VOLTAMMETRIC STUDY OF CORROSION OF MILD STEEL IN DEEP EUTECTIC SOLVENTS

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Systematic data on the physicochemical properties of a new class of ionic liquids, deep eutectic solvents (DES) which are based on mixtures of choline chloride and ethylene glycol or carbamide (Ethaline and Reline, receptively) have been obtained. The temperature dependences of density, electrical conductivity and viscosity of these ionic liquids were obtained and characterized. The main characteristics of the corrosion destruction of mild steel in these DES are established. Using voltammetric method, the rates of corrosion destruction of mild steel have been determined. It has been shown that Ethaline is more corrosive towards mild steel than Reline. The mechanism of corrosion of steel in these ionic liquids was established.

Most of the organic solvents used in modern industry are toxic and corrosive. In order to replace them in modern engineering processes, a new type of ionic liquids (ILs), deep eutectic solvents (DESs), were recently developed [1]. DESs can be considered as a promising alternative to traditional toxic solvents. ILs, unlike most "ordinary" organic solvents, are non-toxic, non-flammable, non-volatile, safe for humans and the environment [2, 3]. It should be noted that among the attractive advantages of the newest type of ionic liquids, DESs, their thermal and chemical resistance, polarity and electrical conductivity are much higher than in most classical ionic liquids; in addition, they are distinguished by a wide "window" of electrochemical stability, high solubility of metal salts, variability in structure and properties [4]. ILs can be used in different branches of industries: in the nuclear fuel cycle, in the oil refining industry, as an environment for organic synthesis and synthesis of nanomaterials, in the electrochemical industry (for electrodeposition of metals, alloys and composites, for electropolishing, for creating new current sources). ILs can be also used in machine and rocket construction, in the field of catalysis and biocatalysis, as traps of CO_2 and H_2S [4-13].

One of the most common components used in the formation of the newest ILs is choline chloride, a cheap nontoxic quaternary ammonium salt that forms deep eutectic mixtures with hydrogen bond donors such as urea, carboxylic acids, and polyhydric alcohols, [8-12]. The most widespread DESs based on choline chloride are Ethaline and Reline. Ethaline is a eutectic mixture of choline chloride (ChCl) with ethylene glycol (Etgl) in a molar ratio of 1 to 2, and Reline is a eutectic mixture of choline chloride with carbamide (urea) in the same molar ratio. These DESs are characterized by extremely low crystallization temperatures, which makes them convenient to use in a wide temperature range.

A large number of publications describe the possible applications of ionic liquids [4-13]. Many of them are devoted to the electrodeposition of various metals from DESs. However, very few papers concern the problems of corrosion and the mechanism of corrosion of structural materials in these ionic liquids. It should be noted that without the solution of these important problems, the full-fledged application of new types of ionic liquids in industry is impossible; therefore the presented work is aimed to solve this problems.

Research methodology

Ethaline and Reline mixtures were prepared by mixing the components at a temperature of 75°C until a homogeneous, colorless liquid was formed. To maintain the temperature, a Flüssigkeitsthermostate Baureihe U/UH8 thermostat (± 0.01°C) was used. After the storage of synthesized liquids for 24 hours, they were filtered under vacuum using a Schott filter.

Density (ρ) of DESs was determined by a pycnometric method (volume of a pycnometer was 5 ml). The dynamic viscosity (η) of the DESs was determined by the capillary flow method using a glass thermostated viscosimeter. The determination of electrical resistance of solutions (R) has been conducted by means of usual ac Wheatstone bridge at a frequency of about 500 Hz. Voltammograms were recorded using Potentiostat/Galvanostat/ZRAReference 3000 (Gamry Instruments, Inc.).

Voltammetric experiments were carried out in a three-electrode glass cell. A steel wire (St3) with a diameter of 2 mm pressed into a teflon holder was served as working electrode. We used a silver wire as a reference electrode. A graphite electrode with a highly developed surface was used as an auxiliary electrode. All experiments were carried out under the conditions of natural aeration.

Results and Discussion

1. Physicochemical characteristics of Ethaline and Reline

Dependences characterizing the effect of temperature on the density of Ethaline and Reline solutions are presented in Figure 1.

As can be seen in Fig. 1, an increase in temperature leads to a decrease in the density of DES, this fact can be explained by an increase in the mobility of ions and molecules in the ionic liquid due to the destruction of hydrogen bonds between them. We note the linear character of temperature dependences of the density both for Ethaline and for Reline.

