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Some Possibilities of the Drop-Volume Method for Investigation of the Water/Oil Phase Interface: Adsorption and Precipitation

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The present paper presents evaluation of the thickness of adsorbed layer (linear dimension of a molecule), the number of monolayers precipitated from the organic and aqueous phases, the densities of crown-ether and its complexes with KSCN, $KAg(CN)_2$. Special attention was paid to the course of interfacial tension isotherms when surface active substance (SAS) adsorbs from water or organic phase; state of substance in solution: dissociation, formation of saturated or supersaturated solution. The thickness of adsorbed layer of complexes between crown ethers and potassium salts equals to 5 – 7 Å and it is comparable to the thickness of a monolayer formed by lying hydrocarbon chains.

Keywords: dicyclohexane-18-crown-6, interface, interfacial tension, isotherm, precipitation.

1. INTRODUCTION

The method of surface pressure isotherms allows to relate the surface and volume properties of surface active substances (SAS). As model systems, some untypical SAS were investigated, i.e., complexes of crown-ether and salts of alkali metals. The penetration of a cation into a cavity of dicyclohexane-18-crown-6 makes the substance diphilic and more surface active, if compare to crown ether. The substance distributes between the aqueous and organic phases. The complex is less soluble in water than a MX salt and in the organic phase than crown-ether. The previous paper evaluated the adsorption work of the complex from the aqueous phase, its distribution between the phases and the value of hydrophilic-lypophilic balance resting upon the surface pressure isotherms obtained by the drop-volume method [1].

2. EXPERIMENTAL DETAILS

The interfacial tension at the water/oil interface was measured by means of the drop-volume method using an instrument constructed for this purpose (Fig. 1). In all cases, a drop of water was formed at the abut of a glass capillary pressed in Teflon. Such a construction makes it possible to use a series of capillaries with different diameters and to avoid wetting of the outer surface of the capillary by water. A drop was pressed out from a capillary by a Teflon pistol, which moved inside a glass cylinder with the help of a micrometer connected to an electric motor. A system of reducers made it possible to vary the rate of drop formation from 0.1 to 0.0001 cm^3/min, thus making it possible to choose a certain drop-forming rate for each case and thus to secure interfacial tension measuring under the conditions close to equilibrium ones. The independence of interfacial tension on the further reduction of drop-forming rate serves as the basis for the statement that adsorption at the interface is close to equilibrium.

The densities of isomer A of dicyclohexane-18-crown-6, its complex with KSCN, a complex of dibenzo-18-crown-6 with $KAg(CN)_2$ were obtained pycnometrically without vacuum processing, over octane.

The value of surface pressure was calculated according to the following equation:

$$\pi = \sigma_o - \sigma, \qquad (1)$$

where σ_o is the interfacial tension at the organic solvent/water interface; σ is the interfacial tension at the interface of crown ether solution in organic solvent and water solution of MX salt.

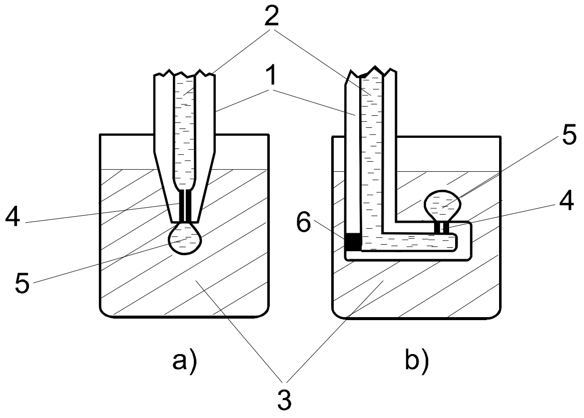

Fig. 1. The scheme of a capillary for the drop-volume method applied to interfacial tension measuring: a – density of the water phase is more than that of the oil phase; b – density of the oil phase is more than that of the water phase; 1 – Teflon tube; 2 – water phase; 3 – oil phase; 4 – glass capillary; 5 – forming water drop; 6 – glass plug

The adsorption of SAS was calculated using the Gibbs equation:

$$\Gamma = -\frac{1}{nRT}\frac{d\sigma}{d\ln a}, \qquad (2)$$

where a is an activity of SAS; $n = 1$ in presence (and it equals to 2 in absence) of background electrolyte having common ion to SAS [2]. The activity of complex in organic phase equals to concentration.

The adsorption work was calculated using the Bets-Pethica equation [3]:

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$$\underset{com}{Wad} = RTln\left(\frac{\pi}{Ccom}\right)_{C\to 0}, \quad (3)$$

where C_{COM} is the concentration of the complex in the organic or water phases. Subscripts w and o denote water and organic phases.

