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The competitive interactions between the anion-receptor, anions and neutral solvent species

A. Plewa-Marczewska, M. Bukat, M. Kalita, A. Sołgała, D. Pourjafarinokande, S. Ketabi, H. Emani, A. Piśniak, M. Siekierski*

Polymer Ionics Research Group, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

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ABSTRACT

In this article, studies on coordinative properties of 5,11,17,23-tetra-*p*-*tert*-butyl-25,27-bis(*N*-*p*-nitrophenylureido-butoxy)-26,28-dipropoxycalix[4]arene (Cx2) are presented. Since this anion-receptor was previously used as an additive to solid polymer electrolytes, the correlation of the data presented here and the role of anion-receptors in this type of electrolytes is discussed. The formation constants of salt–receptor complexes and receptor self-complexation (dimer formation) are estimated in the solution in the non-interacting solvent using ^{1}H and ^{19}F NMR titration. Independently, the affinity of the Cx2 to low molecular weight analogs of PEO and some other organic solvents in this system was tested using the same technique. The estimated values of the formation constants are used in the discussion the role of the anion-receptor in the changes of concentration of ions, ionic agglomerates and complexes of Cx2 in the system comprising salt, solid or liquid matrix and anion-receptor.

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1. Introduction

Despite commercial success, batteries containing lithium still need further development to fulfill market expectations. The main goals to be reached are miniaturization of the batteries, enhancement of their work safety, energy density higher and stable in time as well as life length improvement [1–3]. Some of the above mentioned parameters can be enhanced when (i) transport of the lithium cation in the electrolyte is faster, (ii) resistance of the electrode–electrolyte interface is lower. This problem arises into particular importance when an application of solid polymer electrolytes (SPEs) is taken into consideration. In this case conductivity of the lithium cation is acceptable for application in the lithium battery only in elevated temperatures. Moreover, the lithium transference number in such systems is also low in majority of the systems studied it does not exceed 0.5; usually it is the range of 0.2–0.3 (e.g. [4–7]). These phenomena result in weak performance of the battery and also in a faster growth of the passive layer on the electrode–electrolyte interface. Hence, every approach leading to an increase of the lithium transference number and conductance of the lithium cations in the electrolyte should result in both better stability of the electrode–electrolyte interfaces as well as lower and stable in time inner resistance of the lithium cell.

Several methods of improving cationic conductivity have been applied, unfortunately all of the approaches presented here lead to an increase of the σ_{Li+} and t_{Li+} but none of them has given an ultimate solution until now. The application of the polyelectrolytes in which the anion is part of the polymeric chain and, thus, is fully immobilized led to lowering of the overall conductivity by more than one order of magnitude. Thus, the lithium cation conductivity was lowered in this case. Moreover, several polyelectrolytes, when used in the lithium cell, exhibited fast degradation due to their poor resistivity against oxidation and reduction. This problem was present not only when the cell was cycled but also when it was stored [8–11]. Similar problems with resistivity increase occurred when anionic conductivity was lowered by the application of heavy anions. Other problems occurred when strong Lewis acids such as $AlCl_3$, $SnCl_4$, BF_3, etc. were tested as additives (e.g. [12–14]). In this approach, anions should be partially immobilized due to the formation of anion–Lewis acid complexes. Unfortunately, additives belonging to this class of compounds can also catalyze both the depolymerization of the solid polymeric matrix and the degradation (e.g. polymerization) of the typical solvent used in liquid electrolytes. Another option of this approach is based on the application of weaker Lewis acids such as boranes [15,16], borates [17–19], boronates, trialkylaluminum, or trialkoxyaluminum. In these cases, the Lewis acidity of the anion-receptor is low enough to prevent matrix degradation and can be high enough to form the anion–Lewis acid complex. Indeed, for several systems, lithium transference number enhancement after the receptor

* Corresponding author. Tel.: +48 601 26 26 00; fax: +48 22 628 27 41.
E-mail address: alex@ch.pw.edu.pl (M. Siekierski).

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addition was observed. Another positive effect of the anion-receptor addition was stabilizing the passive layer on the anode–electrolyte interface due to presence of the $LiBO_2$ in this layer (originating from the decomposition of the compounds containing boron) and due to dissolving of the LiF being one of the constituents of this layer (due to the fact that Li[AF] complex salt, where A is an anion-receptor is, contrary to the LiF, soluble in majority of the aprotic solvents). A similar effect was obtained when aza-ethers were added to the solutions. In fact, aza-ethers can also form complexes with the anions. In this case, the only difference is that the receptor binds anion not by a by Lewis acid–Lewis base bond but by a mix of the hydrogen bond-like and ion–dipole interactions [20–23].

In recent years, an alternative strategy was introduced basing on the addition to the electrolyte of anion-receptors interacting with the anion via hydrogen bond. It was proved that also this type of anion-receptors, at least in the case of a solid, PEO-based system, can be applied in order to enhance conductivity and the transference number of the lithium cations [24–27]. Interestingly, the results showing improvement in lithium conductivity were not confirmed by measurements of the same parameters for liquid poly(ethylene glycol) dimethyl ether ($M_w = 500\,g\,mol^{-1}$) PEODME–salt–receptor systems [28]. PEODME is often used as a model solvent due to its coordination and dielectric properties very similar to those of PEO. In order to study the phenomena responsible for this discrepancy, IR, Raman and various nuclei NMR spectroscopy studies were conducted. It was shown that anion-receptors, which were previously studied in the SPEs, can interact not only with the anion but also with the cation and molecules of various solvents including glymes. Moreover, it was proved that the affinity of the receptor to the $CH_3O(CH_2CH_2O)_nCH_3$ molecule changes with the number of the oxyethylene units in the oligomeric chain. These observations are important not only from the point of view of the studies of glyme-based model systems but also, due to increasing interest in "small molecule"-salt complex based "pseudopolymierc" electrolytes [29–31] comprising of well-defined stoichiometric complexes of lithium salts and oligoethers.