In the wide temperature range, the density value for Reline solution was significantly higher than for Ethaline. Apparently, this is due to the different nature and strength of the interaction of the components that form the investigated DESs. It is known that DESs contain vacancies (the so-called "holes"), the size of which determines the density of the liquid. Thus, we can conclude that Reline with a higher density is characterized by significantly smaller vacancies in comparison with Ethaline.

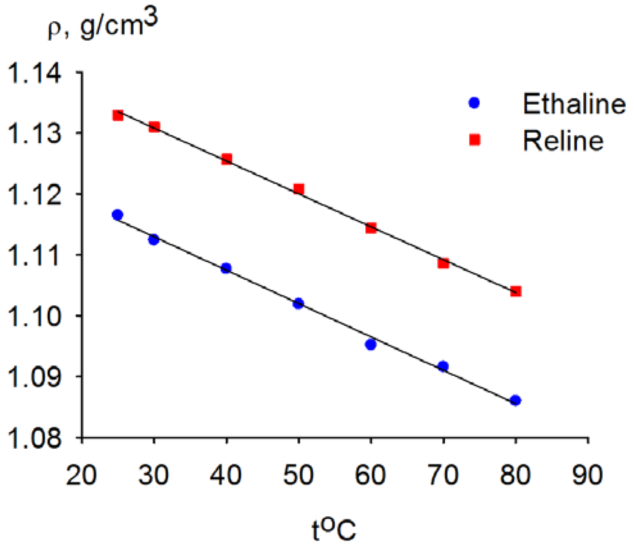

Figure 1. Temperature dependences of the density of Ethaline and Reline mixtures

It can be concluded from Fig. 2 that the different size of "holes" or vacancies in Ethaline and Reline solutions also affects on the viscosity of the solvents.

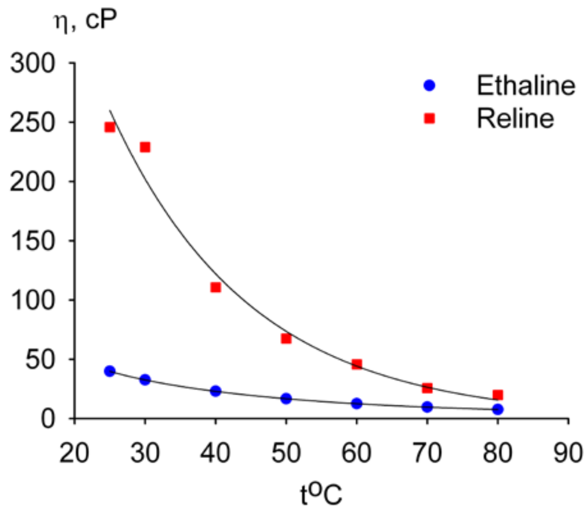

Figure 2. The dependence of the dynamic viscosity of Ethaline and Reline mixtures on temperature

As can be seen from the presented data (Fig. 2), the viscosity of the Reline solution is several times greater than the viscosity of the Ethaline mixture, this difference is especially noticeable at low temperatures. Increasing the temperature of the solutions leads to a regular decrease in the DESs viscosity both in case of Reline and in case of Ethaline. At higher temperatures (ca. 70-80°C), the viscosity of the Reline solution approaches the corresponding value of the Ethaline solution.

The increase in the mobility of ions and DESs molecules with increasing temperature is also reflected in the dependence of the electrical conductivity on temperature (Figure 3).

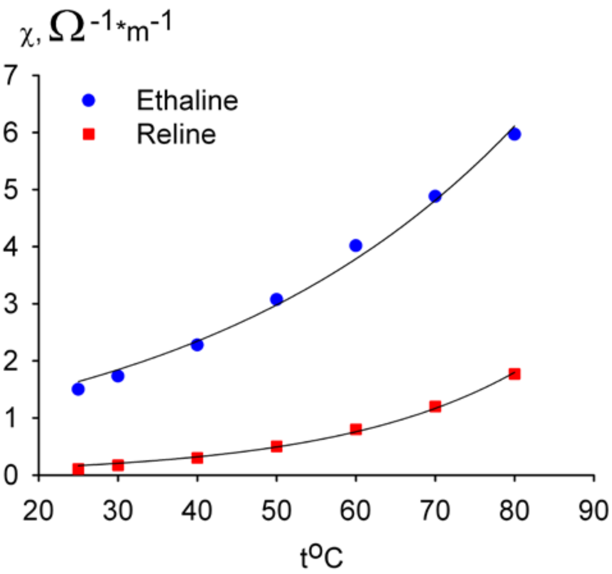

Figure 3. Temperature dependence of the conductivity of Ethaline and Reline mixtures

As can be seen in Fig. 3, the electrical conductivity of the Ethaline solution throughout the temperature range is noticeably greater than the electrical conductivity of the Reline solution, which is certainly also a consequence of various structures of the DESs under consideration and different sizes of vacancies in them.

