Viscosity-Molecular Weight Relationship for Cellulose Solutions in Either NMMO Monohydrate or Cuen

John Eckelt,[1,2] Anja Knopf,[1] Thomas Röder,[3] Hedda K. Weber,[4] Herbert Sixta,[5] Bernhard A. Wolf[1]

[1]Institut für Physikalische Chemie der Johannes Gutenberg-Universität Mainz and Materialwissenschaftliches Forschungszentrum der Universität Mainz, Welder-Weg 13, D-55099 Mainz, Germany
[2]WEE-Solve GmbH, Auf der Burg 6, D-55130 Mainz, Germany
[3]Lenzing AG, Department FE, A-4860-Lenzing, Austria
[4]Kompetenzzentrum Holz GmbH (Wood K plus), A-4021 Linz, Austria
[5]Helsinki University of Technology, 02150 Espoo, Finland

ABSTRACT: The intrinsic viscosities, [η], of nine cellulose samples, with molar masses from 50×10^3 to $1\,390 \times 10^3$ were determined in the solvents NMMO*H$_2$O (N-methyl morpholin N-oxide hydrate) at 80°C and in cuen (copper II-ethlenediamine) at 25°C. The evaluation of these results with respect to the Kuhn–Mark–Houwink relations shows that the data for NMMO*H$_2$O fall on the usual straight line in the double logarithmic plots only for $M \leq 158\ 10^3$; the corresponding $[\eta]/M$ relation reads $\log ([\eta]/\mathrm{mL\ g}^{-1}) = -1.465 + 0.735 \log M$. Beyond that molar mass [η] remains almost constant up to $M \approx 10^6$ and increases again thereafter. In contrast to NMMO*H$_2$O the cellulose solutions in cuen behave normal and the Kuhn–Mark–Houwink relation reads $\log ([\eta]/\mathrm{mL\ g}^{-1}) = -1.185 + 0.735 \log M$. Possible reasons for the dissimilarities of the behavior of cellulose in these two solvents are being discussed. The comparison of three different methods for the determination of [η] from viscosity measurements at different polymer concentrations, c, demonstrates the advantages of plotting the natural logarithm of the relative viscosities as a function of c. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 670–676, 2011

Key words: intrinsic viscosity; cellulose; NMMO hydrate; cuen; Kuhn–Mark–Houwink relation

INTRODUCTION

Intrinsic viscosities, [η], provide valuable information on the spatial extension of isolated polymer coils in a particular solvent and at the given temperature. For industrial purposes, the measurement of [η] offers easy and quick access to the molar mass M of the polymer if the dependence of [η] (M) is known. The polymer handbook is for that reason full of so-called Kuhn–Mark–Houwink relations. In the case of cellulose, this information is lacking for some technically important solvents, such as N-methylmorpholine N-oxide monohydrate (NMMO*H$_2$O) or only known for a limited range of molar masses, like in the case of cuen.

Because of the situation described above, we have measured the intrinsic viscosities of nine different cellulose samples with molar masses ranging from 50 to 1360 kg/mol in NMMO monohydrate and in cuen (copper II-ethlenediamine). Primary data were evaluated according to the traditional lines, that is, in Huggins and in Schulz–Blaschke plots, as well as according to a new procedure introduced for the characterization of polyelectrolyte solutions. The information obtained in the course of these measurements are discussed with respect to hydrodynamic interaction parameters and in view of the possibilities to establish practically useful master curves.

EXPERIMENTAL

Substances

Cellulose samples (fibers or sheets) with low contents of hemicelluloses originate from the Lenzing AG (Lenzing, Austria). Their molar masses were determined[1] by means of gel permeation chromatography in the mixed solvent dimethylacetamide + LiCl; Table I collects their values, which are relative molar masses, that is, dimensionless.

