ADSORPTION OF POLYVINIL ALCOHOLS AT LIQUID-LIQUID INTERFACES

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Abstract

The paper summarizes the authors' experimental results and literature data on the adsorption of high-molecular-weight surfactants forming network structures on the interface. Equations for adsorption on mobile interfaces are derived. The parameters and coefficients in the equations can be calculated or obtained by independent methods and are clearly understandable from the physical point of view. Based on the concept of adsorption in an effective layer, a method is proposed for calculating such an important parameter of the emulsification process as the maximum area stabilized by a fixed amount of high-molecular-weight surfactant. It is shown how the minimum emulsifier concentration required to stabilize the emulsion can be determined from the surface tension isotherm. The description of the emulsification process in combination with the equation relating adsorption values to the structure parameters of the emulsifier reveals the mechanism of adsorption of the high-molecular-weight surfactants.

Introduction

The comprehensive theory of low-molecular-weight surfactants makes it possible to predict properties of systems with mobile interfaces, such as reduction of surface and interface tension, the value of adsorption of the surfactant at the interface, maximum interface area of the emulsification. Methodologies have been developed for such surfactants for the calculation and testing of these properties [2]. Regarding high-molecular-weight

surfactants, for them there is no theory of adsorption or emulsification, and some researchers question the applicability of the Gibbs and Langmuir equations [1,3] to such surfactants. This is because of the irreversible adsorption nature of polymer surfactants on the mobile interfaces [3,4,5] and to the complex structure of the interface layer. There are two types of polymer surfactants:

1) those forming net structures at the interface and 2) those forming globular structures.

The aim of this work is to investigate the regularities of polymer surfactants in liquid-liquid systems for polymers forming a net adsorption layer at the interface. PVA is selected as a specimen of such a high-molecular-weight surfactant.

Experimental details

Emulsions have been obtained and stabilized by PVA with the content of acetate groups X_{ac} = 1.8% and mean value molecular mass $\overline{M}$ = 28000 determined by the procedure described in [6].

Emulsions that reach the maximum specific interface area, and that are broken by the addition of an excess amount of dispersion phase, were considered **Highly Concentrated Emulsions - HCE**. Emulsions that do not reach the maximum specific interface area for a given surfactant concentration were referred to as **non-Highly Concentrated Emulsions - non-HCE**.

The **non-HCE** emulsions were obtained by mixing a two-phase system of water-decane in a glass with an impeller at varied speeds and by whipping it up with a spiral in the cylinder using Kremnev's method [2]. The dispersed phase volume ratio $\alpha_{disp} = V_{disp}/V_{cont}$ was taken arbitrarily. The dispersed phase in the resulting O/W emulsion was decane, the continuous phase - water. The **HSE** emulsions were prepared using Kremnev's method at the highest achievable dispersed phase volume ratio for a given PVA concentration.

The surface tension of the aqueous solutions of the studied sample was measured by the Du Nuy ring. The PVA concentration in the bulk of the continuous phase was determined from the interface tension isotherm. The

interface area value was determined by microscopy [2]. Adsorption Γ in the interface layer was evaluated directly based on the reduction of concentration in the volume of the continuous phase after emulsification, as described in [7].

Results and discussion

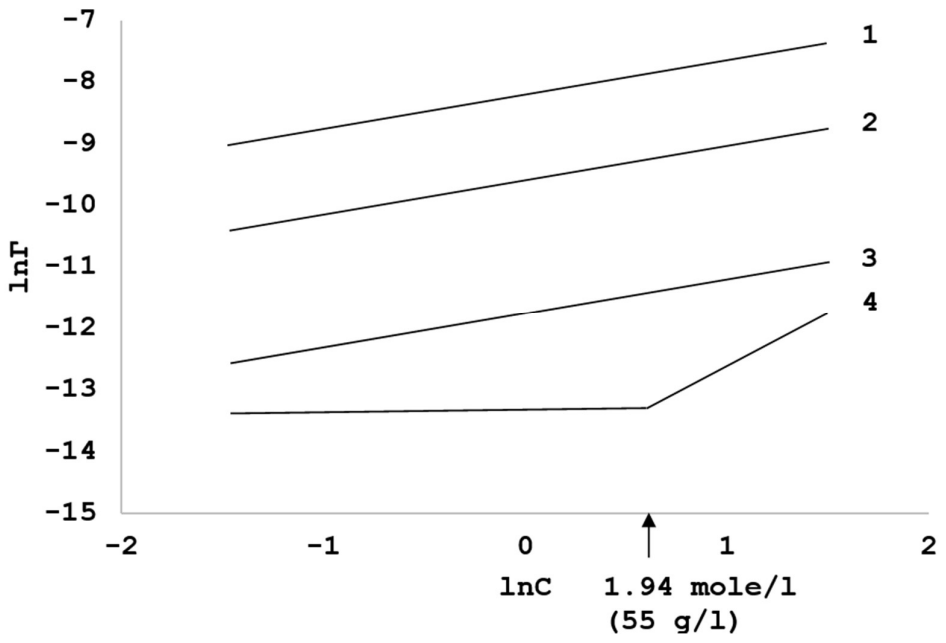
Adsorption in non-HCE emulsions

Based on the results of the experiment, isotherms Γ vs. C were plotted (Fig.1, lines 1,2,3). It can be seen from Figure 1 that in logarithmic coordinates, adsorption isotherms (straight lines 1,2,3) are linear and parallel to each other at various α_{disp} and described by an equation

$$\ln\Gamma = 0.5\ln C + b_\alpha \qquad (1)$$

where Γ is adsorption, mole/m^2; C is concentration, mole/m^3; b_α is a coefficient related to α_{disp}.

Figure 1. Adsorption isotherms for emulsions stabilized by PVA with x_{ac} = 1.8%, $\overline{M}$ = 28000 : 1) α_{disp} = 0.2 in the non-HCE, 2) α_{disp} = 1 in the non-HCE, 3) α_{disp} = 3 in the non-HCE, 4) HCE. Γ – mole/m^2, C – mole/m^3



The equation for the experimental function b_α vs. $\alpha_{disp.}$ was obtained by the procedure [8]:

$$b_\alpha = -14.3 + 6.1 \times e^{-\alpha_{disp}/3} \qquad (2)$$

Based on equation (2), the isotherm of adsorption for a **non-HCE** emulsion stabilized by the PVA sample under investigation may be described by the equation

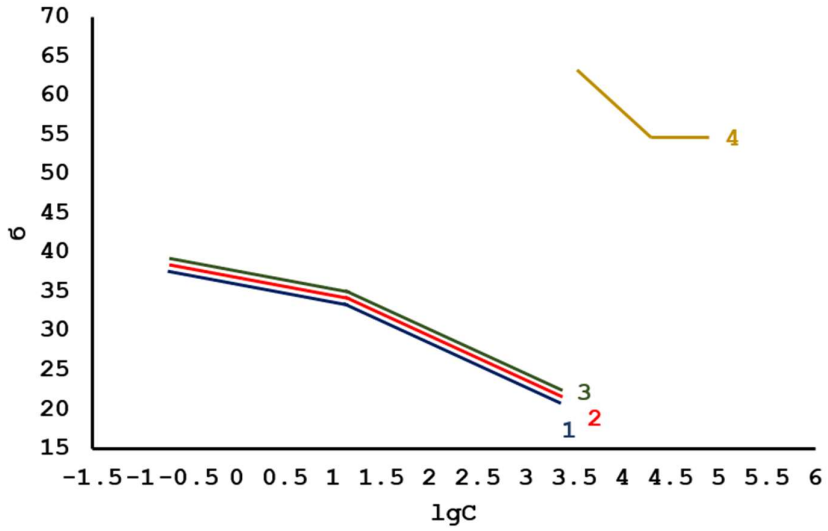
$$\Gamma = 6.15 \times 10^{-7} \times C^{0.5} \times e^{6.1 \exp(-\alpha_{disp.}/3)} \qquad (3)$$

Where Γ, mol/m^2, is adsorption, C, mol/m^3, is the concentration of PVA in water before emulsification.