2. Voltammetric study of the corrosion process

To obtain quantitative parameters of the corrosion process of mild steel in Ethaline and Reline solutions, voltammetric studies of the behavior of steel samples (St3) in these media have been carried out. Voltammograms (VAG) of the steel electrode in the mixtures Ethaline and Reline, obtained at different scan rates, are shown in Figure 4.

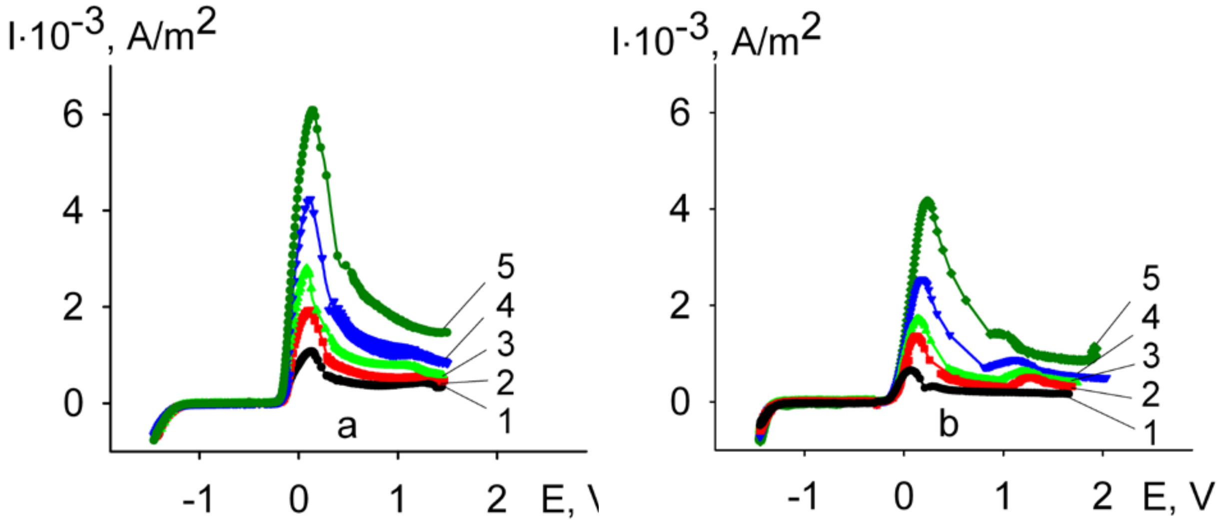

Figure 4. VAG of steel electrode in Ethaline (a) and Reline (b), obtained at different potential scan rate (mV/s): (1) 20, (2) 50, (3) 100, (4) 200, (5) 500, t = 25°C

The electrode potential was scanned at different scan rate from the open circuit potential (OCP) to the cathode region, and then to the anode one. A small current of the electroreduction of oxygen dissolved in DES (as stated above, the experiments were carried out under the conditions of natural aeration) is observed in the cathode region of the VAG (at negative potentials and negative current values). Further, at potentials which are more negative than -1.2 V, sharp increase in the current can be seen in VAG due to the hydrogen electroreduction on the steel surface from proton donors presented in DESs.

In the anode region of the VAG (at potentials more positive than -0.2 V), the current peak of the electrodissolution of steel electrode is observed. In addition, a decrease in current is observed in VAG at further potential scanning to more positive direction. This may be due to the passivation of the electrode surface. A sharp rise of the anode current at potentials of 1.8-2 V is evidently due to the oxidation of some solvent components.

Figure 4 demonstrates that at all potential scan rates the peak currents of the steel dissolution in Ethylene is higher than in Reline.

Figure 5 shows the effect of temperature on the shape of the VAG. As can be seen from the presented data, an increase in temperature leads to an increase in the currents of steel dissolution peaks in both solvents. This means that the electrodissolution rate of steel electrode is higher in Ethaline than in Reline at all temperatures.