N-methylmorpholine-N-oxide monohydrate (NMMO*H$_2$O) was purchased from Sigma Aldrich (Germany) in purum grade (≥95%) and was used without further purification. The melting point was 71–75°C and its density at 80°C was 1.28 g/mL. The

TABLE I
Molar Masses, Molecular Nonuniformity and Intrinsic Viscosities in NMMO*H_2O as Compared
with the Intrinsic Viscosities in Cuen

Sample	Origin	Internal description	$10^{-3} M_w$	M_w/M_n	$[\eta]$ 80°C/mL g^{-1} in NMMO*H_2O	$[\eta]$ 25°C/mL g^{-1} in Cuen
CV	Viscose fiber	FE 76/09–4	50.0	2.50	102	195
PHK 1	Prehydrolysis Kraft pulp	Solucell 270	96.0	2.05	143	270
CMD	Modal fiber	FE 76/09–5	100.0	2.50	155	283
CL 1	Cotton linters	FE 76/09–6	101.0	1.69	186	346
CLY	Tencel® fiber	FE 76/09–9	140.0	2.55	191	370
PHK 2	Prehydrolysis Kraft pulp	24/01–1	158.0	2.82	313	580
CL 2	Cotton linters	FE 76/09–8	360.0	2.16	299	855
CL 3	Cotton linters	FE 76/09–1	620.0	2.15	283	1150
CL 4	Cotton linters	FE 76/09–7	1390.0	1.37	382	2100

cuen solution was purchased from Merck KGaA (Germany) with a copper concentration of 1 mol/L. It's density at 20°C was 1.1 g/mL.

Viscometry

Measurements were made using micro Ubbelohde capillary viscometers of type IIc with a capillary diameter of 0.95 mm, in combination with AVS 310 (Schott, Mainz, Germany). The temperature was 80°C in the case of NMMO monohydrate and 25°C for cuen. In both cases, there was no need to perform Hagenbach corrections.

Solutions in NMMO*H_2O were prepared in the following manner: The cellulose samples were mixed with the solid NMMO*H_2O (white powder) at room temperature to yield concentrations in the rage from 0.3 to 5 mg/mL. The mixtures were then heated to 80°C in a silicone bath and stirred for 2 h to reach homogenous solutions. The solutions were measured without filtration. Three series of independent measurements were performed to check the reproducibility of the data. The errors in the running times lie typically in the order of one per cent.

Solutions in cuen were obtained by suspending cellulose in 25 mL of water for at least 10 min. This step was followed by the addition of 25 mL cuen (1 mol/L in water) and the agitation of the mixture for 15 min. The cellulose solutions were also not filtered before the viscosity measurements.

DATA EVALUATION

Two fundamentally different methods were applied for the determination of the intrinsic viscosities $[\eta]$ from the viscosities η of the polymer solutions at different concentrations c (mass per volume) and from η_o, the viscosity of the pure solvent. According to the usual procedures, the reduced viscosity η_{red} is extrapolated to infinite dilution, either according to eq. (1), the equation of Huggins,[2] or according to eq. (2), the relation proposed by Schulz and Blaschke.[3]

$$\frac{\eta - \eta_o}{\eta_o c} = \frac{\eta_{spec}}{c} = \eta_{red} = [\eta] + k_H[\eta]^2 c \quad (1)$$

The independent variable of eq. (1) is c, whereas it is η_{spec} in eq. (2).

$$\frac{\eta_{spec}}{c} = [\eta] + k_{SB}[\eta]\,\eta_{spec} \quad (2)$$

The parameters k_H (the Huggins constant) and k_{SB} (the Schulz–Blaschke constant) quantify the hydrodynamic interaction between the solute molecules. Normally these two extrapolation methods yield slightly different $[\eta]$ values.

An alternative method[4] for the determination of intrinsic viscosities, formulated in eq (3), was also used here. It was established for polyelectrolytes,[5] because the traditional relations do not account adequately for the electrostatic interactions at high dilution and in the absence of salt, which become very important for the viscometric behavior. This approach avoids the extrapolation to a zero divided by zero situation (i.e., can also be successfully applied to polyelectrolyte solutions in the absence of salt) and uses the fact that the limiting slope of the relative viscosity η_{rel} as a function of c is according to phenomenological considerations[4] identical with the intrinsic viscosity. One of the relations representing the data for polyelectrolyte solutions very well is the following

$$\ln \frac{\eta}{\eta_o} = \ln \eta_{rel} = \frac{[\eta]c + B[\eta][\eta]^{\bullet}c^2}{1 + B[\eta]c} \quad (3)$$

