UDC 544.65

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ADSORPTION PHENOMENA AT THE INTERFACE BETWEEN MERCURY AND SOLUTIONS CONTAINING CHOLINE CHLORIDE, ETHYLENE GLYCOL AND WATER

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Adsorption of the components of deep eutectic solvent ethaline (ethylene glycol and choline chloride) on mercury electrode is investigated by electrocapillary measurements. It is determined that choline cations are mainly adsorbed on the negatively charged surface of mercury, while chloride anions are mainly adsorbed on the positively charged surface. The corresponding values of free energies of adsorption and interactions of adsorbate and solvent with metal are calculated and analyzed. An anomalous increase in both the apparent value of the adsorption at limiting coverage and the free energy of the interaction of the choline cation with mercury is observed in the transition from aqueous to ethylene glycol solutions, which is explained by the formation of complexes in a surface layer that exist in deep eutectic solvents and are capable of adsorbing on the electrode surface. The free energy of interaction with the mercury surface is higher than the energy of squeezing out from the volume of the solution onto its surface, which indicates the specific interaction of the adsorbate with mercury. A marked decrease in interfacial tension on both branches of the electrocapillary curve is observed when water is added to ethaline.

Keywords: adsorption, electrocapillary curve, mercury, deep eutectic solvent, choline chloride, ethylene glycol, adsorption, Gibbs energy.

DOI: 10.32434/0321-4095-2021-138-5-50-58

Introduction

Deep eutectic solvents (DESs), as a new and promising type of ionic liquids, are currently being intensively studied given a number of interesting physicochemical properties and prospects for use in various fields of science and technology [1,2]. In particular, it is extremely important and relevant to study the structure of the electric double layer (EDL), which is formed at the interface between a DES and other phase, and investigate the corresponding adsorption phenomena [3–11]. It is known that the electric double layer formed at the ionic liquid/electrode interface differs in its structure and properties from the layers formed with the participation of «ordinary» aqueous electrolytes [12,13]. The practical use of ionic liquids in systems with charged surfaces is impossible without deep understanding of these features.

Mamme et al. [3] showed that EDL at the interface «the eutectic mixture of choline chloride and urea/graphene electrode» is built of a mixed layer consisting of urea molecules and counterion (choline cations or chloride anions), followed by a layer with a cluster structure containing all components of the DES (choline and chloride ions and urea molecules). The change in electrode polarization significantly affects the particle distribution in the EDL.

Calculations performed by the methods of density functional theory and research by atomic force microscopy [7] showed that the molecular component of a DES is moved away from the surface of a graphite electrode at any electrode potential, whereas chloride and choline ions are localized in the Stern layer in case of positively and negatively charged surface, respectively.

The properties of the electric double layer formed on the surface of platinum, gold and glass carbon electrodes immersed in a DES based on choline chloride and glycerol were studied by cyclic voltammetry and electrochemical impedance spectroscopy [8]. It was shown that the capacitance of the electric double layer weakly depends on the electrode potential but is sensitive to the nature of the electrode material.

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The vast majority of experimental and theoretical studies of the structure of EDL and adsorption in systems based on DESs, were conducted for solid electrodes. One of the few exceptions is work by Costa et al. [9], this study reported the data on the differential capacity of the EDL formed on a mercury electrode in liquid mixtures based on choline chloride with a number of polyols, urea and thiourea. It was concluded that the predominant adsorption of choline cation and chloride ion occurs at very negative and positive potentials, respectively.

Thus, there is currently a clear lack of experimental data on the structure of EDL and the adsorption of DESs components on the surface of liquid mercury. Meanwhile, the mercury electrode, which has long been used in electrochemical research, due to the high hydrogen overvoltage allows measurements in extremely wide ranges of electrode potentials without complications associated with some electrode processes. The results of experiments on a liquid mercury electrode, as a rule, are characterized by high reproducibility and reliability in comparison with the surfaces of solid electrodes. In addition, the use of Hg electrode allows implementing the electrocapillary method of studying the state of a metal surface, which is very informative and visual.

Therefore, the aim of this work was to establish patterns of adsorption phenomena on the surface of mercury in liquid systems containing the main components of a DES, which consists of ethylene glycol and choline chloride (the so-called ethaline [1]), and their aqueous solutions by using electrocapillary measurements.

