

Adsorption distribution of the ion associates and ion-exchange at the water/1,2-dichloroethane interface by extracting with cesium dicarbollyde

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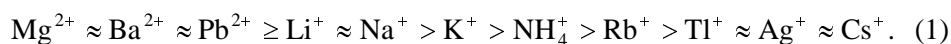
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Abstract. The paper presents evaluation of the distribution ratios of dicarbollylcobaltate (III) of alkali metal salts and of the voluminous constant of exchange of sodium by magnesium on a monolayer. A comparison of these values, calculated by different methods, has been made and the influence of counterions on the surface activity of cesium dicarbollyde is investigated. Interfacial tension isotherms have been used to study the adsorption at the water/1,2-dichloroethane interface and to evaluate the above-mentioned values.

Key words: dicarbollylcobaltate (III) anion, interface, interfacial tension, isotherm, drop-volume method.

1. INTRODUCTION

In this paper we study the properties of monolayers of non-typical cation-exchange extractant dicarbollylcobaltate (III) salts adsorbed at the water/1,2-dichloroethane interface. Even if the system is not extracting in usual meaning, that is, the distribution ratios are small, their values are higher for less hydrated counterions [1]. Cesium dicarbollyde, dissolved in dichloroethane, behaves as the cation-exchanger to the salt of the other metal dissolved in the aqueous phase. The counterions affect the surface activity of this cation-exchange extractant according to an order reverse to the Hofmeister lyotropic series:



The distribution ratios are maximal for the first and last member of the row as shown in [2].

2. MATERIALS AND METHODS

The method of surface pressure isotherms has been used to study the adsorption of dicarbollylcobaltate (III) of monovalent and bivalent metals at the water/1,2-dichloroethane interface. The description of the drop-volume method, including the experimental device, is presented in [3]. The information about dicarbollyde salts and other substances, including salts, water, and 1,2-dichloroethane as well as formulas for calculating surface pressure π from the experimentally measured interfacial tension σ and the work of adsorption (desorption) W , is presented in [2].

The distribution ratio of the salt between organic and water phase $D_{o/w}$ was calculated by an equation derived in [4]:

$$W_{ad}^w - W_{ad}^o = RT \ln D_{o/w}, \quad (2)$$

where W_{ad}^w and W_{ad}^o are the work of adsorption from the water phase and organic phase, respectively, R is the universal gas constant, and T is the absolute temperature.

3. RESULTS

The introduction of a salt of the investigated counterion of a certain concentration that reduces surface pressure by 1 mN/m in the aqueous phase at a constant concentration of the background electrolyte, allowed to define the voluminous ion-exchange constants K_v as a function of the distribution ratios of ion pairs to Cs^+ ions [2]. The concentrations of the introduced counterions are presented in [2].

The isotherms of the surface pressure are presented in Fig. 1.

Great variation of the voluminous constant K_v of ion exchange of the ion of the extractant to the counterion from the water phase (three orders in logarithmic scale) [2] necessitates an immediate definition of the distribution ratio $D_{o/w}$ of the ion associate directly from the surface pressure isotherms. The introduction of counterions in the aqueous phase at the constant ion force 0.1 M $Mg(NO_3)_2$ allows to calculate the work of desorption of dicarbollyde anions (marked as DC^-) to the aqueous phase according to the Betts-Pethica equation. The work of desorption W_{des}^w and $\lg D_{o/w}$ of ion pairs are:

$$W_{des}^w: 13.46 (Li^+); 17.35 (Na^+); 18.68 (K^+); 21.81 (NH_4^+); \\ 23.50 (Rb^+); 28.06 (Cs^+); \text{kJ/mol}; \quad (3)$$

$$\lg D_{o/w}: -4.82 (Mg^{2+}); -3.62 (Li^+); -2.93 (Na^+); -2.69 (K^+); -3.13 (NH_4^+); \\ -1.83 (Rb^+); -1.02 (Cs^+). \quad (4)$$

The extraction rate is maximum for Cs^+ ions.

