The composition of the starting electrolyte also influences the electrosynthesis, and in particular the yield of diesters of the higher dicarboxylic acids. The yield of 1,12-dodecanedioic acid diester increases when the starting concentration of the adipic acid monoester is higher (Fig. 4). This possible is due to enhanced solubility of ethylene in the starting monoester.

A mixture of diesters of higher dicarboxylic acids was similarly obtained in a chemical yield of 96% when electrolyzing monomethyl glutarate in the presence of ethylene under pressure (dimethyl suberate in a yield of 79%, dimethyl sebacate in a yield of 11%, and dimethyl 1,12-dodecanedioate in a yield of 6%).

Thus, by performing the Brown–Walker reaction in the presence of ethylene one can raise the useful conversion of monoester to 92-95%. All products formed can be used for technical purposes: the manufacture of plasticizers, lubricating oils, polyesters, polyamides, and polyurethanes. For plasticizer manufacture one can use both a mixture of dicarboxylic acid diesters and the individual diesters separated by fractional distillation of the mixture.

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INFLUENCE OF D-RIBONO-γ-LACTONE ON THE CATHODIC INCORPORATION OF LITHIUM INTO LEAD AND MERCURY

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Previously it had been shown that there is an interrelation between the electroreduction of a number of organic compounds and the cathodic incorporation of alkali metals into solid electrodes. The suggestion was made, in particular, that reaction between the organic material and the products of cathodic incorporation of the alkali metals is one of the reduction pathways [1]. Here the analogy to reduction at the mercury cathode under conditions of amalgam formation has been stressed. In studies of the above interrelation, organic compounds had been used which could be reduced both at liquid mercury and at different solid electrodes. However, there are materials, in particular D-ribono-γ-lactone (RL), which in aqueous solutions can only be reduced at mercury cathodes under conditions of amalgam formation [2]. At solid electrodes, RL was found to be electrochemically inactive [3]. Therefore in the present work we studied the effect of RL on the cathodic incorporation of lithium into lead and mercury.

The measurements were conducted in 0.5 N $LiClO_4$ solution in propylene carbonate. Crystalline RL was obtained from the technical product via the benzylidene derivative and subsequent recrystallization [4].

Polarization curves were recorded in order to elucidate the effect of RL on the rate of cathodic incorporation of alkali metal and of anodic decomposition of the intermetallic compound. The curves were recorded at lead electrodes of two types. Part of the samples was untreated, i.e., had not undergone preliminary cathodic and anodic polarization. The φ vs log i relations obtained are reported in Fig. 1. Throughout the potential range examined one notices an increase in the overpotential of the cathodic reaction when RL is present; this effect becomes stronger at higher RL concentrations.

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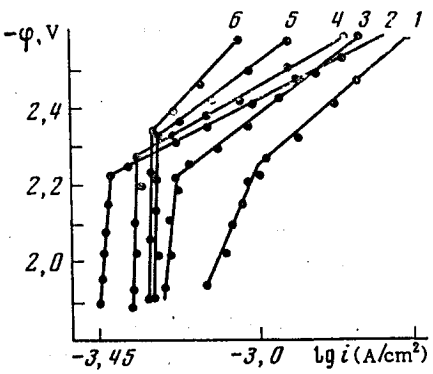

Fig. 1

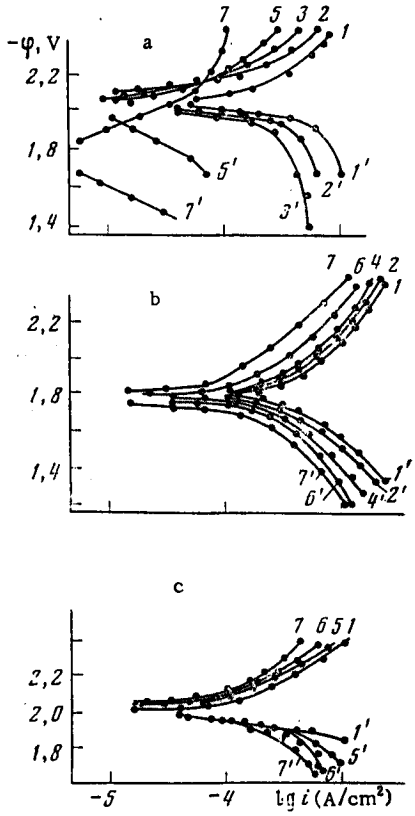

Fig. 2

Fig. 1. Cathodic polarization curves recorded at lead. The RL concentrations: 1) 0, 2) 5×10^{-4}, 3) 10^{-3}, 4) 5×10^{-3}, 5) 10^{-2}, and 6) 10^{-1} M.

