Soft Matter

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/softmatter

Compliance of the Stokes-Einstein Model and Breakdown of the Stokes-Einstein-Debye Model in Urea-based Supramolecular Polymer of High Viscosity

Jolanta Świergiel,*[a] **Laurent Bouteiller,**[b] **and Jan Jadżyn**[a]

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X
DOI: 10.1039/b000000x

The impedance spectroscopy was used for studies of the static and dynamic behavior of the electrical conductivity of the hydrogen-bonded supramolecular polymer of high viscosity. The experimental data are discussed in the frame of the Stokes-Einstein and Stokes-Einstein-Debye models. It was found that the ions translation movement is due to the normal Brownian diffusion, what reveals in a fulfillment of the Ohms law by the electric current and in a strictly exponential decay of the current after removing the electric stimulus. The dc conductivity dependence on the viscosity of the medium quite good fulfills the Stokes-Einstein model. An extension of the model, by including in it the conductivity relaxation time, is proposed in this paper. A breakdown of the Stokes-Einstein-Debye model reveals in the dipolar relaxation time relations to the viscosity and to the dc ionic conductivity. An importance of the C=O···H−N hydrogen bonds in that breakdown is discussed.

1 Introduction

Diffusional motions of molecules and ions are responsible for all fundamental dynamic processes occurring in molecular and macromolecular systems. In the case of molecular species it is the translational and rotational diffusion which correspond for the viscous flow and for the dielectric polarization, while the translational motion of ions is responsible for the electrical conductivity in liquid media. The diffusion processes stand for the fundamentals of the molecular physics of fluids and a significance of these processes extents from the technical aspects, as those based on ions activity in electrolytes, to the biological ones, as the osmosis or transdermal drug delivery. Hence, the nature of diffusional motions and the relationship between the microscopic and macroscopic quantities corresponding to these motions, are still a subject of intense studies both experimental and theoretical.[1,2]

The principal experimental methods which are used for investigations of the diffusional motions in liquids are based on recording of the relaxational processes related to electric field actions on a given system. On the microscopic level, two main effects can be induced when an electric field is applied to a liquid: an orientation of molecular dipoles (dielectric polarization) and an ordered flow of ions (electrical current). A way at which the system relaxes to the new (ordered) state, or, after removing the field - returns to the chaotic (normal) state, is totally controlled by the natural molecular motions occurring in the studied medium, so, the type of those motions can be recognized in experiment. In particular, after removing the electric field, a disappearance of the dipolar polarization and/or the electrical conductivity takes an exponential form (in the time domain) but only in the case when the dipolar rotation and/or the ions translation dynamics are of the normal Brownian diffusion type. An exponential decay of the dipolar polarization and the electrical current can be represented by the time constants (the relaxation times), τ_D and τ_σ, respectively. In the mostly used experimental set-ups an alternating electric field is applied to the cell filled with a liquid and as the frequency of the electric stimulus changes, one records the relaxational spectra.[3] The spectra can be presented as the dielectric $\varepsilon^*(\omega)$, the electric modulus $M^*(\omega)$, the impedance $Z^*(\omega)$ or the conductance $\sigma^*(\omega)$ spectra, depending on the goals of the studies ($\omega = 2\pi f$ denotes the angular frequency of the electric stimulus, f is the frequency in Hz). Then, in the frequency domain, the relaxation processes driven by the normal Brownian diffusion, manifest themselves as the simplest Debye-type relaxational spectrum.[4] Each deviation from that picture denotes a deviation of the molecular or ionic dynamics from the normal Brownian diffusion. It is important to realise that the mentioned above four complex quantities are alternative representation of the same macroscopic relaxation data and can be easily transformed to each other according to the scheme:

---

[a] *Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, PL-60-179 Poznań, Poland. E-mail: swiergiel@ifmpan.poznan.pl*
[b] *UPMC Université Paris 06, UMR 7610, Chimie des Polymères, F-7500335 Paris, France, and CNRS, UMR 7610, Chimie des Polymères, F-75005 Paris, France.*

$$\frac{1}{\varepsilon^{*}(\omega)} = j\omega C_0 Z^{*}(\omega) = M^{*}(\omega) = \frac{j\omega\varepsilon_0}{\sigma^{*}(\omega)} \qquad (1)$$

where $C_0 = k\varepsilon_0$ is the electric capacity of the empty measuring cell, the constant of the cell equals $k = S/l$, where S and l are the electrode surface and the distance between the electrodes, respectively, $\varepsilon_0 = 8.85$ pF/m is the permittivity of free space and $j = \sqrt{-1}$. A theoretical background of the use of different spectral representation in studies of ions and molecules diffusive processes and some examples of the studied complex liquids are presented in recent papers.[5–7]

The present paper concerns an important, from the theoretical and technical points of view, problem of translation and rotation Brownian diffusion in supramolecular polymeric medium of high viscosity.

