

SURFACE TENSION TIME AND CONCENTRATION DEPENDENCIES OF MULTIFARIOUS SURFACTANTS-BASED SYSTEMS CONTAINING POLYVINYLYL ALCOHOL

Zhanar B. Ospanova¹, Kuanyshbek B. Mussabekov¹,
Saule B. Aidarova², Reinhard Miller³, Mirsalim Asadov⁴

¹ Al-Farabi Kazakh National University
71 Al-Farabi str., 050040, Almaty, Kazakhstan
E-mail: zhanospan@mail.ru

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² Kazakh National Technical University after K.I. Satpayev, Almaty, Kazakhstan

³ Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

⁴ Institute of Catalysis and Inorganic Chemistry after M.F. Nagiyev
Azerbaijan National Academy of Sciences, Baku, Azerbaijan

ABSTRACT

This article summarizes the measurements results referring to the surface tension (σ) of two water-based surfactant compounds - sodium dodecylsulphate (SDS) and cetyltrimethylammonium bromide (CTAB). They are of low critical aggregations content in presence of polyvinyl alcohol (PVA). In fact, the increment of polyvinyl alcohol (PVA) concentration in the aqueous solutions within the concentration range from $1 \cdot 10^{-4}$ base-kmol. m^{-3} to $1 \cdot 10^{-1}$ base-kmol. m^{-3} entails a substantial lower surface tension (from 70 mN m^{-1} to 40 mN m^{-1}). The experimental results provide to follow the time and concentration dependencies of water-based surfactants-PVA compounds surface tension (σ). The surfactants-PVA compounds studied provide effective decrease of the surface tension of low surfactants concentrations, i.e. at a relative concentration of components $n = C_{\text{surfactants}}/C_{\text{PVA}} = 1 \cdot 10^{-4} - 1 \cdot 10^{-1}$, where PVA concentration $C_{\text{PVA}} = 1 \cdot 10^{-2}$ base-kmole m^{-3} . A decrement velocity σ in the binary compounds of SDS-PVA and CTAB-PVA appears to be dependent on the surfactants adsorption rate at the interface between the water and air phases. The polymer adsorption layer relaxation time is minimized due to PVA solutions concentration increment which testifies of surface tension relaxation activation. The increase of the surfactants content in the surfactants-PVA compounds results in increase of the relaxation time. The kinetic parameters are defined for the adsorption layers of PVA and surfactants-PVA compounds at the water-air interface at a relative concentration of the compound components $n = 1 \cdot 10^{-4} - 1 \cdot 10^{-1}$ and $C_{\text{PVA}} = 1 \cdot 10^{-2}$ base-kmole m^{-3} . The surface characteristics are estimated for SDS-PVA and CTAB-PVA compounds at the water-air interface.

Keywords: surface tension, Surfactants, water-soluble polymers.

INTRODUCTION

Surfactants and water-soluble polymers (polyelectrolytes) including surfactants-polymers compounds are used in minerals flotation, chemical and biochemical processes, catalysis, and organic synthesis. They can be utilized as flocculants and coagulants for waste treatment, soil stabilizers, and drugs prolongators. They are also used in the cosmetic industry, the oil production technology and other industrial sectors. The wide application

requires knowledge of their physicochemical properties, particularly, of their surface tension concentration and time dependencies. The kinetic studies of compounded non-ionogenic polymers and charged surfactants are still deficient. The investigation of surfactants-polyelectrolytes associates of the foam stabilizing action of sodium dodecylsulphate (SDS) and cetyltrimethylammonium bromide (CTAB) of low critical aggregations content is reported in refs. [1, 2]. The binary hydrous systems SDS-PVA and CTAB-PVA provided foam destruction.

However, the surface tension concentration and time dependences of such water-based systems have not yet been studied. In fact this is the aim of the study reported.