To built a complete image of the interaction in the system of interest another phenomenon must be taken into consideration. The formation of physically bonded receptor agglomerates inactive in anion coordination (e.g. dimers) can be observed in the system [32,33]. Unfortunately, most of data collected, especially when originated from vibrational spectroscopy experiments, were qualitative or at most semi-quantitative. In this study, we try to estimate anion-receptor and receptor–neutral solvent complex formation constants as well as receptor dimer formation constants from multiple nuclei NMR data in order to present the quantitative description of the equilibriums present, firstly, in the model system containing anion-receptor and, secondly, in the respective polymeric electrolyte.

The NMR data are usually used for estimation of various constants using a procedure named "NMR titration" [34]. In this procedure, a series of the measurements is performed for fixed concentration of one specimen (host) while the concentration of another one (guest) is varied[1]. Such a procedure was used first to estimate the values of complex formation between molecules, e.g. between hexamethylbenzene and 1, 3, 5-trinitrobenzene [35–38], benzene and caffeine [39], dimethyltin dichloride and pyridine [40], cyclohexanones and cyclohexanols [41] as well as between more complicated entities [42,43]. In the last two decades, this method was also successfully applied in the studies of the anion-receptor–anion coordination in nonaqueous solutions (usually $CHCl_3$, DMSO, CH_3CN, CH_2Cl_2 or their mixtures were used as the solvents) (e.g. [44–51]). Usually in these studies salts containing bulky organic cation were used and the problems of residual water presence in the system studied (being an important factor for salt solubility) as well as the question of the degree of the salt dissociation (which can be also related to the water issue) have not been addressed. In several other publications, the values corresponding to the interactions of the neutral specimen and the anion-receptor were also presented (e.g. [52]), however, these results were discussed rather in terms of receptor selectivity. In another study the ^{13}C chemical shift of the organic carbonate type solvents was affected by the interaction with the $LiPF_6$ salt [53]. In our case a similar method based on NMR titration will be used in order to study the formation of complexes of anion-receptors with electrically neutral solvent molecules containing polar moieties, namely, organic carbonates and various dimethyl ethers of oxyethylene oligomers. The molecules studied are used in the majority of electrolytes dedicated for lithium batteries.

The results obtained will be used in comparison with previous results published by our group which prove that the anion-receptor can change the conductivity and lithium transference number both in liquid oligomeric [24] and solid electrolyte [54]. We have proved previously that the direct method of the estimation of majority of the anion-receptor complex formation constants in 1,2-dimethoxyethane by means of NMR techniques [55,56] cannot be successfully applied. The possible explanation for the fault observed can be attributed to the formation of the receptor–solvent complex. It was also impossible to measure this constant in solid PEO systems as in samples of this kind the signals obtained are extremely broad and too inaccurate in terms of the chemical shift to apply the numerical procedure leading to K_c estimation. Hence, we will try to estimate the values of the formation constants in the polymeric system with the use of indirect method. This method bases on the estimation of the anion-receptor formation constant in neutral in terms of interactions with the receptor solvent and consequent comparison of this value with the K_c values estimated for receptor–glyme interactions in the same solvent [33][2].

2. Experimental

The dimethyl ethers of mono-, di- and triethylene glycol (glyme, diglyme, triglyme respectively) all anhydrous and purchased from Fluka. Tetraglyme (Aldrich) was doubly distilled under vacuum over molecular sieves 5A type to remove the traces of water. PEGDME $M_w = 1000$ (Aldrich) was dried in high vacuum (temperature equal to 60 °C) for about 100 h. Dimethyl carbonate (DMC) and ethylene carbonate (EC, both battery grade and purchased from Aldrich), 1,4-dioxane, CH_3CN (both POCH, for DNA synthesis, humidity below 50 and 10 ppm, respectively) and $CDCl_3$ (Armar Chemicals, 99.8% D) were used as received. $(C_4H_9)_4NCF_3SO_3$ (TBATf) (Fluka, puriss. electrochemical grade) was dried in vacuum for at least 48 h at 90 °C. Poly(ethylene glycol) dimethyl ether (PEODME, Aldrich, average $M_w = 1000\,g\,mol^{-1}$) was dried in vacuum for at least 150 h at temperature gradually increased to 90 °C. 5,11,17,23-tetra-p-*tert*-butyl-25, 27-bis((*N*-*p*-nitrophenyloureido)butyl)oxy-26,28-dipropoxycalix[4]arene (Cx2, see Fig. 1) was synthesized and dried using the procedures reported elsewhere [24].

^1H and ^{19}F NMR spectra were recorded on a computer interfaced Varian VNMRS 500 MHz spectrometer at 499.9 MHz and 470.4 MHz

[1] The terms "host" and "guest" in this place are arbitrary.

[2] In publication it was proved that the interaction between the studied receptor and various matrices lowers in the order: $CH_3OCH_2CH_2OCH_3 > CH_3O(CH_2CH_2O)_2CH_3 > CH_3O(CH_2CH_2O)_3CH_3 >$ PEODME > PEO. Hence, the coordinating properties of the 1,2-dimethoxyethane differ from those of PEO.

