

Research papers

Properties of AlCl_3 guanidine deep eutectic solvent with addition of polyethylene oxide of different molecular weights supported by quantum-chemical calculation

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ABSTRACT

Deep eutectic solvent of AlCl_3 with guanidine HCl was synthesized in the molar ratio 3:1 in the presence of polyethylene glycols of various molecular weights from 1500 to $5 \cdot 10^6$ g/mol. Concentration of polymer was 2.5 %, 5 % and 10 %. Temperature dependence between 25 and 70 °C of conductivity of each electrolyte was calculated from the cyclic voltammetry of aluminum deposition-stripping measurements. It was found that conductivity increases with molecular weight of polymer in the interval between 2 and 10 kD. This result was interpreted as binding of AlCl_3 guanidine to two different sites which have hydroxyl (chain ends) and ether (middle chain) oxygen with relatively higher and lower binding energy respectively. Polymer with longer chain has more low energy binding sites which causes lesser binding and consequently higher conductivity of electrolyte. B3LYP-D3 and DLPNO-CCSD(T) computations support experimental results. DES are discussed in terms of Pearson HSAB principle.

1. Introduction

Rechargeable batteries have become important as carbon dioxide emission free power sources for electrical vehicles and other applications. However, Li based as they are almost exclusively now, they have critical disadvantages as flammability and scarcity of cathode materials, which necessitates their costly not environmentally friendly recycling. In other words, they are not cheap, and not “green”. So, Li batteries are not exactly fit to the purpose they were introduced from start, which is reflected by recent decrease of EV market.

In view of the above, a number of scientific groups are investigating the possibility of using other metals (Na, K, Mg, Ca, Zn and Al, etc.) in the production of the rechargeable batteries [1]. From mass per exchanging electron, one can immediately conclude that it is Al^{3+} (27/3 = 9 g/mol) which is the closest suitable ion to replace Li^+ (6.9 g/mol).

Chemical current sources based on aluminum have a number of

qualitative advantages. The main one is the electrical capacity of aluminum batteries ($8000 \text{ mAh} \cdot \text{cm}^3$ vs $2000 \text{ mAh} \cdot \text{cm}^3$ for Li-ion). Aluminum is present in the earth's crust in a larger amount when compared to lithium (8 % Al compared to <0.01 % Li). The distinctive parameters of an aluminum-ion battery are: short charging time (less than one minute at a current density of 4000 mA/m^2) and durability (6000–7500 charge-discharge cycles) [2–5]. In addition, it is known that the features of electrochemical processes in aluminum-based electrolytes do not allow the formation and growth of dendrites on the electrodes, which prevents a possible short circuit in the device. It is worth noting that to create this type of battery, it is necessary to use anhydrous electrolytes that can create conditions for a multiple process of dissolution and intercalation of aluminum in the structural parts of a chemical current source.

Successful tests were performed in an electrolyte based on imidazolium and pyrrolidinium chloride ionic liquids, (1-ethyl-3-

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methylimidazolium chloride, [EMIm]Cl [3,6,7], and 1-butyl-3-methylimidazolium chloride [BMIM]Cl and other imidazoliums, mixed with aluminum chloride (AlCl_3) [8], in carbamide (urea) with AlCl_3 [9], in various amides with AlCl_3 [10], and in triethylammonium chloride (Et_3NHCl) with AlCl_3 ionic liquids [11].

Recently new chloroaluminate DES have been proposed [12] based on Pearson HSAB, Hard and Soft Acids and Bases principle [13]. AlCl_3 is typical “hard Lewis acid”. It is defined by low polarizability and large charge. According to HSAB it binds preferably to Lewis base with the same properties. All Lewis bases studied so far were soft bases imidazoliums or urea. It was proposed that hard bases should be tried. Because of their ionic character, they should be searched within Lewis bases with high melting temperature. The following bases have been found acetamidine HCl, guanidine HCl and BMP Cl. They have melting temperatures above 180°C . Which makes them different from imidazoliums with extended π system and $T_m = 60\text{--}70^\circ\text{C}$, or urea $T_m = 110^\circ\text{C}$.

During battery discharge, Al^{3+} binds into stronger ionic compound in DES, thus the final state has lower energy and the current increases.

This paper proceeds with investigation of anodic half reaction from AlCl_3 guanidine DES in different polymer solutions. They are expected to stabilize electrolyte, since it consists of the strongest Lewis acid and base and prone to precipitation and thickening. The results can be useful for electrochemical deposition of Al on its own. Since cathodic half reaction is entirely different subject, it is not touched here, and full cell as well. However, one can say that graphite cathode with pvd/nmp or sodium alginate binders works with this DES but needs improvement. Acetamidine and guanidine batteries were recently reported [5,14].

Polyethyleneoxide/-glycol (PEO, or PEG) of 100–5000 kD molecular weight was found to mix surprisingly well with chloroaluminates ionic liquids, as AlCl_3 EMIM Cl, or AlCl_3 Urea [15–18] as well as acetamidine (also polyamide [5]), guanidine and BMP Cl (unpublished data). Experiment is straightforward: the dry polymer is added either to synthesis batch or to ready DES and heated to $80\text{--}90^\circ\text{C}$. The resulting plastic is conductive and can be exposed to air. Therefore, it is useful for batteries construction. It was found that shorter chains <100 kD do not produce smooth gel. This puzzling observation is the topic of current paper.