The adsorption isotherm for a non-HCE emulsion and the surface tension isotherm

It follows from Figure 2 that the surface tension isotherm at coordinates **б - lnC** is linear in a wide range of concentrations, which is consistent with the literature data [3].

Figure 2. Surface tension isotherms of the aqueous PVA solutions
PVA – Paraffin – water: 1) X_{ac} = 1.5%, $\overline{M}$ = 13000; 2) X_{ac} = 1.5%, $\overline{M}$ = 72000; 3) X_{ac} = 1%, $\overline{M}$ = 105000; paraffin – Merck A.G., PVA – Wacker
PVA – water - air: 4) X_{ac} = 1.8%, $\overline{M}$ = 28000; PVA – Plastpolymer, Leningrad.
б – mN/m, **C** – g/m^3.



In the case of high-molecular-weight surfactants, the direct use of the Gibbs equation to calculate adsorption values from the surface tension isotherms is questionable because of the irreversibility of adsorption. Lankveld explained the irreversibility of polymer adsorption by the fact that a polymer molecule is attached to the interface by many active groups simultaneously. Desorption of a polymer macromolecule would mean simultaneous desorption from the surface of all elementary links attached to it, which is highly improbable. Adsorption of the individual elementary link is reversible, and local equilibrium is achieved for the elementary links. From the numerous facts reported by Lyklema and Lankveld [3,4], it follows that in the study of adsorption processes involving polymers, it is advisable to operate with elementary links rather than with whole high-molecular-weight chains.

Then, considering the adsorption process in terms of elementary links, one can apply the statistical thermodynamics of reversible processes to these systems. Considering the elementary links of polymer chains as analogues of the low molecular surfactants, it is necessary to draw attention to the similarity of the mechanism of their action. At each fixed concentration of the surfactants (elementary links) in the volume of the aqueous phase, a certain number of molecules (elementary links) corresponding to this concentration are simultaneously present at the interface. The local interface tension at the contact points of the active groups with the surface is considerably smaller than on the free surface. The decrease in surface tension is determined by: **A.** The statistic factor is the number of molecules

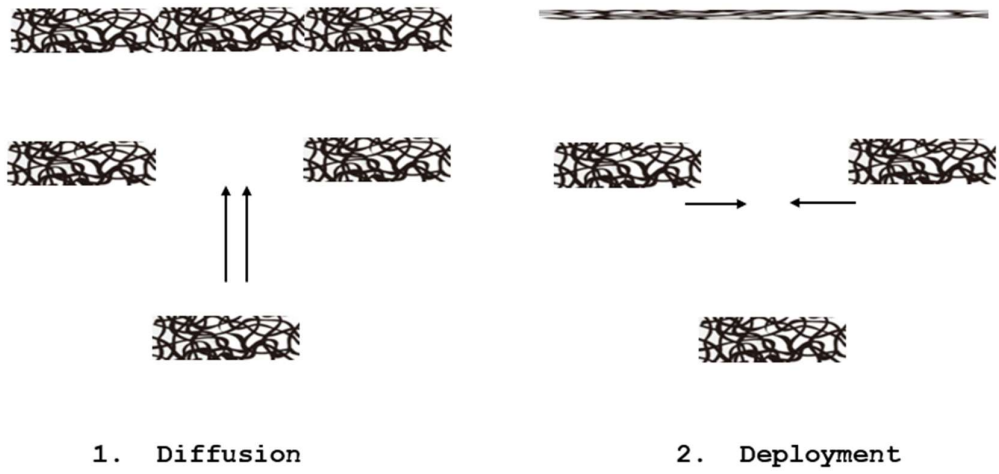
(elementary links) adsorbed at the interface. When an adsorption-desorption equilibrium has set in, their number is certain for concentration at each point in time. This allows considering the interface layer in static. In this case, the decrease of surface tension is affected only by molecules (elementary links) that are at the distance from the surface, not exceeding the range of action of the intermolecular forces. For liquids, this value is estimated to be equal to ~$10 \cdot 10^{-10}$ m. This is the value many researchers take as the thickness of the adsorption layer of the surfactants, considering that beyond this thickness, active groups cannot effectively reduce surface tension [1]. **B.** The kinetic factor determining the value of decrease in surface tension is the frequency of contacts of active groups with the interface. It depends on the rate with which, in the adsorption process, a new active group occupies a vacancy at the interface resulting from the desorption. The frequency of contacts is determined by the diffusion of the surfactant molecules (elementary links) from the volume of the aqueous phase, the latter depending on the concentration and hydrophobic-hydrophilic properties of the surfactant molecules (elementary links).

For low-molecular-weight surfactants, once the interface is saturated (maximum adsorption Γ_m at a certain concentration C_m for each surfactant), the static factor (**A.**) remains constant with a further increase in concentration. Therefore, after the C_m concentration, only the kinetic factor (**B.**) associated with diffusion increases with an increase in the concentration. Therefore, after the concentration of C_m, the surface tension isotherm of the low-molecular-weight surfactant becomes linear at the coordinates of $\sigma - \ln C$. For PVA, the kinetic factor is not limited to the diffusion mechanism of providing the surface with elementary links. The adsorption of elementary links can also be achieved through the deployment of twisted chains partially adsorbed on the surface (Fig. 3). This mechanism is realized at very low concentrations of PVA in the volume of the aqueous phase [3.4]. Then the rate of the deployment of polymer chains exceeds the rate of diffusion from the volume. With a further increase in concentration, polymer molecules will find it more difficult to deploy their chains on the surface, as nearby vacancies will be occupied by faster diffusion from volume. Lankveld considers [3] that the deployment mechanism is realized up

to a certain concentration (very small) of PVA in the bulk of the aqueous phase. As a result, a saturation of the interface with elementary links by deployment chains leads to a flat structure of the interface layer.

Therefore, in the case of low concentrations of polymer surfactant, the static factor is constant, and the kinetic factor has little effect on the reduction in surface tension. This determines the nature of the adsorption isotherm; it is linear with a slight slope. Then, at a certain concentration, the diffusion mechanism becomes dominant and, as in low-molecular-weight surfactants at a constant static factor, the surface tension isotherm has a constant slope. Lyklema and Lankveld thus explain the inflection on surface tension isotherms in the low concentration range [3,4].

Figure 3. Polymer molecules input mechanism at the interface between two phases: 1) Diffusion 2) Deployment.



Surface tension for isomers 1,2,3 in the low concentration range is shown in Fig.2 [9]. It can be seen from Fig.2 that these isotherms are linear, parallel, and have an inflection at $25 \cdot 10^{-3}$ g/l.

Experience has shown that emulsions stabilized by PVC are formed at relatively high concentrations, i.e., when the diffusion mechanism provides the surface with elementary links [3]. Thus, based on the interpretation proposed by Lyklema and Lankveld to explain the shape of the surface tension isotherms of aqueous PVA solutions, it is possible to better understand the linear character of the isotherms in the concentration intervals

corresponding to the formation of stable emulsions. The isotherm for the test sample is shown in Fig.2 (line 4). Over the range of high concentrations there is an inflection of isotherm, which turns into a plateau at C = 55 g/l. For low-molecular-weight surfactants, a similar inflection point means either a solubility limit or a critical concentration of micelles formation, after which further increases in the concentration of surfactants are spent on micelles formation rather than on increased diffusion.