The impressive progress which is observed in supramolecular chemistry, is related to a demand of novel polymeric materials of special properties.[8,9] Supramolecular polymers, in which the monomers are linked by highly directional secondary interactions, such as hydrogen bonds, metal coordination or charge-transfer, combine many essential and attractive features of conventional polymers with the reversibility originating from a relative low energy of the non-covalent interactions. In the most cases that energy does not surpass a few k_BT, k_B is the Boltzmann constant and T is the absolute temperature. The reversibility, which appears to be due to an efficiency of the thermal energy k_BT in competing with the hydrogen bonds energy, determines all essential properties of supramolecular ensembles - their structure and dynamics as well as the susceptibility on the external stimuli. Especially important are diffusion-controlled electric and dielectric properties, as they determine a usefulness of polymeric materials for rapidly expanding applications of the plastic electronics in various devices of the every-day uses.

sym-Disubstituted derivatives of the urea, (N,N'-dialkylureas, R-NH-CO-NH-R,) seem to be very promising compounds[10–16] for designing new supramolecular materials of some specific purposes, especially when the existence of linear polymeric chains is desired. That type of polymeric entities are formed in solutions of dialkylureas, which are the solids at room temperature. N,N'-di(2-ethylhexylurea (EHU), R =$CH_2CH(C_4H_9)C_2H_5$, the subject of our present studies, is a rare exception: at the room temperature, it does not crystallize and remains a liquid of high viscosity.[17]

Due to *trans*-conformation of the ureide group, –NH.CO.NH–, and its proton-donor and proton-acceptor abilities, a strong unidirectional self-association develops in dialkylureas solutions due to the bifurcated C=O···H−N hydrogen bonds formation between the monomers.[18] The reversible supramolecular chains formed are in the dynamic equilibrium with the non-linked molecules, as sketched in Figure 1. Among the physical properties of such hydrogen-bonded linear structures, the electrical conductivity seems to be of a great interest.

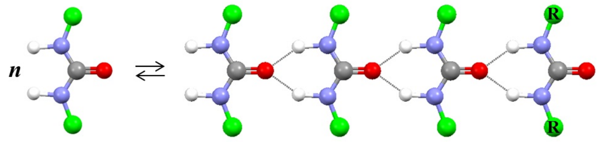


Fig. 1 Sketch presenting an equilibrium between the reversible supramolecular polymer chain formed by hydrogen-bonded N,N'-disubstituted urea molecules and the free monomers. The equilibrium constant of that reaction depends on the result of a competition between the thermal energy k_BT and the energy of C=O···H−N hydrogen bonds.

In recent paper,[19] we have presented the results of the dielectric relaxation studies performed for neat EHU and its solutions in non-polar solvent. Unexpectedly, the simplest dipolar relaxation process (the Debye-type spectra) was recorded for the concentrated solutions, included the neat EHU, i.e. for apparently the most structurally complex systems. In particular, it was roughly estimated the mean size of that fragments of EHU polymers which reveal in the dielectric relaxation spectrum. That part of the polymers is composed of about five hydrogen-bonded EHU molecules. The dipolar relaxation picture recorded in our experiments quite well agreed with the theoretical predictions presented by Stukalin and Freed.[20] In particular, it was shown that the concentration evolution of the dielectric response of hydrogen-bonded supramolecular polymers formed by EHU in non-polar medium well corresponds to the self-association model evolution, from the simplest model of the frozen (unbreakable) chains in diluted solutions to the monomer-mediated and the scission-recombination models in concentrated solutions, including neat EHU.

It seems to be important our finding that in the concentrated solutions and neat EHU, the activation energy for the dipolar reorientation presents the value of about 60 kJ/mol (14 kcal/mol), which corresponds to the energy required for interruption of two C=O···H−N hydrogen bonds.

The present paper concerns mainly the static and dynamic behavior of the translational diffusion of ions immersed in a highly viscous medium formed by the self-associated EHU molecules. The obtained results on the electrical conductivity and its relaxation, together with the results previously obtained[19] for the diffusional rotational dynamics of the dipolar species immersed in the same as the ions medium, will be discussed in the frame of the Stokes-Einstein or the Stokes-Einstein-Debye models.[4,21–25] The studied system was not doped with any electrolyte, i.e. the conductivity background was investigated. There are two circumstances which make such studies valuable. First of all, it is a low ions concentration which efficiently reduces the ion-ion interactions, so, one can use the simple models which neglect these interactions. Secondly, in the strongly hydrogen-bonded systems, the electrical conductivity may also result from the proton translocation across the intermolecular hydrogen bonds.[26,27] The effect can be expected mainly for the cases when the chain-like multimolecular entities are formed. The electric conductivity in such hydrogen-bonded liquids should exhibit some correlations with the dynamics of the H-bonds, as the process of proton release requires the breaking of the bond. After breaking, the molecule in its diffusional motion, can reform hydrogen bonding with another molecular partner.