In this work, the effect of additives of PEG polymer macromolecules (PEG–1500; PEG–2000; PEG– CH_3 –2000; PEG–4000; PEG–9000; PEG–20000; PEG–5 million) on the process of electrochemical deposition-dissolution of aluminum as a function on the temperature of the electrolyte was studied. Polymers were added to the system in mass concentrations from 2.5 % to 10 %, which, together with obtaining results on the temperature effect on voltage and current density, allowed us to find Activation Energy values (E_a) for each electrochemical system. Fittings were created to build diagrams reflecting the results of the process. In the course of experimental studies, after obtaining laboratory results, during analytical processing it is planned in this article to apply the ionic conductivity equation to create fittings and plot graphs and curves of the activation energy dependences on molecular weight. The equation describes a mathematical model of the process and has been tested in a number of studies and has repeatedly confirmed its effectiveness [12,15,19].

2. Materials

All reagents used in this study are chemicals with an analytical degree of purity. Polyethylene glycol (PEG) with different molecular weights ($M_n = 1500\text{--}5\text{mln g/mol}$) was produced and supplied by Sigma Aldrich, BASF and Thermoscientific, respectively. Guanidine hydrochloride/GuanHCl ($\text{CH}_5\text{N}_3\text{--HCl}$) 98 % was purchased by Alfa Aesar. Aluminum chloride (AlCl_3) was purchased from Q-BASF. All reagents were used without additional purification. Melts of samples-electrolytes of amidine solutions were compiled and used immediately for experimental purposes. Aluminum anode CA–III–B (Al–Zn–Si, B–) containing tin (Sn) 5.5–7.0 %, boron (B) 0.025–0.035 %, silicon (Si) 0.1–0.15 %, iron

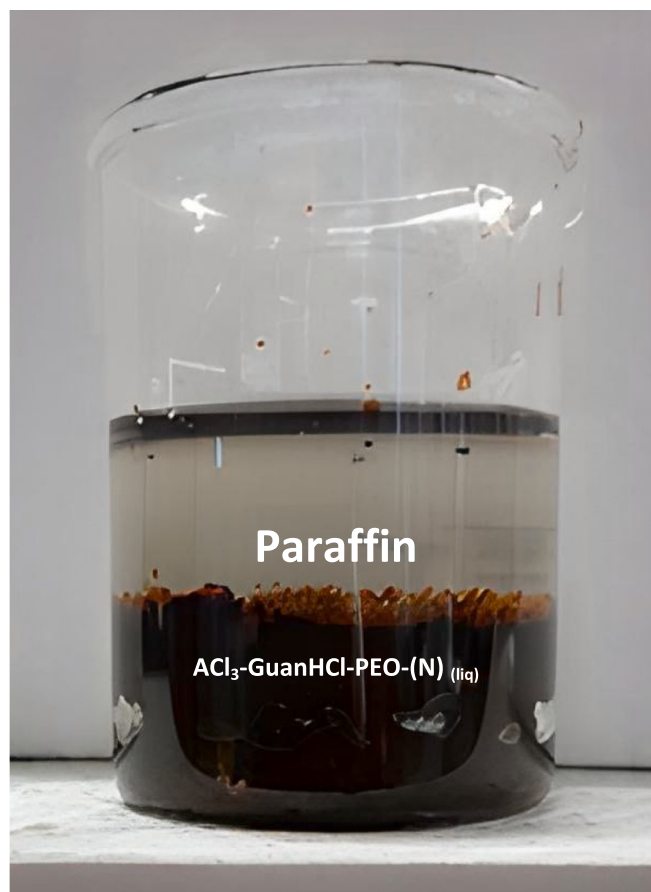


Fig. 1. A typical AlCl_3 guanidine HCl DES.

(Fe) 0.09 % and 0.006 % copper (Cu) were used as elements of the galvanic cell; pure copper and brass were used as cathodes and an aluminum wire as reference electrode.

3. Methodology

To conduct an experiment to determine the activation energy and identify the phase transition in the GuanHCl – AlCl_3 – polymer system (Fig. 1), a number of electrolyte solutions with a molar ratio of GuanHCl: $\text{AlCl}_3 = 1:3$ was compiled. That was based on the successful results in previous study [12], however the ratio was increased to assure that AlCl_3 during heating is always in saturating concentrations. The analyzed amounts of polymers were added, from 2.5 to 10 wt%. The used experimental procedure was as following: Selection of a container for mixing reagents and filling it with 10 % of the volume of a hydrocarbon in liquid form [12] to create an insulating film on the surface of the system. The procedure was run on bench, not in glove box, therefore isolation from air and humidity was necessary. The hydrocarbon also provided better contact and heat exchange between solid reactants. The calculated masses of reagents are introduced into the container alternately, first aluminum chloride, then GuanHCl, and at the end – a certain mass of polymer.