In this relation, B quantifies the hydrodynamic interaction by analogy to k_H and k_{SB}. The additional parameter $[\eta]^{\bullet}$, is only required in the case of polyelectrolytes; for uncharged polymers it becomes zero. In the case of sufficiently dilute solutions the parameters B and k_H are interrelated by the following equation
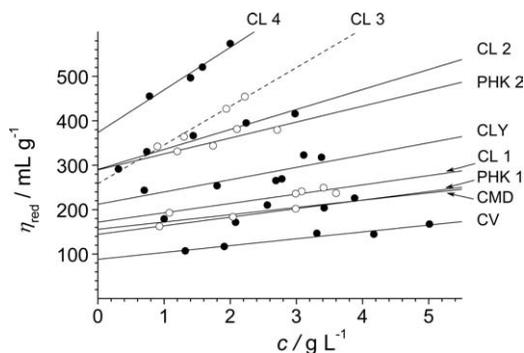
$$k_H = \frac{1}{2} - B \quad (4)$$

Figure 1 Huggins plots [eq. (1)] for cellulose solutions in NMMO*H$_2$O and 80°C.

Because of the different mathematical expressions used to model the influences of composition, this expression fails at higher c values.

The intrinsic viscosities as function of the molar mass of the polymer are usually formulated according to the Kuhn–Mark–Houwink[6] in terms the weight average M_w as

$$\log [\eta] = K + a \, \log M_w \qquad (5)$$

where K and a are system specific constants for a given solvent and temperature.

RESULTS AND DISCUSSION

The following parts deal with the determination of intrinsic viscosities according to the different methods described in the previous section and with the evaluation of the resulting data regarding the Kuhn–Mark–Houwink relations.

Intrinsic viscosities

NMMO*H$_2$O

All three methods are exemplified for this solvent. Figure 1 shows the Huggins evaluation, Figure 2 the Schulz–Blaschke plots, and Figure 3 depicts the evaluation according to eq. (3). For the sake of clarity no molar masses are stated at the individual lines; they can, however, be easily allocated by means of Table I. Irrespective of the kind of data evaluation the cellulose sample CL 3 deviates from the general trend as emphasized by the dotted lines. In the Huggins and Schulz–Blaschke plots the line for this polymer intersects lines for other samples, which should not be the case for a homologous series, even if the molecular weight distribution varies, and in the Wolf plot the curvature does not follow the general trend. The reason for this exceptional behavior is not yet clear.
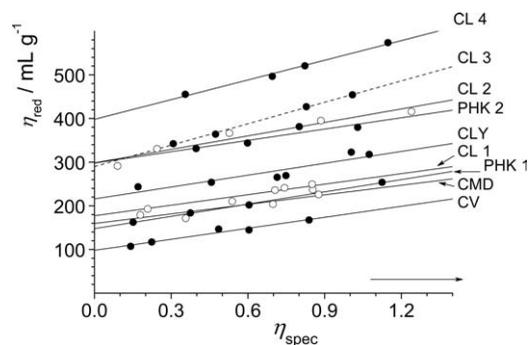
Figure 2 Schulz–Blaschke [eq. (2)] plots for cellulose solutions in NMMO*H$_2$O and 80°C.

Cuen:

The intrinsic viscosities of the different cellulose samples in this solvent were obtained by means of single point measurements according to standard routines used in industry (SCAN method: SCAN-CM 15:99).

The reliability of the industrial procedure described above and its equivalence to the evaluation according to eq. (3) will be demonstrated in the next section comparing the new data treatment with the traditional methods and studying the possibilities for a reduced representation of all data, irrespective of the molar mass of the polymer.

Comparison of evaluations

Equation (1)—for which the polymer concentration c constitutes the independent variable—can be rewritten in terms of a dimensionless reduced concentration by dividing each side by the intrinsic viscosity [η] yielding eq. (6).

$$\frac{\eta_{\text{red}}}{[\eta]} = 1 + k_H[\eta] \, c \qquad (6)$$

The reduced variable c [η] must not be confused with the coil overlap parameter; for the latter
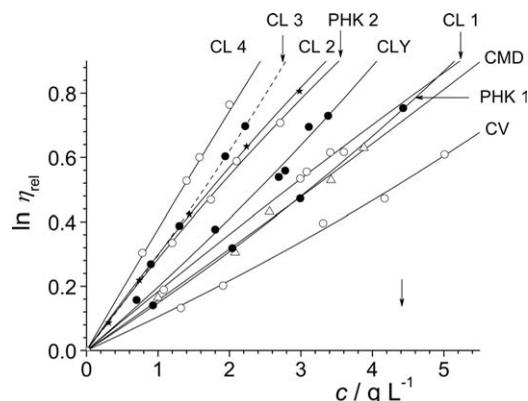

