EFFECT OF TRITON X100 ON TETRAMETHYLAMMONIUM ION TRANSPORT KINETICS THROUGH THE WATER/NITROBENZENE INTERFACE

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The tetramethylammonium cation (TMA^+) transport through the water/nitrobenzene interface modified by the Triton X100 (TX100) adsorption has been investigated using cyclic voltammetry and interfacial tension measurements. Obtained results indicate the strong adsorption of TX100 and its responsible effect on the TMA^+ ion transfer. Adsorption data have been fitted to six theoretical adsorption isotherm equations with the best fitting for the Frumkin isotherm. The mechanism of facilitating effect of TX100 on the TMA^+ transfer has been proposed. The suggested mechanism is different from that developed by other authors.

The history of the studies of the liquid/liquid interface between immiscible electrolyte solutions in water and in an organic solvent (ITIES) has lasted almost twenty years. Hundreds publications have appeared on the subject since the Gavach's and Guastalla's work[1] who were the first to apply the electrochemical methods to the interface separating immiscible electrolyte solutions (ITIES). The literature of the subject was reviewed by Vanysek and Buck[2] and by Koryta[3]. The papers mainly dealt with interface polarization phenomena[4–6], with charge transport through the ITIES (refs[7–11]) with double layer structure[12–14] and with adsorption of ions and neutral molecules in the interfacial region[15–19].

Recently, the investigators working in the domain have indicated the ways of applying their results in practice. An interesting practical aspect of the studies of ITIES is the prospect to apply them in analysis, particularly in constructing new ion-selective electrodes. Now, the most commonly used electrodes are those with polyvinyl chloride gel membrane in an organic solvent containing suitable ions to assure its good selecti-

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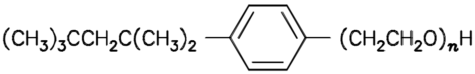
**On leave from the Department of Chemistry, Warsaw University, ul. Pasteura 1, 02-093 Warsaw, Poland vity, sensitivity and electric conductance. Such techniques were applied to construct the electrodes sensitive to tetramethylammonium and acetylcholinium ions[20–23]. The results of the studies of the adsorption on ITIES were also applied to improve e.g. the parameters of electrodes sensitive to lanthanide ion[24] or to alkali metal ions[25,26]. It was attained by modifying the solution composition from which the ion-selective membranes were obtained and the inner solution composition. The modifications consisted in adding substances changing the interface state due to specific adsorption. This group of substances contains various surfactants like Tritons X, Tween 20, crown ethers.

The results of the studies of the effect of Triton X100 (TX100) on tetramethylammonium ion (TMA^+) transport kinetics through the water/nitrobenzene interface are presented in this work. Triton X100 is a non-ionic surfactant, it belongs to polyethers of general formula



where *n* is 9 or 10 in the case of TX100. The studies cover the adsorption of TX100 on the water/nitrobenzene interface and the TMA ion transport through the interface in the presence of TX100 in the aqueous phase. It has been the purpose of the study to determine if TX100 affects the tetramethylammonium ion transfer across the ITIES between water and nitrobenzene and what is the mechanism of this influence.

EXPERIMENTAL

Apparatus: The adsorption studies were carried out by measuring interfacial tension. The stalagmometric method modified in our Laboratory[27] to liquid/liquid interfacial tension measurements was used to this aim. Chronovoltammetric studies were carried out using a four-electrode potentiostat[28,29]. The experimental results, both electrocapillary (maximum determinations) and chronovoltammetric (transition peak position and height determinations) were processed by differentiating the obtained curves numerically.