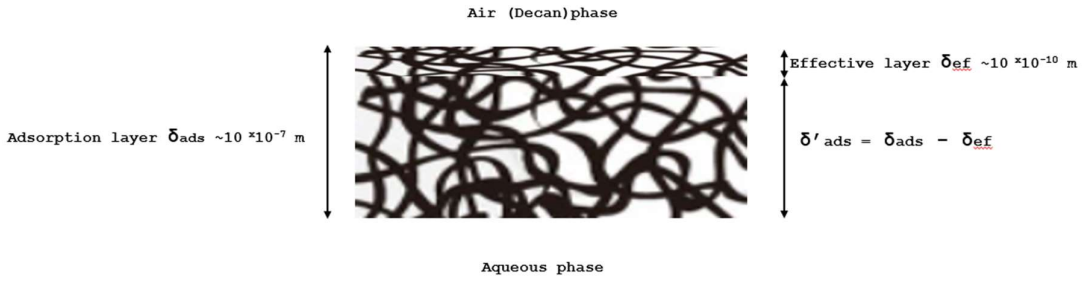
Since for PVA the solubility limit is reached much later and it is not possible to form micelles from polymer molecules, it is clear that the critical concentration of $C_{crit.}$ = 55 g/l, at which the surface tension becomes a constant, is associated with some other structural property of the adsorption layer of the PVA. As shown below, at $C_{crit.}$ the maximum interface area is reached in emulsions stabilized by different PVA samples (see p. 18). Since, following [3.4], we have proposed the possibility of using the Gibbs equation for the PVA when considering the process in terms of adsorption of the elemental links; it remains to determine the units of measurement to be used in estimating the value of the Γ_m. It is evident that the units of adsorption directly used by the Gibbs equation will be the MOLE OF PVA ELEMENTRY LINKS PER UNIT OF INTERFACE AREA. In this case, there is no difference in the units in which the PVA concentration C in the aqueous phase will be measured, as it is part of the Gibbs equation in logarithmic form. By calculating the adsorption from the reported relationship (Figure.2, line 4) and using the Gibbs equation, $\Gamma_m = 12.3 \cdot 10^{-7}$ mol/m^2 was obtained. Interestingly, for a sample of PVA with X_{ac} = 10% the value Γ_m , as determined by Gibbs' equation, is the same [10], and the value Γ_m as determined by the isotherms 1.2.3 (Figure 2), is $11.9 \cdot 10^{-7}$ mol/m^2. Turning to the adsorption equation (3), we see it contains an empirical factor of exactly $0.5 \cdot \Gamma_m$.

For high-molecular-weight surfactants, the thickness of the adsorption layer on the surface of stable emulsions is known to be 100 nm [1].

However, it has been determined that only part of the adsorption layer ~ $10 \cdot 10^{-10}$ m effectively influences the reduction of the interphase tension. The effect of the rest of the adsorption layer is within the experimental error

limits. This thin layer, related to the range of action of the intermolecular forces, we call THE EFFECTIVE LAYER (figure 4).

Figure 4. Model of the polymer adsorption layer in emulsion



The PVA concentration in the volume of the effective layer can be estimated from the Γ_m value determined from surface tension and the thickness of the effective layer δ_{ef}:

$$C_{ef} = \Gamma_m : \delta_{ef} : \overline{M}_{e.l.}, \ g/m^3 \qquad (4)$$

Considering that Γ_m = 12.3·10^{-7} mole/m^2, δ_{ef} = 10·×10^{-10} m and the molecular mass of the PVA elementary link $\overline{M}_{e.l.}$ is equal 44 we got C_{ef} = 55 g/l. This value agrees with the mass concentration of PVA in the volume of the aqueous phase corresponding to the inflection point in which the surface tension isotherm σ gets a constant value, as well as with the concentration of the maximum interphase area in the emulsions stabilized by PVA (see p. 18). Then the agreement between C_{ef} and C_{crit} has a definite physical sense. Thus, the Γ_m value for PVA is the concentration in the effective layer expressed in the moles of elementary links. Therefore, it is better to refer to the Γ_{ef}. Then the adsorption equation (3) can be written as:

$$\Gamma = 0.5\,\Gamma_{ef} \cdot C^{0.5} \cdot e^{6.1 \exp(-\alpha_{disp}/3)} \qquad (5)$$

The minimum concentration of emulsification

It is shown that, for low-molecular-weight surfactants, a minimum concentration sufficient to stabilize emulsions C_e is the concentration of

saturating the surface monolayer C_m, i.e. the point at which the isotherm of the surface tension becomes a straight line [1]. Following the same logic, based on the Lyklema and Lankveld concepts, high-molecular-weight surfactants can be expected to stabilize emulsions at very low concentrations. In fact, we got an unstable emulsion at PVA concentration before emulsification in the volume of the continuous phase of $57.8 \cdot 10^{-5}$ g/l. We got a stable emulsion only from the concentration of $25 \cdot 10^{-3}$ g/l, which corresponds to the first inflection point of the surface tension isotherm (Figure 2, lines 1,2,3). The flat structure of the polymer molecules at the interface seems to contribute much less to the stabilization of the emulsions than the volume structure of the interface formed by the interwoven loops of the macromolecules. Therefore, for practical, it is advisable to take the point of inflection of surface tension isotherms in the small concentration range as the C_e of the polymer surfactants.

Adsorption in HCE emulsions

Fig.1 shows the experimental adsorption isotherm (line 4) in an **HCE** emulsion stabilized by the tested sample of PVA. From this figure (line 4), at the concentration of PVA in the continuous phase before emulsification $C \leq C_{crit}$. adsorption value at the interface of the **HCE** emulsion Γ_∞ is constant and equal to $13.1 \cdot 10^{-7}$ mole/m^2. Starting with the critical concentration C_{crit}, Γ_∞ increases. It follows from Fig. 1 that for each concentration, the adsorption in the **HCE** emulsion is minimal at the maximum phase ratio α_{disp} achievable under given emulsification conditions. Γ_∞ for each PVA sample (with various X_{ac} and $\overline{M}$) is constant up to the concentration C_{crit} = 55 g/l, because in this concentration range, the maximum interface area is directly proportional to the concentration of PVA in the bulk of the aqueous phase [11]. Table 1 shows the comparison between the minimum adsorption G for the test sample and other PVA samples for at C_{crit} . Adsorption Γ was

determined from the maximum interface area [11]. From table.1, the Γ_∞ values are different at various X_{ac} and . The question is what a relationship exists between Γ_∞ and X_{ac} and $\overline{M}$.

Table 1. Adsorption in Highly Concentrated Emulsion HCE stabilized by PVA

$\overline{M}$ PVA	C PVA Mol/m^3	Adsorption $\Gamma_\infty^{(exp)} \cdot 10^7$ Mol/m^2	Adsorption $\Gamma_\infty^{(calc)} \cdot 10^7$ from eq. (19) Mol/m^2	X_{ac} %	N_{ac}	K_{MN} from eq. (20)
11000	5.0	6.5	6.6	10	0.08	0.54
28000	1.96	2.5	2.5	10	0.08	0.20
48000	1.15	1.6	1.5	10	0.08	0.12
28000	1.96	13.1	13.1	1.8	0.01	1.07
28000	1.96	2.5	2.5	10	0.08	0.20
28000	1.96	1.3	1.4	18.7	0.16	0.11
28000	1.96	2.8	2.3	25.3	0.23	0.10
28000	1.96	2.8	2.2	33	0.32	0.07

The polymer molecule formula is $(-CH2-CH(OCO-CH3)-)_n(-CH2-CH(OH)-)_m$. The mean molecular mass of PVA and PVAc elementary links is 44 and 86 respectively. Considering the molecular mass of the polymer: $\overline{M} = 86 \cdot n + 44 \cdot m$, the number of acetate links is:

$$n = 0.01 \cdot X_{ac} \cdot \overline{M} / 59 \qquad (6)$$

(59 is the molecular mass of an acetate group), and the mole fraction of the acetate link in the polymer is: $N_{ac} = n / (n + m)$, a formula linking the mole fraction of the acetate link in the polymer to the content of acetate groups is obtained:

$$N_{ac} = 1 : [(134.1/X_{ac}) - 0.95] \qquad (7)$$

The dependence of adsorption in an HCE emulsion on the content of acetate groups

Table 1 lists the N_{ac} values estimated by equation (7). From these data the relationship Γ_∞ vs. N_{ac} is plotted for PVA samples with $\overline{M}$ = 28000 at $C \leq C_{crit}$ (curve 1, Fig.5).

