First Studies on the Influence of Methylated *β*-Cyclodextrin on the Rheological Behavior of 1-Ethyl-3-methyl Imidazolium Acetate

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The rheology of solutions of randomly methylated (1.8) *β*-cyclodextrin (*β*-CD) in 1-ethyl-3-methyl imidazolium acetate ([EMIM][Ac]) was studied in detail by rotational and oscillatory shear measurements. It was found that a gel structure was formed even at a relatively low *β*-CD concentration, which induced intriguing results in oscillation experiments. The solutions showed abrupt changes of the structurally dependent rheological moduli and reproducible transitions from gel to sol state at specific shear stress. For all *β*-CD solutions, a non-Newtonian flow behavior including shear thinning was obtained. The influence of temperature and *β*-CD concentration on the flow behavior was studied for all solutions, and the flow activation energies were calculated from the logarithmic form of the Arrhenius equation for nonassociating electrolytes.

1. Introduction

Cyclodextrins (CDs) are cyclic oligoamyloses based on α-1,4-linked D-glucose units. Due to their conical, tubelike shape, CDs are able to enclose suitable hydrophobic molecules reversibly.[1−3] In the past decade, a large number of applications in pharmaceutical and analytical chemistry, food technology, chemical synthesis, and catalysis have been developed.[4,5]

As a new type of "green solvent", ionic liquids (ILs) are currently in the focus of increasing scientific interest. Their distinguished physical properties, such as excellent thermal stability, negligible vapor pressure, and high electrical conductivity and a great potential as a special solvent, open a broad field of applications. This includes the improved solubility of cellulose and CDs in ILs.[6−12] Since the interaction between ILs and CDs plays a crucial role in analytical chemistry and material synthesis,[13−15] the understanding of the rheological properties of CD/IL solutions is an important prerequisite for a successful processing. A survey of the relevant literature reveals that no further investigations on the rheological behavior of CD dissolved in IL have been made.

In this work, we therefore present a comprehensive investigation on the rheological properties of randomly methylated (1.8) *β*-cyclodextrin (*β*-CD)/1-ethyl-3-methyl imidazolium acetate ([EMIM][Ac]) solutions, including oscillatory and rotational shear experiments as well as the influence of temperature. *β*-CD concentrations were varied in a wide range from dilute (5 wt %) to an almost saturated state (25 wt %). Furthermore, some rheological data of [EMIM][Ac] are shown for comparison.

2. Experimental Methods

2.1. Materials. [EMIM][Ac] was obtained from BASF SE, Ludwigshafen, Germany. The amount of water and free acid was determined as 4100 ppm by coulometric Karl Fischer titration using Hydranal Coulomat AG from Fluka as anolyte. Randomly methylated (1.8) *β*-cyclodextrin (CAVASOL W7M, technical grade) was obtained from Wacker-Chemie GmbH, Burghausen, Germany. Prior to use, *β*-CD was dried in a CEM Sam 255 microwave drying system and stored in a desiccator under vacuum over sicapent.

2.2. Methods. Karl Fischer titration was carried out on a 831 KF Coulometer from Metrohm, Deutsche METROHM GmbH & Co. KG, Germany.

[EMIM][Ac] and *β*-CD were mixed in a sealed reaction vessel, and the mixture was stirred at room temperature for at least 24 h under nitrogen atmosphere. Clear solutions were obtained for all applied *β*-CD concentrations varying from 5 to 25 wt %. The complete dissolution was proven by polarization microscope images.

The rheological behavior was studied using a Thermo Scientific HAAKE Mars II rheometer equipped with plate−plate geometry (plate diameter = 35 mm) and a temperature control system DC30/K10 from Thermo scientific to ensure constant temperatures with deviations of ±0.1 °C. All measurements were carried out with a gap width of 1 mm.

Steady shear measurements were performed for all solutions to achieve viscosity curves. Controlled shear rate tests were performed at varying shear rates from 0.002 to 800 s⁻¹ and varying temperatures from 23 to 70 °C. Controlled shear stress tests were performed at varying shear stresses from 0.1 to 300 Pa up to a shear rate of 800 s⁻¹ and at a temperature of 23 °C.