Experimental

Ethylene glycol (99.9%, AR, Belgium), choline chloride (99%, Acros Organics) and sodium chloride (99.99%) were used in this study. Bidistilled water was used to prepare aqueous solutions. The procedures of solution preparation are described in detail elsewhere [11].

Electrocapillary curves at the mercury/solution interface were recorded by measuring the drip period of the mercury electrode using a PU-1 polarograph and a three-electrode electrochemical cell. The working electrode was a mercury drip electrode and the auxiliary electrode was a platinum electrode. The reference electrode was a saturated silver chloride electrode and a silver wire in the cases of aqueous solutions and ethaline-based solutions, respectively. All measurements were made at a constant temperature of 298 K (Flussigkeitsthermostate Baureihe U/UH8 thermostat, Prufgerate-Werk Medingen GmbH, Germany). The lifetime of the droplet was recorded in 0.1 V increments and readings were recorded for at least 3 droplets for each electrode potential value. The experiments were performed three times and the average value was calculated. The reproducibility of the results was at least 95%.

Results and discussion

Adsorption of choline chloride on mercury from aqueous solutions

As can be seen from the electrocapillary curves obtained in aqueous solutions of choline chloride of different concentrations (0.1 M NaCl was used as a supporting electrolyte) (Fig. 1), the cathode branches of the curves show a significant decrease in interfacial tension, indicating the adsorption of choline cation on mercury surface. A decrease in interfacial tension is also observed on the anode branch of the electrocapillary curve, which is probably due to the adsorption of chloride anions. In general, the results correspond to those reported earlier in the study of similar systems [14].

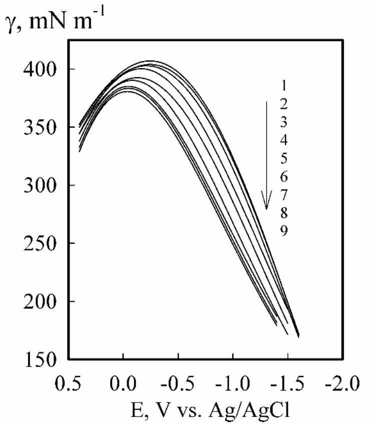


Fig. 1. Electrocapillary curves recorded in aqueous solutions containing 0.1 M NaCl (supporting electrolyte) and choline chloride (mol dm^{-3}): 1 – 0; 2 – $1.00\cdot10^{-3}$; 3 – $3.00\cdot10^{-3}$; 4 – $5.00\cdot10^{-3}$; 5 – $7.00\cdot10^{-3}$; 6 – 0.010; 7 – 0.050; 8 – 0.100; 9 – 0.150. The arrow indicates the order of numbering of the curves

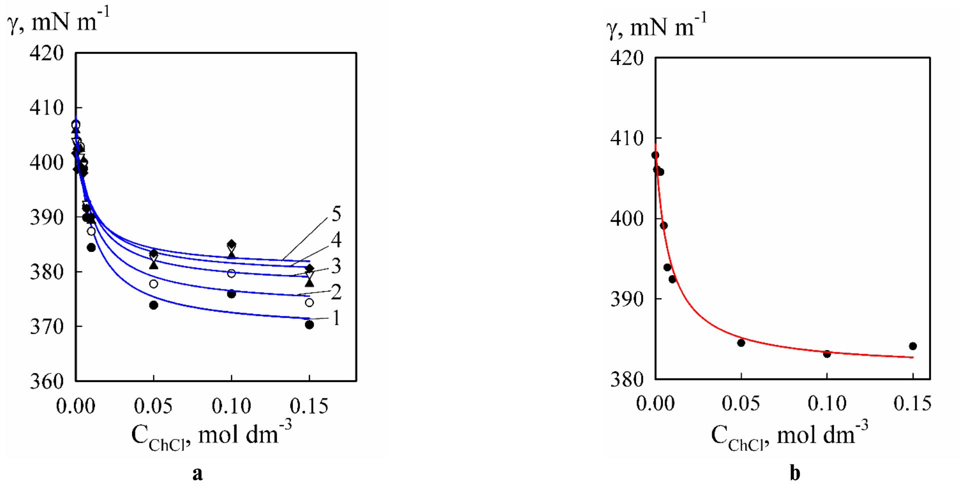
Adsorption of ionic constituents of choline chloride causes a decrease in interfacial tension at the maximum of the electrocapillary curve and a corresponding shift of this maximum towards positive potentials with increasing concentration of choline chloride (Fig. 1, Table 1). This indicates that the adsorption of choline cations is not only purely electrostatic, but also to some extent caused by specific interactions.