As it was shown in some papers,[3,5] among the above listed four complex electrical quantities which can be used for description of the experimental frequency dependence of several properties of dielectric materials placed in an external electric field, only the impedance and the electric modulus show the relaxational behavior with the time constant describing the relaxation of the ionic current, τ_σ. As the impedance spectra contain also explicitly the direct current conductivity (σ_{DC}) of the studied system, the usefulness of that formalism in analysis of the static and dynamic conductivity of EHU is obvious.

2 Experimental Section

2.1 Materials

The studied supramolecular polymer is N,N'-di(2-ethylhexyl)urea (EHU), R-NH-CO-NH-R, R=$CH_2CH(C_4H_9)C_2H_5$. Figure 2 presents the chemical structure of the studied compound. Synthesis and purification of EHU were described previously.[11,28]

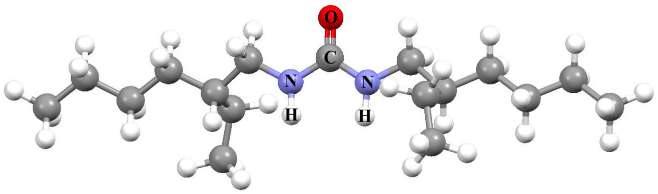


Fig. 2 Chemical structure of N,N'-di(2-ethylhexyl)urea.

2.2 Characterization

The impedance spectra were recorded with the use of an HP 4194A impedance/gain phase analyzer in the frequency range from 500 Hz to 100 MHz. A measuring capacitor consisted of three plane electrodes: one central and two grounded on each side, with a distance between them of about 0.2 mm. Electrical heating of high performance with the use of a Scientific Instruments temperature controller, model 9700, assured very good temperature stabilization (at milikelvin level). Such equipment allows one to determine the impedance with an uncertainty less than 1%. The details on the experimental set-up used are described previously.[19]

3 Result and Discussion

Figure 3 presents, as an example, the real (a) and imaginary (b) parts of the impedance spectra $Z^*(\omega) = Z'(\omega) + jZ''(\omega)$ recorded for neat EHU, at different temperatures. According to equation 1, these spectra are related to the dielectric spectra, which were analyzed in our previous paper,[19] through a simple transformation $1/\varepsilon^*(\omega) = j\omega C_0 Z^*(\omega)$. In Figure 4 the spectra are presented in the complex plane (Z'', Z').

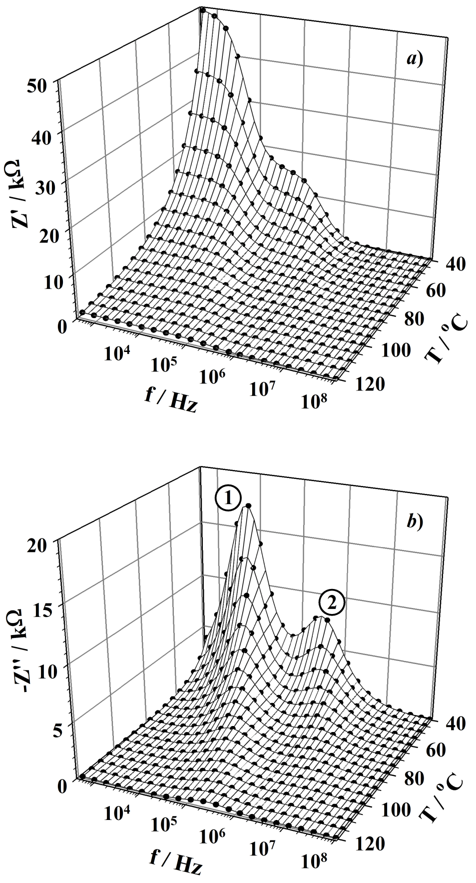


Fig. 3 The real (a) and imaginary (b) parts of the impedance spectra recorded for neat EHU, at different temperatures. The bands correspond to the ionic current (**1**) and the displacement current (**2**). The solid lines represent the best fit of two Debye-type equations to the experimental data (points). The ionic conductivity relaxation spectrum (**1**) is described with equations (2) and (3).

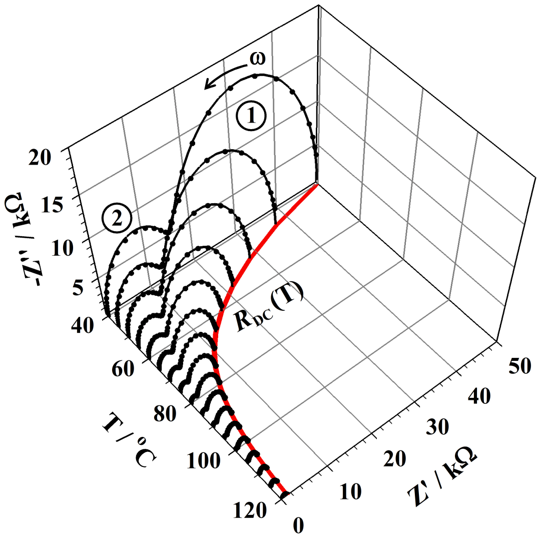


Fig. 4 The impedance spectra from Figure 3 presented in the complex plane. R_{DC} denotes the dc resistivity of the sample. Direction of the frequency increase of the electric stimulus (ω), is marked in the figure.