Section I ($N_{ac} < 0.16$) of this curve straightens in logarithmic coordinates (line 2, figure 5) and is described by the equation:

$$\Gamma_\infty = 0.33 \cdot 10^{-7} (N_{ac})^{-0.8} \quad (8)$$

For section III ($N_{ac} \geq 0.25$), adsorption in an HCE emulsion is constant Γ_∞ = $2.8 \cdot 10^{-7}$ mole/m^2. Section II ($0.16 \leq N_{ac} < 0.25$) is interjacent one.

From our research and data in [1], it is known that Γ_{ef} = $12.3 \cdot 10^{-7}$ mole/m^{2}at $X_{ac} \leq$ 10%. From the same work [1] the Γ_{ef} = $24 \cdot 10^{-7}$ mole/m^2 at X_{ac}=25.3% (N_{ac} = 0.23) and Γ_{ef} = $32 \cdot 10^{-7}$ mole/m^2 at X_{ac} = 68% (100% PVAc). Thus, there is a correlation between the Γ_{ef} and Γ_∞ depending on N_{ac}. It can be expected that the linear nature of $\ln\Gamma_\infty$ vs. $\ln N_{ac}$ (line 2, Fig.5) for sections I and III is related to the constancy of Γ_{ef} for these sections, and the Γ_{ef} value is included in the equation for Γ_∞ . This is plotted in Fig.6. Then the Γ_{ef} change for interjacent section II ($0.16 \leq N_{ac} < 0.25$) is described by the equation:

$$\Gamma_{ef} = 0.5 \cdot 10^{-4} N_{ac}^2 \quad (9)$$

For section I (Fig.5) Γ_{ef} = $12.3 \cdot 10^{-7}$ mole/m^2 and equation (8) can be given:

$$\Gamma_\infty = 0.027 \cdot \Gamma_{ef} \cdot (N_{ac})^{-0.8} \quad (10)$$

Placing formula (9) for the Γ_{ef} for section II (Fig.5) in equation (10) gives:

$$\Gamma_\infty = 1.35 \cdot 10^{-6} (N_{ac})^{1.2} \quad (11)$$

For the upper bound of section II (N_{ac} = 0.25), one gets from equation (11) the value $\Gamma_\infty = 2.6 \cdot 10^{-7}$ mole/m^2. For section III, Γ_∞ can also be calculated by equation (10), with N_{ac} = 0.25 and $\Gamma_{ef} = 32 \cdot 10^{-7}$ mole/m^2. Here, we get the same value $\Gamma_\infty = 2.6 \cdot 10^{-7}$ mole/m^2. The experimental Γ_∞ for N_{ac} = 0.25 is $2.8 \cdot 10^{-7}$ mole/m^2 (Fig.5). Thus, for a PVA sample with $\overline{M}$ = 28000 at $C \leq C_{crit}$, the relationship between Γ_∞ and N_{ac} is described by equation (10). In this case, the Γ_{ef} for the sections $N_{ac} < 0.16$ and $N_{ac} > 0.25$ is a constant, and at $0.16 \leq N_{ac} \leq 0.25$ can be estimated from equation (9). At higher values of N_{ac}, the acetate elementary links, because of their hydrophobic nature, will displace the PVA elementary links from the interface. Starting with a certain N_{ac} value, the interface becomes fully saturated only with acetate elementary links. The effective layer can then be considered as the PVAc layer rather than formed by PVA. In this case, because of the insolubility of PVAc in water the acetate links are located relative to the interface above the water phase. As shown in [1], this results in an increase in the thickness of the effective layer defining surface tension. These changes in the effective layer (Γ_{ef}, δ_{ef}, $\overline{M}$e.l.) have the opposite effect on the volume concentration C_{ads} in it (see equation (4)). Considering that C_{crit}, at which the largest maximum interface area and the inflection of the adsorption isotherms in the HCE emulsions are observed, remains 55 g/l with the content of acetate groups in PVA 33% (N_{ac} = 0.32) [1], one may assume that C_{ef} also does not change at higher values of N_{ac}.

According to the literature, until the PVA concentration in the continuous phase reaches the C_{crit} value the interlayer thickness between the drops decreases, and after reaching C_{crit} increases [1]. This can be explained by contacting the protective layers of two droplets at $C = C_{crit}$. The adsorption layer receives the entire volume of the continuous phase, i.e., the concentration of PVA in the volume of the continuous phase after reaching C_{crit} becomes equal to the concentration in

the volume of the adsorption layer C_{ads}. The concentrations in the volume of the adsorption layer and in the bulk of the effective layer also coincide:

$$C_{ads} = C_{ef} = C_{crit} = C \qquad (12)$$

It should be noted that formula (12) is valid for **HCE** emulsions at the C_{crit} in MASS EXPRESSION only since the mean molecular mass of the elementary link in the volume of the adsorption layer (and continuous phase) differs from $\overline{M}_{e.l.}$ in the volume of the effective layer at high N_{ac} values.

In a **non-HCE** emulsion, when the concentration in the bulk of the continuous phase reaches Crete, there is no contact between the adsorption layers, so there is nothing to prevent their convergence at concentrations above C_{crit}. This results in a straight-line (no inflections) character of the adsorption isotherm of a **non-HCE** emulsion (Fig. 1, lines 1, 2, 3).

Dependence of adsorption in HCE emulsions on the PVA mean molecular mass

The dependence of Γ_∞ on $\overline{M}$ (Fig7) is based on the data given in Table 1, for PVA samples with X_{ac} = 10% (N_{ac} = 0.08) at $C \leq C_{crit}$. This relationship is described by an equation

$$\Gamma_\infty = 7.25 \cdot 10^{-3} / \overline{M} \qquad (13)$$

By analogy with the dependence of Γ_∞ on N_{ac}, we extract from equation (13) the value of Γ_{ef}, which at N_{ac} = 0.08, is $12.3 \cdot 10^{-7}$ mole/m^2. Then equation (13) can be taken as:

$$\Gamma_\infty = (59 \cdot 10^2 / \overline{M}) \cdot \Gamma_{ef} = (M_{ac} / \overline{M}) \cdot 10^2 \cdot \Gamma_{ef} \qquad (14)$$

where M_{ac} = 59 is the molecular mass of the acetate group.