Figure 2 demonstrates the isotherms of the interfacial tension at different values of the electrode

Table 1

Potential of zero charge ($E_{q=0}$) of the mercury electrode in aqueous solutions of choline chloride (ChCl) of different concentration (0.1 M NaCl as a supporting electrolyte)

C_{ChCl}, mol dm^{-3}	0	0.001	0.003	0.005	0.007	0.010	0.050	0.100	0.150
$E_{q=0}$, V	–0.23	–0.23	–0.19	–0.16	–0.11	–0.05	–0.02	–0.02	–0.01



a b

Fig. 2. Isotherms of interfacial tension at the mercury/aqueous solution interface at different concentrations of choline chloride (0.1 M NaCl as a supporting electrolyte): a – plotted at the electrode potentials (1) –0.23 V; (2) –0.19 V; (3) –0.16 V; (4) –0.11 V; and (5) –0.05 V; b – plotted for the surface of uncharged mercury ($E_{q=0}$)

potential. To determine the adsorption parameters by differentiating the isotherms of the interfacial tension, a certain value of the electrode potential should be selected, for which the corresponding calculations will be performed according to the Gibbs adsorption equation. In this study, in accordance with the recommendation [15], an isotherm of interfacial tension was constructed at the potential of zero charge (i.e., $E_{q=0}$) of each given electrolyte (Fig. 2, b), which allowed determining the adsorption characteristics of choline cation on the uncharged mercury surface by the adsorption Gibbs equation (Table 2).

Table 2

Thermodynamic parameters of adsorption of choline cation from aqueous solution on mercury *

Parameter	Value
$\Gamma_\infty \cdot 10^6$, mol m^{-2}	2.61
B, m^3 mol^{-1}	0.50
ΔG^0, kJ mol^{-1}	–8.24
$\Delta G^0_{A/S}$, kJ mol^{-1}	–28.88
$\Delta G^0_{S/Me}$, kJ mol^{-1}	–21.00
$\Delta G^0_{A/Me}$, kJ mol^{-1}	–0.36

* Note: Γ_∞ is the adsorption at limiting coverage; B is the equilibrium constant of adsorption; ΔG^0 is the standard free energy of adsorption. The values of $\Delta G^0_{A/S}$, $\Delta G^0_{S/Me}$ and $\Delta G^0_{A/Me}$ are explained in text.

The adsorption of choline cation on the mercury surface at limiting coverage (Γ_∞=2.61·10^{-6} mol m^{-2}) is slightly lower than at the solution/air interface (Γ_∞=3.10·10^{-6} mol m^{-2} [11]). This may indicate certain differences in the orientation of choline cations in EDLs formed at different phase interfaces.

It should be noted that the value of ΔG^0 in Table 1 is the free adsorption energy of choline cation on mercury, which was determined on the basis of the calculated adsorption equilibrium constant B (Langmuir equation). As is known [16], this value characterizes the change in the free energy of the system in the process of competitive adsorption of a surfactant on the electrode and is determined by the following equation:

$$\Delta G^0 = \Delta G^0_{A/Me} + \Delta G^0_{A/S} - \Delta G^0_{S/Me},$$

where $\Delta G^0_{A/S}$ is the free energy of interaction of the organic adsorbate with the solvent, which with satisfactory accuracy corresponds to the free energy of adsorption of a surfactant at the solution/air interface; $\Delta G^0_{A/Me}$ and $\Delta G^0_{S/Me}$ are the free energies of interaction of the adsorbate and the solvent with the metal, respectively.

The value of $\Delta G^0_{A/S}$ was taken from the data given in our previous work [11]. The value of $\Delta G^0_{S/Me} = -21.00$ kJ mol^{-1} for the interaction of mercury and water was borrowed from studies [17,18].

The value of $\Delta G^0_{A/Me}$ was calculated by Eq. (1).

A comparison of the values of the constituents of ΔG^0 in Eq. (1) shows (Table 1) that the main contribution to the change in the Gibbs energy during the adsorption of the choline cation is made by the interaction between the organic cation and the solvent (i.e. squeezing the cation out from the bulk solution onto its surface); the contribution of the interaction of the surface-active ion with the metal is much smaller.