Oscillatory shear measurements were performed for all solutions to achieve amplitude sweeps and frequency sweeps. Controlled shear stress tests were recorded at a constant frequency (1 Hz) and shear stresses varying from 0.1 to 300 Pa and were additionally performed with cycles of increasing and decreasing shear stress to prove reproducibility. Frequency sweeps were recorded at a constant shear stress of 0.5 Pa with frequencies varying from 0.01 to 20 Hz. All oscillatory measurements were performed at 23 °C.

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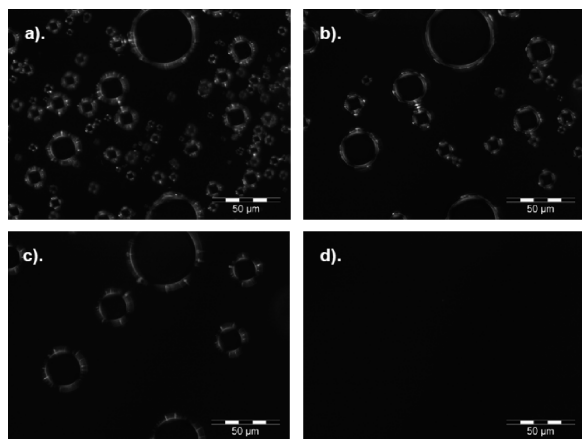† Heinrich-Heine-Universität.
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Figure 1. PLM images of the chronological sequence of β-CD (5 wt %) dissolution in [EMIM][Ac]. $t =$ (a) 0, (b) 15, (c) 45, and (d) 90 min.
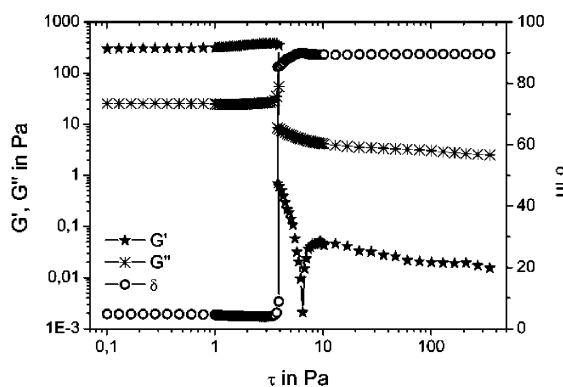

Figure 2. Amplitude sweep results for a solution of 15 wt % β-CD in [EMIM][Ac] at 23 °C.

Figure 3. Storage modulus, G'; loss modulus, G''; and phase shift angle, δ, as functions of the frequency, f, exemplary for a 15 wt % solution at a shear stress of 0.5 Pa.

Figure 4. Cycles of amplitude sweeps for a 15 wt % β-CD/ [EMIM][Ac] solution at 23 °C.

3. Results and Discussion

3.1. Dissolution Process. The dissolution behavior of randomly methylated (1.8) β-CD in [EMIM][Ac] at different weight percentages was investigated, due to a better solubility as compared with unmodified β-CD. Since the change in electrostatic interactions and the formation of ordered structure of an ionic liquid dominates the ability to dissolve β-CD,[16] [EMIM]-[Ac] should be the appropriate solvent because of its weak anion/cation interactions. It was found that [EMIM][Ac] dissolves β-CD up to 25 wt % at room temperature to obtain transparent and viscous solutions. Solutions of lower concentrations (e.g., 5 wt % β-CD) could be obtained in minutes, whereas the dissolution of 25 wt % β-CD in [EMIM][Ac] took several hours.

Because of the high degree of crystallinity of β-CD, the dissolution process in the isotropic IL could be observed by polarized light microscopy (PLM), as shown in Figure 1. In the undissolved state, the coronas of widespread crystals of chiral β-CD units were observed.

