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ҚАЙЫРЫМДЫЛЫҚ ҚОРЫ
HALYK
CHARITY FOUNDATION

«ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ» РҚБ
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ИЗВЕСТИЯ

РОО «НАЦИОНАЛЬНОЙ АКАДЕМИИ
НАУК РЕСПУБЛИКИ КАЗАХСТАН»
ЧФ «Халық»

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ЧФ «ХАЛЫҚ»

В 2016 году для развития и улучшения качества жизни казахстанцев был создан частный Благотворительный фонд «Халык». За годы своей деятельности на реализацию благотворительных проектов в областях образования и науки, социальной защиты, культуры, здравоохранения и спорта, Фонд выделил более 45 миллиардов тенге.

Особое внимание Благотворительный фонд «Халык» уделяет образовательным программам, считая это направление одним из ключевых в своей деятельности. Оказывая поддержку отечественному образованию, Фонд вносит свой посильный вклад в развитие качественного образования в Казахстане. Тем самым способствуя росту числа людей, способных менять жизнь в стране к лучшему – профессионалов в различных сферах, потенциальных лидеров и «великих умов». Одной из значимых инициатив фонда «Халык» в образовательной сфере стал проект Ozgeris powered by Halyk Fund – первый в стране бизнес-инкубатор для учащихся 9-11 классов, который помогает развивать необходимые в современном мире предпринимательские навыки. Так, на содействие малому бизнесу школьников было выделено более 200 грантов. Для поддержки талантливых и мотивированных детей Фонд неоднократно выделял гранты на обучение в Международной школе «Мирас» и в Astana IT University, а также помог казахстанским школьникам принять участие в престижном конкурсе «USTEM Robotics» в США. Авторские работы в рамках проекта «Тәлімгер», которому Фонд оказал поддержку, легли в основу учебной программы, учебников и учебно-методических книг по предмету «Основы предпринимательства и бизнеса», преподаваемого в 10-11 классах казахстанских школ и колледжей.

Помимо помощи школьникам, учащимся колледжей и студентам Фонд считает важным внести свой вклад в повышение квалификации педагогов, совершенствование их знаний и навыков, поскольку именно они являются проводниками знаний будущих поколений казахстанцев. При поддержке Фонда «Халык» в южной столице был организован ежегодный городской конкурс педагогов «Almaty Digital Ustaz.

Важной инициативой стал реализуемый проект по обучению основам финансовой грамотности преподавателей из восьми областей Казахстана, что должно оказать существенное влияние на воспитание финансовой грамотности и предпринимательского мышления у нового поколения граждан страны.

Необходимую помощь Фонд «Халык» оказывает и тем, кто особенно остро в ней нуждается. В рамках социальной защиты населения активно проводится работа по поддержке детей, оставшихся без родителей, детей и взрослых из социально уязвимых слоев населения, людей с ограниченными возможностями, а также обеспечению нуждающихся социальным жильем, строительству социально важных объектов, таких как детские сады, детские площадки и физкультурно-оздоровительные комплексы.

В копилку добрых дел Фонда «Халык» можно добавить оказание помощи детскому спорту, куда относится поддержка в развитии детского футбола и карате в нашей стране. Жизненно важную помощь Благотворительный фонд «Халык» оказал нашим соотечественникам во время недавней пандемии COVID-19. Тогда, в разгар тяжелой борьбы с коронавирусной инфекцией Фонд выделил свыше 11 миллиардов тенге на приобретение необходимого медицинского оборудования и дорогостоящих медицинских препаратов, автомобилей скорой медицинской помощи и средств защиты, адресную материальную помощь социально уязвимым слоям населения и денежные выплаты медицинским работникам.

В 2023 году наряду с другими проектами, нацеленными на повышение благосостояния казахстанских граждан Фонд решил уделить особое внимание науке, поскольку она является частью общественной культуры, а уровень ее развития определяет уровень развития государства.

Поддержка Фондом выпуска журналов Национальной Академии наук Республики Казахстан, которые входят в международные фонды Scopus и Wos и в которых публикуются статьи отечественных ученых, докторантов и магистрантов, а также научных сотрудников высших учебных заведений и научно-исследовательских институтов нашей страны является не менее значимым вкладом Фонда в развитие казахстанского общества.