EXPERIMENTAL

The substances used included an anionic surfactant (sodium dodecylsulphate, CMC, of $8.3 \cdot 10^{-3} \text{ mole} \cdot \text{l}^{-1}$) and a cationic surfactant (cetyltrimethylammonium bromide, CMC of $9.2 \cdot 10^{-4} \text{ mole} \cdot \text{l}^{-1}$) products of Fluka, Germany. The non-ionic polymer (polyvinyl alcohol of a molecular mass $M_n = 1 - 2.6 \cdot 10^4$) was purchased from Alfa Aesar, Germany. The surface tension (σ , $\text{mN} \cdot \text{m}^{-1}$) of the water-based PVA, surfactants and their compounds was measured by method of the immersed Wilhelm's plate. A platinum plate was used in this case. All experiments were carried out at a room temperature.

RESULTS AND DISCUSSION

Figs. 1 - 3 show the time dependences of σ of the water-based systems SDS, CTAB, PVA and their

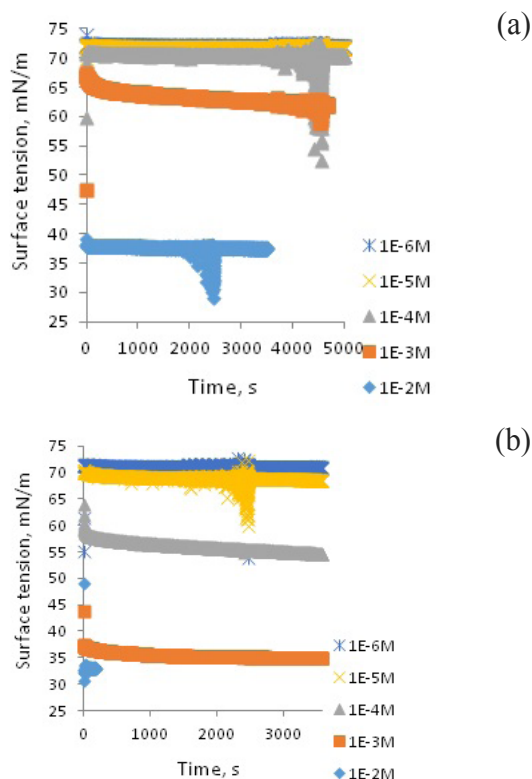


Fig.1. Concentration-time dependencies of the surface tension of SDS (a) and CTAB (b) at the water-air interface.

compounds SDS-PVA and CTAB-PVA. As seen from Fig. 1, the surface tension of the surfactants solutions decreases within the first seconds only and reaches quickly its equilibrium value. The water-based surfactants concentration increase results in σ sharp decrease from $\sim 70 \text{ mN} \cdot \text{m}^{-1}$ to $\sim 37 \text{ mN} \cdot \text{m}^{-1}$ for SDS and $\sim 32 \text{ mN} \cdot \text{m}^{-1}$ for CTAB varying the concentration from $1 \cdot 10^{-6} \text{ kmol} \cdot \text{m}^{-3}$ to $1 \cdot 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$.

The kinetic curves presented show that the surface tension decreases more slowly and requires longer time to reach its equilibrium value when compared to the results referring to the surfactants solutions (Fig. 2).

Fig. 3 presents the time dependences of σ of the binary compounds SDS-PVA and CTAB-PVA in case of a relative components concentration $n = C_{\text{surfactants}}/C_{\text{PVA}} = 1 \cdot 10^{-4} - 1 \cdot 10^{-1}$. The value of CPVA remains constant equal to $1 \cdot 10^{-2} \text{ base} \cdot \text{kmole} \cdot \text{m}^{-3}$.

Fig. 3 shows that σ decrease in presence of surfactants-PVA compounds is basically defined by the association of the non-ionic PVA with the surfactants due to the formation of hydrogen bonds and the further stabilization of the hydrophobic interactions. Fig. 3 shows also that the surfactants concentration increase results in σ decrease to the relaxation level leading to the equilibrium state establishment. The latter is described by the exponential equation:

$$\sigma_t = \sigma_\infty + (\sigma_0 - \sigma_\infty) \cdot e^{-K \cdot t} \quad (1)$$

where σ_t is the surface tension of the solution at time t , σ_0 is the initial surface tension, σ_∞ is the equilibrium