3.2. Oscillatory Measurements. Prior to the dynamic rheological measurements, amplitude sweeps were recorded with a constant frequency of 1 Hz and a shear stress varying from 0.1 to 300 Pa for all β-CD/[EMIM][Ac]-solutions. The weight percentages of β-CD in [EMIM][Ac] solutions were between 5 and 25 wt %. In Figure 2, storage modulus, G'; loss modulus, G''; and phase shift angle, δ, of a 15 wt % solution are shown. Since $G' > G''$ at low shear stress, the system turns out to be a soft, solid gel. A linear viscoelastic (LVE) plateau was observed up to 1% of strain, where the initial gel structure broke, resulting in a sharp transition. δ shifted from 5° to
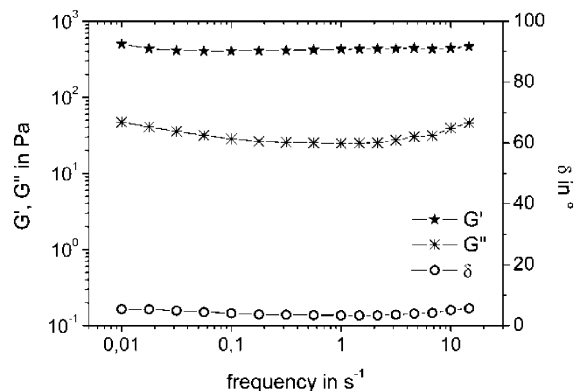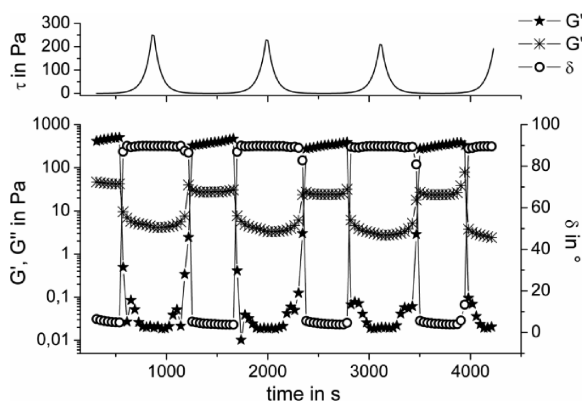
90° by only a slight change of shear stress of 0.2 Pa. Thus, the system shows an astonishingly abrupt change from almost ideal elastic to an ideal viscous behavior. At higher shear stress, G'' outweighed G'.

As Figure 3 implies, the corresponding plot of the frequency sweep proves the gel structure of the system as G' and G'' occurred in parallel straight lines throughout the entire frequency range. The values for G' were at least one decade higher than those for G''. Thus, the system behaves like a rigid gel with a high degree of physical cross-linking, for example, energetic interactions. The shape of the curves is comparable to that indicated by cross-linked polymers, since both structures show a structural network. In contrast to that, frequency sweeps at a higher shear stress value, for example, 100 Pa, showed a typical sol behavior with $G'' > G'$ and a constant phase shift angle, δ, of 90°.

To verify the reproducibility of this uncommon abrupt gel–sol transition, multiple cycles of amplitude sweeps were measured between 0.1 and 300 Pa (Figure 4). For all cycles, the three-dimensional network structure collapsed at a shear stress of 3.96 ± 0.1 Pa, whereas the gel-structure was rebuilt immediately when the shear stress reached lower values (1.82 ± 0.01 Pa). Since the cycles were measured without a recovery phase, the small hysteresis provides evidence for pure shear thinning behavior and excludes thixotropy.

The abrupt gel–sol transition was achieved for all β-CD/ [EMIM][Ac] solutions with increasing shear stress, τ. The yield point, τ_0 ($G' = G''$), in dependency on the weight percentage of β-CD is shown in Figure 5. With increasing amounts of β-CD, a larger number of cross-linking points and, therefore, a
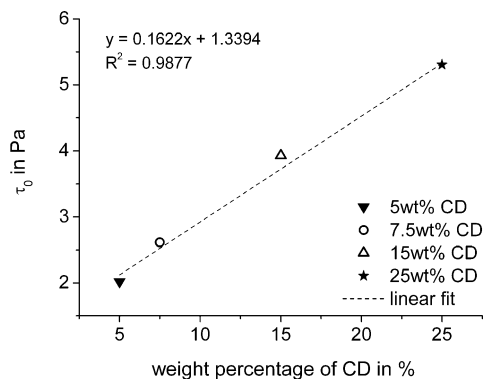
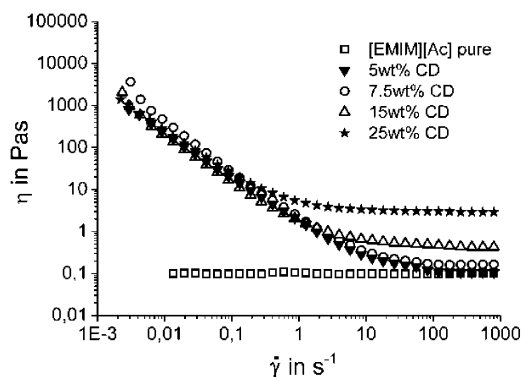**Figure 5.** Yield point, τ_0, as a function of β-CD weight percentage.