The state of an ideal two-dimensional gas (corresponding to the Henry adsorption isotherm) with a surface pressure being 1 mN/m and that of 1 M ideal solution [4] have been accepted as a standard state.

The thickness of an adsorption layer (linear dimension of a molecule) was calculated using the equation:

$$l = \frac{\Gamma_{max} \cdot M}{\rho}, \quad (4)$$

where Γ is expressed in mol/cm^2; M is the molecular mass of a substance; ρ is the density of substance in g/cm^3 [5]. The constant of substance distribution and the hydrophilic-lypophilic balance value were calculated due to equation and value are shown in [1].

The isomer A (cis-sin-cis conformation) and B (cis-anti-cis) of dicyclohexane-18-crown-6 were separated out of a mixture of diasterseomers following to the procedure given in [6].

The analytic grade inorganic salts were twice recrystallized from water. MCl and M_2SO_4 salts were kept at 600 °C during 20 hours.

Twice distilled water with a surface tension of 72.5 mN/m (20 °C) was used in all experiments.

1,2-Dichloroethane was purified in a similar way [7] and the fractions with a boiling point of 83.4 – 83.5 °C were used. Toluene and n-octane were distilled without further purification.

The interfacial tension of mutually saturated liquids was 34.8 mN/m for the water/toluene interface; 28.5 – for the 1,2-dichloroethane/water interface.

3. RESULTS

Surface pressure is a function of two parameters: concentration of crown-ether in organic phase lgC_A^o and activity of distributed complex A·KX in aqueous phase lga_{KX}^w. The background electrolyte doesn't display any surface activity, so the surface activity during the adsorption from water phase must be related to the activity of distributed complex.

The surface tension grows monotonously as the concentration of crown ether increases. Adsorption achieves the maximum value at the point "C" (Fig. 2, 3). The solubility of the complex is achieved too, i.e. a saturated solution forms. Sometimes, but not always, a straight portion can be found in isotherms after the "C" point. The precipitation of the substance begins for non-micelle forming SAS i.e., the formation of polylayers at the phase interface. The interface is in equilibrium with the supersaturated solution. The concentration of monomers increases insignificantly and is fixed by the run of tangential "CB" to the point "C" (Fig. 2, 3). The location of the point "C" is related to the solubility of the complex in each phase and in fact does not depend on the concentration of crown ether or electrolyte. The number of layers m from either border of every phase is different at the time of drop break: from a monolayer at $m = 1$ to $m = 42$. It is calculated as the ratio of maximum adsorption to the adsorption at a given experimental point as it has been suggested by A. Popov for calculating the degree of SAS association in the organic phase volume [3].

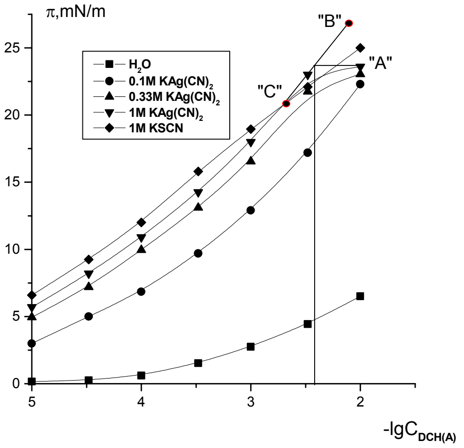

Fig.2. Surface pressure isotherms for DCH(A) solutions in toluene at the interface with water solutions: 1 – H_2O, 2 – 0.1 M $KAg(CN)_2$, 3 – 0.33 M $KAg(CN)_2$, 4 – 1 M $KAg(CN)_2$, 5 – 1 M KSCN

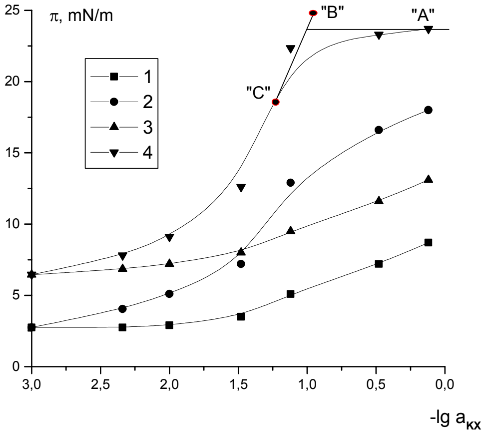

Fig. 3. Surface pressure isotherms for potassium compounds water solutions at the interface with 10^{-3} M (1, 2) and 10^{-2} M (3, 4) solutions of dicyclohexane-18-crown-6 (isomer A) in toluene: 1, 3 – KOH; 2, 4 – $KAg(CN)_2$