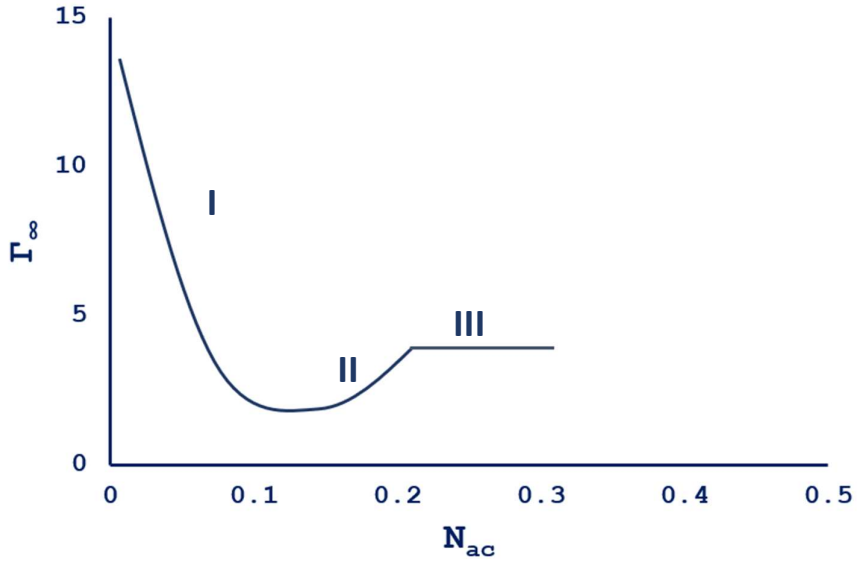
A comparison of equations (10) and (14) shows that from the available data (Table 1) the equations for adsorption of Γ_∞ depending on the structure of the PVA and Γ_{ef}, are obtained at fixed parameters of polymer structure N_{ac} and $\overline{M}$:

at N_{ac} = const = 0.08: $\Gamma_\infty = K_M \cdot \Gamma_{ef}$, where $K_M = (M_{ac} / \overline{M}) \cdot 10^2$ (15)

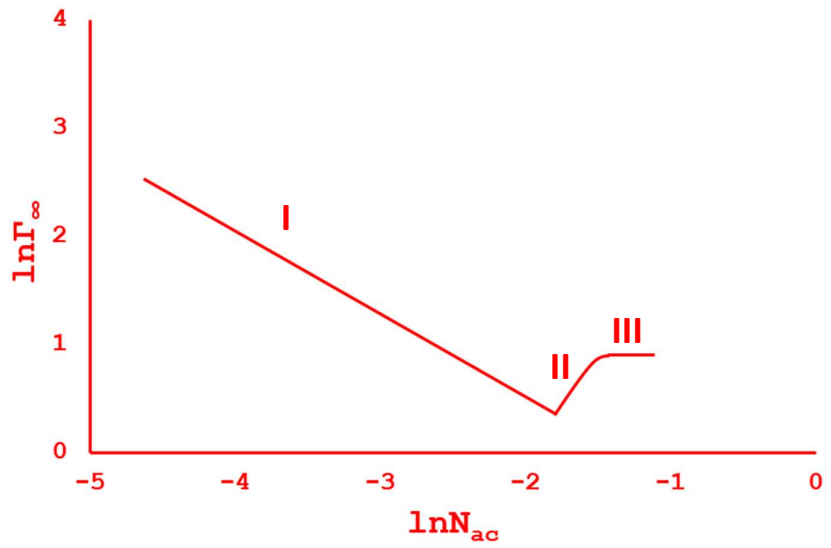
at $\overline{M}$=const=28000: $\Gamma_\infty = K_N \cdot \Gamma_{ef}$, where $K_N = 0.027 \cdot (N_{ac})^{-0.8}$ (16)

Figure 5. Dependence of PVA adsorption at the interface of HCE emulsions on the mole fraction of the acetate links in PVA molecule (a PVA concentration C before emulsification in the volume of the continuous phase is 55 g/l):

1) on coordinates $\Gamma_\infty - N_{ac}$ 2) on coordinates $\ln\Gamma_\infty - \ln N_{ac}$. $\Gamma_\infty - 10^{-7} \cdot$ mole/m^2



1) $\Gamma_\infty = f(N_{ac})$



2) $\ln\Gamma_\infty = f(\ln N_{ac})$

Figure 6. **Dependence of the PVA adsorption in the effective layer in HCE emulsion on the mole fraction of the acetate links in the polymer molecule on coordinates $\ln\Gamma_{ef} - \ln N_{ac}$. Γ_{ef} - mole/m^2**

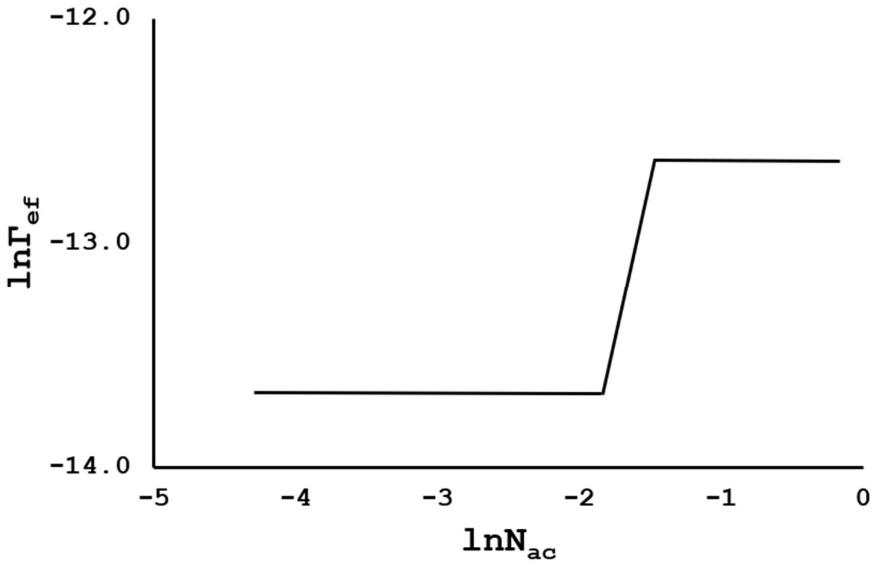
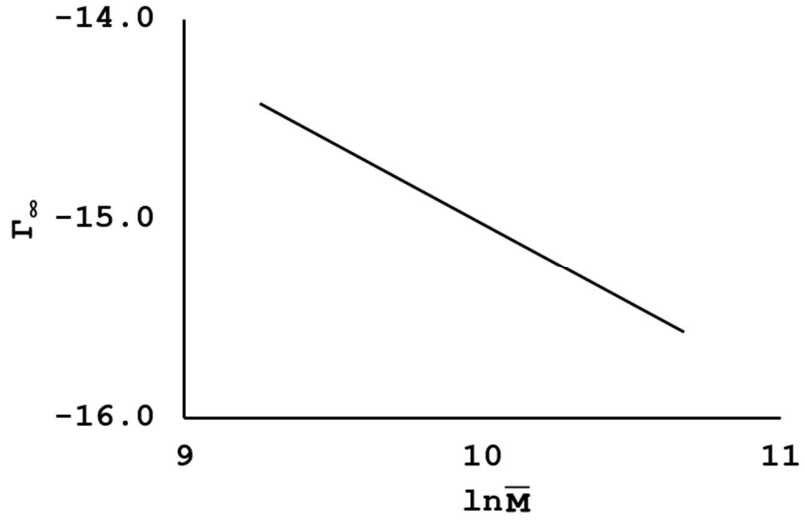


Figure 7. **Dependence of the adsorption of PVA at the interface of HCE emulsions on the mean molecular mass of PVA (a PVA concentration C before emulsification in the volume of the continuous phase is 55 g/l) on coordinates $\ln\Gamma_\infty - \ln\overline{M}$. Γ_∞ - mole/m2.**



To express the dependence of Γ_∞ on the structure of PVA and Γ_{ef} at simultaneous variations of the N_{ac} and $\overline{M}$ parameters, it is necessary to reduce this dependence to the conditions under which equations (15) and (16) were obtained. It follows from equation (14) that:

$\Gamma_\infty^{\overline{M}}/\Gamma_\infty^{(2800)} = 2800/\overline{M}$, that is:

$$\Gamma_\infty^{\overline{M}} = \Gamma_\infty^{(2800)} \cdot 2800/\overline{M} = K_N \cdot \Gamma_{ef} \cdot 2800/\overline{M} \quad (17)$$