Fig. 2. Polarization curves recorded, a) at the intermetallic compound of lead with lithium produced electrochemically, b) at mercury, and c) at the intermetallic compound of lead with sodium produced by fusion of the elements. The RL concentrations: 1) 0, 2) 5×10^{-4}, 3) 10^{-3}, 4) 2×10^{-3}, 5) 5×10^{-3}, 6) 10^{-2}, and 7) 10^{-1} M.

Other lead electrodes were prepolarized to −2.4 V in the working solution in order to accumulate intermetallic compound. Then potentials more negative and more positive than the equilibrium potential of the intermetallic compound were alternatingly applied to the electrode, and the corresponding values of the current recorded. The polarization curves obtained at electrodes prepared in this way (with an excess of vacancies in the layer of intermetallic compound) are reported in Fig. 2a. The linear relation between i and φ observed here is characteristic for those cases of incorporation where chemical reaction between alkali metal and cathode metal is the rate-limiting step [5]. The displacement of the cathodic and anodic i vs φ straight lines toward lower current densities which is found to occur in the presence of RL and also the increase in their slope are indications for inhibition, both of incorporation and of ionization of the alkali metal, which can be explained by coating of part of the electrode surface by molecules of the organic material.

A decrease in the rate of the cathodic process was not observed when incorporation of alkali metals was studied under the influence of other organic compounds also capable of reacting with the intermetallic compound [1].

It must be noted that at the RL concentration of 0.1 M, in addition to inhibition one observes a displacement of the equilibrium potential of the intermetallic compound to less negative values, which reaches 0.3 V (Fig. 2a). It follows from these results that in the presence of RL, the intermetallic compound is produced not only in lower quantities but also in different composition, with lower activity of the alkali metal.

The influence of RL on the rate of incorporation and ionization near the equilibrium potential is also found when measuring the impedance of the lead electrode. Figure 3 shows the dependence of reactive on resistive component of impedance, both measured in series substitution. The increase in radius of the semi-

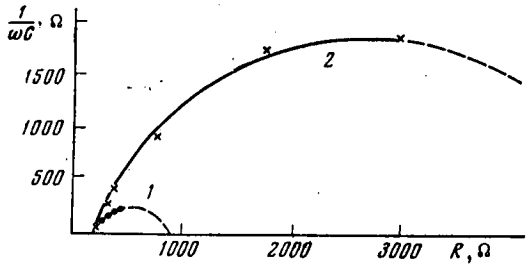

Fig. 3. The reactive impedance component of the lead electrode as function of the resistive component, both measured in series substitution at different frequencies near the equilibrium potential ($\varphi = -2.3$ V): 1) base electrolyte, 2) base electrolyte $+5 \times 10^{-4}$ M RL.

circle which results upon addition of RL to the solution indicates that the electrochemical step of incorporation becomes about one order of magnitude slower when this compound is present. At high frequencies the ohmic components are the same in solutions with and without RL, which indicates that poorly conducting layers are not present on the electrode surface.

Since the behavior of the mercury electrode as cathode for RL reduction is substantially different from that of the lead electrode [2, 3], it was of interest to examine the effect of RL on the cathodic formation and anodic decomposition of alkali metal alloys with mercury. Polarization curves were recorded at mercury following the procedure described above, including cathodic prepolarization of the electrode (Fig. 2b). At low RL concentrations, the curves obtained at mercury are similar to those obtained at lead. But at RL concentrations above 10^{-2} M, the behavior of the electrodes is substantially different; the displacement of equilibrium potential to the positive side which was observed for the lead electrode is not seen with mercury.

Under the aspect of the formation of intermetallic compounds, solid and liquid electrodes differ in the distribution of this compound at the surface and in the interior of the electrode. Therefore, we also recorded polarization curves at Na–Pb alloy obtained thermally (Fig. 2c). The polarization curves obtained at the thermal alloy look like the curves for mercury.

The effect of RL on the electrochemical reaction rates at potentials between -1.7 and -2.4 V can be attributed to the adsorption of RL molecules in this potential range, which appears to be near the zero-charge potential of the intermetallic compound. The results of [6] confirm that the zero-charge potential of an intermetallic compound is displaced to more negative values when alkali metal is incorporated with the formation of intermetallic compound.

Thus, a decrease in the rate of incorporation of alkali metal ions is observed for all the electrodes studied, both solid and liquid, viz., lead, intermetallic compounds obtained both electrochemically (with lithium) and thermally (with sodium), and also mercury, when lactone is present in the propylene carbonate solution.

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