As the studied conducting molecular system exhibits the reorientational dipolar relaxation within the frequency range of the used probing field,[19] the impedance spectrum is composed of two bands related to the two electric currents occurring in such type of systems.[7] The low-frequency band (**1**) represents the relaxation of the ionic current flowing through the sample placed between the electrodes of the measuring cell. That part of the impedance spectrum is a subject of our interest. The high-frequency band (**2**) corresponds to the relaxational changes of the electric charge density on surfaces of the cell electrodes, caused by the dipolar reorientation relaxation occurring in the system. The current related to band (**2**), i.e. the displacement current, reflects the electrons movement in the external circuit supplying the measuring cell and it will be not discussed in this paper.

The numerical analysis have shown that the two bands appearing in the impedance spectrum of EHU, as presented in Figure 5, are both of the Debye-type in the whole temperature range used. So, in the complex plane the two bands present two semi-circles with centers placed on the real axis of the impedance, as depicted in Figure 5b.

As shown in a recent paper,[5] the equations for the real and imaginary parts of the impedance related to the band (**1**), have the following form:

$$Z'(\omega) = \frac{R_{\mathrm{DC}}}{1+\omega^2\tau_\sigma^2}, \tag{2}$$

$$Z''(\omega) = -\frac{R_{\mathrm{DC}}\,\omega\tau_\sigma}{1+\omega^2\tau_\sigma^2}, \tag{3}$$

where the conductivity relaxation time is equal to:

$$\tau_\sigma = \frac{\varepsilon_0\varepsilon_s}{\sigma_{\mathrm{DC}}}. \tag{4}$$

Fitting of equations 2 and 3 to the band (**1**) of the impedance spectra yields the values of two quantities which are fundamental in our investigations: *i*) the dc resistivity of the sample, R_{DC} ,which usually is expressed as the dc conductivity, $\sigma_{DC} = 1/kR_{DC}$, where k is the constant of the measuring cell mentioned above and *ii*) the relaxation time of the ionic current, τ_σ, which, according to equation 4, is proportional to the ratio of the static permittivity (ε_S) and the static (dc) electrical conductivity (σ_{DC}) of the system under investigation. The solid lines in Figures 3-5 show how perfectly two Debye-type functions reproduce the experimental impedance spectra of EHU.

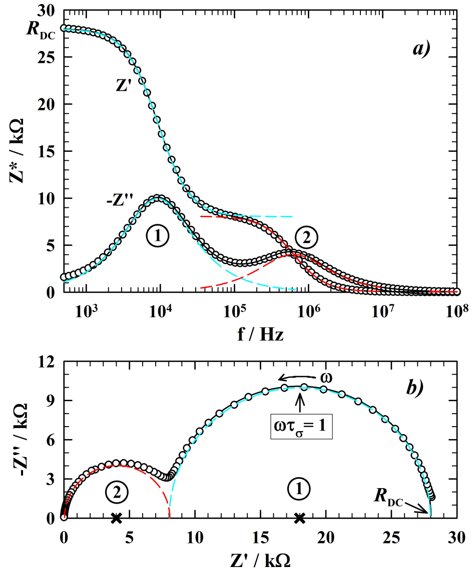


Fig. 5 An example of the resolution of the impedance spectrum recorded for EHU at 50°C into two Debye-type bands corresponding to the ionic current (**1**) and the displacement current (**2**).

The first conclusion arising from the results presented above concerns the dynamics of charge carriers in EHU. A strictly Debye-type behavior of the impedance spectrum (**1**), for which an equivalent picture in the time domain is an exponential conductivity decay when the electric field suddenly disappears, reveal the normal Brownian translational diffusion as a natural dynamics of the ions immersed in supramolecular medium formed by EHU molecules. From the macroscopic point of view that conclusion is identical with the statement that the ionic current flowing through that supramolecular system perfectly fulfills the Ohm's law.[29]

The quantities σ_{DC} and τ_σ determined in our experiment are the functions of two parameters: the viscosity of the medium and the temperature. As we mentioned before, EHU is a liquid of high viscosity,[19] which varies from 4 Pa·s, at 30°C (for comparison, it is roughly the viscosity of fresh cold honey) to 0.2 Pa·s, at 90°C. In Figure 6 are presented the dependences of the above mentioned quantities related to the electrical conductivity in EHU versus the viscosity of the medium. Besides, in the picture the viscosity dependence of the dipolar relaxation time measured in EHU,[19] is also shown.