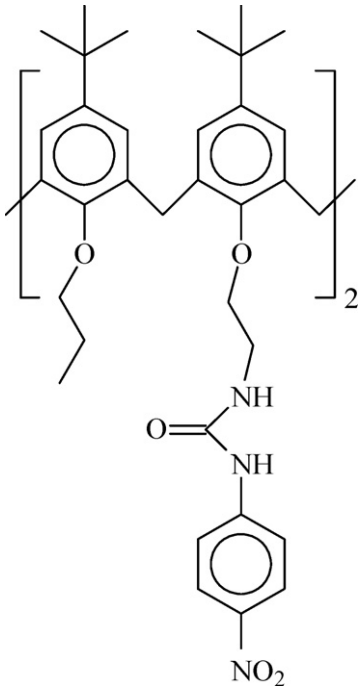

Fig. 1. Cx2 formula.

respectively. All the measurements were performed at 25 °C. The spectra were analyzed using MestReNova 5.1.0 software. The estimation of the solvent–receptor complex formation was reported elsewhere [32]. In the case of glymes and PEGDME the estimation of the constant was performed (on the basis of the same experimental data) in two modes, one of which takes into consideration the ratio between receptor and oligo(ethylene glycol)dimethyl ether molecules concentration while the other is based on the ratio between the receptor and the oxylethylene units. The same procedure and equations were used in the case of anion-receptor complex formation.

A very similar procedure was used to estimate the formation of the anion-receptor dimers. The following function should be minimized in this case:

$$F_{(\delta_S,\delta_D,K_a)} = \left(\frac{2(1-x_s^i)\delta_D + x_s^i\delta_S}{2-x_s^i} - \delta_i^{exp}\right)^2, x_s^i = \frac{\sqrt{1+8K_Dc_R}-1}{4K_Dc_R}$$

where δ_S is the chemical shift of a given atom in the "free" receptor, δ_D is the chemical shift of a given atom in the receptor dimer, K_D is dimer formation constant, and c_R is receptor concentration. Using the least square method, for given K_D, δ_D and δ_S can be estimated from equations as follows:

$$\delta_S = \frac{1}{W}\left(\sum_i \delta_i^{exp}\frac{x_s^i}{2-x_s^i}\sum_i \frac{4(1-x_s^i)^2}{(2-x_s^i)^2} - \sum_i \delta_i^{exp}\frac{2(1-x_s^i)}{2-x_s^i}\sum_i \frac{2(1-x_s^i)x_s^i}{(2-x_s^i)^2}\right)$$

$$\delta_D = \frac{1}{W}\left(\sum_i \frac{(x_s^i)^2}{(2-x_s^i)^2}\sum_i \delta_i^{exp}\frac{2(1-x_s^i)}{2-x_s^i} - \sum_i \delta_i^{exp}\frac{x_s^i}{2-x_s^i}\sum_i \frac{2(1-x_s^i)x_s^i}{(2-x_s^i)^2}\right)$$

$$W = \sum_i \frac{(x_s^i)^2}{(2-x_s^i)^2}\sum_i \frac{4(1-x_s^i)^2}{(2-x_s^i)^2} - \sum_i \frac{2(1-x_s^i)x_s^i}{(2-x_s^i)^2}\sum_i \frac{2(1-x_s^i)x_s^i}{(2-x_s^i)^2}$$

K_D can be estimated using the bubbling algorithm by minimizing the function F.

The error of the dimer constant formation estimation did not exceed 7% (see Table 1).

Table 1
Estimated values of the association constant for various dimethyl ethers of poly(ethylene glycols). Estimated values are for the NH aliphatic (first value) and NH aromatic (second value). The constant is here defined as follows: $K_a = [Cx2_{complex}]/([Cx2_{free}]\cdot[S])$ where $[S]$ is the concentration of the active solvent. The results were gathered upon the assumption that $[S]$ value is calculated per mole of the solvent molecules (middle column) and per mole of the —(CH_2CH_2O)— structural repeating units (second column).

	$S = CH_3O(CH_2CH_2O)_NCH_3$	$S = —(CH_2CH_2O)—$
Glyme	8.3/8.1	8.3/8.1
Diglyme	14/12.6	6.3/6.1
Triglyme	17.1/18.5	5.1/5.5
Tetraglyme	18.4/18.4	4.4/4.4
PEODME 1000	37.0/40.0	1.5/1.6

3. Results

3.1. Formation of the anion-receptor dimers

The phenomenon of the anion-receptor dimer formation is typical for calix[4]arene derivatives substituted with urea or urethane groups either in the wide or narrow rim (e.g. [57–59,47,60]). Two identical molecules interact with each other through the formation of intermolecular hydrogen bonds between the donor and acceptor parts of the dangling moieties if an appropriate geometrical fitting is fulfilled in terms of symmetry and steric hindrances. We also observed such a tendency previously in the IR studies of the molecule of interest [32,33]. Thus, for the understanding of complexation equilibriums existing in the system, the concentration of "free" molecules of the anion-receptor instead of the overall receptor concentration should be taken into consideration. As the dimer formation process is dynamic and fully reversible due to the fast kinetic of the process in the electrolyte solution. Dimerized and single receptor molecules are both present in the equilibrium concentrations. Thus, dimerization is an additional party in the competition between the receptor interactions with the solvent and the anions. Therefore, we decided to estimate the dimer formation constant firstly. This value was estimated from the NMR experiments in which the chemical shift of the interaction sensitive protonic signals (originating from both NH groups in the receptor molecule) was plotted against receptor concentration (see Fig. 2). The value of K_D obtained according to the above described numerical procedure is equal to 39 mol^{-1} dm^3. Additionally, the plot shows a plateau at extremely low receptor concentrations (below 10^{-3} mol dm^{-3}) showing only weak interactions in this concentration range. Thus, in the next titration, in which we estimated the complexation of the receptor with anions and neutral solvent species, we take the receptor concentration between 0.001 and 0.0005 mol dm^{-3}. In such a concentration range, only 5% of the receptor molecules are agglomerated to dimers. Moreover, the titrations (excluding ^{19}F NMR experiments) were performed for constant concentration of the receptor[3].