Reagents: Tetramethylammonium chloride (analytical grade, Fluka), lithium chloride (analytical grade, POCh, Poland), and Triton X100 (analytical grade, POCh, Poland) were used without purification. Tetrabutylammonium tetraphenylborate (TBATPhB) was prepared from sodium tetraphenylborate (analytical grade, Fluka) and tetrabutylammonium chloride (analytical grade, Fluka) using the procedure described by Gavach et al.[30]. Tetrabutylammonium chloride (pure, Fluka) was purified by twofold crystallization from 1 : 1 dioxan–ethyl ether mixture. Nitrobenzene (POCh, Poland) was purified by fractional distillation at reduced pressure. Triply distilled water saturated with nitrobenzene and nitrobenzene saturated with water were used to prepare solutions. Each partition system was stored for 2 h before the measurement for partition equilibrium completion.

Electrocapillary measurements were carried out using the cell:

$$\mathrm{Ag, AgCl} \mid \mathrm{LiCl + TX100[aq]} \mid \mathrm{TBATPhB[nb]} \underset{2}{\mid} \mathrm{TBACl[aq]} \mid \mathrm{AgCl, Ag} \qquad (I)$$

Chronovoltammetric studies were carried out using the cell:

$$\text{Ag, AgCl} \mid \text{LiCl + TMACl + TX100[aq]} \mid \text{TBATPhB[nb]} \underset{2}{\mid} \text{TBACl[aq]} \mid \text{AgCl, Ag} \qquad \text{(II)}$$

Supporting electrolytes were lithium chloride in the aqueous phase and tetrabutylammonium tetraphenylborate in the nitrobenzene phase. The interface marked by "2" in the diagrams I and II were the so-called reference interfaces; the potential difference of the studied interface was measured with respect to it.

RESULTS AND DISCUSSION

Electrocapillary Measurements

Electrocapillary curves recorded from the studied partition systems for various Triton X100 concentrations in the aqueous phase are presented in the Fig. 1. The TX100 concentration in the systems presented by the Fig. 1 increased from 0.165 to 1.654 mmol dm^{-3}. Electrocapillary maxima were determined by fitting experimental points to the curves described by the polynomial of third order, then the curves obtained were differentiated in a potential range comprising a wide vicinity of the maximum point (100–350 mV). Zero points were determined with an accuracy 2 mV. The procedure described above allows in our opinion to significantly decrease the possible experimental errors. Interfacial tension decreases with increasing TX100 concentration as it is reflected by lowering electrocapillary maxima; in addition, the maximum position shifts to positive potentials. The occurrence of such an effect, called the Esin–Markov (E–M) effect[27,31], is a good criterion for determining if specific adsorption takes place in the studied system.

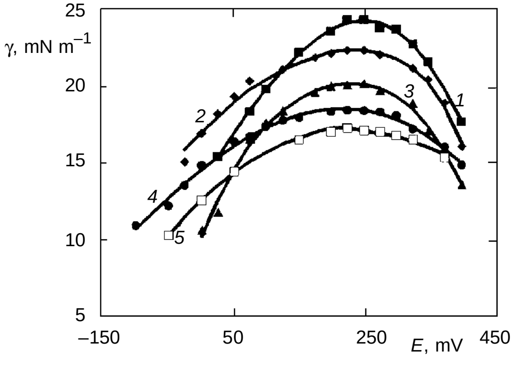


FIG. 1
Electrocapillary curves in the LiCl + TX100(aq)/TBATPhB(nb) system. Consecutive curves were recorded for the following TX100 concentrations in the aqueous phase: *1* 0.165, *2* 0.414, *3* 0.827, *4* 1.241, *5* 1.654 mmol dm^{-3}

The term “specific adsorption” means, both for ions and neutral molecules, the adsorption other than electrostatic. In the case of adsorption of non-ionic substances, the E–M effect is comparable with that of ion adsorption if dipole moments of the adsorbed molecules are large. If the dipole moment is small then the E–M effect is small, too, regardless the energy of adsorption. The magnitude of the effect is presented in Fig. 2 where the dependence of the potential of electrocapillary maximum on TX100 concentration natural logarithm is presented for the studied partition system. The experimental slope of the line describing the dependence is equal to 14 mV per logarithm unit. It indicates that the Triton X100 molecules are adsorbed on the water/nitrobenzene interface. The slope is relatively small but TX100 is a non-ionic substance and in such a case the adsorption is evidenced by mere electrocapillary maximum shifts.