Figure 6. Viscosity curves of various β-CD/[EMIM][Ac] solutions in comparison to the applied shear rate at 23 °C.

Figure 7. Viscosity curves of various β-CD/[EMIM][Ac] solutions in comparison to the applied shear stress.

Figure 8. Complex oscillation viscosity, $|\eta^*|$, and shear viscosity, η, as a function of the angular frequency, ω, and the shear rate, $\dot{\gamma}$, respectively, exemplary for a 15 wt % solution of β-CD in [EMIM][Ac] at a shear stress of 0.5 Pa at 23 °C.

denser physical interconnected gel structure was obtained. An approximated linear correlation was found.

3.3. Rotational Measurements. The results of the shear viscosity in dependency of the shear rate $\dot{\gamma}$ for various β-CD/[EMIM][Ac] solutions are shown in Figure 6. For a better comparison, the rheological behavior of pure [EMIM][Ac] was evaluated, as well. As can be seen, the viscosity decreased with increasing shear rates over 3−4 decades for all β-CD solutions before η became constant, which is typical for shear-thinning substances. With increasing β-CD weight percentages, the plateau viscosities reached higher values. Such a shear thinning behavior derived from the degradation of the physical networks by increasing shear force until the viscosity showed a nearly Newtonian behavior. In the literature, it has already been described that dispersions of hematite in [C$_2$MIM][EtSO$_4$], hydrophobic silica nanoparticles in [BF$_4$] anion-based ILs, and dispersions of single-walled carbon nanotubes (SWCNTs) in [C$_4$mim][BF$_4$] show similar shear thinning.[17−19] In contrast, viscosity curves of pure [EMIM][Ac] showed Newtonian behavior over the whole range of shear rates (0.01−1000 s^{-1}).[20]

In Figure 7, the results of shear stress controlled viscosity curves are shown. At lower shear stress regions, scattering of viscosities was recorded. These irregularities can be allocated to the chosen measurement setup. At a critical shear stress value, an abrupt change occurred, and constant viscosity plateaus were reached. Therefore, slippage of the sample can be excluded, since no further shoulders or steps were observed during the transition from high to low viscosities.[21] The plateau values showed the same dependency on β-CD concentrations as those obtained in the shear rate controlled measurements shown in Figure 6.

3.4. Cox−Merz Rule. The empirical rule of Cox and Merz states that the complex oscillation viscosity, $|\eta^*|$, and the shear viscosity, η, agree for polymer melts and homogeneous solutions
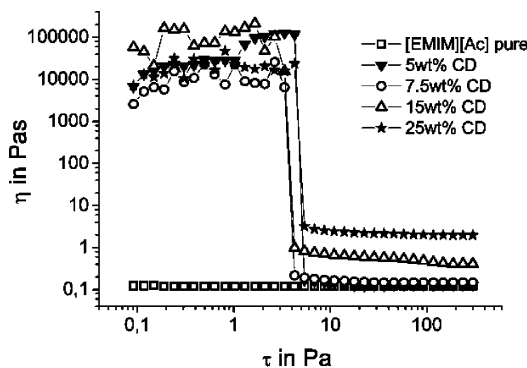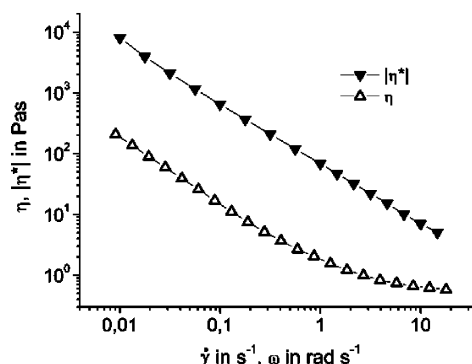
with no energetic interactions if they are plotted against angular frequency, ω, and shear rate, $\dot{\gamma}$ (eq 1), respectively.[22]