Adsorption of ethylene glycol on mercury from aqueous solutions

As expected, the electrocapillary curves obtained in an aqueous solution of ethylene glycol have the appearance typical of nonionic surfactants: there is a decrease in interfacial tension on both branches of the curve due to adsorption. The electrode potential corresponding to the uncharged surface (at the maximum of the curve) changes insignificantly (Fig. 3, Table 3).

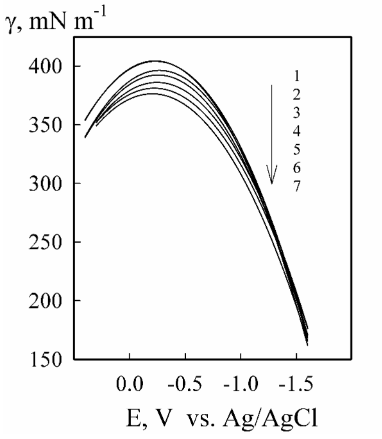


Fig. 3. Electrocapillary curves recorded in aqueous solutions containing 0.1 M NaCl (supporting electrolyte) and ethylene glycol (mol dm^{-3}): 1 – 0; 2 – $1.00\cdot10^{-3}$; 3 – $5.00\cdot10^{-3}$; 4 – 0.010; 5 – 0.050; 6 – 0.100; 7 – 0.200. The arrow indicates the order of numbering of the curves

The interfacial tension isotherm of uncharged mercury (Fig. 4) derived from electrocapillary curves, as in the previous case, was processed using the Gibbs adsorption equation and the Langmuir adsorption isotherm. The results of the calculations are summarized in Table 4.

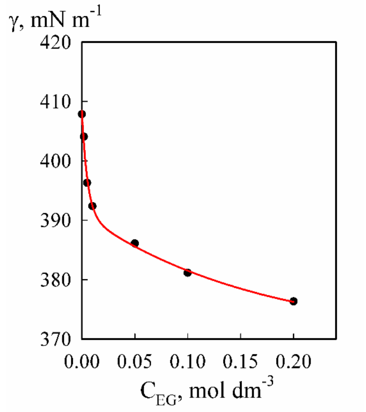


Fig. 4. Isotherm of interfacial tension at the mercury/aqueous solution interface at different concentrations of ethylene glycol (0.1 M NaCl as a supporting electrolyte) on the surface of uncharged mercury ($E_{q=0}$)

It should be noted that the value of $\Delta G^0_{A/S}$=14.46 kJ mol^{-1} was determined by standard methods based on surface tension isotherms of aqueous solutions of ethylene glycol (the data are not shown). It follows from the comparison of the results given in Tables 2 and 4 that ethylene glycol has significantly lower tendency to adsorption at the «aqueous solution/air» interface as compared with the choline cation. However, the free energy of interaction of ethylene glycol with the mercury surface is significantly higher than in the case of choline cation, and this component makes the main contribution to the change in Gibbs energy during adsorption at the interface «aqueous solution/ mercury». Probably, ethylene glycol molecules are prone to specific adsorption on mercury.

Interestingly, the value of ΔG^0=–6.01 kJ mol^{-1} for adsorption of ethylene glycol on mercury found in this work is close to the value reported earlier for adsorption of the same adsorbate from solutions of similar composition (about –8 kJ mol^{-1}) [19]. In a first approximation, the calculated free energy of the interaction of ethylene glycol with the mercury surface (–41.47 kJ mol^{-1}) approaches the value defined earlier (about –50 kJ mol^{-1}) [17]. A significantly higher absolute value of $\Delta G^0_{A/Me}$ for ethylene glycol, as compared with water (according to both this study and the results given in previous work [17]), means that ethylene glycol molecules are able to effectively displace water molecules by adsorbing on the surface of the mercury electrode.

Table 3

Potential of zero charge ($E_{q=0}$) of the mercury electrode in aqueous solutions of ethylene glycol of different concentration (0.1 M NaCl as a supporting electrolyte)

$C_{ethylene\ glycol}$, mol dm^{-3}	0	0.002	0.005	0.010	0.050	0.100	0.200
$E_{q=0}$, V	–0.23	–0.23	–0.25	–0.25	–0.25	–0.24	–0.22

Table 4

Thermodynamic parameters of adsorption of ethylene glycol from aqueous solution on mercury *

Parameter	Value
$\Gamma_{\infty}\cdot10^6$, mol m^{-2}	2.60
B, m^3 mol^{-1}	0.20
ΔG^0, kJ mol^{-1}	–6.01
$\Delta G^0_{A/S}$, kJ mol^{-1}	14.46
$\Delta G^0_{S/Me}$, kJ mol^{-1}	–21.00
$\Delta G^0_{A/Me}$, kJ mol^{-1}	–41.47

* Note: The designations are the same as in Table 2.