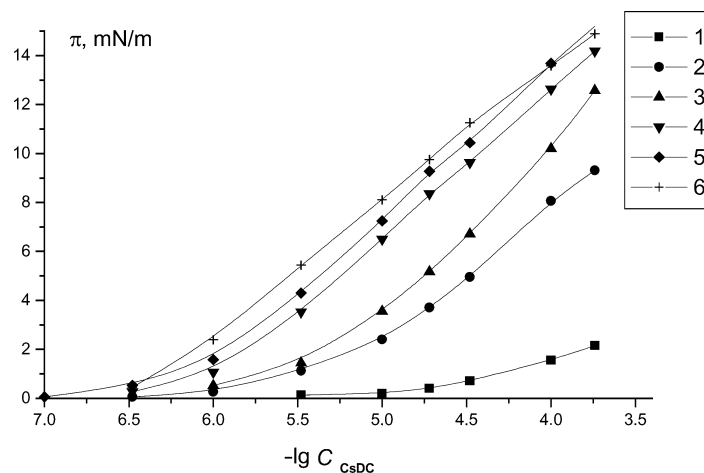


Fig. 1. Surface pressure isotherms at 20°C for dicarbollycobaltate (III) cesium solutions in 1,2-dichloroethane at the interface with aqueous solutions: 1 – 0.1 M CsNO₃; 2 – 0.1 M Mg(NO₃)₂ + 5 × 10⁻⁴ M CsNO₃; 3 – 0.1 M Mg(NO₃)₂ + 10⁻⁴ M CsNO₃; 4 – 0.1 M Mg(NO₃)₂ + 5 × 10⁻⁵ M CsNO₃; 5 – 0.1 M Mg(NO₃)₂ + 10⁻⁶ M CsNO₃; 6 – 0.1 M Mg(NO₃)₂.

The work of adsorption from the organic phase W_{ad}^0 CsDC_o is 33.78 kJ/mol. It is the work calculated from the initial fragment of the isotherm 4 in Fig. 1, CsDC_o/(0.1 M Mg(NO₃)₂ + 10⁻⁵ M CsNO₃)^w. It is an isotherm, for which the surface tension at the point 10⁻⁴ M DCCs is by 1 mN/m less than for the isotherm 6. The value of $D_{o/w}$ for Mg²⁺ was determined independently.

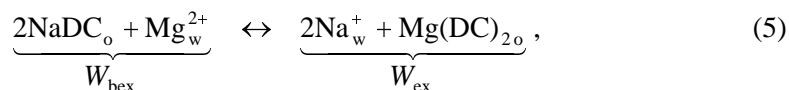
Figure 2 presents the isotherms for the solutions of dicarbollyde salts, dissolved in dichloroethane at the interface with 0–0.1 M corresponding salts in the aqueous phase, i.e., for individual dicarbollydes of metals MDC.

The ions Cs⁺, Rb⁺, and K⁺ (Fig. 2) are desorbed and extracted better in a composition of ion pairs.

The $D_{o/w}$ for the Na-salt was evaluated as a ratio of the salt solubilities in organic and aqueous phases over the points of maximum adsorption on the isotherms NaDC_o/0.1 M NaCl^w and 10⁻⁴ M NaDC_o/(0–0.1 M NaCl)^w presented in Fig. 2. ($\lg D_{o/w}$ was –2.70).

The works of adsorption from the organic phase for individual metal dicarbollydes are: 36.20 kJ/mol for Mg(DC)₂ and 33.1 kJ/mol for NaDC [2]. From the water phase they are 16.05 kJ/mol for NaDC and 21.33 kJ/mol for Mg(DC)₂, respectively. They were calculated from the initial parts of the isotherms 4 and 5 (Fig. 2).

If sodium dicarbollyde is dissolved in the organic phase and Mg²⁺ salt (in the aqueous one), the reaction of ion-exchange takes place in the interface zone:



where W_{bex} and W_{ex} denote back extraction and extraction of Na⁺, respectively.