Figure 3 Wolf plots [eq. (3)] for cellulose solutions in NMMO*H$_2$O and 80°C.
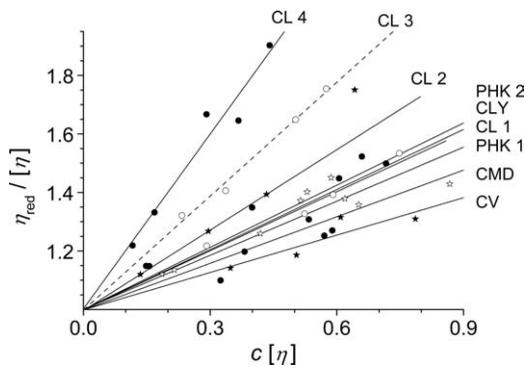
Figure 4 Reduced Huggins plot according to eq. (6) for solutions of the different cellulose samples in NMMO*H$_2$O at 80°C.

quantity it is necessary to account for possible changes in the coil dimensions with polymer concentration. An analogous restatement for the Schulz–Blaschke eq. (2) is impossible, because the independent variable is no longer c but the specific viscosity. Equation (3), on the other hand, is already formulated in terms of c [η]; for uncharged polymers $[η]^{\bullet} = 0$ and the relation reduces to

$$\ln \; η_{rel} = \frac{[η]c}{1 + B[η]c} \qquad (7)$$

In both cases one would obtain molecular weight independent master curves in terms of c [η], if it were not for the hydrodynamic interaction parameters k_H and B, which may vary more or less pronouncedly with the molar mass of the solute.

The representation of the same primary data, obtained for cellulose solutions in NMMO*H$_2$O, according to eq. (6) (Fig. 4) and according to eq. (7) (Fig. 5) demonstrates that k_H depends much more on M than B. This feature can be seen more explicitly from Figure 6 plotting the hydrodynamic interaction parameters as a function of log (M). In this context, it is interesting to note that the sequence of the sam-
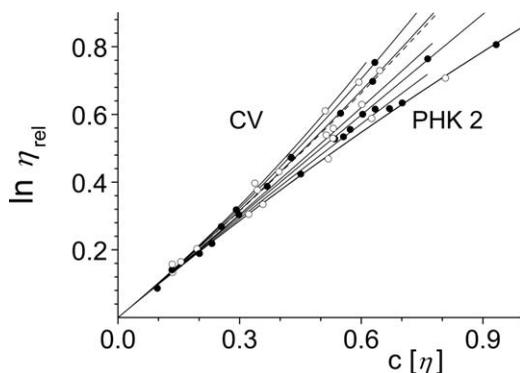

Figure 5 Reduced Wolf plot according to eq. (7) for solutions of the different cellulose samples in NMMO*H$_2$O at 80°C. The broken line refers to CL 3 again.
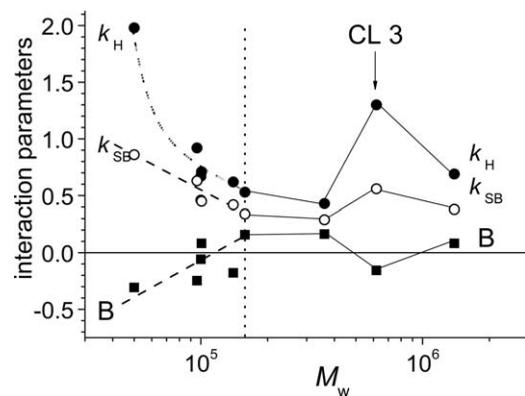

Figure 6 Viscometric interaction parameters of eqs. (1)–(3) for cellulose solutions in NMMO*H$_2$O at 80°C. The vertical line indicates at which molar mass the Kuhn–Mark–Houwink relation deviates from the straight line (cf. Fig. 8).

ples of different molar mass may change in the reduced plots of Figures 4 and 5 when compared with Figure 1 and that the cellulose sample CL 3 does no longer fall out of the general pattern. However, this polymer retains its exceptional role as far as the molecular weight dependence of the interaction parameters is concerned (cf. Fig. 6).