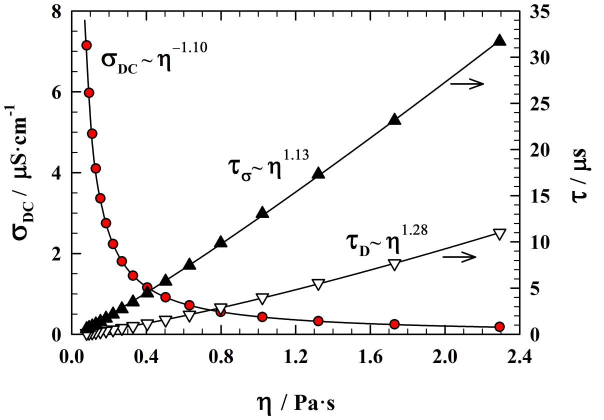


Fig. 6 Experimental dependences of the dc electrical conductivity σ_{DC}, the conductivity relaxation time τ_σ and the dipolar relaxation time τ_D,[19] on the viscosity of EHU. The solid lines are the best fits of the function of the $y \propto x^m$ type to the experimental data (points).

As can be seen in Figure 6, with increasing viscosity of the medium, the dc conductivity decreases in a way very close to be exponential, whereas both relaxation times show an inverse behavior - an increase close to a linear dependence. Now, it will be interesting to confront these experimental results with predictions of the Stokes-Einstein and Stokes-Einstein-Debye models which relate the diffusion coefficients, expressed in the quasi-macroscopic hydrodynamic approximation taken from the Stokes theory,[30] to the microscopic quantities being a subject of our present consideration. Namely, the Stokes-Einstein model, with the use of the Nernst-Einstein equation,[31] links the translation diffusion coefficient (D_{tr}) with the ionic dc conductivity (σ_{DC}) in the following way:

$$D_{tr} = \frac{k_{\mathrm{B}}T}{6\pi\eta r_{ion}} \propto T\sigma_{\mathrm{DC}}, \tag{5}$$

The Stokes-Einstein-Debye model, in turn, links the rotational diffusion coefficient (D_{rot}) to the dielectric relaxation time (τ_D) for the molecular dipoles reorientations:

$$D_{rot} = \frac{k_{\mathrm{B}}T}{8\pi\eta r_{dip}^3} \propto \frac{1}{\tau_{\mathrm{D}}}. \tag{6}$$

In these models the translating ion or rotating dipolar molecule are represented by a sphere of radius r_{ion} or r_{dip}, respectively, which are moving in a continuum medium of the shear viscosity η.

The Stokes-Einstein model (5) predicts a linear dependence of $T\sigma_{DC}$ vs η/T with a slope of -1, in log-log scale. Figure 6 shows that in the studied medium of high viscosity, the prediction of that model is fulfilled nearly perfectly. Next, the Stokes-Einstein-Debye model (6) predicts a linear dependence of τ_D vs η/T with a slope equal to 1. Figure 7 shows that the prediction of the Stokes-Einstein-Debye model is fulfilled significantly worse than it was in the case of the Stokes-Einstein model.

Unfortunately, there is no model predicting behavior of the conductivity relaxation time τ_σ on the medium viscosity. Still, taking into account similarities in the experimental behavior of τ_σ and τ_D, as it is shown in Figure 6, and the relation (4), we propose, in analogy to the Stokes-Einstein-Debye model (6), the following extension of equation (5):

$$D_{tr} = \frac{k_B T}{6\pi\eta r_{ion}} \propto \frac{1}{\tau_\sigma}. \tag{7}$$

The data presented in Figure 7 show that the τ_σ vs. η/T dependence fulfils the prediction of such formulated extension of the Stokes-Einstein model even better than that of τ_D in Stokes-Einstein-Debye model.

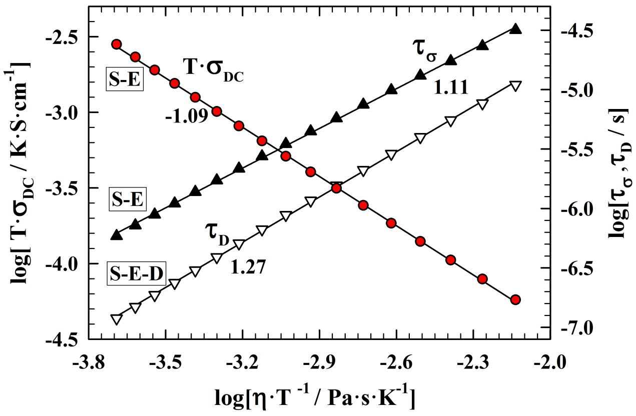


Fig. 7 Experimental dependences of the dc electrical conductivity, its relaxation time and the dipolar relaxation time on the viscosity of supramolecular polymer EHU as an illustration of the Stokes-Einstein (S-E) and Stokes-Einstein-Debye (S-E-D) models (equations 5-7). The slopes of the lines are depicted in the figure.