It follows from equation (10) that:

$\Gamma_\infty^{(Nac)} / \Gamma_\infty^{(0.08)} = (N_{ac}/0.08)^{-0.8}$, that is:

$$\Gamma_\infty^{(Nac)} = \Gamma_\infty^{(0.08)} \cdot (N_{ac}/0.08)^{-0.8} = K_M \Gamma_{ef} \cdot (N_{ac}/0.08)^{-0.8} \quad (18)$$

Since equations (17) and (18) allow the calculation of the same Γ_∞ value, then

$(\Gamma_\infty)^2 = \Gamma_\infty^{\overline{M}} \cdot \Gamma_\infty^{(Nac)}$, or:

$$\Gamma_\infty = (\Gamma_\infty^{\overline{M}} \cdot \Gamma_\infty^{(Nac)})^{1/2} = (7.66 \cdot 10^2 \cdot (N_{ac})^{-0.8}/\overline{M}) \cdot \Gamma_{ef} = K_{MN} \cdot \Gamma_{ef}, \quad (19)$$

where $K_{MN} = 7.66 \cdot 10^2 \cdot (N_{ac})^{-0.8}/\overline{M}$ (20)

Table 1 summarizes the values of K_{MN} calculated from equation (20) and Γ_∞^{calc} from equation (19), Γ_{ef} is defined from equation (9). Γ_∞^{exp} is taken from our work and from Ref.[11]. Table 1 shows a good agreement between Γ_∞^{calc} and Γ_∞^{exp}, which confirms the correctness of the proposed calculation method. Thus, equations (19) and (20) make it possible to calculate Γ_∞ for the entire class of PVA.

By comparing the equation of adsorption in the **HCE** emulsion (19) with that in the **non-HCE** emulsion (5), one can see that equation (5) includes both the Γ_{ef} and indirectly the mean molecular mass $\overline{M}$ (which is part of the mole concentration). By

analogy with the **HCE** emulsions, it is expected that the equation (5) should also include the second characteristic of the PVA structure – N_{ac}. When N_{ac} is introduced as the structural coefficient K_N, calculated from equation (16), we obtain K_N = 1.07 for the tested sample. This value differs from value 1 within the experimental error, therefore it could not be immediately identified. For the other tested sample, with X_{ac} = 10% and $\overline{M}$ = 56000, K_N is 0.2. The experimental values for this sample are presented in Table 2 and were obtained by us at α_{disp} = 1 and at three varying concentrations. Also included are the Γ^{calc} values, estimated from equation (5), with the coefficient K_N = 0.2. Table 2 shows a good agreement between the experimental and calculated data. Thus, the equation of adsorption in the **non-HCE** emulsion with the considered polymer structure is:

$$\Gamma = 0.5 \cdot K_N \cdot \Gamma_{ef} \cdot C^{0.5} \cdot e^{6.1 \exp(-\alpha_{disp}/3)} \qquad (21)$$

Table 2. Adsorption in non-Highly Concentrated Emulsion non-HCE stabilized by PVA. $\overline{M}$=56000, X_{ac}=10%, N_{ac}=0.08, K_N=0.2 (from eq.16), α_{disp} = 1

$C \cdot 10^2$ PVA Mol/m^3	Adsorption $\Gamma_\infty^{(exp)} \cdot 10^6$ Mol/m^2	Adsorption $\Gamma_\infty^{(calc)} \cdot 10^6$ Mol/m^2
2.4	1.3	1.5
6.6	2.2	2.5
18.0	4.5	4.1

Thus, we have obtained equations linking the adsorption values in the **non-HCE** emulsion (equation (21)) and the **HCE** emulsion (equation (19)) to the Γ_{ef} value determined by an independent method from the surface tension isotherm or calculated from equation (9). For the **HCE** emulsions, Γ_∞ at $C \leq C_{crit}$, is not concentration dependent. Regarding the **non-HCE** emulsions,

it follows from equation (21) that adsorption in weight expression is proportional to $(\overline{M})^{1/2}$, which is consistent with the data of Lankveld [3].

Maximum interface area

The maximum interface area S_∞ to be stabilized by PVA was evaluated for the tested sample by microscopy [2]. Fig.8 shows the experimental dependence of S_∞^{sp} on **C** for this sample (curve 1). The same figure also shows experimental S_∞^{sp} relationships to **C** for PVA samples with X_{ac} = 10% (curve 2) and X_{ac} = 18.7% (curve 4), taken from Ref. [10] and evaluated similarly. S_∞^{sp} is the interface area in the **HCE** emulsion calculated per 1 ml of continuous phase. As seen from Fig.8, a characteristic feature of PVA is the linear growth of S_∞^{sp} to the maximum point $MaxS_\infty^{sp}$ at $C = C_{crit}$ = 55 g/l followed by a reduction of S_∞^{sp} with further growth of **C**. It is known that the interface area in emulsions is described by equation [1]:

$$S = [(C - C_{eq}) \cdot V_{cont}] / \Gamma_\infty, \qquad (22)$$

where **C** is the initial surfactant concentration in the volume of the continuous phase before emulsification; C_{eq} is the equilibrium surfactant concentration in the volume of the continuous phase formed after emulsification. In the **HCE** emulsion $C_{eq} \ll C$, therefore equation (22) for the **HCE** emulsion for S_∞^{sp} is transformed into:

$$S_\infty^{sp} = C/\Gamma \qquad (23)$$

The left branch of the experimental curve 1 (Fig.8) for the test sample is described by equation (23) when substituting $\Gamma_\infty = 13.1 \cdot 10^{-7}$ mol/m^2. The right branch of the same curve straightens in coordinates $S_\infty^{sp} - 1/C$ (curve 6, Fig.8) and is described by equation:

$$S_\infty^{sp} = 2.91/C, \text{ where } C - \text{mole/m}^3 . \quad (24)$$

On the other hand, the right branch of curve 1 (Fig.8) can also be described by equation (23), where Γ_∞ is a variable. Equating equation (23) with equation (24) gives the equation for the test sample at concentration $C \geq C_{crit}$:

$$\Gamma_\infty = 3.44 \cdot 10^{-7} \cdot C^2 \quad (25)$$

Since the adsorption layers of the droplets in a PVA stabilized emulsion are in contact when C_{crit} is reached (Fig.9), the interface area can then be determined by the formula:

$$S_\infty = 2 \cdot V_{cont} / 2 \cdot \delta_{ads} = V_{cont}/\delta_{ads} \quad (26)$$

Equating equation (24) to (26) gives the following for the tested PVA sample:

$$C \cdot V_{cont} / \delta_{ads} = 2.91, \quad (27)$$

where $V_{cont} = 1 \cdot 10^{-6}$ m^3, δ_{ads} is the thickness of the adsorption layer.

In the HCE emulsion at $C \geq C_{crit}$ the interlayer thickness between the droplets δ is $2 \cdot \delta_{ads}$ (Fig.9). From (27) it follows that:

$$C \cdot V/\delta = const \quad (28)$$

As seen from equation (28), after the adsorption layers have come into contact, THE QUANTITY OF HIGHMOLECULAR WEIGHT SURFACTANT PER UNIT THICKNESS OF THE INTERLAYER BETWEEN DROPLETS (AND PER UNIT THICKNESS OF THE ADSORPPTION LAYER) in the unit volume of the continuous phase is a constant value. Since this value is related to the structure of the PVA (it is different for various samples) we call the constant estimated by the formula (27) at V_{cont} = 1 ml, as the structure coefficient K_s of the adsorption layer. Then (24) can be written as:

$$S_\infty^{sp} = K_s/C \quad (29)$$

The constancy of K_s after reaching C_{crit} means that with constant V_{cont} according to the formula (27) δ_{ads} increases with increase of C, i.e.

$$\delta_{ads} = k \cdot C, \quad (30)$$

where k is the proportionality factor.