3.2. Formation of the complexes between Cx2 and organic carbonates

The estimated values of the complex formation constants of Cx2-organic carbonates in $CDCl_3$ are equal to 13 mol^{-1} kg in the case of

[3] This procedure is not fully satisfactory due to fact that the concentration of the "free" receptor molecules and receptor dimers decreases when the complex between the receptor and neutral solvent or anion is formed. The estimation would be more accurate if the parallel formation of dimer and complex was assumed. On the other hand, the influence of the dimers on the chemical shift calculated is in the case of ^1H NMR titrations lower than 0.05 ppm when the difference between complex and "free" receptor in the chemical shift is at the level of 0.5.

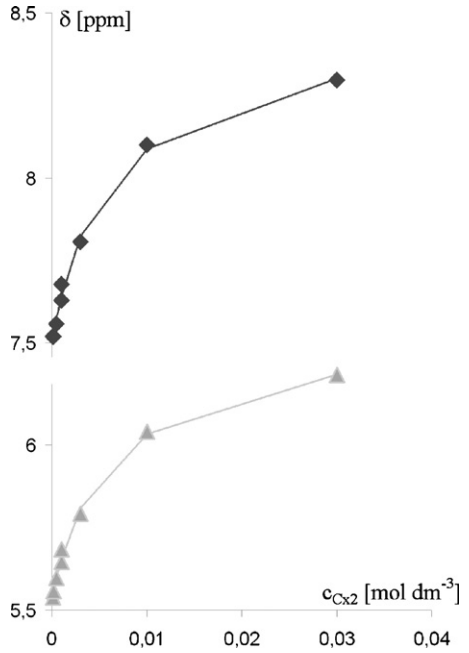

Fig. 2. Chemical shift changes for protons of the ureid group in Cx2 molecule as a function of the molecule concentration change. The points present measured values and the lines the numerical fit.

ethylene carbonate and 25 mol^{-1} kg in the case of dimethyl carbonate. This rather surprising result takes into consideration similar or even slightly higher donor properties of EC (EC is characterized by donor number equal to 16.4 while DN of DMC is equal to 15.1 [61]). The phenomenon observed can be explained by steric factors which are much more important for interactions with large supramolecular entities in comparison with the solvent–cation interactions for the evaluation of which the DN value was created. DMC is a linear molecule capable of interacting with the urea group of the receptor by oxygen belonging to two OCH_3 moieties (known from our previous research for good geometrical fitting [32,58]). Contrastively, EC molecule exhibiting cyclic geometry must interact with the receptor either through one of the ether or carbonyl oxygen.

3.3. Formation of the complexes between Cx2 and oxyethylene oligomers

The results of the NMR titration of Cx2 with oligooxyethylene compounds characterized by various chain lengths are shown in Fig. 3a. Fig. 3b shows an exemplary fit (solid line) leading to the estimation of the Cx2–glyme complex formation constants in $CDCl_3$ which are given in Table 1 (middle column shows the results for which the molecule concentration is taken into consideration while calculating the receptor:solvent ratio). As one can clearly see, in this approach the formation constant values are between 8 and 40 mol^{-1} kg and grow with the raising length of the oligooxyethylene chain. This tendency in the complex formation values is contrary to the tendencies in the change of the maxima of the NH and C=O stretching bands in previous infrared spectroscopy studies [32,33]. The discrepancy observed here can be attributed to the fact that in the case of IR studies the strength of the interaction was compared for identical concentrations of oxyethylene units and not the molecules themselves. In consequence the molecular concentration of PEGDME M_w = 500 g mol^{-1} was ten times lower in comparison with glyme. To compare these results a new approach was introduced. The estimated values were recalculated according to the rule that the ratio between the receptor and the solvent is calculated not on the molecular basis but on the repetitive unit concentration one. Thus, in consequence, the molecular concentrations were divided by *n* factor equal to 1 in the case of glyme, 2 in the case of diglyme and, finally, 22 in the case of PEGDME M_w = 1000 g mol^{-1}. In contrast to the previous results the values (gathered in the right column of Table 1) decrease monotonically from 8.3 to 1.5 mol^{-1} kg