It seems to be interesting to compare the slopes of the dependences presented in Figure 6 and the corresponding exponents from Figure 6. One can notice practically no difference between these quantities, so, it shows that in the highly viscous systems the temperature is not the main factor which determines the basic dynamic properties of the system but that is the viscosity of the medium. In the literature the most often that simpler presentation, as in Figure 6, is used and rather the dependence $\sigma_{DC} \propto \eta^{-1}$ is taken as the criterion of fulfilment of the Stokes-Einstein model than the $T\sigma_{DC} \propto \eta^{-1}$ dependence.

A similar simplification is applied in presentation of the dependence

$$T\sigma_{\mathrm{DC}} \cdot \tau_{\mathrm{D}} = const, \tag{8}$$

resulting from comparison of equations 5 and 6. The most often rather

$$\sigma_{\mathrm{DC}} \cdot \tau_{\mathrm{D}} = const \tag{9}$$

dependence is discussed in the literature and its fulfilment is considered as a correctness of the Stokes-Einstein-Debye model for a given system. Indeed, as shown in Figure 8, the slopes corresponding to these two dependences are quite close to each other, however, the slope of the $T\sigma_{DC}$ vs τ_D dependence is distinctly closer to the value predicted by the models.

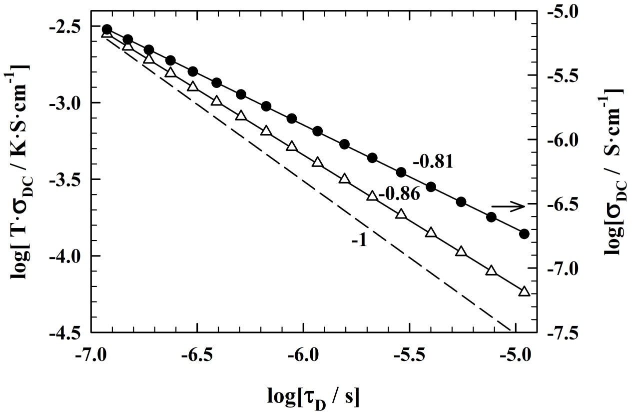


Fig. 8 Two used approximations in the electrical conductivity vs. the dipolar relaxation time dependence related to the Stokes-Einstein-Debye model: $T\sigma_{DC} \propto (\tau_D)^{-0.86}$ and $\sigma_{DC} \propto (\tau_D)^{-0.81}$. The dashed line represents the prediction of the model.

A quite good fulfillment of the Stokes-Einstein model allows one to formulate the following conclusions, *i*) the charge carriers existing in the studied supramolecular medium can be well approximated by the entities of a sherical shape and, *ii*) the dynamics of these carriers, related both to the electrical current and to its relaxation, is well described by the hydrodynamic model of particles moving in a fluid of shear viscosity η. On the other side, a breakdown of the Stokes-Einstein-Debye model, what manifests itself as a quite meaningful deviation from unity of the exponent in relation $T\sigma_{DC} \propto (\tau_D)^{-0.86}$ [or $\sigma_{DC} \propto (\tau_D)^{-0.81}$], may results from the evidently non-spherical shape of the rotating dipolar entities, as it was discussed in the previous paper.[19] Anyway, the similar values of that exponent have been obtained for many various molecular systems, and in such the cases, the model is often labelled as the fractional Stokes-Einstein-Debye model.[32–39]

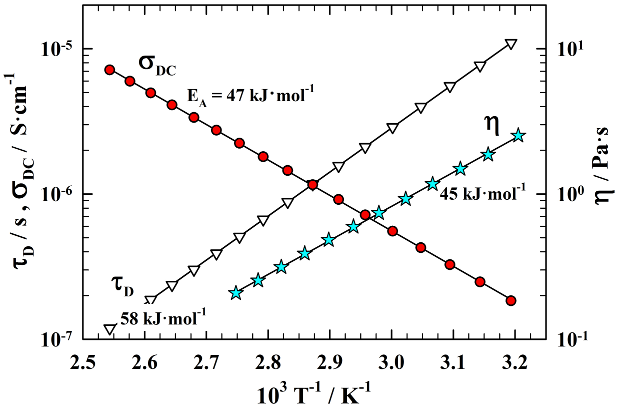


Fig. 9 Arrhenius plot of the dc conductivity measured for neat supramolecular EHU. The dependences for dipolar reorientation relaxation time and for the shear viscosity of EHU are added for comparison. The values of the activation energy are given in the picture.