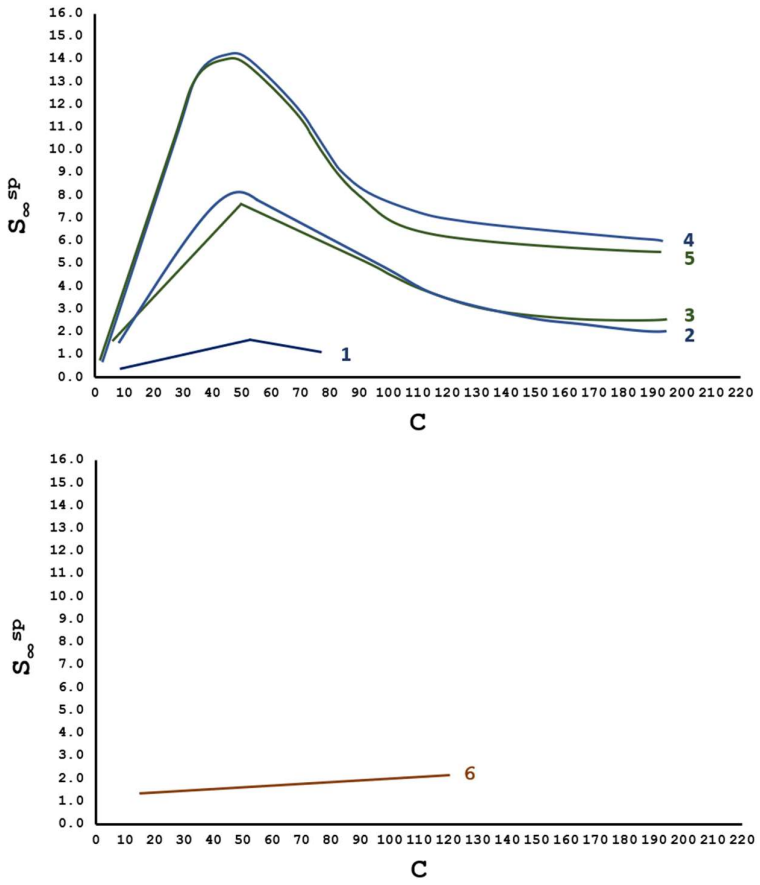
Figure 8. Dependence of the specific maximum interface area in HCE emulsion on the PVA concentration C before emulsification in the volume of the continuous phase:

1, 2, 4 – experimental relationships S_∞^{sp} vs. C for PVA with 1) x_{ac} = 1.8%, $\overline{M}$ = 28000 2) x_{ac} = 10%, $\overline{M}$ = 28000 4) x_{ac} = 18.7%, $\overline{M}$ = 28000.

3, 5 – calculated relationships S_∞^{sp} vs. C for PVA with 3) x_{ac} = 10%, $\overline{M}$ = 28000 5) x_{ac} = 18.7%, $\overline{M}$ = 28000.

6 – experimental relationship S_∞^{sp} vs. 1/C for PVA with x_{ac} = 1.8%, $\overline{M}$ = 28000.

S_∞^{sp} – m^2/ml, C – g/l.



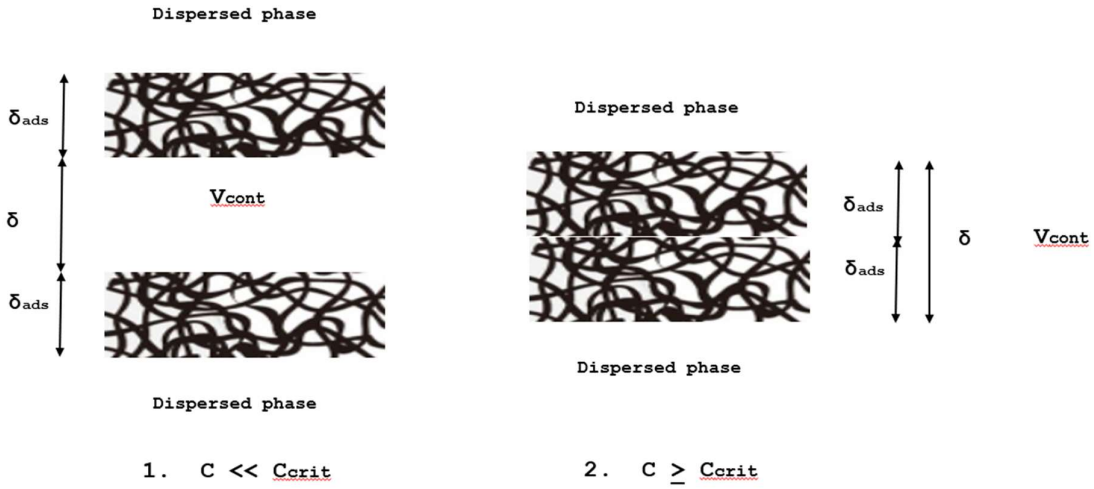
The adsorption in the HCE emulsion may be described by the formula

$$\Gamma_\infty = C_{ads} \cdot \delta'_{ads} + C_{ef} \cdot \delta_{ef}, \qquad (31)$$

where δ'_{ads} is the thickness of the part of layer with concentration C_{ads} (Fig.4). It is calculated as follows:

$$\delta'_{ads} = \delta_{ads} - \delta_{ef}. \qquad (32)$$

Figure 9. Model of the interlayer between droplets in emulsion stabilized by polymer surfactant: 1) when $C < C_{crit}$ 2) when $C \geq C_{crit}$.



Since $\delta_{ads} \gg \delta_{ef}$, formula (31) can be given to:

$$\Gamma_\infty = C_{ads} \cdot \delta_{ads} \qquad (33)$$

Since at $C \geq C_{crit}$ conditions (12) and (30) are fulfilled, then

$$\Gamma_\infty = k \cdot C^2 \qquad (34)$$

The constant k in equation (34) is easily evaluated if $C = C_{crit}$, at which Γ_∞ is defined by equation (19)

$$K = K_{MN} \cdot \Gamma_{ef} / C^2_{crit(m)}, \qquad (35)$$

where $C_{crit(m)}$ is the critical concentration in molar expression. By substituting (35) in (34), we got:

$$\Gamma_\infty = K_{MN} \cdot \Gamma_{ef} \cdot (C / C_{crit(m)})^2, \qquad (36)$$

where K_{MN} is calculated with the formula (20). By substituting (36) in (23), we obtained:

$$S_\infty^{sp} = [C^2_{crit(m)} / (K_{MN} \cdot \Gamma_{ef})] \cdot 1/C \qquad (37)$$

Comparing (37) to (29), we see that

$$C^2_{crit(m)} / (K_{MN} \cdot \Gamma_{ef}) = K_s. \qquad (38)$$

Thus, equation (29) describes adsorption in the **HCE** emulsion at $C \geq C_{crit}$, K_s is defined from equation (38). Fig.8 presents the calculated dependencies of S_∞^{sp} on C for the PVA sample with X_{ac} = 10%, $\overline{M}$ = 28000 (curve 3), and for that with X_{ac} = 18.7%, $\overline{M}$ = 28000 (curve 5). The left branches of these curves were calculated by equation (23), Γ_∞ was calculated by equation (19), and the right branches were calculated by equation (29), in which K_s was defined by equation (38). Fig.8 shows good agreement between the calculated curves 3,5 derived from the equations obtained for the tested sample and experimental curves taken from the work [11].