It has been attempted to state the criterion for forming the limit-saturated monolayer at the phase interface. The following condition is fulfilled for adsorption of the crown-ether·$KAg(CN)_2$ complex:

$$W_{ad}^o / W_{ad}^w = 1/2\, \Gamma_{max}^w / \Gamma_{max}^o, \quad (5)$$

where W_{ad} is the work of adsorption and Γ_{max} is the maximum adsorption from the organic and aqueous phases. It means that the work of covering by the limit-saturated monolayer is equal both from the organic and aqueous phases. Maximum adsorption from the organic phase equals ½ of that from the aqueous phase for KSCN, KCl salts and it is 1 for KOH. This fact is in accord with the molecular ratio of substances in precipitate being 1:1 at

Table 1. Parameters of the adsorption at the temperature 20 °C

N	Aqueous phase	ρ, g/cm^3 (18 °C)	W^o_{ad}, kJ/mol	W^w_{ad}, kJ/mol	$\Gamma^w_{max}/2$, mol/cm^2	Γ^o_{max} mol/cm^2	l, Å	W^w_{ad} exp kJ/mol	m^o	m^w
1	1 M $KAg(CN)_2$		35.40	13.74	$4.23\cdot10^{-10}$	$1.76\cdot10^{-10}$			8	42
2	0.1 M $KAg(CN)_2$		32.80	13.74	$4.23\cdot10^{-10}$	$1.86\cdot10^{-10}$			1	11
3	1 M KSCN	1.155	35.10	12.71	$1.12\cdot10^{-10}$	$1.17\cdot10^{-10}$	4.7		1	3
4	0.1 M KSCN		30.80	12.71	$0.92\cdot10^{-10}$	$1.17\cdot10^{-10}$			1	1
5	1 M KCl		32.40	11.28	$0.78\cdot10^{-10}$	$0.99\cdot10^{-10}$		12.03	1	1
6	1 M KOH		30.80	10.61	$\Gamma^w_{max} = 0.80\cdot10^{-10}$	$0.88\cdot10^{-10}$			1	4
7	0.1 M KOH		26.60	10.61	$\Gamma^w_{max} = 0.80\cdot10^{-10}$	$0.94\cdot10^{-10}$			1	1
8	0.1 M $KClO_4$		32.40	12.65	$\Gamma^w_{max} = 1.56\cdot10^{-10}$	$1.22\cdot10^{-10}$		12.13	1	1
9	Water/DCH(A) in toluene	1.102	20.70			$0.91\cdot10^{-10}$	3.0			
10	0.1 M $KAg(CN)_2$/ DBK in benzene	1.530	33.00			$1.95\cdot10^{-10}$	7.1			

the phase interface independent on the ion pair dissociation in the aqueous phase. It was shown previously [1] that a nine times excess of the background electrolyte does not suppress the dissociation of a complex in the aqueous phase.

It is known for the adsorption of SAS homologous series that the thickness of the adsorption layer affecting the surface tension equals to 12Å [5]. The corresponding values found for the experimental systems (3 – 7 Å) are comparable with the thickness of a monolayer formed by lying hydrocarbon chains. The number of monolayers allows to evaluate the thickness of precipitate. It is known that the area of cross-section of a hydrocarbon tail is 18 – 19 Å^2, the diameter of this circle is about 5Å. When crown ether is not complexed, the thickness is much smaller. The number of monolayers allows to evaluate the thickness of the precipitate. The data for 10^{-2} dibenzo-18-crown-6 (DBK) in benzene/1M $KAg(CN)_2$ are given under number 10 after [8] in Table 1.

Table 1 presents the density of complex DCH(A)·KX ρ, the work of adsorption of the complex from the organic phase W^o_{ad}, the work of adsorption of the complex from the water phase W^w_{ad}, maximum adsorption of the complex from water Γ^w_{max}, maximum adsorption of complex from the organic phase Γ^o_{max}, the thickness of an adsorption layer l at the phase interface 10^{-2} M crown ether in toluene/water solutions KX, the work of adsorption of the complex measured experimentally from the aqueous phase W^w_{ad}, exp, the number of layers precipitated from the organic phase m^o, the number of layers precipitated from the aqueous phase m^w.

4. CONCLUSIONS

1. The following condition is proposed as a criterion for forming the limit-saturated monolayer at the phase interface: $W^o_{ad} / W^w_{ad} = 1/2\Gamma^w_{max} / \Gamma^o_{max}$. The work of covering by the limit-saturated monolayer is equal both for the organic and aqueous phases.

2. The molecular ratio of substances in precipitate is 1:1 at the phase interface for all investigated compounds.

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