1. The mixing process begins in parallel to local heating, which was applied from an external source (heating tile or heat gun), in order to dissolve the reagents and to obtain a homogeneous viscous liquid.
2. When the critical temperature of dissolution of the reagents in the system is reached, a transition occurs to the termination of the heat supply and the continuation of mixing until a homogeneous consistency in the solution;

3. Separation of the solution from the liquid hydrocarbon with an extraction glass-pipette;
4. Assembling an electrochemical cell (aluminum anode, aluminum reference electrode and copper cathode); some layer of aforementioned hydrocarbon always remained on top, since it had lower density. It was well separated and allowed to run experiments on bench, not in glovebox, without altering the data [20].
5. Electrolyte introduced into the cell (approximately 20 ml) and contacting the electrodes to a BioLogic SP150 potentiostat;
6. Conducting all experimental processes on EC-Lab V11.30 and recording cyclic voltammograms (CV) of the studied electrolytes in the temperature range from 25 °C to 70 °C. The cathodic current, which corresponds to the process of aluminum deposition, and the anodic peak, which characterizes the dissolution of aluminum on the cathode surface, have been analyzed.

An exponential equation was used for fitting the current density and potential recorded during the anodic scan (Eq. (1)). The activation energy of electrolytes based on their composition and temperature was thus calculated.

4. Computational methodology

Quantum-chemical computations were employed to assess the gas-phase enthalpy (H^{gas}) and Gibbs free energy (G^{gas}) of non-covalent intermolecular interactions formation. (The superscript gas denotes a gas phase standard state at 298.15 K and 1 atm.) Namely, such an analysis was carried out for the formation reaction of the Guan- $AlCl_3$ dimer and the Urea- $AlCl_3$ dimer (Table 2). Additionally, we use the reaction of trimer formation from a Guan- $AlCl_3$ complex and one small molecule (oligomer) as a model to evaluate non-covalent intermolecular interactions between the Guan- $AlCl_3$ complex and the PEG polymer. As an oligomer simulating functional groups and fragments of the macromolecules of the PEG polymer, we are testing compounds such as ethanol, ethylene glycol, dimethyl ether, 1,2-dimethoxyethane (Table 3). Ethanol and ethylene glycol molecules model the terminal parts of the PEG polymer, while dimethyl ether and 1,2-dimethoxyethane describe its internal portions.

DFT calculations were performed using Gaussian09, Revision D.01 [21]. An initial 100 structures were randomly generated for each of the molecular complexes modeled in this work using the «kick» algorithm [22,23]. Geometry optimizations have been performed using the B3LYP hybrid functional [24,25] complemented by the D3 dispersion correction [26]. The 6-31+G(d,p) all electron basis set have been used for all elements [27]. Frequency calculations have been carried out to verify that the optimized structures are true minima. Thermochemical corrections to H^{gas} and G^{gas} were calculated using the entropic quasi-harmonic treatment with frequency cut-off value of 100.0 wave-numbers [28]. The individuality of the found conformers was confirmed using an energy criterion $\Delta E_{tot} > 10^{-7}$ Hartree and comparing geometries by distances between each atom and the centroid point [29–31]. Following previous studies on organometallic compounds [32–34], we performed single point B3LYP-D3 calculations for found conformers with a more extended basis set 6-311++G(2df,2p) to analyze the DFT energies in Tables 2 and 3. Additionally, single point energies have subsequently been calculated with the DLPNO-CCSD(T) method [35,36] as implemented in ORCA 5.0.4 [37] in combination with the cc-pVTZ and cc-pVQZ basis sets, followed by extrapolation to the complete basis set (CBS) limit to DLPNO-CCSD(T)/CBS total energies [35,38]. Enthalpies and free energies at 298.15 K have then been obtained through combination of the single point total energies with thermochemical corrections calculated at the B3LYP-D3/6-31+G(d,p) level before.