$$|\eta^*|(\omega) = \eta(\dot{\gamma}) \qquad (1)$$

As Kulicke et al. described, deviations from the Cox−Merz rule occur if a superstructure in the relaxed state is destroyed by the imposed shear force.[23] In that case, the complex viscosity, $|\eta^*|$, is higher than the shear viscosity, η. Figure 8 shows a corresponding plot of $|\eta^*|$, obtained from dynamic oscillatory shear measurements, and η for a 15 wt % solution of β-CD in [EMIM][Ac]. This plot confirms strong physical interactions as $|\eta^*|$ is more than a decade higher than η. Furthermore, the $|\eta^*|$ function rose to an infinitely high value, confirming a gel character and, therefore, form stability at rest.

3.5. Temperature Dependence and Flow Activation Energy. Okoturo and VanderNoot showed that the viscosity of pure ILs is drastically changed by variation of temperature.[24] Therefore, the influence of temperature on the shear-thinning behavior was studied for all weight percentages of β-CD. Figure 9 shows the temperature dependency of η of a 15 wt % β-CD/[EMIM][Ac] solution. In the region of lower shear rates, the viscosities proceeded independent of the temperature up to 50 °C. Obviously, the physical interactions in the network structure were dominating the hydrodynamic forces in the IL. In contrast to this, a significant decrease in the plateau viscosities could be observed for increasing temperatures. It appears that for higher shear rates, the physical interactions became less important, and the hydrodynamic properties of the IL were prevailing. At temperatures above 50 °C, a decrease in viscosity could already be observed at lower shear rates. This indicates that the gel
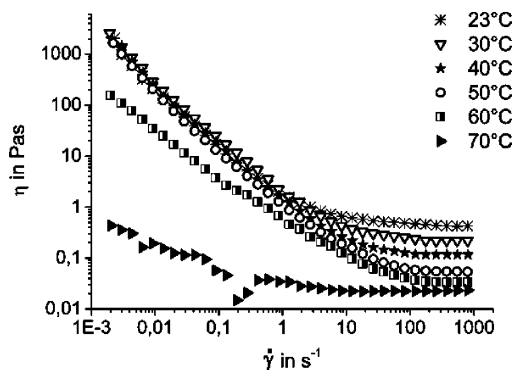
Figure 9. Temperature dependence of viscosities for 15 wt % β-CD in [EMIM][Ac].

TABLE 1: Dependency of Plateau Shear Viscosities (mPa's) and Flow Activation Energies for Solutions of β-CD in [EMIM][Ac] on Weight Percentage of β-CD and Temperature

wt % β-CD	23 °C	30 °C	40 °C	50 °C	E_η (kJ/mol)	R^2
0	99.6	52.9	29.4	18.3	49.19 ± 3.99	0.9806
5	106.5	62.4	34.0	23.2	45.06 ± 3.69	0.9802
7.5	163.6	104.5	59.1	31.8	45.94 ± 1.90	0.9949
15	440.3	223.2	117.3	55.4	59.73 ± 2.62	0.9942
25	2929	1542	554.3	180.7	82.19 ± 3.78	0.9937

structure is sensitive to high temperatures, and it can be assumed that for temperatures above 70 °C, the curves resemble the Newtonian behavior of pure [EMIM][Ac].

A common way to analyze the viscosity–temperature dependence for nonassociating electrolytes is to use the logarithmic form of the Arrhenius equation (eq 2),[24] where E_η is the activation energy for viscous flow, R is the universal gas constant, and η_∞ is the viscosity at infinite temperature.

$$\ln \eta = \ln \eta_\infty + \left(\frac{E_\eta}{RT}\right) \qquad (2)$$

Therefore, the values for the plateau viscosities were determined at higher shear rate regions between 23 and 50 °C (Table 1).