Now, let us consider the temperature behavior of the quantities related to the electric and dielectric dynamic properties of EHU. In spite of the natural linkage between temperature and viscosity, what unables one to separate the contribution arising from these two quantities on the physical properties of a given molecular system, the thermal activation energies can be a valuable data in the interpretation of the dynamic behavior of molecular systems. Figure 9 presents, in a form of the Arrhenius plots, the temperature dependences of the dc electrical conductivity and the dielectric relaxation time measured for the supramolecular EHU. In the figure is also presented the plot for the viscosity of EHU. The results presented in Figure 9 confirm the previously formulated conclusions on the role of the medium viscosity in the process of the ionic conductivity in EHU: the activation energy of σ_{DC} is practically equal to that of the viscosity. On the other side, as it was discussed in details in a previous paper,[19] the activation energy of the dipolar relaxation time (τ_D) is fully determined by the energy of C=O···H−N hydrogen bonds. In particular, it has been shown that breaking of two hydrogen bonds (the energy of about 60 kJ/mol) is required for the reorientation of the formed dipolar entity being a part of long polymeric chain. The Arrhenius activation energy of τ_D is quite close to that 60 kJ/mol.[19]

So, there is an essential difference between the two diffusional processes occurring in the studied supramolecular polymer, namely, the conductivity which is fully controlled by the bulk viscosity of the medium, and the dipolar relaxation, which is controlled by the energy of hydrogen bonds linking the basic units of the supramolecular polymer.

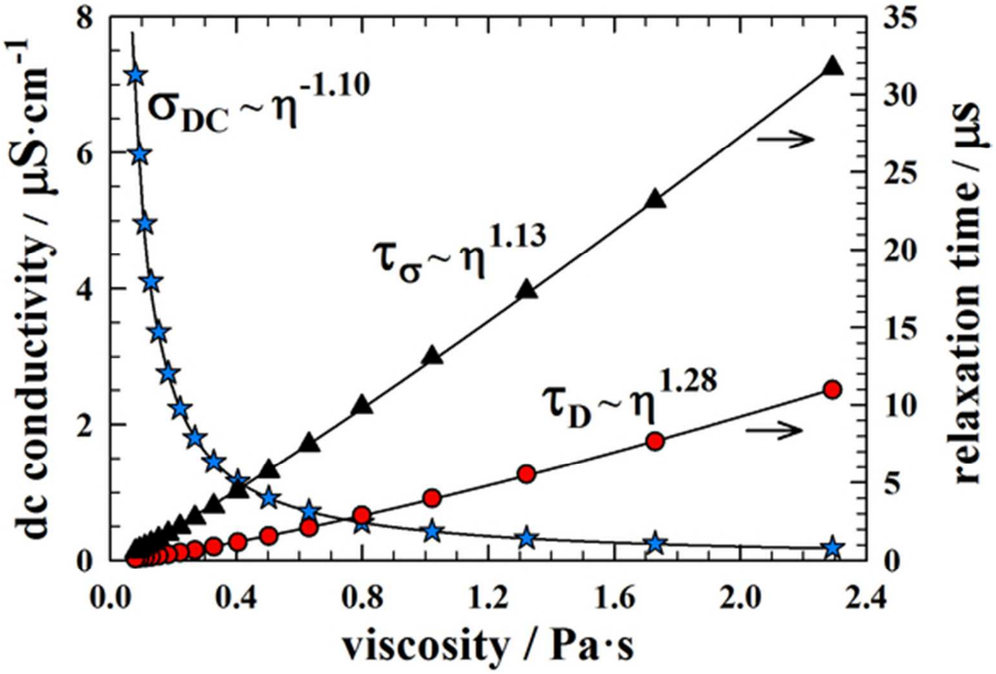
That difference seems to be the reason of different behavior of the Stokes-Einstein and Stokes-Einstein-Debye models in confrontation with the experimental data obtained in the present studies.

4 Conclusions

The results presented in this paper have shown that even in the complex medium of a high viscosity, the relaxational processes, both translational and rotational, can exhibit the simplest possible behavior. That behavior, in its intuitive form presents an exponential decay of the ionic current and the dielectric polarization when the electric stimulus disappears abruptly. It seems to be important that the thermal activation energy of the conductivity is similar to the viscosity activation energy which points out rather for the ions impurities as the charge carriers occurring in the polymeric EHU. It is important to realize that the highly polar EHU (the permittivity is equal to about 46 at 40°C) is a medium very conducive to ionic dissociation of any electrolytic impurities existing in that medium. However, the results presented in this paper cannot definitely decide on the nature of the charge carriers in such strongly hydrogen-bonded system as studied urea-based supramolecular polymer. An empirical extension of the Stokes-Einstein model by including the conductivity relaxation time, as proposed in equation 7 of the present paper, makes that model open to correlations of the macroscopic quantities, such as the viscosity of the medium, to the conductivity dynamics, similarly to the Stokes-Einstein-Debye model which includes the reorientational dynamics of dipolar molecules.