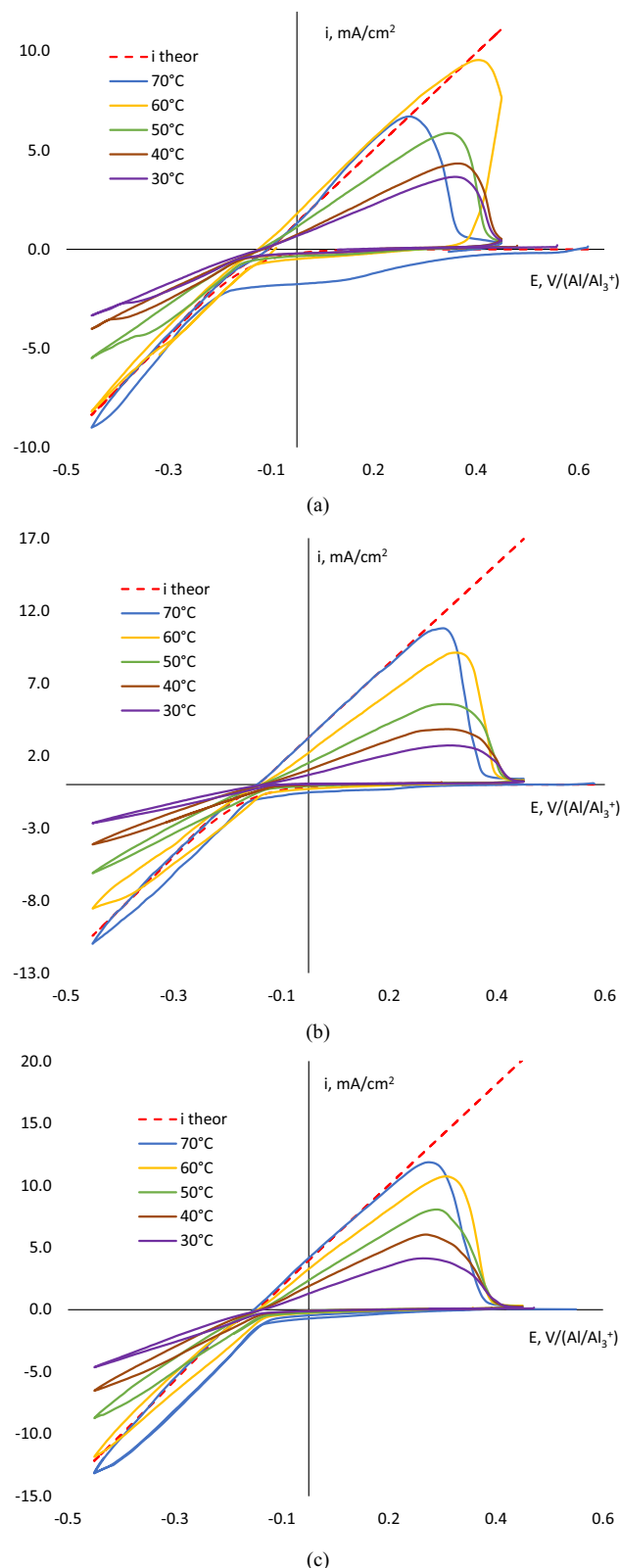


Fig. 2. Typical experimentally obtained cyclic voltammetry at different temperatures and its corresponding calculated theoretical approximation (red line) for (a) GuanHCl – $AlCl_3$ – PEG-5million(kk) (5 % w/w); (b) GuanHCl – $AlCl_3$ – PEG(CH_3)₂-2000 (5 % w/w); (c) GuanHCl – $AlCl_3$ – PEG-9000 (5 % w/w). Scan rate = 20 mV/s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

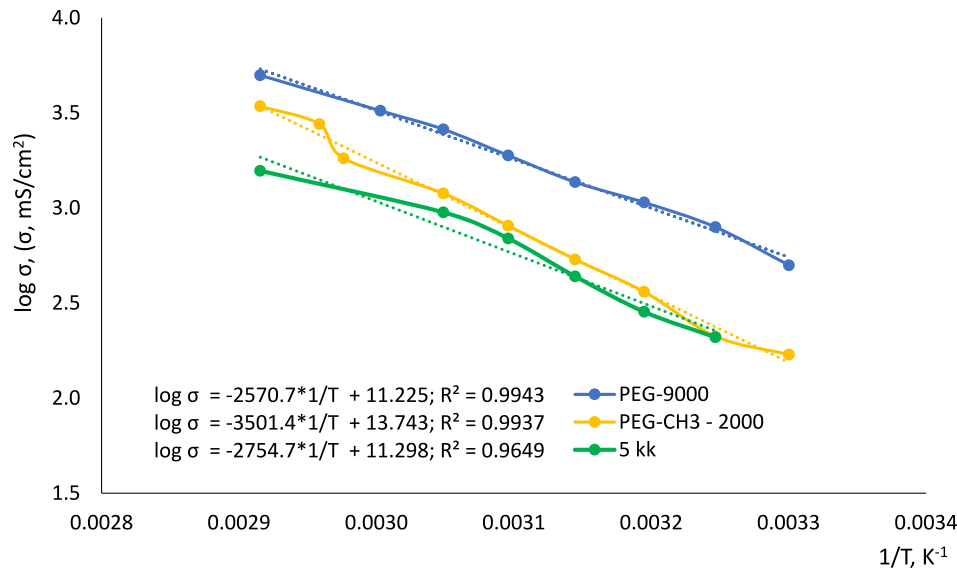


Fig. 3. A typical Arrhenius dependence of logarithm ionic conductivity on inverse temperature. The concentration of polymers is 5 % (w/w).

5. Experimental part

The experiments were carried out in the temperature range from 70 °C to 30 °C, the cooling occurring under normal conditions. Cyclic voltammograms were recorded at a scan rate of 20 mV/s in the voltage range from −0.4 V to +0.4 V vs Al/Al³⁺ RE. The step of recording the indicators was set to 5 °C. In addition, the physical properties of the electrolyte (color, viscosity) were qualitatively noticed. The cathode plate was investigated by bare eyes after the deposition was completed, in order to see if metal deposition (aluminum) occurred on it, the quality and color of the deposit, and in rare cases, its thickness. This inspection was of interest in terms of identifying the effect of added polymer molecules in the electrolyte. PEG could act as structuring agents for the electrolyte, as well as additives in the near-electrode region during the diffusion of aluminum compounds to/from the electrical double layer.