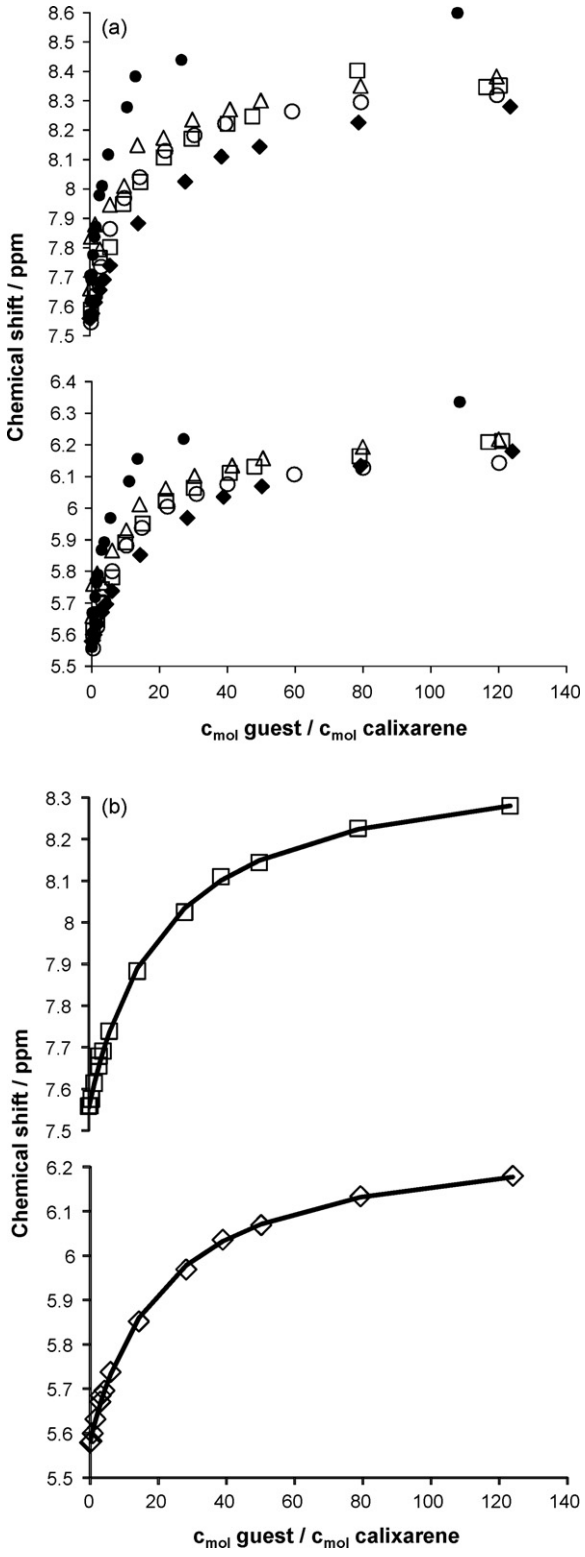

Fig. 3. ^{1}H NMR titration curves of Cx2 molecule for different oligoglyme active solvent (♦: monoglyme, □: diglyme, △: triglyme, ○: tetraglyme, ●: PEGME 1000) (a) and an exemplary numerical fit leading to the estimation of K_a for monoglyme (□: NH aromatic, ◊: NH aliphatic, the lines represent the numerical fit) (b).

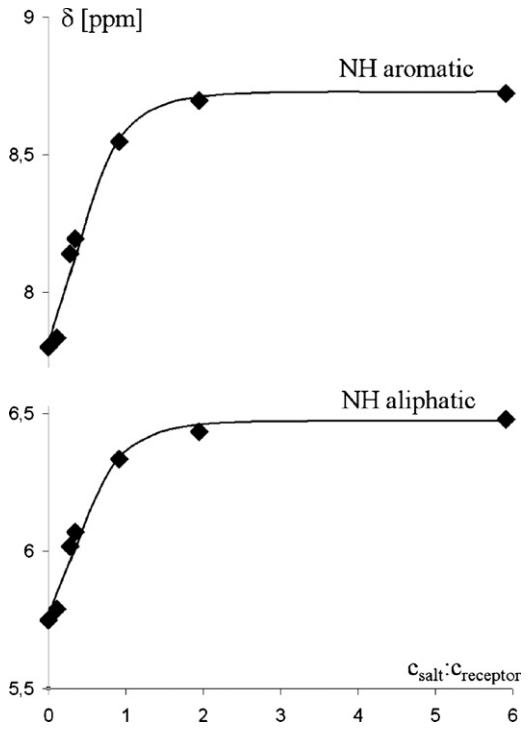

Fig. 4. ^{1}H NMR titration curve of Cx2 s with *n*-$Bu_4NCF_3SO_3$ in $CDCl_3$. The points present the measured values, the lines numerical fit.

with the increase of the molecule chain length. In this case the obtained tendency stays in agreement not only with the previous IR results but also with our other observations reported in [32]. Moreover, the per molecule complex formation constants for glymes are very similar to those for Cx2-organic carbonates. This observation is also rather surprising, as the DNs of the ethers which are taken into consideration here are higher than these of EC and DMC (DN of the studied systems is between 19 and 24).

3.4. Formation of the complexes between Cx2 and other solvents

The formation constant of Cx2-CH_3CN and Cx2-1,4-dioxane in $CDCl_3$ are below 1 and 0.01 mol kg^{-1} respectively. The corresponding chemical shift change is extremely small in the first case and not observable in the second. Therefore, the values presented only have an indicative meaning as they are far below the sensitivity of the method used. Additionally, it is worth noting that 1,4-dioxane is characterized by a similar donor number (characterizing the ability of molecules to form a complex with cation or the moiety being acidic hydrogen donor). This fact confirms the role of enthropic effects, e.g. geometrical fitting between the molecule and the receptor in the formation of the anion–solvent complex.

3.5. Formation of the complexes between Cx2 and anions

The anion-receptor complex formation constants were estimated at about $9{\cdot}10^4$ for Cx2–$CF_3SO_3^-$ complex[4]. The value obtained is the result of approach typical for supramolecular chemistry approach based on the NMR titration (see Fig. 4) performed in a solvent of low polarity and properties promoting weak salt dissociation (e.g. $CDCl_3$). Additionally, a bulky organic cation salt is used to achieve solubility. The estimated constant value is about four orders of magnitude higher than the constants of receptor–neutral specimen formation reported herein. This result stands in contrast with our previous result [55] where complex formation constant for Cx2 and $LiCF_3SO_3$ was determined to be in range 700–800 (depending on the dielectric constant) for the dioxane–acetonitrile mixtures tailored to have dielectric constant 5.5 and 7.1. In this case a "reverse" ^{19}F NMR spectroscopy titration was used with fixed salt concentration and the receptor being the guest molecule. To resolve this discrepancy some other NMR titration experiments were performed. In the first one identical mixtures of acetonitrile and dioxane were used for a classic ^{1}H NMR experiment with lithium salt being the guest molecule. In this case the obtained K_c values are even lower and remain in range 200–250 for the same solvent proportions as above. The observed difference between fluorine and protonic-based estimations can be explained by the fact that even for a weakly interacting solvent such as acetonitrile some solvent-originating blocking of the receptor molecules can be assumed. In this case protonic chemical shift changes can be partially suppressed which assumption is not true for the fluorine ones.