References

1 H. J. V. Tyrrell and K. R. Harris, *Diffusion in Liquids*, Butterworths, Sevenoaks, 1984.
2 A. N. Borodin and P. Salminen, *Handbook of Brownian motion. Facts and formulae*, Birkhäuser Verlag, Basel, 2nd edn, 2002.
3 E. Barsoukov and J. R. Macdonald, *Impedance Spectroscopy: Theory Experiment & Applications*, John Wiley & Sons, London, 2nd edn, 2005.
4 P. Debye, *Polar Molecules*, Chemical Catalog Co., New York, 1929.
5 J. Świergiel and J. Jadżyn, *Ind. Eng. Chem. Res.*, 2011, **50**, 11935–11941.
6 J. Jadżyn and J. Świergiel, *Ind. Eng. Chem. Res.*, 2012, **51**, 807–813.
7 J. Świergiel, L. Bouteiller and J. Jadżyn, *Ind. Eng. Chem. Res.*, 2013, **52**, 11974–11979.
8 J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim, 1995.
9 A. Ciferri, *Supramolecular Polymers*, Taylor & Francis, Boca Raton, 2nd edn, 2005.
10 L. Bouteiller, *Adv. Polym. Sci.*, 2007, **207**, 79–112.
11 F. Lortie, S. Boileau and L. Bouteiller, *Chem. Eur. J.*, 2003, **9**, 3008–3014.
12 F. Lortie, S. Boileau, L. Bouteiller, C. Chassenieux and F. Lauprêtre, *Macromolecules*, 2005, **38**, 5283–5287.
13 S. Abed, S. Boileau and L. Bouteiller, *Macromolecules*, 2000, **33**, 8479–8487.
14 A. Arnaud and L. Bouteiller, *Langmuir*, 2004, **20**, 6858–6863.
15 L. Bouteiller, O. Colombani, F. Lortie and P. Terech, *J. Am. Chem. Soc.*, 2005, **127**, 8893–8898.
16 F. Vonau, D. Aubel, L. Bouteiller, G. Reiter and L. Simon, *Phys. Rev. Lett.*, 2007, **99**, 086103.
17 N. Lou, Y. Wang, X. Li, H. Li, P. Wang, C. Wesdemiotis, A. P. Sokolov and H. Xiong, *Macromolecules*, 2013, **46**, 3160–3166.
18 J. Jadżyn, M. Stockhausen and B. Żywucki, *J. Phys. Chem.*, 1987, **91**, 754–757.
19 J. Świergiel, L. Bouteiller and J. Jadżyn, *Macromolecules*, 2014, **47**, 2464–2470.
20 E. B. Stukalin and K. F. Freed, *J. Chem. Phys.*, 2006, **125**, 184905.
21 A. Einstein, *Investigations on the Theory of the Brownian Motion*, Dover, New York, 1956.
22 R. A. L. Jones, *Soft Condensed Matter*, Oxford University Press, Oxford, 2002.
23 G. M. Mazza, N. Giovambattista, H. E. Stanley and F. W. Starr, *Phys. Rev. E*, 2007, **76**, 031203.
24 G. P. Johari and O. Andersson, *J. Chem. Phys.*, 2006, **125**, 124501.
25 G. Power, J. K. Vij and G. P. Johari, *J. Phys. Chem. B*, 2007, **111**, 11201–11208.
26 D. Marx, *ChemPhysChem*, 2006, **7**, 1848–1870.
27 R. Vuilleumier and D. Borgis, *Nature Chemistry*, 2012, **4**, 432–433.
28 S. Boileau, L. Bouteiller, F. Lauprêtre and F. Lortie, *New J. Chem.*, 2000, **24**, 845–848.
29 C. J. F. Böttcher and P. Bordewijk, *Theory of Electric Polarization: Dielectric in Time-Dependent Fields*, Elsevier, Amsterdam, 1992, vol. 2.
30 G. Stokes, *Trans. Cambridge Philos. Soc.*, 1856, **9**, 5.
31 J. P. Hansen and J. R. McDonald, *Theory of Simple Liquids*, Academic Press, New York, 1991, p. 399.
32 A. Voronel, E. Veliyulin, V. S. Machavariani, A. Kisliuk and D. Quitmann, *Phys. Rev. Lett.*, 1998, **80**, 2630–2633.
33 S. R. Becker, P. H. Poole and F. W. Starr, *Phys. Rev. Lett*, 2006, **97**, 055901.
34 S. H. Bielowka, T. Psurek, J. Ziolo and M. Paluch, *Phys. Rev. E*, 2001, **63**, 062301.
35 D. A. Turton and K. Wynne, *J. Phys. Chem. B*, 2014, **118**, 4600–4604.
36 K. R. Harris, *J. Chem. Phys.*, 2009, **131**, 054503.
37 K. L. Ngai, *Philos. Mag.*, 1999, **79**, 1783–1797.
38 P. P. Jose, D. Chakrabarti and B. Bagchi, *Phys. Rev. E*, 2006, **73**, 031705.
39 J. Świergiel and J. Jadżyn, *Phys. Chem. Chem. Phys.*, 2011, **13**, 3911–3916.



Viscosity dependences of dc conductivity, conductivity relaxation time and dipolar relaxation time, measured for neat hydrogen-bonded supramolecular polymer N,N′-di(2-ethylhexyl)urea (EHU).
49x36mm (300 x 300 DPI)