A fitting on the experimentally obtained current densities and potential curves was performed with MS Excel program (with a pre-installed Solver package) according to Eq. (1) and also used the logarithm of pre-exponent equation of ionic conductivity, compiled to solve similar problems [15]:

$$i = \frac{\sigma \varphi i_0 \left(\exp\left(\frac{nF(1-\alpha)\varphi}{RT}\right) - \exp\left(\frac{-nF\alpha\varphi}{RT}\right) \right)}{\sigma \varphi + i_0 \left(\exp\left(\frac{nF(1-\alpha)\varphi}{RT}\right) - \exp\left(\frac{-nF\alpha\varphi}{RT}\right) \right)} \quad (1)$$

where R – universal gas constant, F – Faraday constant, T – temperature, n (=3) – the number of electrons, $\varphi = E - E_0$ – potential with respect to potential of zero current E_0 , σ – electrical conductivity, α – transfer coefficient.

The obtained current density values were compared according to the composition of the electrolyte, in particularly, to the polymer macromolecules added in the solution (with molecular weight from 1500 to 5 million). When recording the values from the potentiostat, the step was determined by the temperature value and was a difference of 10 °C, which made it possible to apply the Arrhenius law to the presented systems.

A typical graph for the experimental obtained data and the data obtained by the fitting with Eq. (1) is shown in Fig. 2.

As it can be seen from the Fig. 2, the experimentally obtained data are in agreement with the theoretical assumption formed by the mathematical fitting model for the cathodic sweep. The activation energy (E_a) values predicted by the Arrhenius equation Eq. (2) reflect the studied

Table 1

The E_a , R^2 (correlation factor) and $\log k$ (logarithm of pre-exponent) values calculated for the system GuanHCl:AlCl₃ = 1:3 from the cyclic voltammograms experiments; dE/dt = 20 mV/s. A copper cathode (56 mm² geometrical area) was used.

System GuanHCl-AlCl ₃	E_a , kJ/mol	R^2	$\log k$
Without additive of the polymer	18.7	0.98	10.1
+2.5 % PEG-1500	28.8	0.97	14.6
+2.5 % PEG-4000	21.0	0.98	11.5
+2.5 % PEG-5 million	22.0	0.96	11.3
+2.5 % PEG-(CH ₃) ₂ -2000	28.0	0.99	13.8
+2.5 % PEG-9000	20.6	0.99	11.2
+5 % PEG-9000	24.8	0.99	12.0
+5 % PEG-20000	26.4	0.98	13.3
+5 % PEG-2000	33.5	0.95	16.2
+5 % PEG-(CH ₃) ₂ -2000	20.6	0.98	11.7
+5 % PEG-4000	22.6	0.96	12.5
+5 % PEG-1500	31.7	0.90	14.8
+5 % PEG-5 million	41.5	0.99	18.4
+10 % PEG-2000	27.3	0.99	12.5
+10 % PEG-1500	25.5	0.99	11.9
+10 % PEG-20000	35.3	0.97	15.5
+10 % PEG-(CH ₃) ₂ -2000	28.6	0.98	13.3
+10 % PEG-9000	30.4	0.99	14.3

values for each GuanHCl – AlCl₃ – Polymer system in a given voltage range.

$$\sigma = k e^{\frac{E_a}{RT}}; \quad (2)$$

The value of the activation energy (E_a) for each system in the specified temperature range was determined from graphical representation of the temperature dependence of the ionic conductivity. Such a curve used to calculate the E_a values is shown in Fig. 3.

Fig. 3 shows an Arrhenius dependence curve of the GuanHCl-AlCl₃ system with polymers PEG-9000, PEG-5million(kk) and PEG-(CH₃)₂ with a molecular weight of 2000 and a specific concentration of polymer in the system of 5 %. All experimental and computational studies of all types of electrolytes investigated here are summarized in Table 1.

As it can be seen from the Table 1, the obtained activation energy values (E_a) have a high calculated accuracy, based on $R \geq 0.95$ (except for the experiment with PEG-20000 2.5 % weight.). All this confirm the assumption that the introduction of a polymer as additive into the ionic liquid electrolyte qualitatively affects the ionic conductivity.