To discuss the discrepancy observed between the results of the experiment one and three one must take into consideration the following issues: (i) the difference in the kind of the cation and, in consequence, its size, surface charge density and hardness, (ii) the difference in the coordination properties of the solvents and, in consequence, in ionic states of the dissolved salts, (iii) the amount of residual water. The first of the issues presented is quite obvious and needs no further comments. As it comes to the second it must be stressed that even in the situation when the dielectric constant values are similar 4.73 for $CHCl_3$ and 5.5 for the dioxane–acetonitrile mixture studied the latter, contrastively to $CHCl_3$, is able to solvate cations and, thus, to separate them from anions. Therefore, salt dissociation is promoted. The last and most important issue is related to the residual water content. For deuterated chloroform this value is equal to 50 ppm which makes a 3 mmol dm^{-3} solution of water in the organic solvent. Taking into consideration that the receptor concentration is equal to 0.5 mmol dm^{-3} and the salt:receptor ratio varies in one experimental series from 0.2 to 6.0 we can easily estimate the water:salt molecular ratio of the series of solutions to change from 30:1 for the lowest salt concentration to 1:1 for the highest one. Taking into consideration the fact that water is a preferred coordination sphere builder for both cation and anion this variation results in a total change in the coordination spheres. For low salt:receptor ratios we predominantly deal with hydrated salt constituents being either free ions or solvent-separated ionic pairs. For the highest ratio used the situation is just opposite and no significant amount of water can be incorporated into the structure. In consequence, there is a difference in availability of anions for the receptor and it decreases with the increase of salt concentration. Thus, the observed shape of the curve depicting the dependence of the chemical shift on the salt to receptor ratio can be affected in a manner which leads to the final increase of the estimated K_a value.

Finally, an experiment expected to be the NMR titration of the same anion was performed for $LiCF_3SO_3$ salt in $CDCl_3$ CD_3CN 9:1 mixture by means of ^{1}H NMR spectroscopy. In this case the solubilization of the lithium salt ich achieved by its dissolution in the polar solvent while the receptor is primarily dissolved in chloroform. Both solvents present in the system reveal rather weak coordination properties for the lithium cation while the average dielectric constant of the system is similar to those characteristic for various glymes. In this case the dependence of the chemical shift of proton belonging to ureid moiety of the receptor on the salt to receptor ratio is more complicated (see Fig. 5) and not forming a typical titration curve. For the lower range of ratios (below 1) the

[4] In the literature it is suggested that values of the anion-receptor association constant above 10^5 mol^{-1} dm^3 cannot be measured. Thus, the error of the estimation is at the level of 30%.

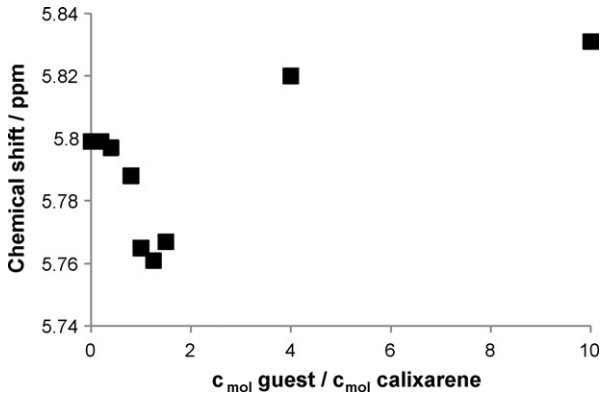

Fig. 5. Changes of the chemical shift for protons of the ureid group in cx2 molecule as a function of the $LiCF_3SO_3$ concentration change.

monotonic decrease of the chemical shift is observed and a minimum is reached. For higher salt concentrations an increase of it is observed once again. This atypical behavior can be correlated with changes in the ^{1}H NMR spectrum of Cx2. Fig. 6 shows the NMR signals attributed to protons belonging to $-C_6H_4NO_2$ moiety of the receptor molecule. For pure calixarene solution (a) a multiplet (1) is observed while for the sample containing a large amount of salt (c) another multiplet (2) containing the same number of constituents can be observed. For an intermediate case (b) a superposition of both multiplets can be observed. Additionally, the chemical shift of the signal of the other proton belonging to the ureid moiety does not shift gradually with the salt:receptor ratio change but a step change is observed in the same range of ratios. This noncontinuous behavior can be also correlated with the situation when two separate signals originating from the same proton can be observed (see Fig. 6(b)). This situation can be explained by the conformational change of the receptor molecule related to the interactions with the salt. This phenomenon can result from the interaction between the cation and the receptor molecule as calix[4]arenes can interact with the cations by Lewis acid–Lewis base type interactions. At least two groups can form such a complex. Firstly, ether groups directly linked to the calixarene narrow rim can coordinate the cation. Such interaction was observed for several calixarene derivatives [62–65]. Secondly, such interaction between the cation and the carbonyl oxygen from the urea group and/or oxygen from the nitro group might be observed. Due to a higher enthalpy of such interaction, the cation exchange is much slower. Therefore, in consequence, the signals originating from the "free" and "cation-bonded" receptor molecules can be observed separately not forming a weighted average of all constituents. The observation of the cation–receptor interaction for this system can be attributed to the previously mentioned weak cation coordination properties of the solvent used. Further studies are here needed to answer the question upon the nature of the species originating from salt (independent free cation and anion, contact or solvent-separated ionic pairs or cation and anion belonging to two different ionic pairs) taking part in the described process.

As a supplement to the organic carbonate complexation studies a "reverse" ^{19}F NMR titration of $LiPF_6$ solution with Cx2 was performed in acetonitrile as a polar and weakly receptor-interacting solvent. The chemical shift dependence together with the numerical fit is shown in Fig. 7. The estimation reveals K_c equal to about 80. The lower (in comparison with $LiCF_3SO_3$) value can be related to firstly weaker geometrical fit of the PF_6^- anion to Cx2 molecule in combination with partial blocking of the receptor even by only slightly interacting solvent. The second explanation can be additionally confirmed by relatively small changes of the fluorine chemical shift upon titration.