A dependence shown at negative potentials of electrocapillary curves presented in Fig. 1 is really unusual for systems containing metal/solution interface (including mercury/solution one), but not for the ITIES. Such the electrocapillary curves crossing was obtained by other authors interested in these problems, for example by Senda et al.[32]. However, one should take into account that the interfacial region at the ITIES has much more complicated structure than that in the metal/solution interface. Schiffrin et al.[33] noted that the main difference between both interfaces is that there is present no sharp dielectric termination between phases at the ITIES. In our opinion this fact has a very important meaning if adsorption phenomena are discussed. It is discussible that at strong polarization conditions if adsorption of an amphiphilic molecule is discussed, tendencies of the hydrophilic and hydrophobic parts of such a molecule to adsorption should be considered separately inasmuch as these tendencies can play an important role in the final picture. One can observe only a final effect of such phenomena, but it should be born in mind that this effect can not be a simple linear combination of the tendencies of both parts of the molecule to the adsorption, especially at the strong polarization. For example, the adsorbate molecule can move perpendicularly to the interface toward one phase or another, dependently on the polarization. In our opinion

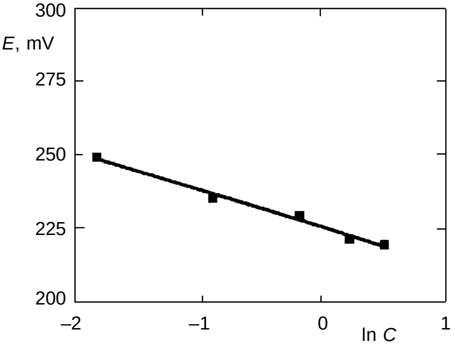


FIG. 2
The Esin–Markov effect for the LiCl + TX100(aq)/TBATPhB(nb) system. a = 13 mV

interfacial tension changes can be unexpected in such conditions. For the above reasons it is possible to obtain the randomly crossing electrocapillary curves at the ITIES contrary to the metal/solution interface. The explanation proposed above is not as precise and clear as it should be, but the problem discussed needs more detailed experiments and is rather marginal from the point of view of the main aim of this work because it relates to the region outside of the zero charge point region.

In general, the presence of adsorbed anions provokes the electrocapillary maximum shift to negative potentials and the presence of surface-active cations shifts the electrocapillary potential to positive potentials. In the case of a non-ionic surfactant, the shift direction depends on the surfactant molecule orientation at the interface. With the discussed partition system, it can be deduced from the direction of electrocapillary maximum shift that the Triton molecules are oriented at the interface with the positive pole of the molecule pointing at the nitrobenzene phase. This conclusion has been reached from the TX100 molecule structure analysis. The long chain containing ether bridges constitutes the negative pole of the molecule because of numerous lone electron pairs of the oxygen atoms. From the same reason, the chain has strongly hydrophilic properties implying its orientation to the aqueous phase. The short, branched aliphatic chain attached to a benzene ring is the positive end of the dipole. The effect of the benzene ring on the TX100 molecule polarity should also be stressed: the ring attracts both the aliphatic and etheric chain electrons making the positive and negative charge centres of gravity approach one another and reduce the Triton X100 molecule polarity.

Relative surface excesses of Triton on the water/nitrobenzene surface were determined by the Parsons method[34]. As earlier[27,35] the surface excess values were calculated at constant surface charge in the electrocapillary maximum point. The calculation results are presented graphically in the Fig. 3 as the dependencies of the Triton relative surface excess, Γ, on its bulk concentration in water. The experimental surface excess