In the reduced presentation of Figure 5, the curvature changes from positive for the low molecular weight cellulose sample to negative as M is raised, where CL 3 does again not follow the general trend. The little deviations of the individual curves at low reduced concentrations, shown in Figure 5, suggest an easy way for obtaining first information concerning [η] without the need to correct for hydrodynamic interactions. From measured ln $η_{rel}$ values in the range of 0.5 (corresponding to an increase of ∼ 20–25% in the viscosity of the cellulose solution as compared with the viscosity of NMMO*monohydrate) it is possible to read the reduced concentration from Figure 5. Knowing the cellulose concentration c this information can be easily converted into intrinsic viscosities. The uncertainty in [η] is only about ±5%, despite the neglect of the influence of B, because of the small correction for the viscometric interactions as formulated in eq. (3) (cf. Fig. 6) in comparison with k_H or k_{SB}.

Figure 6 collects the molecular weight dependence of different hydrodynamic interaction parameters. The strong reduction of k_H with rising M agrees well with early reports[7] on this dependence, according to which this diminution is typical for polymer solutions in thermodynamically favorable solvents [cf. Fig. 2(a) of Ref. 7].

The exceptional position of the cellulose sample CL 3 becomes very obvious in Figure 6, as opposed to the reduced plots shown in Figures 4 and 5. Hydrodynamically CL 3 behaves as if its molar mass
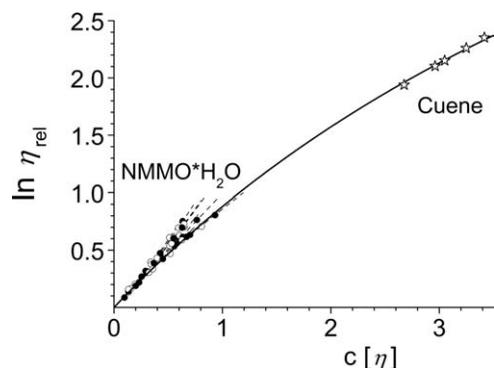
Figure 7 As Figure 5 but including the results for cellulose solutions in cuen. In contrast to NMMO*H₂O, where each dotted line represents the composition dependence of the viscosity for one given cellulose sample, the full line connects the data of single point measurements for the solutions of different polymer samples in cuen.

were approximately one order of magnitude lower than it actually is. In the case of k_H, we may assume that its value is proportional to the product of the pull-along effect[8] (favorable interaction between polymer segments) and the probability of intersegmental contacts between different polymer chains (strongly decreasing for a given value of c [η] with rising M). Under this premise the exceptionally large value of k_H for CL 3 could mean that the polymer contains some alien groups which interact with each others in a particularly favorable manner.

The composition dependence of the viscosity of the polymer solutions was not studied in detail for the system Cuen/Cellulose as stated earlier. In this case, the intrinsic viscosities were determined from single point measurements. Figure 7 demonstrates that this procedure yields data that are in full agreement with the results for the system NMMO*H₂O/cellulose if plotted according to eq. (7), despite the three times larger reduced concentrations. This observation demonstrates once more the superiority of the new method for the determination of intrinsic viscosity, because the hydrodynamic interaction parameters, obeying the following inequality $B < k_{SB} < k_H$ (cf. Fig. 6), remain inconsequential up to comparatively large polymer concentrations.

Kuhn–Mark–Houwink relations

The present results concerning the intrinsic viscosities of nine cellulose samples in either NMMO*H₂O or cuen plus the information on their molar mass (cf. Table I) permit the establishment of the dependencies of [η] on M. The data for NMMO*H₂O are—in contrast to the normal situation—not located on a straight line in the usual double logarithmic plot as shown in Figure 8, but deviate from it once the molar mass of the polymer surpasses a critical value.

Furthermore all intrinsic viscosities are for given cellulose samples in this solvent at 80°C considerably lower than in cuen at 25°C. For the linear part of the relation for NMMO*H₂O at 80°C the following expression holds true.

$$\log([\eta]/\text{mL g}^{-1}) = -1.465 + 0.735 \log M \quad (8)$$

It is interesting to note that the slope of this line is within experimental error the same as that for the system cuen/cellulose at 25°C, for which the dependence is linear in the entire M-range. This relation reads

$$\log([\eta]/\text{mL g}^{-1}) = -1.185 + 0.735 \log M \quad (9)$$

In order to emphasize the exceptional behavior of cellulose solutions as compared with the solutions of typical synthetic polymers, Figure 8 also shows some results for polystyrene.