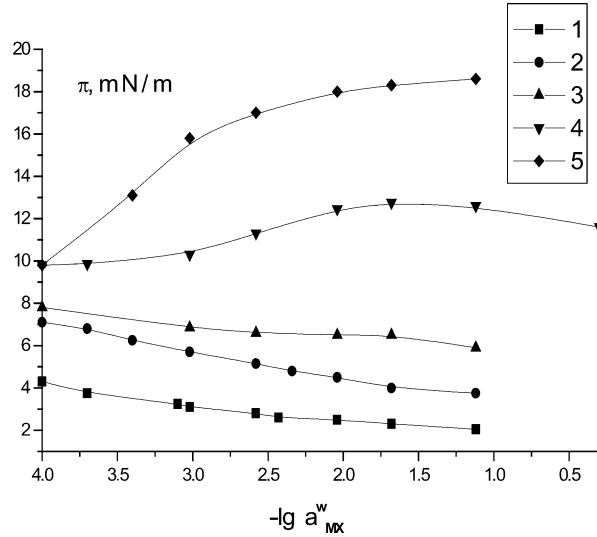


Fig. 2. Surface pressure isotherms at 20°C for 10^{-4} M dicarbollycobaltate (III) metal solutions in 1,2-dichloroethane at the interface with 0–0.1 M water solutions of salts: 1 – CsNO_3 ; 2 – RbCl ; 3 – KNO_3 ; 4 – NaCl ; 5 – $\text{NaDC}_0/\text{Mg}(\text{NO}_3)_2^w$; the values of π coincide with those for the interface with water and 10^{-4} M salt solutions; 1.7×10^{-4} M NaDC_0 ; 1.3×10^{-4} M RbDC_0 ; 10^{-4} M KDC_0 and 10^{-4} M CsDC_0 were used; a_{MX}^w is the activity of the salt MX in water.

The exchange rate of sodium to magnesium is

$$K_{v\text{Na}^+/\text{Mg}^{2+}} = \frac{D_{o/w\text{Mg}^{2+}}}{D_{o/w\text{Na}^+}^2}, \quad -\lg K_v = 2\lg D_{o/w\text{Na}^+} - \lg D_{o/w\text{Mg}^{2+}}. \quad (6)$$

The straight reaction is back extraction of Na^+ ; the reverse reaction is extraction of Na^+ . The works W_{bex} and W_{ex} can be calculated for each of them. The difference of these works $\Delta W = W_{\text{bex}} - W_{\text{ex}}$ is related to K_v as $\Delta W = RT \ln K_{v\text{Na}^+/\text{Mg}^{2+}}$, $\lg K_v = 1.49$. The value found from the selectivity coefficients of the ion-selective electrode [2] is 1.38. It confirms that the values of the exchange constant, found by different methods, are close. The value of $\lg K_{v\text{Na}^+/\text{Ba}^{2+}}$ is 1.5 for the interface with nitrobenzene [5].

This approach has been found applicable to different extractants [1] and allows relative calculations of the ions in an existing ion-exchanger (H^+ or Na^+ for cation-exchangers or Cl^- for salts of quaternary ammonium bases).

4. CONCLUSIONS

1. The distribution ratio of the ion associate is maximum for cesium dicarbollyde and minimum for magnesium dicarbollyde at the Hofmeister lyotropic series of counterions.

2. If sodium dicarbollyde is dissolved in organic phase and the magnesium salt in the aqueous one, the reaction of ion-exchange takes place and is characterized by a constant K_v . The value of $\lg K_v$ (1.49) is in accordance with the constants found by two other methods.

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Adsorptsioon ja ionvahetus vee ja 1,2-diklooretaani eralduspinnal tseesiumdikarboliidi ekstraktsioonil diklooretaaniks

Tatjana Borissova

Artiklis vaadeldakse dikarboliitkoobaltiidi (III) jaotust, naatriumi magneesiumiga monokihiks muundamise konstanti ja selle väärtuste arvutamist erinevatel meetoditel ning vastasioonide mõju tseesiumkarboliidi pinna aktiivsusele. Nii märgitud suuruste määramisel kui ka adsorptsiooni uuringutel vesi/1,2-diklooretaani eralduspinnal kasutati pindpinevuse isotermi.