The calculated activation energies (E_a) as a function of the

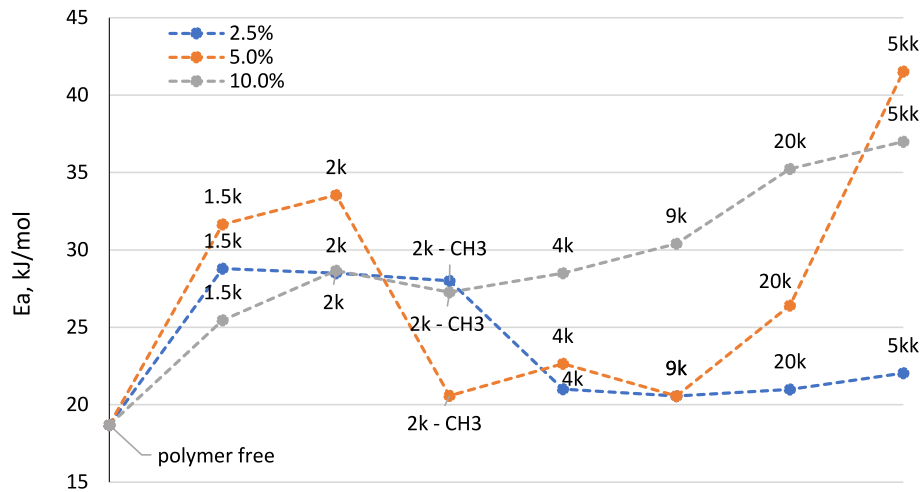


Fig. 4. The graphical representation of the E_a as a function of the molecular weight of the PEG molecule and its amount added in the system $\text{GuanHCl}:\text{AlCl}_3 = 1:3$; $dE/dt = 20 \text{ mV/s}$; a copper cathode (56 mm^2 geometrical area).

*k – 1000, kk – million (the molecular weight);

** The vertical line on the right side of the Fig. indicates a gap that separates points with a high polymer molecular weight.

composition of the electrolytes are illustrated in Fig. 4.

6. Model for binding and dependence on polymer length

The data in Fig. 4 can be explained using a statistical model. As shown above, there are two types of binding sites of $\text{GuanHCl}:\text{AlCl}_3$ on polymer: on the ending, hydroxyl groups and in the inner “middle” ether sites. Let the binding energy be E_{end} and E_{mid} respectively. Then, for the polymer consisting of N units: $N = M/44$, where M is polymer molecular mass, and 44 g/mol is the mass of a single unit. Each unit is equivalent binding site with energy E_{mid} . The same will be activation energy for leaving the site. Two ending sites have binding and activation energies for leaving E_{end} . The following equation applies for the effective binding energy E_{eff} , which is also activation energy measured in the experiment: (Eq. (3))

$$(N+2)\exp\left(\frac{E_{\text{eff}}}{RT}\right) = 2\exp\left(\frac{E_{\text{end}}}{RT}\right) + N\exp\left(\frac{E_{\text{mid}}}{RT}\right) \quad (3)$$

This leads to equation for effective activation energy at $N \gg 1$: (Eq. (4))

$$E_{\text{eff}} = RT \ln \left(\frac{2}{N} \exp\left(\frac{E_{\text{end}}}{RT}\right) + \exp\left(\frac{E_{\text{mid}}}{RT}\right) \right) \quad (4)$$

which provides dependence on polymer length N in terms of binding

energies on 2 types of sites. This equation can be directly compared with Fig. 4 data. Fitting to 2.5 concentration data gives 34.4 , 21.9 kJ/mol for E_{end} and E_{mid} respectively. For 5 % concentration 37.9 , 24.0 kJ/mol for E_{end} and E_{mid} . 10 % solutions already exhibit viscous behavior and do not obey this model. The values obtained are quite far from those provided in quantum chemical calculations. This difference stems from the simplified molecular structures used in the quantum chemical calculations. Also, DFT and CBS calculation access thermodynamic values, whereas conductivity activation energy is a kinetic parameter. Though one would expect that stronger binding implies escape higher barrier, as follows from linear relation of free energies principle.

7. Computational results

The use of enthalpy (ΔH^{gas}) or Gibbs free energy (ΔG^{gas}) for comparison is not an obvious point in this study. On the one hand, the use of Gibbs free energy (ΔG^{gas}) values for comparison are justified by the fact that the coupling constant between molecules is the logarithm of free energy, therefore the entropy factor is considered. On the other hand, the computational model used in the study for DFT is intentionally reduced to a chain of a few atoms (functional radicals). In view of this, the entropy factor, which directly depends on the number of atoms, will have incorrect values. At the same time, the values when comparing the enthalpy will have a smaller error (based on the given model), since the

Table 2

The calculated Boltzmann averaged ΔH^{gas} and ΔG^{gas} values in kJ/mol of dimer formation reactions. The best by ΔH^{gas} conformers found are shown.