Adsorption of choline chloride on mercury from ethylene glycol solutions

Electrocapillary curves recorded on mercury in ethylene glycol solutions of choline chloride (Fig. 5) show that the interfacial tension decreases on both branches. Obviously, the adsorption of chloride ion causes a corresponding decrease in interfacial tension on a positively charged surface. Adsorption of the choline cation probably causes a significant reduction in interfacial tension on the negatively charged surface of mercury.

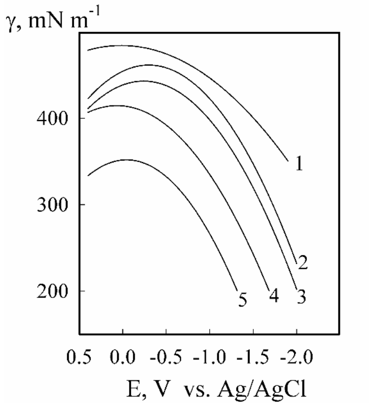


Fig. 5. Electrocapillary curves recorded in ethylene glycol solutions containing 0.1 M NaCl (supporting electrolyte) and choline chloride (mol dm^{-3}): 1 – 0; 2 – 1.0·10^{-2}; 3 – 5.0·10^{-2}; 4 – 0.100; 5 – 0.500

Experimentally measured potentials of zero charge of the mercury electrode in ethylene glycol solutions of choline chloride are given in Table 5. It is clear that the dependence $E_{q=0}$ vs. C_{ChCl} is non-monotonic, which is probably due to the competitive nature of the adsorption of choline cation and chloride anion in this case. Nevertheless, we can note a tendency to shift the potential of zero charge towards more positive values, which is obviously determined by the predominant adsorption of choline cation. The interfacial tension isotherm (Fig. 6) was constructed to determine the adsorption parameters (Table 6).

Table 5

Potential of zero charge ($E_{q=0}$) of the mercury electrode in ethylene glycol solutions of choline chloride of different concentration (0.1 M NaCl as a supporting electrolyte)

C_{ChCl}, M	0	0.010	0.050	0.100	0.500
$E_{q=0}$, V	–0.12	–0.32	–0.24	–0.07	–0.09

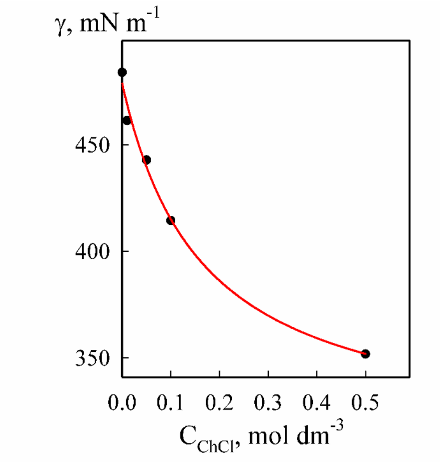


Fig. 6. Isotherm of interfacial tension at the mercury/ethylene glycol solution interface at different concentrations of ethylene glycol (0.1 M NaCl as a supporting electrolyte) on the surface of uncharged mercury ($E_{q=0}$)

Table 6

Thermodynamic parameters of adsorption of choline from ethylene glycol solution on mercury *

Parameter	Value
$\Gamma_{\infty}\cdot10^6$, mol m^{-2}	11.2
B, m^3 mol^{-1}	0.12
ΔG^0, kJ mol^{-1}	–4.70
$\Delta G^0_{A/S}$, kJ mol^{-1}	–16.43
$\Delta G^0_{S/Me}$, kJ mol^{-1}	–41.47
$\Delta G^0_{A/Me}$, kJ mol^{-1}	–29.74

* Note: The designations are the same as in Table 2.

