulation to ascertain the errors produced by the various methods that we have been considering. In summary, these methods are:

- Single-point Solomon–Ciuta, Eq. 4
- Corrected single-point Solomon–Ciuta, Eq. 23
- Huggins extrapolation to zero concentration

In the simulation, we generate reference values of the relative viscosity η_r, for given values of k_H and $C = [\eta]c$. We suppose that, in the real experiment, these values are affected by an experimental, relative error $\delta\eta_r$. Then, a random error is added to the reference as a Gaussian random number of zero mean and standard deviation $\Delta\eta_r = \eta_r\delta\eta_r$. In the two single-point Solomon–Ciuta methods, this is done for a single value of C. In the dilution–extrapolation procedures, mimicking experimental protocols [8], six values from C down to $C/3$ values are generated and used to get the intercept from a linear least-squares fit. The relative difference between the value so obtained and the reference is the relative error in $[\eta]$. This process is repeated many times, and the final result for the relative global error, $e([\eta])$, is the root-mean-square value of the results of each repetition.

Results for the relative global errors for the three procedures listed above are plotted in Figs. 2b, and 3a, b. For standard glass-capillary viscometry, we estimate a typical experimental error in η_r, $\delta\eta_r$ (arising from errors in falling times, temperature fluctuations, etc.) of 1%, so that, for the reported results, we took $\delta\eta_r = 0.01$.

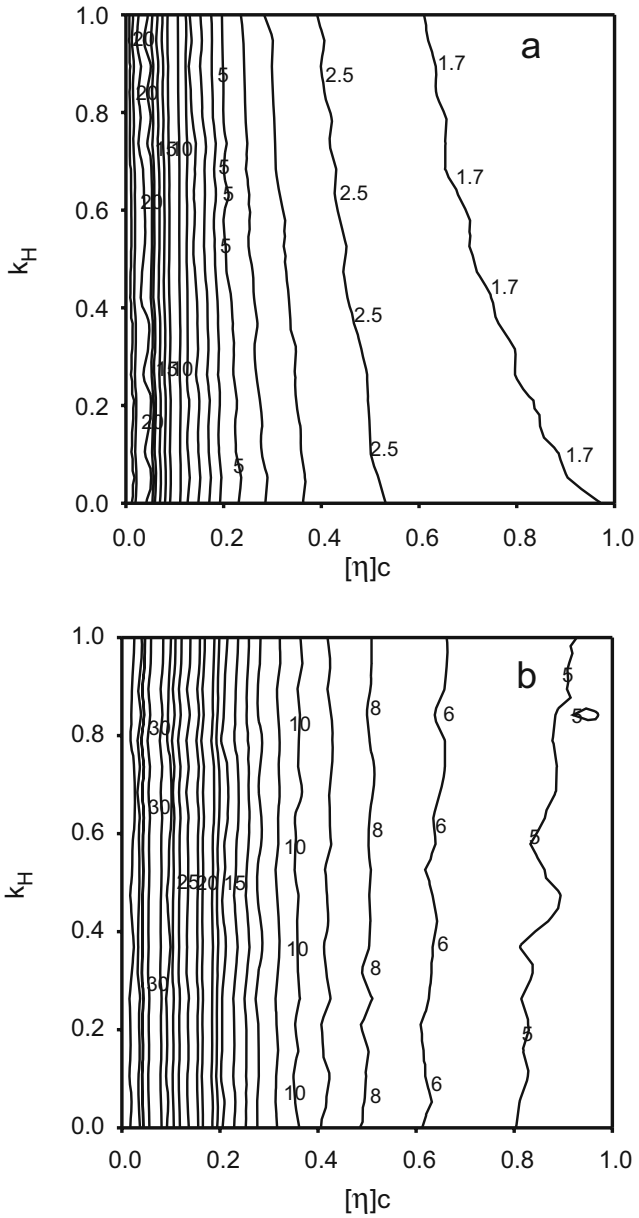

Fig. 3 **a** Relative global error of the corrected single-point Solomon–Ciuta method. **b** Relative global error of the extrapolated Huggins method

Anyway, $e([\eta])$ can be recalculated for any other $\delta\eta_r$ because $e([\eta])$ is proportional to $\delta\eta_r$. We also recall that the errors do not depend on c and $[\eta]$ separately but on the product $[\eta]c$.

Discussion and concluding remarks

We first note the similarity between the global error of the single-point Solomon–Ciuta (Fig. 2b) and the theoretical systematic error (Fig. 2a); actually, most of the global error is due to the systematic component, except for very dilute solutions, where the accidental part is dominant. Figure 2b can serve to estimate

the error expected from a single-point Solomon–Ciuta determination.