A first attempt to explain the anomalous results for the solutions in NMMO*H₂O as an artifact must be ruled out because the data have been reproduced by independent experiments and by different persons. Furthermore, an interpretation of the lower intrinsic viscosities in NMMO*H₂O as compared with cuen in the usual manner via a lower solvent quality appears difficult in view of practically the same parameter a (eq (5)) for both solvents and the particularities for NMMO*H₂O at high M values.

Because of these observations we confine the discussion to considerations based on the immediate physical meaning of [η], i.e. on the specific hydrodynamic volume of isolated polymer coils. The observed reduction of the intrinsic viscosities upon an augmentation of M in the range of truly high molecular weight cellulose can be interpreted in two different ways. (i) Either the addition of further polymer segments (prolongation of the chain) does
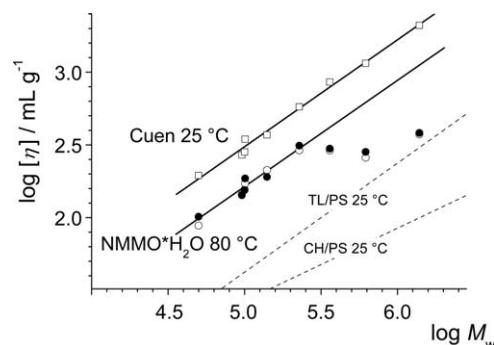

Figure 8 Kuhn–Mark–Houwink plot for the systems cuen/cellulose at 25°C and NMMO*H₂O/cellulose at 80°C. Open circles: Evaluation according to eq. (1), and full circles according to eq. (3). For comparison this graph also shows the corresponding dependencies for polystyrene solutions in the thermodynamically favorable solvent toluene and for the theta solvent cyclohexane at 34°C.
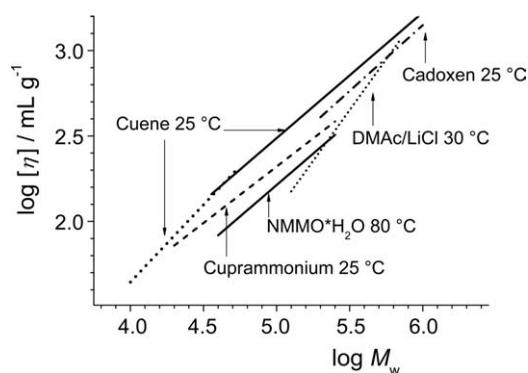
Figure 9 Comparison of the Kuhn–Mark–Houwink relations for cellulose in the solvents and at the temperatures indicated in the graph; DMAc: dimethylacetamide. The molecular weight ranges covered by the experiments are indicated by the length of the lines. For NMMO*H$_2$O this graph shows the linear dependence at low M values only.

not increase the volume of an isolated coil because favorable intramolecular interactions with other segments become possible as a result of the declining restrictions of chain stiffness with rising M or (ii) the experimental [η] values do not refer to isolated polymer molecules, because of the increasing importance of intermolecular interactions, which become at sufficiently high molar masses so strong that the different polymer molecules cannot individualize upon dilution but form long lived aggregates. Light scattering data[9,10] for solutions of cellulose samples with molar masses in the range of anomalous behavior indicate that option (ii) is likely holding true. Similar observations[11] were also made for the solution of cellulose in Cd-tren. These scattering experiments have produced apparent M values only, which are considerable larger than the corresponding data obtained from measurements in cuen.

Based on the above consideration we can tentatively conclude that the particularities in the Kuhn-Mark-Houwink relation for the system NMMO*H$_2$O/cellulose are caused by a pronounced intermolecular association tendency, which becomes so dominant with rising M that only cellulose below a critical molar mass can form isolated coils upon the dilution of moderately concentrated solution. In other words: Once this critical value is exceeded such a separation is seriously handicapped by the increasing number of intermolecular contacts between polymer segments.