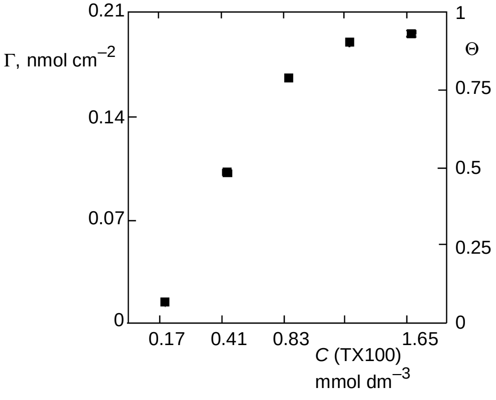


FIG. 3
The dependence of the relative surface excess of TX100 and of the interface coverage fraction by the TX100 molecules on TX100 concentration in the aqueous phase

values are much higher than those obtained for the same partition system containing the supporting electrolytes only[27]. It is the evidence that the adsorption of Triton takes place on the interface and it supports the conclusions from the E–M effect analysis.

The experimental data were fitted to a theoretical model of adsorption in order to determine the parameters of Triton X100 adsorption on the water/nitrobenzene interface. To this aim, the maximum surface excess of TX100 was determined by extrapolating the dependence given by $\Gamma = f(C_{\mathrm{TX100}})$ and then the coverage fractions of the surface by the surfactant molecules were calculated. The dependence of coverage fraction on bulk Triton concetration in the aqueous phase is presented in Fig. 3. Six isotherms of adsorption were selected for fitting. The fitting was done by the least squares method after transforming the equations describing the isotherms to a linear form. The results with the fit error and the standard free energy of adsorption values are presented in Table I.

It can be concluded from Table I data that the best fit of the experimental data was obtained with the Frumkin isotherm. The mean fit error was about 9% for this isotherm while it was much higher with other models (see Table I). Mentioned errors are the mean deviation of the fitted values from its experimental equivalents expressed in percents. The intermolecular interaction constant calculated for the TX100 molecules from the Frumkin isotherm fit indicates mutual attraction of the TX100 molecules at the interface. In addition, the equilibrium constant of the process suggests a relatively strong adsorption. It has been supported by standard free energy of adsorption value as determined from the relationship:

TABLE I
Values of parameters of Triton X100 adsorption at the water/nitrobenzene interface for six theoretical adsorption isotherms

Isotherm	a[a]	b	ΔG_{ads} kJ mol^{-1}	Error %
Frumkin	–3.27	378.2	–14.7	8.91
Virial	–0.44	539.4	–15.6	13.69
Volmer	–	–	–	<100
Langmuir	–	–	–	<100
Flory–Huggins	–4.65	$1.56 . 10^{-5}$	–21.7	32.65
Henry	–	0.68	–1.0	14.58

[a] The r parameter values are given in this column for the Flory–Huggins isotherm.
a Intermolecular interactions constant; b adsorption equilibrium constant; ΔG_{ads} free enthalpy of adsorption.

$$\beta = \exp\left(\frac{\Delta G^{0}_{\mathrm{ads}}}{RT}\right) . \qquad (1)$$

It is equal to 14.7 kJ mol^{-1}. It can be concluded from the comparison of the present results with earlier results on supporting electrolyte adsorption at the water/nitrobenzene interface[27,35] that the adsorption of Triton X100 is rather strong.

Describing adsorption phenomena the standard state of the adsorbate at the interface should be properly defined. It is important because values of the standard Gibbs energy of adsorption obtained from different isotherms are comparable if they are related to the same standard state. For the isotherms used in this work the following standard states were chosen:

1. Frumkin isotherm: $\Theta = 0.5$;
2. Virial isotherm: $\Gamma = 1$ molecule/cm^2;
3. Langmuir isotherm: $\Theta = 0.5$;
4. Flory–Huggins isotherm: $\Theta = 0.5$, $r = 1$ (it means the same size of solvent and adsorbate molecule).

The above list shows standard states for the isotherms that gives the fitting error less than 100% (see Table I). The standard Gibbs energy values given in Table I does not correspond to the same standard state and for this reason they are not comparable. It results from the main aim of this work that is only to find the best isotherm for the description of the adsorption in the system examined. So only the parameters given for the Frumkin isotherm are valid in our opinion.