The results of the Arrhenius plots are shown in Figure 10 for all weight percentages of β-CD. The flow activation energies could be deduced from the slope of the linear fit of $\ln(\eta)$ versus inverse temperature and are presented in Table 1.
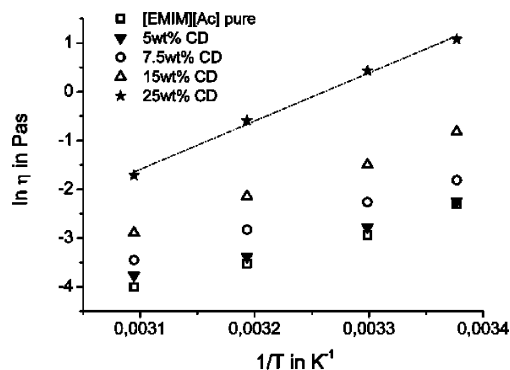

Figure 10. Arrhenius plot for β-CD/[EMIM][Ac] solutions at different weight percentages. The dashed line corresponds to the Arrhenius approximation.
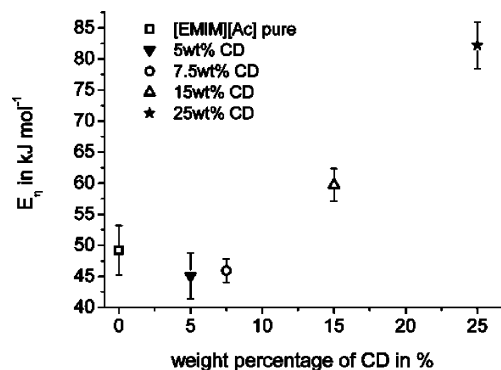

Figure 11. Flow activation energy as a function of β-CD weight percentage dissolved in [EMIM][Ac].

The E_η value for pure [EMIM][Ac] was in a good agreement with those already reported in the literature for similar ILs (e.g., $E_\eta = 49.33$ kJ mol^{-1} for 1-butyl-3-methyl imidazolium acetate ([BMIM][Ac]) or $E_\eta = 49$ kJ mol^{-1} and $E_\eta = 52$ kJ mol^{-1}, respectively, for [EMIM][Cl]).[25−27] As can be seen in Figure 11, E_η obtained for low β-CD percentages were slightly smaller than E_η of pure [EMIM][Ac] due to the disruption of ionic interactions in the IL. With increasing amounts of β-CD, a continuous increase in the activation energies could be observed. This behavior could be explained by the increase in the physical interactions between β-CD molecules and, therefore, stronger network structures. Since physical interactions of the glycopyranose units of β-CD in IL should be the same as for cellulose, the results for E_η were compared with those already reported by Budtova et al. for cellulose dissolved in ILs.[20] It was found that the values of E_η for microcrystalline cellulose (DP = 300) dissolved in [EMIM][Ac] were of the same magnitude as the results shown above and that the flow activation energies also increased with concentration.

Conclusion

The rheological behavior of β-CD in [EMIM][Ac] was systematically studied under rotational and oscillatory shear. It was found that even in low β-CD concentration, gel structures were formed. Oscillatory measurements showed an abrupt gel–sol transition at certain shear stress values, depending on β-CD weight percentages. These processes were both reproducible and reversible. The gel showed a frequency-independent behavior and a structural break-up at very small strains (1%). In addition, rotational shear experiments revealed the characteristics of gel-like systems with shear thinning behavior and plateau viscosities, depending on the amount of β-CD and the temperature. The comparison of the complex oscillatory viscosity and the shear viscosity according to Cox and Merz verified the existence of a three-dimensional physical network. Furthermore, the temperature dependency of the viscosity was investigated. It was shown that the β-CD/[EMIM][Ac] solutions were sensitive to temperatures above 50 °C. Using the logarithmic Arrhenius equation, a correlation between β-CD concentration and flow activation energy could be established. A systematic study involving the network structure of the system is in progress.

List of Symbols:

E_η	(kJ/mol) flow activation energy
f	(1/s) frequency
G'	(Pa) storage modulus
G''	(Pa) loss modulus

R	(J/Kmol)	gas constant
T	(K)	temperature
δ	(°)	phase shift angle
η	(Pa's)	shear viscosity
$|\eta^*|$	(Pa's)	complex viscosity
ω	(rad/s)	angular frequency
τ_0	(Pa)	yield point
$\dot{\gamma}$	(1/s)	shear rate

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