The systematic deviation is suppressed by either extrapolation in the Huggins method or by correction in our corrected single-point Solomon–Ciuta procedure, and the purely accidental errors do not depend on the k_H value, as shown in Fig. 3a, b, but only on how dilute the solutions are. Comparing, as it was, the main purpose of this paper, the Huggins extrapolation procedure with the single-point Solomon–Ciuta determination, one reaches a most satisfactory finding about the latter: using our corrected single-point Solomon–Ciuta procedure, the errors of the single-point method are even smaller than those of the full extrapolation; thus, the errors in the corrected single-point Solomon–Ciuta method can be smaller than 5% for a concentration of $c = 0.25/[\eta]$, while the more laborious Huggins extrapolations for a series of dilutions starting from that concentration would yield errors larger than 10%.

The possibility of employing the corrected single-point Solomon–Ciuta procedure relies on the previous knowledge or accurate estimation of k_H. With the information available (reviewed in the previous section) on the Huggins constant, this may be possible in a number of cases, for instance, when the $[\eta]$ measurement is just intended to determine the molecular weight or molecular dimensions of a solute of well-known structure and solution behavior (e.g., a flexible polymer in a good solvent). This capability of the corrected single-point Solomon–Ciuta procedure enhances the utility of the single-measurement, pressure-imbalance differential viscometers. There will be other cases where the k_H value may be ignored or presumably abnormal, and then, a single-measurement determination of $[\eta]$ would be dangerous. It can be noted, however, that – as we have indicated above – such cases are commonly associated to heterogeneity in the solute. Then, the modern set-ups of SEC or FFF with viscosity detection (SEC/VIS or FFF/VIS) may be extremely valuable: the instrument determines the $[\eta]$ values for the components of the heterogenous solute as single species, previously separated in the SEC or FFF separation, and such values can be eventually corrected as we have proposed. Finally, we should also recall that there are special but relevant circumstances, which have been reviewed above, where the dilution/extrapolation procedures would be the proper choice.

Computer programs

Fortran code and executable programs to evaluate the corrected Solomon–Ciuta intrinsic viscosity, and to estimate the systematic and global errors expected for the various procedures mentioned in this work, will be freely available from our web site, leonardo.inf.um.es/macromol/, where other related programs can be found.

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References

1. Elias HG (1977) Macromolecules, vol. 1. Wiley Interscience, New York
2. Billmeyer FW Jr (1984) Textbook of polymer science, 3rd edn. Wiley Interscience, New York
3. Munk P, Aminabhavi TM (2002) Introduction to macromolecular science, 2nd edn. Wiley, New York
4. Harding SE (1997) Prog Biophys Mol Biol 68:207–262
5. van Holde KE, Johnson W, Ho P (1998) Principles of physical biochemistry, 2nd edn. Prentice Hall, Upper Saddle River
6. Hunter RH (2001) Foundations of colloid science. Oxford University Press, Oxford
7. Bohdanecký M, Kovár J (1982) Viscosity of polymer solutions. Elsevier, Amsterdam
8. Kulicke WM, Clasen C (2004) Viscosimetry of polymers and polyelectrolytes. Springer, Berlin
9. Graessley WW (2004) Polymeric liquids and networks: structure and properties. Garland Science, New York
10. García Bernal JM, Tirado MM, García de la Torre J (1991) Macromolecules 24:593–598
11. Freire JJ, Prats R, Pla J, García de la Torre J (1984) Macromolecules 17:1815–1821
12. Freire JJ (1999) Adv Polym Sci 143:35–112
13. Pamies R, López Martínez MC, Hernández Cifre JG, García de la Torre J (2005) Macromolecules 38:1371–1377
14. Yamakawa H, Fujii M (1974) Macromolecules 7:128–135
15. Bohdanecký M (1983) Macromolecules 16:1483–1492
16. Ortega A, García de la Torre J (2007) Biomacromolecules 8:2464–2475
17. Ortega A, García de la Torre J (2003) J Chem Phys 119:9914–9919
18. García de la Torre J, Del Río Echenique G, Ortega A (2007) J Polym Sci B Polym Phys Ed 111:955–961
19. Huggins ML (1942) J Am Chem Soc 64:2716–2720
20. Sandler SR, Karo W, Bonestel J, Perace E (1998) Polymer synthesis and characterization. A laboratory manual. Academic, New York
21. Lee J, Tripathi A (2005) Anal Chem 77:7137–7147
22. Solomon OF, Ciuta IZ (1962) J Appl Polym Sci 6:683–686
23. Solomon OF, Gotesman BS (1967) Makromol Chem 104:177–184
24. Haney MA (1985) Am Lab 17:41–56
25. Haney MA (1985) Am Lab 17:116–126
26. Dutta PK, Hammons K, Willibey B, Haney MA (1991) J Chromatogr 536:113–121
27. Bevington PR (1969) Data reduction and error analysis for the physical sciences. McGraw-Hill, New York