Chronovoltammetric Measurements

Typical cyclic chronovoltammetric curves recorded from the water/nitrobenzene partition system in the cell presented diagramatically by (II) are presented in the Fig. 4. Supporting electrolyte concentration in the chronovoltammetric measurements was 0.05 mol dm^{-3} in both phases, tetramethylammonium chloride concentration in the aqueous phase was kept constant and amounted to 5 . 10^{-4} mol dm^{-3} and the Triton X100 concentration in the aqueous phase varied from 0.165 to 1.654 mmol dm^{-3}. All the curves were recorded at polarization rates 5, 10, 25 and 50 mV s^{-1}. The TMA$^+$ peaks of transport from water to nitrobenzene and of its back-transport from the organic to the aqueous phase are well shaped in all the curves.

Essential information which can be obtained from chronovoltammetric studies is the determination of character of the charge transport through the interface. The criterion most frequently used to this aim is the relationship[36]:

$$\Delta E^{\mathrm{bp}}_{\mathrm{p}} = E_{\mathrm{p}} - E_{\mathrm{bp}} = 2.22\,\frac{RT}{nF} \ , \qquad (2)$$

where E_p is the peak potential, E_{bp} is the back-transport peak potential and the meaning of other symbols is as commonly accepted. At 298 K, the difference amounts to 57 mV (for a univalent ion) for a reversible process, i.e. where the charge transport rate is higher than the diffusion rate. This criterion is met in the case of the TMA^+ ion transport through unmodified water/nitrobenzene interface[37] whereas in the presence of Triton X100 the difference between the transport and back-transport peak potentials varies with the Triton concentration in the aqueous phase. At the same time, the difference value is higher than that defined by Eq. (*2*). The ΔE_p^{bp} difference of the TMA^+ transport in the presence of TX100 in the interfacial region for a TMA^+ ion concentration at the 25 mV s^{-1} polarization rate are collected in Table II.

Another criterion of reversibility of the ion transfer process in the chronovoltammetry is the difference between the transport peak potential and half-peak potential

TABLE II

$\Delta E_p^{p/2}$ and ΔE_p^{bp} values for the TMA^+ ion transfer across the water/nitrobenzene interface modified by Triton X100. The TMA^+ ion concentration is equal to 5 . 10^{-4} mol dm^{-3} and polarization rate is 25 mV s^{-1}

C_m(TX100) mmol dm^{-3}	$\Delta E_p^{p/2}$ mV	ΔE_p^{bp} mV
0.0	44	61
0.165	46	65
0.414	46	64
0.827	47	61
1.241	47	59
1.654	47	56

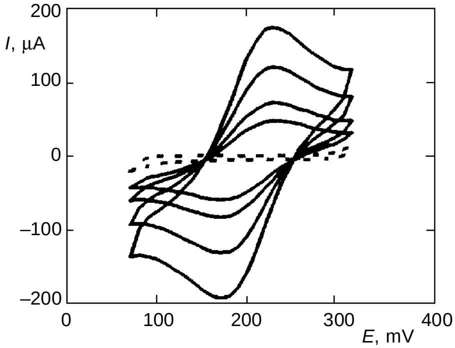


FIG. 4

The chronovoltammetric curve of the TMA^+ ion transport across the water/nitrobenzene interface modified by Triton X100. The TX100 concentration amounts to 0.827 mmol dm^{-3}. The TMA^+ concentration is equal to 1 . 10^{-3} mol dm^{-3}

ΔE_p^{bp}. At 298 K it amounts to 56 mV (ref.[36]) for reversible processes. The values obtained for the discussed partition system suggest the reversible character of the process (the values are given in Table II), i.e. they are contradictory to the earlier given criterion. However, the above criterion of charge transport reversibility should not be applied to estimation of the character of the process occurring on the specific adsorption modified interface because of the effect of the double layer thickness on the slope of the rising part of the chronovoltammetric curve.