When discussing the data from Table 6, it should be noted that the value of $\cdot\Delta G^0_{A/S}=-16.43$ kJ mol^{-1} is taken from our previous work [11] and the value of $\Delta G^0_{S/Me}=-41.47$ kJ mol^{-1} is given in Table 4. A significant (almost fivefold) increase in the adsorption corresponding to limiting coverage is noteworthy. An essential increase in the value of free energy of interaction between choline ion and mercury surface is indicative: it reaches $\Delta G^0_{A/Me}=-29.74$ kJ mol^{-1} in case of ethylene glycol solution, while it is only -0.36 kJ mol^{-1} (Table 2) for aqueous solution, which implies a considerable increase in the surface activity of the choline cation in ethylene glycol.

The revealed anomalies (an increase in the values of Γ_∞ and $\Delta G^0_{A/Me}$) in the transition from aqueous solutions to ethylene glycol ones can be interpreted within the framework of an explanation given earlier [11]. According to that concept, in a system containing both choline chloride and ethylene glycol even at their ratios far from eutectic, some complexes can be formed in the adsorption surface layer, which are similar to those that exist in the bulk of a liquid deep eutectic solvent. This is due to the concentration of components in the adsorption surface layer and the formation of hydrogen bonds between them. Obviously, this phenomenon may occur not only at the solution/air interface as was reported in work [11], but also at the ethylene glycol solution of choline chloride/mercury interface. The formation of the above complexes promotes an increase in surface activity (which means a growth of $\Delta G^0_{A/Me}$) and an increase in the apparent value of the adsorption at limiting coverage (Γ_∞). Given the fact that not the individual ions, but some complexes are adsorbed on the surface of the mercury electrode, the data shown in Fig. 6 and in Table 6 have a semi-quantitative character. However, there is no doubt that the observed tendencies of changes in the corresponding thermodynamic parameters correctly reflect the main features of physicochemical processes occurring during adsorption of choline chloride from ethylene glycol solutions.

Effect of the addition of water to ethaline on adsorption phenomena on the mercury surface

Given the known data that the addition of water to deep eutectic solvents significantly affects the adsorption characteristics [11], it was interesting to follow the nature of changes in the appearance of the electrocapillary curves at different concentrations of water added to ethaline (Fig. 7). As can be seen, there is a decrease in the interfacial tension on both branches of the electrocapillary curve with increasing water content. When interpreting the obtained data, it should be borne in mind that the introduction of water into ethaline gradually destroys the complexes formed in DESs due to the hydrogen bonds and promotes the solvation of the released particles by water molecules [20]. On a positively charged mercury surface, the decrease in interfacial tension is caused mainly by the adsorption of chloride anions. Hydrated choline cations, whose share increases with increasing water concentration, are adsorbed on the negatively charged Hg surface.

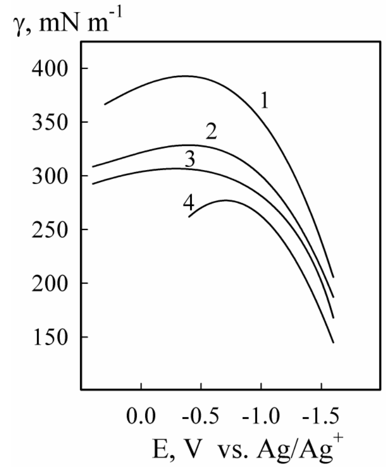


Fig. 7. Electrocapillary curves recorded in ethaline with the addition of water (wt.%): 1 – 0; 2 – 20; 3 – 40; 4 – 60

However, it should be noted that the obtained data are semi-quantitative and they should be treated with caution due to the fact that there is an uncontrolled change in the diffusion potential at the interface «electrolyte under study/solution into which the reference electrode is immersed» when water is introduced. Considering this circumstance as well as uncontrolled changes in the nature of particles adsorbed on the mercury surface, the quantitative processing of the data in Fig. 7 using the Gibbs adsorption equation and the Langmuir isotherm was not performed. For the same reasons, it is largely pointless to discuss the shift of the potential of zero charge of mercury when adding water to ethaline.

Conclusions

Electrocapillary measurements showed that choline cations are adsorbed on the negatively charged surface of mercury and chloride ions are adsorbed on the positively charged one in both aqueous and ethylene glycol solutions.