28. Kraemer EO (1938) Ind Eng Chem 30:1200–1203
29. López Martínez MC, Díaz FG, Ortega A, García de la Torre J (2003) J Chem Ed 80:1036–1038
30. Elias HG (1999) Makromoleküle chemische, struktur und synthesen. Wiley-VCH, Weinheim
31. Kurata M, Tsunashima Y (1989) Viscosity-molecular weight relationships and unperturbed dimensions of linear chain molecules, 3rd edn. Wiley, New York
32. Yamakawa H (1961) Macromolecules 34:1360–1372
33. Harvey JD, Geddes R, Wills PR (1979) Biopolymers 18:2249–2260
34. Harrington WF, Burke M (1972) Biochemistry 11:1448–1455
35. Tirrell M, Middleman S (1979) Biopolymers 18:59–72
36. Riseman J, Ullman R (1951) J Chem Phys 19:578–584
37. Sakai T (1968) J Polym Sci 6:1535–1549
38. Ahmad F, Salahuddin A (1974) Biochemistry 13:245–249
39. Sandell, LS, Goring DAI (1970) Macromolecules 3:50–54
40. Geerinssen H, Schutzeichel P, Wolf BA (1991) Macromolecules 24:304–309
41. Batchelor GK (1977) J Fluid Mech 83:97–117
42. Peterson JM, Fixman M (1963) J Chem Phys 39:2516–2523
43. Jones DAR, Learly B, Boger DV (1991) J Colloid Interface Sci 147:479–495
44. Monkos K (1994) Int J Biol Macromol 16:31–35
45. Monkos K (2005) Biochim Biophys Acta 1748:100–109
46. Sato T, Norisuye T, Fujita H (1984) Macromolecules 17:2696–2700
47. Kashiwagi K, Norisuye T, Fujita H (1981) Macromolecules 14:1220–1125
48. Kuwata M, Murakami H, Norisuye T, Fujita H (1984) Macromolecules 17:2731–2734
49. Monkos K (1999) Int J Biol Macromol 26:155–159
50. Kotera A, Saito P, Mizuno H, Taki N (1975) Bull Chem Soc Jpn 48:1176–1179
51. Emes CH, Rowe A (1978) Biochim Biophys Acta 537:110–124
52. Lederer K, Schurz J (1972) Biopolymers 11:1989–1993
53. Lavialle F, de Foresta B, Vacher M, Nicot C, Alfsen A (1979) Eur J Biochem 95:561–567
54. Gabriel DA, Hadler NM (1981) J Biol Chem 256:3240–3244
55. Fang Y, Takahashi R, Nishinari K (2004) Biopolymers 74:302–315
56. Nandi P, Bhattarai A, Das B (2007) J Polym Sci B Polym Phys Ed 45:1765–1770
57. Rholan M, Nicolas P, Cohen P (1982) Biochemistry 21:4968–4973
58. Wierenga AM, Philipse AP (1996) J Colloid Interface Sci 180:360–370
59. Arias C, Yagüe A, Rueda C, García Blanco F (1998) Biophys Chem 72:307–312
60. Hermans J Jr (1962) J Colloid Sci 17:638–648
61. Berry DH, Russel WB (1987) J Fluid Mech 180:475–494
62. Huidt S, Ferry JD, Roelke DL, Greaser ML (1983) Macromolecules 16:740–745
63. Graf C, Kramer H, Deggelmann M, Hagenbüchle M, Johner C, Martin C, Weber R (1993) J Chem Phys 98:4920–4928
64. Aharoni SM (1987) Macromolecules 20:2010–2017
65. Pamies R (2006) Ph.D. thesis, Universidad de Murcia
66. Ma XD, Pawlik M (2007) Carbohydr Polym 70:15–24
67. Kaneda I, Kobayashi A, Miyazaw K, Yanaki T (2002) Polymer 43:1301–1305
68. Davis RM, Russel WB (1987) Macromolecules 20:518–525