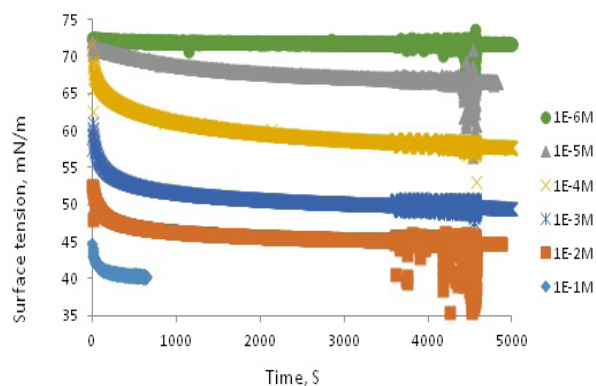


Fig. 2. Concentration and time dependencies of the surface tension σ ($\text{mN} \cdot \text{m}^{-1}$) of water-based PVA at 298 K at the water-air interface.

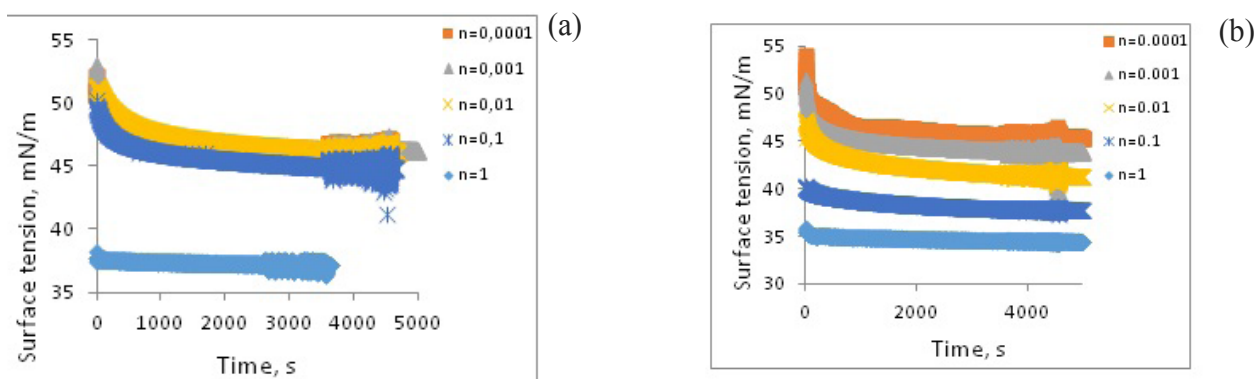


Fig. 3. Concentration and time dependencies of the surface tension σ (mN m^{-1}) of the water-based systems SDS–PVA (a) and CTAB–PVA (b) at 298 K and a relative concentration $n = [\text{surfactants}]/[\text{PVA}]$ of: 1 – 10^{-4} ; 2 – 10^{-3} ; 3 – 10^{-2} ; 4 – 10^{-1} ; 5 – 1. PVA = $1 \cdot 10^{-2}$ base-kmole m^{-3} .

Table 1. Values of the relaxation times τ_r of the aqueous solutions of surfactants, PVA and surfactants-PVA compounds at relative concentration $n = 1 \times 10^{-4}$ –1.

System	$\tau_r, \text{c.}$
SDS, kmole/ m^3	
10^{-6}	8.68E+15
10^{-5}	2.17E+16
10^{-4}	4.34E+17
10^{-3}	4.34E+15
10^{-2}	2.17E+15
CTAB, kmole/ m^3	
10^{-6}	4.34E+16
10^{-5}	6.20E+15
10^{-4}	4.82E+15
10^{-3}	2.17E+15
10^{-2}	4.34E+15
PVA, base-kmole/ m^3	
10^{-6}	6.20E+03
10^{-5}	1.45E+03
10^{-4}	1.09E+04
10^{-3}	7.24E+02
10^{-2}	2.17E+03
$n = [\text{SDS}]/[\text{PVA}]; \text{PVA} = 1 \cdot 10^{-2}$ base-kmole· m^{-3}	
10^{-4}	7.24E+03
10^{-3}	5.43E+04
10^{-2}	2.17E+03
10^{-1}	4.82E+03
1	2.17E+04
$n = [\text{CTAB}]/[\text{PVA}]; \text{PVA} = 1 \cdot 10^{-2}$ base-kmole· m^{-3}	
10^{-4}	7.24E+04
10^{-3}	6.20E+04
10^{-2}	8.68E+03
10^{-1}	2.17E+03
1	4.34E+03

Table 2. Kinetic parameters referring to the adsorption layers of PVA and surfactants–PVA compounds at the water-air interface with a relative concentration $n = 1.10^{-4}-1$.