To obtain a more general picture of the Kuhn–Mark–Houwink relations known for cellulose solutions in different solvent,[12] Figure 9 shows some typical examples. This graph demonstrates that the largest intrinsic viscosities of cellulose are observed with cuen at 25°C; literature reports for this solvent but lower M values[13] match the present result well and yield a relation spanning almost two decades in con-

trast to the other solvents. The Kuhn–Mark–Houwink exponents for cadoxen[14] and cuprammonium[15] are similar to those for cuen and NMMO*H$_2$O, whereas the mixed solvent dimethylacetamide + LiCl[16] behaves in a totally different manner. The reasons for this exceptional position are presently unclear; it may be due to the fact that cellulose acts like a polyanion[17] in this solvent.

CONCLUSIONS

Out of the different solvents for cellulose, NMMO*H$_2$O is according to the present measurements unique because of its uncommon Kuhn–Mark–Houwink relation. The data points are only below a critical polymer mass located on a straight line and only in this M-range the values of the K and a constants are comparable with the corresponding data for cuen, cadoxen, or cuprammonium. A further increase of the molar mass does not lead to the expected augmentation of [η], probably because of strong interactions between the polymer segments impeding the formation of isolated coils upon dilution. This observation prompts a number of questions, some of which are of industrial relevance. For basic research it would be interesting to investigate, whether the particularities disappear as the measuring temperature is increased; a positive answer could support the tentative explanation formulated above. For practical purposes, it might also be helpful to know whether a critical molar mass separating normal from anomalous behavior also exists for the rheological properties of more concentrated cellulose solutions in NMMO*H$_2$O as employed for fiber production. Another interesting question in this context concerns the flow behavior of the solutions of mixtures of cellulose samples with subcritical and supercritical molar masses.

The hydrodynamic interaction between dissolved cellulose molecules depends on their molar mass in the same way as between synthetic polymers. In this context it is, however, worthy to note that out of the nine cellulose samples one material drops out of the general pattern. This feature may offer an opportunity to detect characteristic differences either in the structure of these biopolymers or with respect to their purity.

Another noteworthy finding of the present work concerns the aptitude of different methods for the evaluation of viscometric data: Equation (3) has a number of advantages among which the most import lies in its applicability to polyelectrolyte solutions. Another benefit consists in its ability to describe the viscometric behavior of dilute solutions up to about three times higher polymer concentrations than the Huggins or the Schulz–Blaschke relation with only one hydrodynamic interaction parameter. This attribute

makes eq. (3) particularly valuable for the precise determination of intrinsic viscosities by means of single point measurements.

References

1. Schelosky, N.; Röder, T.; Baldinger, T. Papier 1999, 53, 728.
2. Huggins, M. L. J Am Chem Soc 1942, 64, 2716.
3. Schulz, G. V.; Blaschke, F. J Prakt Chem 1941, 158, 130.
4. Wolf, B. A. Macromol Rapid Commun 2007, 28, 164.
5. Eckelt, J.; Knopf, A.; Wolf, B. A. Macromolecules 2008, 41, 912.
6. Elias, H.-G. Makromoleküle; Hüthig & Wepf Verlag: Basel, 2001.
7. Gundert, F.; Wolf, B. A. Makromol Chem 1986, 187, 2969.
8. Wolf, B. A.; Geerissen, H.; Jend, R.; Schmidt, J. R. Rheol Acta 1982, 21, 505.
9. Röder, T.; Morgenstern, B. Polymer 1999, 40, 4143.
10. Arndt, K. F.; Morgenstern, B.; Roder, T. Macromol Symp 2000, 162, 109.
11. Saalwachter, K.; Burchard, W. Macromolecules 2001, 34, 5587.
12. Kurata, M.; Tsunashima, Y. In Polymer Handbook, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley: New York, 1999.
13. Immergut, E. H.; Ranby, B. G.; Mark, H. F. Ind Eng Chem 1953, 45, 2483.
14. Henley, D. Ark Kemi 1962, 18, 327.
15. Gralén, N.; Svedberg, T. Nature 1943, 152, 625.
16. Mccormick, C. L.; Callais, P. A.; Hutchinson, B. H. Macromolecules 1985, 18, 2394.
17. Stryuk, S.; Eckelt, J.; Wolf, B. A. Cellulose 2005, 12, 145.