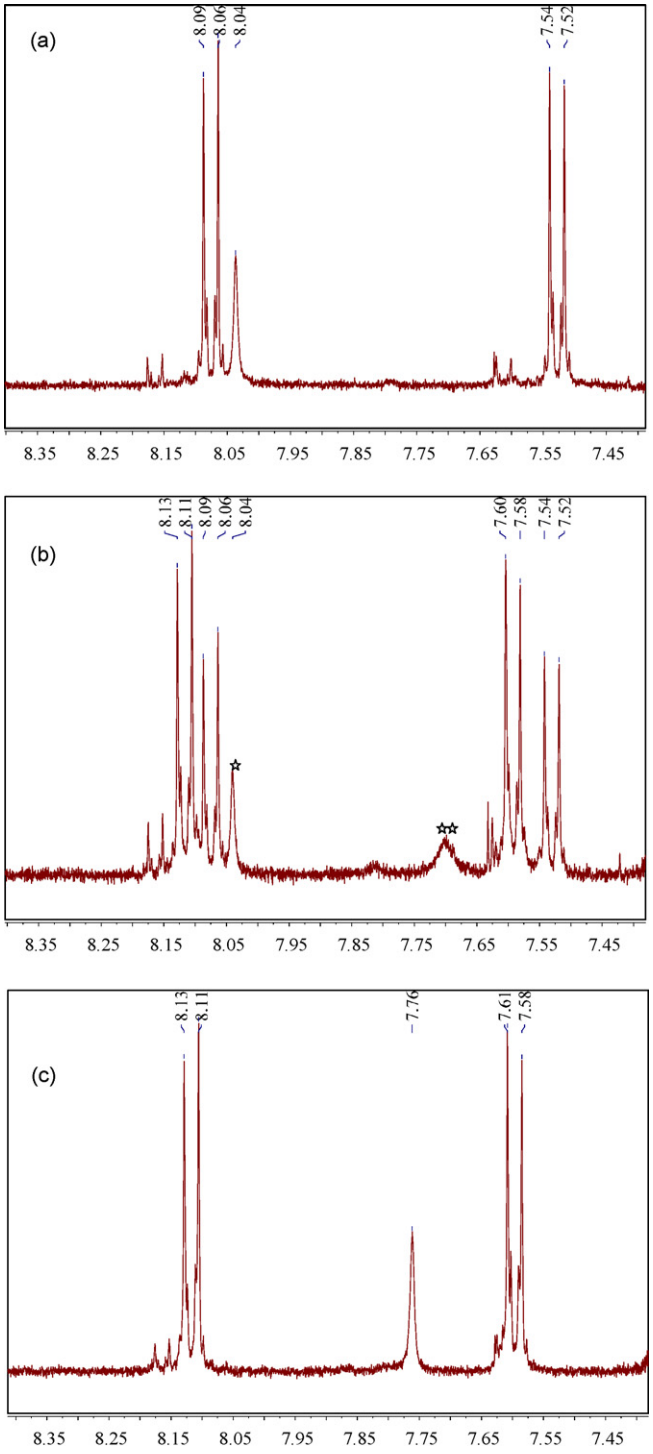

Fig. 6. Fragment of the ^{1}H NMR spectra of the Cx2 molecule representing signals originating from side $-C_6H_4NO_2$ moiety. Pure Cx2 solution (a), $LiCF_3SO_3$:Cx2 ratio = 0.8. Signal marked with (*) is characteristic for all lower ratios while the one marked with (**) for all higher (b), $LiCF_3SO_3$:Cx2 ratio = 10 (c).

4. Discussion

The set of estimated equilibria constants presented above even if measured in conditions "far from reality" can provide us with some image of ionic states of solid polymeric electrolytes. The first assumption here is that the $CDCl_3$ (or $CHCl_3$) does not interact with the anion and, additionally, the receptor–anion and receptor–polar specimen (active solvent) complexes have 1:1 stoichiometry (which

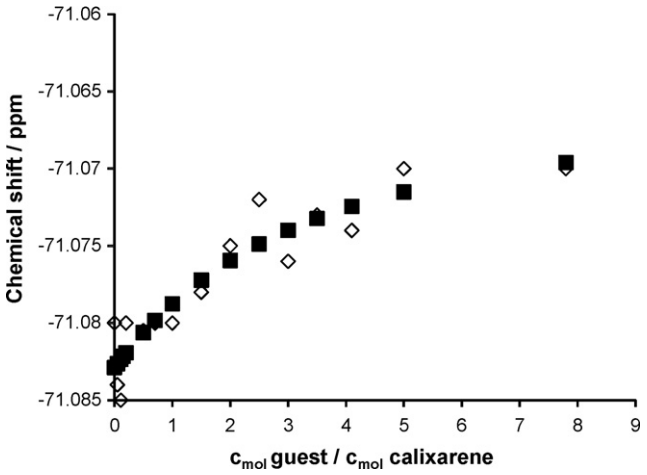

Fig. 7. ^{19}F NMR titration curve of Cx2 s with $LiPF_6$ in CH_3CN (◊: average measured values, ■ : numerical fit.

is realistic in the case of chloroform-based solutions but might be not valid in case of the corresponding polymeric system). Thus, in consequence, the concentrations and ratios between various species of interest can be described as follows. Firstly, the concentration of the $-CH_2CH_2O-$ units in pure glymes, PEODME oligomers and in solid PEO is about 22 mol dm^{-3} and in majority of the composite polymeric electrolytes studied[5] previously it is above 10. Therefore, if we take into consideration the estimated values of K_a for glymes and PEODME, the resulting ratio between "free" receptor molecules and molecules complexed with the oligomeric chain should be at the level of 200 for $n = 1$ and 40 for $n = 22$. On the other hand, taking into consideration the K_D value and temporarily forgetting about the interactions with solvent, the ratio between "free" receptor molecules and anion-receptor dimers calculated for the system in which receptor:EO molar ratio is equal 60 (a typical composite SPE composition is $([PEO]_{20}LiX)_3(Cx2)_1$ is at the level of 5 (this ratio lowers when the receptor concentration is lowered). The comparison of the values obtained confirms the fact that the formation of the polymeric matrix–Cx2 complexes is significantly more pronounced than the formation of the receptor dimers even in high receptor concentrations. The discussion presented above is also valid for systems based on EC–DMC mixture as the respective K_a is even higher. Thus, the presence of anion-receptor dimers will not be further discussed neither for EO based systems nor for the liquid organic carbonates based ones.