System	K , adsorption rate constant	m , constant
PVA	0.8–1.9	0.1–0.4
SDS–PVA	0.2–3.3	0.1–0.2
CTAB–PVA	1.2–2.4	0.1–0.3

surface tension, K is the adsorption rate constant, while m is a numeric constant.

The logarithmic form of Eq. (1) is:

$$\lg(\sigma_t - \sigma_\infty) = \lg(\sigma_0 - \sigma_\infty) - \frac{Kt^m}{2.303} \quad (2)$$

It is assumed that $K = (1/\tau_r)$ and $m = 1$ aiming to define the relaxation time τ_r , i.e. the time, when σ decreases e times. Thus Eq. (2) becomes:

$$\lg(\sigma_t - \sigma_\infty) = \lg(\sigma_0 - \sigma_\infty) - \frac{t}{2.303 \cdot \tau_r} \quad (3)$$

The application of Eq. (3) provides to obtain the values of τ_r listed in Table 1. It is evident that the increase of PVA water-based polymer concentration brings about τ_r decrease. This is an evidence of surface tension relaxation activation. The values of τ_r increase with increase of

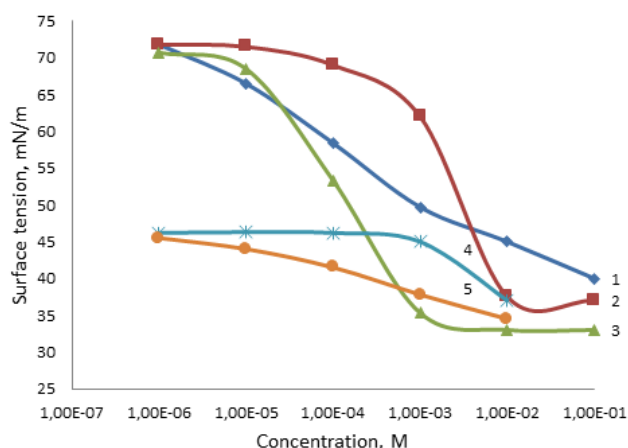


Fig. 4. Surface tension (σ in mN m^{-1}) isotherms of water-based PVA and surfactants–PVA compounds at 298 K: PVA (1); SDS (2); CTAB (3); compound SDS–PVA $n = [\text{SDS}]/[\text{PVA}] = 10^{-4}-1$ (4); compound CTAB–PVA $n = [\text{CTAB}]/[\text{PVA}] = 10^{-4}-1$ (5). PVA concentration in the compound of 1×10^{-2} base-kmole m^{-3} .

PVA content of the surfactants–PVA compounds. This is explained by the macromolecules adsorption determined by the enhanced intra- and intermolecular actions (hydrogen bonds formation and hydrophobic reactions). The surface characteristics of SDS–PVA and CTAB–PVA compounds are also evaluated by isotherms of Surface tension of water-based PVA and surfactants–PVA compounds (Fig.4). Eq. (2) is further modified aiming to determine adsorption rate constant K and constant m :

$$\lg \left[2.303 \cdot \lg \frac{\sigma_0 - \sigma_\infty}{\sigma_t - \sigma_\infty} \right] = \lg K + m \lg t \quad (4)$$

The dependence $\lg \left[2.303 \cdot \lg \frac{\sigma_0 - \sigma_\infty}{\sigma_t - \sigma_\infty} \right]$ vs. $\lg t$ provides the estimation of K and m for PVA adsorption layers and surfactants–PVA compounds at the water-air interface. The values obtained are presented in Table 1.