As it is seen from Fig. 5 the peaks of the transfer current does not shift with the TX100 aqueous bulk concentration changes. This fact has an important meaning, because the occurrence of that shift can be an evidence of the complexation of transferring ions by the surfactant molecules in the interfacial region. No shift is obtained for the TMA^+–TX100 system and in our opinion such a complexation does not take place in the system.

The peak currents of the TMA^+ transfer vs the aqueous bulk TX100 concentration are presented in Fig. 6. It can be unexpectedly concluded from the plot that the presence of a small number of TX100 molecules in the double layer blocks the TMA^+ ion transport across the interface (the drop of the transfer current for the low TX100 concentration), while the increase of the bulk TX100 concentration results in the facilitation of the TMA^+ transport (the rise of the transfer current for high TX100 concentration). It should be noted, that the rise of the transfer peak current corresponds with maximum surface coverage by TX100 molecules. Moreover, it results from the data collected in Table II that the process has rather irreversible character at low TX100 concentrations where the interface is still not saturated by the surfactant molecules as determined by the electrocapillary data. It means that the ion transport through the interface itself is the slowest stage of the process. Only the increase in TX100 concentration in the bulk aqueous phase to the value at which the interface is maximally covered by the surfac-

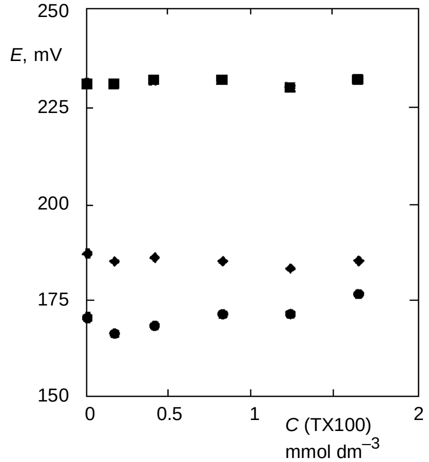


FIG. 5
The dependence of peak potential E_p (■), half-peak potential $E_{p/2}$ (◆), and back-transport peak potential E_{bp} (●) of TMA^+ ion transport through the water/nitrobenzene interface modified with TX100 on TX100 concentration in the aqueous phase. The polarization rate is equal to 25 mV s^{-1}. The TMA^+ concentration is equal to 1 . 10^{-3} mol dm^{-3}

tant molecules makes the TMA^+ transport process to be reversible, i.e. to be limited by the ion diffusion to the interfacial region. As it can be concluded from the plot presented in Fig. 3, this TX100 concentration value is about 1.65 mmol dm^{-3}.

Yoshida and Kihara[38] proposed and ionophoric mechanism of the Triton action on charge transport through the liquid/liquid interface involving a [surfactant–ion] complex formation in the electric double layer and the ion being transported in this form into the other phase. The model seems to have been well supported by other authors' data[25,39,40] on Triton-modified selective electrodes sensitive to various ions. However, the mechanism has been proposed for alkali metal cations.

Another mechanism of action of the Triton X100 molecules adsorbed on the interface can be proposed taking our results into account. The TX100 molecules lower the energy barrier of ion resolvation in the double layer. At a sufficiently high surface concentration of Triton, the etheric chains of its molecules are simultaneously solvated by water and nitrobenzene. Such a state is energetically disadvantageous because of highly hydrophilic character of the chains. If hydrated hydrophilic–hydrophobic ion approaches the interface from the aqueous phase side then the solvation sphere of the ion and of the adsorbed Triton are exchanged and the transported ion is, to say so, sucked in by hydrophilic fragments of the ionophore molecules into the mixed solvents layer where its aqueous solvation layer is replaced by the nitrobenzene layer; as the result, the ion passes into the organic phase. According to the proposed mechanism, the Triton molecules promote the TMA^+ ion transport not leaving the mixed solvents layer. On the other hand, the interface is blocked for the TMA^+ ion transport at the low surfactant concentration. There are at least three possible reasons for this phenomenon. This first reason is that the double layer thickness is much greater in the presence of adsorbed Triton X100 molecules than with an unmodified interface. The second cause