The problem of competition between the complexation of the anion-receptor in oligoether solutions and formation of anion-receptor complexes can be addressed in two different approaches. One of them requires several assumptions. It needs to be assumed that: (i) full dissociation of $(C_4H_9)_4NCF_3SO_3$ in $CDCl_3$ occurs (or, which is much more realistic, the bonding between the anion and the t-Bu_4N^+ cation contact ion pair is weak enough to make the receptor break it—which is absolutely not true for lithium salts); (ii) the stoichiometry of the receptor–anion and receptor–matrix complexes is 1:1 (the last term means here that one Cx2 molecule interacts with one oxyethylene unit only), (iii) for the equilibria studied, the influence of the phenomena related to the second coordination sphere can be neglected, (iv) the anion-receptor does not interact with cations (which is not realistic for the $CDCl_3$ solutions but is valid for a surrounding which coordinates the cation well) and contact ionic pairs. In the case of glymes and PEODME, the cation–anion contact ionic pair formation constant for lithium salt is at the level 10^3–10^4 mol^{-1} dm^3 and for the tetraalkylamonium salts it is at the level of 10^2 mol^{-1} dm^3 [66,67]. Thus, the concentration of the free anions in the 1 mol dm^{-3} solution of $LiCF_3SO_3$ is at the level of $3{\cdot}10^{-2}$ and in the case of 10^{-3} mol dm^{-3} solution of $(n\text{-}C_4H_9)_4NCF_3SO_3$ the concentration of "free" anions is about 10^{-3} mol dm^{-3}. Therefore, taking into consideration the estimated K_a value for a $CDCl_3$ n-$Bu_4NCF_3SO_3$ system and the above calculated concentration of free ions in the system the ratio between anion-receptor complexes and "free" receptor molecules (once again temporarily neglecting the receptor solvent interactions) in oligoethers is at the level of 3000 in the case of 1 mol dm^{-3} $LiCF_3SO_3$ and 90 in the case of 10^{-3} mol dm^{-3} n-$Bu_4NCF_3SO_3$. Finally, when both previously estimated values are compared (the ratio between the "free" receptor molecules and anion-receptor complexes is about 3000 and the respective ratio between the "free" receptor molecules and complexes of the receptor and polymeric/oligomeric solvent is below 80) one can conclude that the ratio between the anion-receptor complexes and the complexes of the receptor and the polymer should be[6] above 12. From the same data we can estimate the anion-receptor complex formation for about 700 mol^{-1} dm^3.

This observation can easily explain why the phenomena of the lithium transference number enhancement in PEO [68] or PEODME [28] were observed. Moreover, also the unsuccessful trial of the Cx2 titration in glyme [56] (where the ratio between the "free" receptor molecules and anion-receptor complexes is about 90 and the respective ratio between the "free" receptor molecules and the complexes of the receptor and the solvent is above 180; thus the ratio between the anion-receptor complexes and the complexes of the receptor and the solvent is lower than 0.5) can be explained through the same argumentation.

An alternative approach to the same data (leading finally to the same conclusions) can be based on the following data: the solvent receptor association constant K_{ao} for glyme is about 15 whereas for PEODME it is below 2 and the anion-receptor equlibria is characterized by the constant K_{aa} in range of 700–800 (^{19}F NMR data and the estimation above. Additionally, it must be assumed that the receptor is capable of interacting with free anions and ionic triplets but not with the ionic pairs [69]. Additionally, we assume that under NMR titration regime (c_{salt} around 10^{-3} mol dm^{-1}) salt is predominantly dissociated and in the "battery regime" (c_{salt} above 1 mol dm^{-1}) the amount of free ions is small and the concentration of ionic triplets plays an important role being at least in the range of 20% of the total salt amount [70]. Therefore, in the first case K_{aa} to K_{ao} is equal to 50 while the "available anion" to solvent concentration ratio is equal to about 10^{-4} while in the second one K_{aa} to K_{ao} equals to 375 and the respective concentration ratio is 0.01. Thus, the relation between the receptor bonded to the solvent and to the anion should be in range of 200:1 in the first case and 100:375 in the second one.

Contrastively, in the case of electrolyte based on organic carbonates and $LiPF_6$ the preliminary data show that the addition of the anionic receptor should not reveal an important influence on the ionic equilibriums present in the system but this issue needs further experimental confirmation.

[5] If we take into consideration the presence of salt–polymer complexes such as $(PEO)_3(LiCF_3SO_3)_1$ in the system, the concentration of "free" oxyethylene units in all membranes previously studied is above 5 mol dm^{-3}.

[6] The real values of the ratio between the anion-receptor and the anion-matrix are lower due to fact that the assumptions made are not fully fulfilled and this not complete fulfillment of these assumptions leads to lowering of this ratio. Moreover, the argumentation presented here does not take into consideration the fact that the amount of cation is equal to the sum of anions and anion-receptor complexes and, thus, is higher than that of anions. Thus, anion concentration is lower than the one given here.

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