The decrease of σ of PVA aqueous solutions at $m \leq 0.5$ is determined [3] by the macromolecules diffusion rate from the bulk of the solution to the interface. This provides the conclusion that this is the rate-determining step of the adsorption of PVA and surfactants–PVA compounds [4, 5].

The isotherms referring to SDS–PVA and CTAB–PVA provided the estimation of CMC, the surface activity values at CMC (G_{CMC}), the Gibbs maximum permissible adsorption (G) and the area (S_{CMC}), occupied by surfactants molecule in presence of PVA (Table 3). Furthermore, the values of the standard free energy of micelle formation ΔG_M^0 and adsorption ΔG_a^0 at the water-air interface are calculated. This was done in correspondence with Eqs. (6) and (7):

$$\Delta G_M^0 = RT \ln C_{\text{CMC}} \quad (5)$$

$$\Delta G_a^0 = RT \ln C_{\text{CMC}} - \pi_{\text{CMC}} \cdot S_{\text{CMC}} \cdot N_A \quad (6)$$

where R is the gas constant, T is the temperature, π_{CMC} and S_{CMC} are the surface pressure and the area occupied by the surfactants molecule in the adsorption layer at a concentration equal to CMC (C_{CMC}), while N_A is the Avogadro's number. The results obtained are summarized in Table 3. It is evident that SDS–PVA and CTAB–PVA water-based systems have a high surface activity. In other words, these compounds are in full capacity to decrease the surface tension of the corresponding aqueous solutions even at their lowest concentrations.

Table 3. Estimated surface characteristics of surfactants–PVA compounds at the water-air interface at $n = [1 \times 10^{-6} - 1 \times 10^{-2} \text{ kmole} \times \text{m}^{-3} \text{ Surfactants}] / [1 \times 10^{-2} \text{ base-kmole} \times \text{m}^{-3} \text{ PVA}]$.

System	C_{CMC} , $\text{kmole} \cdot \text{m}^{-3}$	σ_{CMC} , $\text{mN} \cdot \text{m}^{-1}$	$G_{CMC} \times 10^{-4}$, $\text{mN} \cdot \text{m}^2 \cdot \text{kmole}^{-1}$	$G \times 10^9$, $\text{kmole} \cdot \text{m}^{-2}$	$S_{CMC} \times 10^{20}$, m^2	$-\Delta G_M^0$,	$-\Delta G_a^0$,
						$\text{kJ} \cdot \text{mole}^{-1}$	
SDS–PVA	$2 \cdot 10^{-4}$	30	20	3	56	21	35
CTAB–PVA	$3 \cdot 10^{-5}$	42	98	2	84	26	41

CONCLUSIONS

The increase of PVA concentration in its aqueous solutions from $1 \cdot 10^{-6}$ to $0.1 \text{ base-kmole m}^{-3}$ provides surface tension decrease from 70 mN m^{-1} to 40 mN m^{-1} .

The time and concentration dependencies of surface tension of SDS–PVA and CTAB–PVA are determined. It is found that the surface tension is decreased even at a relative concentration of the components $n = [\text{Surfactants}] / [\text{PVA}] = 1 \cdot 10^{-4} - 1 \cdot 10^{-3}$, PVA concentration in the compound of $1 \cdot 10^{-2} \text{ base-kmole m}^{-3}$.

The σ decrease of the binary compounds SDS–PVA and CTAB–PVA depends primarily on the surfactants adsorption at the water–air interface. The relaxation time of the polymer adsorption layer decreases with increase of PVA concentration which is attributed to the surface tension relaxation activation. The relaxation time of the surfactants–PVA compounds increases with increase of the surfactants content.

The kinetic parameters referring to the adsorption layers of PVA and surfactants–PVA compounds at the water-air interface in case of a relative compound components concentration $n = [1 \cdot 10^{-6} - 1 \cdot 10^{-2} \text{ kmole m}^{-3} \text{ surfactants}] / [1 \cdot 10^{-2} \text{ base-kmole m}^{-3} \text{ PVA}]$ are determined. The surface characteristics of SDS–PVA and CTAB–PVA compounds are also evaluated by isotherms of surface tension. One of the important properties of such composites is their use as foaming agents.

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