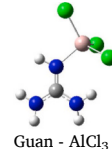
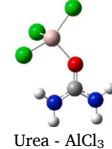
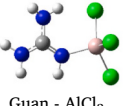
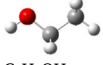
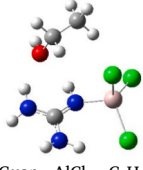
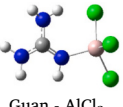
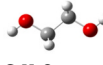
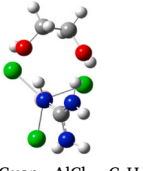
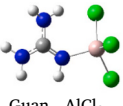
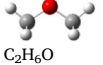
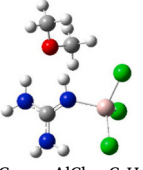
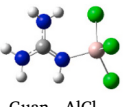
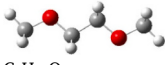
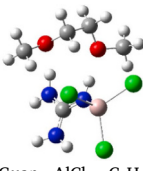
Reactant 1	Reactant 2	Product	DFT		CBS	
			ΔH^{gas}	ΔG^{gas}	ΔH^{gas}	ΔG^{gas}
 Guan (CH_5N_3)	 AlCl_3	 Guan - AlCl_3	-207.7	-160.7	-212.5	-165.4
 Urea ($\text{CH}_4\text{N}_2\text{O}$)	 AlCl_3	 Urea - AlCl_3	-171.4	-124.9	-181.4	-134.9

Table 3

The calculated Boltzmann averaged ΔH^{gas} and ΔG^{gas} values in kJ/mol of trimer formation reactions. The best by ΔH^{gas} conformers found are shown.

Reactant 1	Reactant 2	Product	DFT		CBS	
			ΔH^{gas}	ΔG^{gas}	ΔH^{gas}	ΔG^{gas}
 Guan - AlCl ₃	 C ₂ H ₅ OH (ethanol)	 Guan - AlCl ₃ - C ₂ H ₅ OH	-54.0	-3.2	-47.0	3.7
 Guan - AlCl ₃	 C ₂ H ₆ O ₂ (ethylene glycol)	 Guan - AlCl ₃ - C ₂ H ₆ O ₂	-74.8	-19.0	-64.7	-9.1
 Guan - AlCl ₃	 C ₂ H ₆ O (dimethyl ether)	 Guan - AlCl ₃ - C ₂ H ₆ O	-48.7	-2.1	-43.8	2.7
 Guan - AlCl ₃	 C ₄ H ₁₀ O ₂ (1,2-dimethoxyethane)	 Guan - AlCl ₃ - C ₄ H ₁₀ O ₂	-75.1	-18.6	-66.3	-9.8

interaction with the nearest atoms is considered admittedly accurately. In addition, if we compare full-sized molecules, the entropy factor will be approximately the same, since the influence of the functional groups of radicals H-O-C- / -C-O-C- will be insignificant based on the ratio of their number of several units per several thousand atoms in the complete chain of the molecule, while the enthalpy will be noticeably different and have approximate values to the model taken in this study.

The reaction of Guan and AlCl₃ was primarily investigated (as well as comparison with the reaction of Urea and AlCl₃). The computational results are presented in Table 2. In the best conformer of Guan-AlCl₃

complex, the non-covalent intermolecular interaction Al-N is more favorable with the nitrogen atom bonded to only one hydrogen (Table 2). In case of Urea-AlCl₃ complex, the interaction between Al-O is more favorable in terms of thermodynamics, which has also been noted by other authors [17]. The enthalpy of interaction between Guan and AlCl₃ is by about -35 kJ/mol lower than between Urea and AlCl₃, which is to be expected given that the oxygen atom is more electronegative than the nitrogen. This also indicates that the Guan molecule is a better Lewis base (better electron donor) than the Urea molecule.

Molecules of ethanol, ethylene glycol, dimethyl ether, and 1,2-

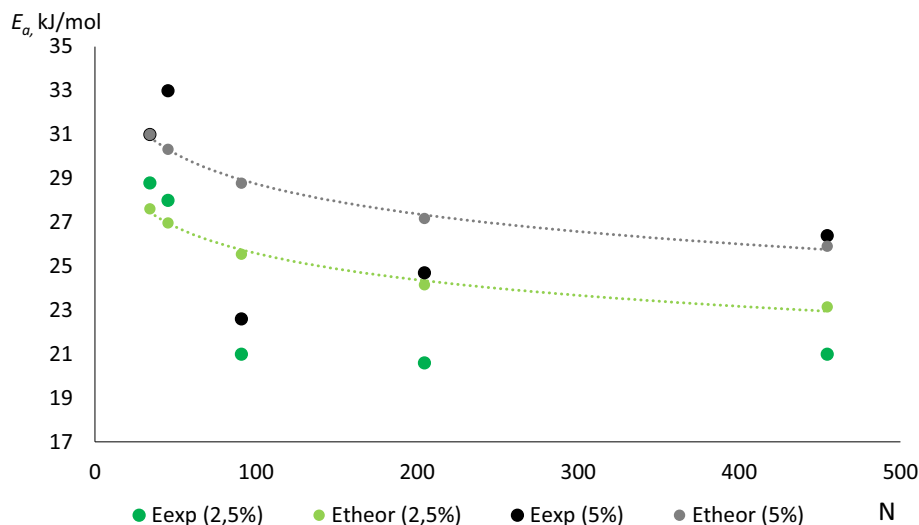


Fig. 5. The graphic representation of the fitting results for activation energy values N (the number of subunits, defined in the text).

dimethoxyethane were used as a model of solvent-fragment (oligomer) interacting with Guan- AlCl_3 complex. We found that in all studied Guan- AlCl_3 -oligomer complexes, in their best conformers, oligomer tends to form intermolecular hydrogen bonds of the N-H...O type with the Guan molecule. Hydrogen bonds of the same type were observed by the authors [17] when modeling complexes with Urea molecules.