The emulsification mechanism

Thus, we got equations (19) and (36) for isotherms of adsorption Γ_∞ in a wide range of concentrations. The analysis of these equations makes it possible to explain and calculate the peak of dependence of S_∞^{sp} on C, and together with the equation obtained for adsorption in the **non-HCE** emulsion (21), sheds light on the emulsification mechanism involving PVA as an emulsifier. In summary, it can be concluded that the isotherm of adsorption of polymer surfactants in emulsions is described by the equation:

$$\Gamma = K^* \cdot \Gamma_{ef}, \qquad (39)$$

where K^* for the **non-HCE** emulsion depends on the concentration and structure of the surfactant and the dispersed phase volume ratio; for the **HCE** emulsion before reaching critical concentration, it depends only on the structure of the high-molecular-weight

surfactant, and above C_{crit} on both its structure and concentration. The value of the Γ_{ef} depends only on the structure of the polymer surfactant.

To describe the adsorption mechanism of the high-molecular-weight surfactants at the emulsion interface, we arbitrarily divide the adsorption process into three stages:

1. The adsorption layer is first formed at the interface. The effective part of the layer near the interface is characterized by the concentration C_{ef}, the rest of the adsorption layer is characterized by the concentration C_{ads} and the volume of the aqueous phase is characterized by equilibrium concentration $C_{eq}=C$ (the concentration before emulsification).

2. In case of the **non-HCE** emulsion at a constant initial concentration and a constant dispersed phase volume ratio α_{disp}, the adsorption of surfactant in the layer is constant (Fig.1, lines 1,2,3), i.e. a change in emulsification conditions, causing an equilibrium concentration change in the volume of the aqueous phase, results in a proportional change in **S** because of a change in dispersity under different emulsification conditions:

$(C - C_{eq}) \sim S$ (equation 22).

This means that the entire amount of surfactant that has moved from the volume to the interface is spent on stabilizing the newly formed interface. Obviously, in this case, the thickness of the layer is constant.

If under these conditions the amount of the dispersed phase increases, i.e., α_{disp} increases (at **C** = const), then adsorption decreases (Fig.1, lines 1,2,3), i.e the thickness of the layer is reduced. This is because of the faster growth of **S** compared to

$(C - C_{eq})$ (formula (22). Thus, stabilization of the new interface is achieved not on1y by the intake of polymer molecules from the volume of the continuous phase, but also by the reduction of the amount of surfactant in the adsorption layer. In this case, such a deployment of the polymer chains results in an increase in the fraction of elementary polymer links in direct contact with another phase, until an ultimate emulsion is formed when further reorientation of adsorbed molecules is unlikely, and the aqueous phase volume reserve is exhausted: $(C - C_{eq}) \rightarrow C$, $C_{eq} \rightarrow 0$.

If in the **HCE** emulsion the initial concentration **C** in the volume of the continuous phase increases (at constant α_{disp}), the adsorption increases (Fig.1, lines 1,2,3), indicating an increase in the thickness of the adsorption layer or C_{ads} (or both). In this case, the increase of $(C - C_{eq})$ contributes not only to the formation of a new interface but also to the increase in adsorption, i.e., the growth of $(C - C_{eq})$ is greater than the growth of **S** (see formula 22).

3. In the **HCE** emulsion, an increase in surfactant concentration is accompanied by an increase in the maximum achievable dispersed phase volume ratio (under constant emulsification conditions), i.e., two trends are superimposed, one increasing, and the other reducing adsorption. Therefore, the value of the HCE adsorption Γ_∞ remains constant, and the entire amount of surfactant that enters the adsorption layer due to increased $(C - C_{eq})$ is used to stabilize the new interface.

In the **HCE** emulsion, the growth of the interface area with an increase in the initial concentration and a constant volume of the continuous phase leads to a decrease in the interlayer's thickness between the droplets (Fig.9). In this case, the equilibrium concentration $C_{eq} \ll C_{ads}$. When adsorption layers of two droplets touch, a unique situation occurs: the concentration in the layer

and in the volume of the continuous phase is immediately aligned $C_{ads} = C_{eq}$, that is C_{eq} immediately reaches the initial value of C. This happens at $C = C_{crit} = C_{eq}$, i.e., all concentrations in the aqueous phase cross-section are equalized: $C = C_{ads} = C_{ef}$.
A further increase in C in the **HCE** emulsion leads to about proportional increase in the thickness of the adsorption layer. Then the adsorption Γ_∞ of the **HCE** increases proportionally to the square of the concentration (see formula (12)).
For low-molecular-weight surfactants, because of the monomolecular nature of the adsorption layer, only the interface area increases proportionally Γ_m value. In this case C_{ads} is always much higher than C_{eq}. Since contact of monomolecular layers is most often unlikely because of their tiny thickness, equilibrium concentration in the volume of continuous phase and concentration in the adsorption layer are also unlikely to equalize. This is the fundamental difference between the polymer adsorption layer and the monomolecular layer.

Summary

1). The concept of effective layer is introduced, and it is shown that its most important property is the value of adsorption of high molecular surfactants in the effective layer. This value is included in equations describing adsorption of high-molecular-weight surfactants in emulsions.
2). It is shown that, from the Gibbs equation and surface tension measurements, the value of effective adsorption of high-molecular-weight surfactants can be obtained by an independent method.
3). For **non-Highly Concentrated Emulsions non-HCE** stabilized by PVA, an equation of adsorption isotherm has been obtained,

considering such parameters of PVA structure as the content of acetate groups and the mean molecular mass.

4). For **non-HCE** emulsions, stabilized PVA, the isotherm adsorption equations have been obtained, allowing the calculation of the adsorption values in a wide range of concentrations.

5). It has been shown that in Highly Concentrated Emulsions **HCE**, until the critical concentration of high-molecular-weight surfactant in the volume of the continuous phase is reached, adsorption at the interface is independent of concentration. After reaching the critical concentration, the adsorption increases proportionally to the concentration in the square.

6). The description of the emulsification process and the resulting equations disclose, in the example of PVA, the mechanism for adsorption of polymeric surfactants, which form net structures at the interface.

NOTATIONS

C – concentration of surfactant before emulsification in the volume of the continuous phase

$\mathbf{C_{eq}}$ – equilibrium concentration of a surfactant in the volume of the continuous phase

$\mathbf{C_{crit}}$ – critical concentration of the polymer surfactant

$\mathbf{C_{ef}}$ – concentration in the effective layer

$\mathbf{C_{ads}}$ – concentration in the adsorption layer besides of its **effective part**

$\mathbf{C_m}$ – critical micelle concentration of low-molecular-weight surfactant

$\mathbf{C_e}$ – minimum concentration of emulsification

$\mathbf{K_S}$ **–** coefficient, considering the structure of the adsorption layer

$\mathbf{K_N}$ **–** coefficient, considering $\mathbf{N_{ac}}$

K_M – coefficient, considering $\overline{M}$

K_{MN} – coefficient, considering both N_{ac} and $\overline{M}$

$\overline{M}$ - mean molecular mass of the PVA

$\overline{M}_{e.l.}$ - molecular mass of the elementary link of a polymer chain

N_{ac} – mole fraction of acetate links in PVA molecule

S_∞ - maximum interface area

S_∞^{sp} – specific maximum interface area (per unit volume of the continuous phase)

V_{disp} – volume of the dispersed phase

V_{cont} – volume of the continuous phase

X_{ac} – content of acetate group, %

α_{disp} – dispersed phase volume ratio

Γ – adsorption value in non-Highly Concentrated Emulsion **non-HCE**

Γ_∞ – adsorption value in Highly Concentrated Emulsion **HCE**

Γ_{ef} – adsorption value in the effective layer

Γ_m – maximum adsorption value of low-molecular-weight surfactant

δ_{ef} – thickness of the effective layer

δ_{ads} – thickness of the adsorption layer

δ – thickness of the interlayer between droplets in the emulsion

δ' – thickness of the adsorption layer besides of its effective part

σ – surface tension

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