When adsorbing a choline cation from an aqueous solution on mercury, the main contribution to the Gibbs energy change is made by the interaction of the organic cation with the solvent (i.e. by squeezing the cation out from the bulk solution onto the surface) and the contribution of the interaction between surfactant ion and the metal surface is much smaller. Quite the contrary, the free energy of interaction between ethylene glycol molecules and the mercury surface in aqueous solution is significantly higher than in the case of choline, and this component makes the main contribution to the change in Gibbs energy during adsorption at the «aqueous solution/mercury» interface.

It is significant that during the transition from aqueous solutions to ethylene glycol ones, there is a considerable increase in the value (modulo) of the free energy of the interaction between choline cations and the mercury surface, which indicates a significant increase in the surface activity of the choline cation. This phenomenon may be caused by the formation of hydrogen bonds and the formation of complexes in the adsorption surface layer, which are similar to those that exist in the bulk volume of deep eutectic solvents. It was found that this effect is observed not only at the «solution/air» interface, but also at the «ethylene glycol solution of choline chloride/mercury electrode» interface. The free energy of interaction with the mercury surface is higher than the free energy of squeezing out from the bulk solution onto its surface, which indicates a certain specific interaction of the adsorbate (choline cation) with mercury.

When water is introduced into ethaline, the complexes existing in the DES are gradually destroyed and the released particles are solvated by water molecules. As a result, the formed solvated particles are adsorbed on the mercury surface and the interfacial tension on both branches of the electrocapillary curve is reduced.

Acknowledgments

This work was financially supported by the Ministry of Education and Science of Ukraine (project no. 0121U109551).

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Received 30.04.2021

АДСОРБЦІЙНІ ЯВИЩА НА МЕЖІ РТУТІ І РОЗЧИНІВ, ЩО МІСТЯТЬ ХОЛІН ХЛОРИД, ЕТИЛЕНГЛІКОЛЬ І ВОДУ

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Досліджена адсорбція компонентів низькотемпературного евтектичного розчинника ethaline (етиленгліколю та холін хлориду) на ртуті методом електрокапілярних вимірювань. Встановлено, що на негативно зарядженій поверхні ртуті переважно адсорбуються катіони холіну, а на позитивно зарядженій – хлорид-аніони. Обчислені та проаналізовані відповідні значення вільних енергій адсорбції та взаємодій адсорбата і розчинника з металом. Показано аномальне зростання уявної величини граничної адсорбції та вільної енергії взаємодії катіона холіну зі ртуттю при переході від водного розчину до етиленгліколевого, що пояснено утворенням у адсорбційному поверхневому шарі комплексів, аналогічних тим, що існують в об'ємі низькотемпературних евтектичних розчинників, і здатних адсорбуватися на електродній поверхні. Вільна енергія взаємодії зі ртутною поверхнею є вищою, ніж енергія «витискування» з об'єму розчину на його поверхню, що вказує на специфічну взаємодію адсорбату зі ртуттю. Виявлено, що при додаванні води до ethaline у результаті адсорбції спостерігається помітне зниження поверхневого натягу на обох гілках електрокапілярної кривої.

Ключові слова: адсорбція, електрокапілярна крива, ртуть, низькотемпературний евтектичний розчинник, холін хлорид, етиленгліколь, адсорбція, енергія Гіббса.

ADSORPTION PHENOMENA AT THE INTERFACE BETWEEN MERCURY AND SOLUTIONS CONTAINING CHOLINE CHLORIDE, ETHYLENE GLYCOL AND WATER

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Adsorption of the components of deep eutectic solvent ethaline (ethylene glycol and choline chloride) on mercury electrode is investigated by electrocapillary measurements. It is determined that choline cations are mainly adsorbed on the negatively charged surface of mercury, while chloride anions are mainly adsorbed on the positively charged surface. The corresponding values of free energies of adsorption and interactions of adsorbate and solvent with metal are calculated and analyzed. An anomalous increase in both the apparent value of the adsorption at limiting coverage and the free energy of the interaction of the choline cation with mercury is observed in the transition from aqueous to ethylene glycol solutions, which is explained by the formation of complexes in a surface layer that exist in deep eutectic solvents and are capable of adsorbing on the electrode surface. The free energy of interaction with the mercury surface is higher than the energy of squeezing out from the volume of the solution onto its surface, which indicates the specific interaction of the adsorbate with mercury. A marked decrease in interfacial tension on both branches of the electrocapillary curve is observed when water is added to ethaline.

Keywords: adsorption; electrocapillary curve; mercury; deep eutectic solvent; choline chloride; ethylene glycol; adsorption; Gibbs energy.

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