When going from ethanol to ethylene glycol, the effect of the second oxygen is visible and the enthalpy of trimer formation decreases, because in the Guan- AlCl_3 - $\text{C}_2\text{H}_6\text{O}_2$ complex energetically more favorable intermolecular hydrogen bonds are formed between the oligomer and Guan. The same effect is observed when moving from dimethyl ether to 1,2-dimethoxyethane. That is, instead of forming two hydrogen bonds with one oxygen atom of the $\text{N}_{\text{amino}}\text{-H}\dots\text{O}\dots\text{H}\text{-N}_{\text{imino}}$ type, the most energetically preferable would be the formation of two hydrogen bonds: one for each oxygen atom of the $\text{N}_{\text{amino}}\text{-H}\dots\text{O}$ type and $\text{N}_{\text{imino}}\text{-H}\dots\text{O}$.

Comparing the calculated energies of formation of complexes with such oligomers as ethanol and dimethyl ether, we see that the interaction energy weakly depends on which oxygen atom hydrogen bonds are formed with: with oxygen of the hydroxy group or with ether oxygen. This is also true for ethylene glycol and 1,2-dimethoxyethane.

The direct comparison with experimental data analysis in Fig. 5 should be done using ethanol (entry 1) and dimethyl ether (entry 3) which contains single oxygen. Second oxygen gives an artifact of bunding to both of them. The DFT calculation gives binding enthalpies -58.8 and -53.9 kJ/mol for ethanol and dimethyl ether respectively, while the CBS method gives -46.8 and -43.8 kJ/mol. Experimental values are for activation energies being correspondingly 34.4 , 21.9 kJ/mol for 2.5 % PEO and for 5 % concentration 37.9 , 24.0 kJ/mol for E_{end} and E_{mid} . Now, the “end” position should be associated with ethanol (entry 1) whereas the “mid” one the emulated by dimethyl ether. The difference in the calculated enthalpies is 3–5 kJ/mol, whereas activation energies are shifted by 13 kJ/mol. The sign is correct, so the absolute value is not, albeit by reasonable margin for simplicity of treatment both of experimental data and modeling.

Comparing with AlCl_3 -urea-PEO [16,17] and AlCl_3 -Emim-PEO [15] current system behaves as elastomer, or the former. Emim system and solidifies due to 5 coordinated Al [15]. Correspondingly our DFT model resembles more used in [17].

Finally, PEO 2000 with both methyl at the ends has lower activation energies. Though to analyze better this result one needs more data with different molecular weights.

8. Conclusions

It was found in this study that the addition of polymer macromolecules affects the structure of the electrolyte in the system with GuanHCl- AlCl_3 complex. The activation energy (E_a) values were calculated for a GuanHCl- AlCl_3 system with PEG additives of various molecular weights (from 1500 to 5 million). Quantum-chemical computation showed a difference in the values of enthalpy (ΔH^{gas}) or Gibbs free energy (ΔG^{gas}) in the formation of a complex both between of Guan and AlCl_3 as well as comparison with the reaction of urea and AlCl_3 , and comparison of Guan- AlCl_3 with various functional groups of polymers. It can be concluded, that the internal resistance of the electrolyte decreases with an increase in the molecular weight of the added polymer (such as polymer macromolecules), in the concentration range from 2.5 to 10 % (which is confirmed by the minimum value of the activation energy in a certain area). The method presented in this paper is related to the measurement of the temperature dependence of the ionic conductivity of electrolytes for polymers with different chain lengths. Further from the indicated Arrhenius law is the activation energy, which determines the contribution of the functional groups located in the polymer chain, as well as the terminal functional groups. Polymer with longer chain has more low energy binding sites which causes lesser binding and consequently higher conductivity of electrolyte. As a result of the conducted

research, the experimental data have been obtained that determine unexpected conclusions about the nature of the processes. It is planned to conduct further research to clarify the patterns in model systems - electrolytes of a similar nature, for example acetamidine, with additives of the corresponding polymers.

Computational analysis revealed that the Guan- AlCl_3 complex exhibited a more favorable interaction compared to Urea- AlCl_3 , indicating Guan's superior Lewis basicity. The study extended to Guan- AlCl_3 complexes with solvent-fragment oligomers, highlighting the impact of additional oxygen atoms on the energetics of trimer formation. Interestingly, the calculated energies showed a weak dependence on the specific oxygen atom involved, emphasizing the versatility of the interactions studied across different oligomers. Overall, these findings contribute to a deeper understanding of the molecular interactions involved in these systems.

CRedit authorship contribution statement

Roman Tangalychev: Writing – original draft, Investigation, Formal analysis, Data curation. **Vasilii Korotenko:** Writing – original draft, Investigation, Formal analysis. **Igor Efimov:** Writing – review & editing, Formal analysis, Conceptualization. **Oleg N. Efimov:** Methodology, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Igor Efimov reports financial support was provided by Alexander von Humboldt Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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