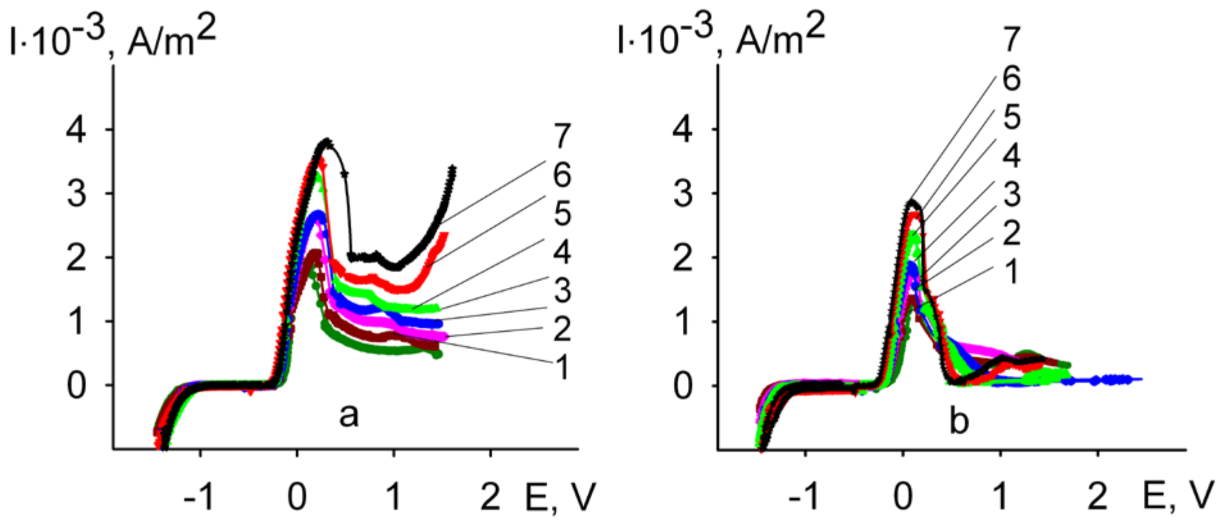

Figure 5. VAG of the steel electrode in Ethaline (a) and Reline (b) obtained at different temperatures (°C): (1) 25, (2) 30, (3) 40, (4) 50, (5) 60, (6) 70, (7) 80), v = 50 mV/s

The processing of the obtained VAGs (Fig. 4 and Fig. 5) allowed calculating the parameters of the corrosion process (Table). One can see in Table that the corrosion potentials of the steel electrode at all the investigated temperatures in the Ethaline solution are more negative compared to the potentials of the same electrode in Reline, this indicates higher corrosion activity of Ethaline towards mild steel.

Table. Corrosion potentials (E_{corr}) and corrosion currents (i_{corr}) of a steel electrode in Ethaline and Reline

t°C	$-E_{corr}$,mV	$i_{corr}\cdot10^{-3}$, A/m^2	E_{corr},mV	$i_{corr}\cdot10^{-3}$, A/m^2
	Ethaline		Reline	
25	-459	11.8	-445	8.7
30	-463	13.7	-453	9.6
40	-469	14.1	-462	10.2
50	-476	14.5	-466	10.4
60	-483	16.2	-470	11.4
70	-490	16.3	-484	15.1
80	-498	17.8	-496	17.2

It should be noted that the values of corrosion potential becomes more negative with increasing temperature. Thus, at high temperatures, the corrosive activities of the mixtures Ethaline and Reline become practically the same. The corrosion rates (in current units) over the wide temperature range are higher in Ethaline than in Reline. However, at temperatures of 70-80°C, the values of corrosion rates of steel in Ethaline and Reline become practically the same.

The voltammetric experiments showed that oxygen dissolved in Ethaline and Reline is a depolarizer in the process of corrosion. Various corrosion potentials and corrosion rates of steel in Ethaline and Reline are likely due to the differences in the amounts of depolarizer in the DESs. The amount of dissolved depolarizer depends on the physicochemical properties of the liquids. Analyzing the data given above, one can conclude that Ethylene and Reline significantly differ in their physicochemical properties, and these differences in properties are decreased with increasing temperature. Thus, the differences in the corrosivity of Ethaline and Reline are primarily due to the differences in their physicochemical properties.

Conclusions

It was found that the investigated ionic liquids differ in their physicochemical properties. The eutectic mixture Ethaline throughout the wide temperature range has a lower density and viscosity and a noticeably higher electrical conductivity than Reline. We note that with increasing temperature the difference in the parameters becomes not so pronounced.

The voltammetric study revealed that Ethaline is a more corrosive liquid (corrosion rate at all temperatures is higher). The difference in corrosion activity is probably due to the differences in physicochemical parameters of the studied DESs. The corrosion process in these eutectic mixtures proceeds with oxygen depolarization. The content of dissolved oxygen evidently depends on the nature of the medium. Thus, this quantity for Ethaline should be larger resulting in increasing corrosion rate. With increasing temperature, the physicochemical parameters of the systems under study become closer and their corrosive activities also approach.

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