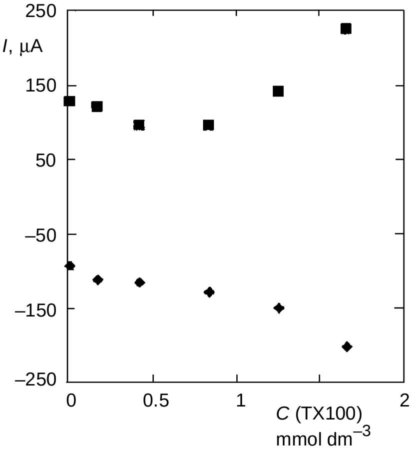


FIG. 6
The dependence of peak current I_p (■) and back-transport peak current I_{bp} (◆) of TMA^+ ion transport through the water/nitrobenzene interface modified with TX100 on TX100 concentration in the aqueous phase. The polarization rate is equal to 25 mV s^{-1}. The TMA^+ concentration is equal to 1 . 10^{-3} mol dm^{-3}

is connected to the fact that at the sufficiently low surfactant concentration all the solvation centres of the hydrophilic part of the surfactant molecule are occupied by water molecules present in the mixed solvents layer. The surfactant–ion interactions are then shielded by water molecules. The third reason of the blocking effect discussed is the orientation of the surfactant molecules at the interface. As it results from our data[41] this orientation is strictly dependent on a difference between the electrical permittivity of the adjoining phases of the partition system. For the system considered this difference is as low that for the low surfactant concentration the hydrophilic parts of the Triton X100 molecules are rather parallel than perpendicular to the interface. This fact causes that the interface is blocked for the TMA^+ ions transport.

The mechanism postulated by us is complementary to that of Yoshida and Kihara[38]; it merely explains how Triton X100 facilitates the transport of ions of similar affinity to both partition system solvents. Yoshida and Kihara studied alkali metal cations which are rather small and strongly hydrophilic. The ions that we examined rather of greater radius and for this reason can not be complexed with Triton X100. This phenomenon was observed by the authors cited for Mg^{2+} cations. Moreover, strong hydrophilic properties of the ions studied by Yoshida and Kihara causes that water molecules hydrating oxygen atoms in polyoxyethylene chains of TX100 can be easier detached providing higher reactivity of the surfactant molecule to the complex formation.

CONCLUSIONS

It has been determined on the ground of experimental studies that kinetics of ion transport through the interface in the studied partition system is markedly affected by the presence of Triton X100. The effect depends on the bulk TX100 concentration in the aqueous phase implying its concentration in the interfacial zone. The interface is blocked for the ion transport by the presence of TX100 concentrations not assuring the interface saturation and the increase in bulk surfactant concentration, i.e. in the double layer, too, to the value assuring maximum interface coverage has a ionophoric effect on the TMA^+ ion transport through the interface.

It has also been shown that the effect of the TX100 presence at the water/nitrobenzene interface on the TMA^+ ion transport from one phase to the other is not only due to a [surfactant–ion] type complex formation. This transport, especially at incomplete interface coverage, can be caused by interaction of the hydrophilic part of the Triton molecule with the hydration sphere of the transported ion and finally by stripping it out, what lowers resolvation barrier. Our mechanism explains the effect of interface blockade at incomplete interface coverage by the TX100 molecule, and as it was pointed out earlier, is complementary to the mechanism postulated by Yoshida and Kihara[38].

The Triton X100 adsorption at the water/nitrobenzene interface is well described by the Frumkin isotherm with negative intermolecular interaction constant which, according to the literature data, is as rule most adequate to description of non-ionic substance adsorption. It means that the molecules of this surfactant attract each other in the double layer and that the adsorption is strong enough to be not negligible, i.e. it is impossible to describe the adsorption by the Langmuir isotherm.

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