С уважением,
Благотворительный Фонд «Халык»

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EFFECT OF IONIC AND NONIONIC SURFACTANTS ON WETTING OF SULFUR SURFACE

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Abstract. This study presents the experimental results on dynamic contact angles of pure surfactants on the sulfur surface. Dynamic contact angles were measured for the aqueous solution of three different surfactants: cetyltrimethylammonium bromide (CTAB), sodium dodecylbenzenesulfonate (SDBS), and Triton X-100 (TX-100) using the sessile drop method. The interfacial tension and critical concentration of CTAB, SDBS TX-100 at the water/air interface measured by the method of Vilgemi, using surface tensiometer (DCAT-21, Date physics, Germany) at room temperature 25 °C . Based on the data, the adhesion work on the sulfur surface was calculated and its adsorption mechanism was discussed. The results show that the surface tension and contact angle are smaller for SDBS and TX-100, whereas their calculated adhesion work values are higher compared to CTAB. This shows that the wetting ability of SDBS and TX-100 solutions at the sulfur surface is better than that of CTAB. The adsorption mechanism of the same three surfactants on the sulfur surface was also studied.

Keywords: sulfur surface, contact angle, wetting, surfactants, adsorption

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ИОНДЫҚ ЖӘНЕ ИОНСЫЗ БЕТТІК АКТИВТІ ЗАТТАРДЫҢ КҮКІРТ БЕТІНЕ ЖҰҒУ ӘСЕРІ

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Аннотация: Бұл зерттеуде күкірт бетіндегі таза беттік активті заттардың динамикалық жанасу бұрыштары бойынша тәжірибелік нәтижелер көрсетілген. Үш түрлі беттік активті заттардың судағы ерітіндісі үшін динамикалық жанасу бұрыштары өлшенді: цетилтриметиламмоний бромиді (CTAB), натрий додецилбензолсульфонаты (SDBS) және Triton X-100 (TX-100) тамшы отырғызу әдісімен. CTAB, SDBS, TX-100 су/ауа интерфейсіндегі фазааралық кернеу мен критикалық концентрациялары Вилгеми әдісімен, беттік тензиометрді (DCAT-21, Date physics, Германия) 25°C бөлме температурасында пайдалана отырып өлшенді. Алынған мәліметтер негізінде күкірт бетіндегі адгезия жұмысы есептеліп, оның адсорбциялық механизмі талқыланды. Нәтижелер SDBS және TX-100 үшін беттік керілу және жанасу бұрышы кішірек, ал олардың есептелген адгезия жұмыс мәндері CTAB-мен салыстырғанда жоғары екенін көрсетеді. Бұл SDBS және TX-100 ерітінділерінің күкірт бетіндегі сулану қабілеті CTAB-ге қарағанда жақсырақ екенін көрсетеді. Сондай-ақ күкірт бетіндегі үш бірдей беттік активті заттардың адсорбциялық механизмі зерттелді.

Түйін сөздер: Күкірт беті, жанасу бұрышы, сулану, беттік активті заттар, адсорбция

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ВЛИЯНИЕ ИОННЫХ И НЕИОННЫХ ПАВ НА СМАЧИВАНИЕ ПОВЕРХНОСТИ СЕРЫ

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Аннотация. В данной работе представлены экспериментальные результаты по динамическим краевым углам смачивания чистых поверхностно-активных веществ на поверхности серы. Динамические краевые углы были измерены для водного раствора трех различных поверхностно-активных веществ: бромида цетилтриметиламмония (ЦТАБ), додецилбензолсульфоната натрия (ДБС) и тритона X-100 (TX-100) методом сидячей капли. Межфазное натяжение и критическую концентрацию ЦТАБ, ДБС TX-100 на границе вода/воздух измеряли по методу Вилгеми с помощью поверхностного тензиометра (DCAT-21, Date Physics, Германия) при комнатной температуре 25 °С. На основании полученных данных рассчитана работа адгезии на поверхности серы и обсужден механизм ее адсорбции. Результаты показывают, что поверхностное натяжение и контактный угол меньше для ДБС и TX-100, тогда как их расчетные значения работы адгезии выше по сравнению с ЦТАБ. Это показывает, что смачивающая способность растворов ДБС и TX-100 на поверхности серы лучше, чем у ЦТАБ. Исследован также механизм адсорбции тех же трех ПАВ на поверхности серы.

Ключевые слова: поверхность серы, контактный угол, смачивание, поверхностно-активные вещества, адсорбция

Introduction

Solutions of various surfactants are frequently used in the synthesis of sulfur nanoparticles. Thus, it is important to study the properties of surfactants such as wetting, contact angle, and adsorption on the sulfur surface (Prabhu et al, 2009; Zhao et al., 2010). The reason for this lies in the fact that a surfactant can significantly reduce the surface tension of a solution and effectively wet the sulfur surface. This leads to the formation of the sulfur nanoparticles and hydrophilization of the sulfur surface. As such, the use of different surfactants plays a key role in improving the way sulfur nanoparticles are obtained (Turganbay et al. 2013). Besides, surfactants play an important role in many industrial processes including the synthesis of nanocomposites for lithium batteries (Yanjun et al, 2016; Huang et al, 2015; Qu et al., 2015), fungicides in agriculture (Vineeta Parihar et al., 2019), biomedical and food packaging fields (Duncan et al., 2011), synthesis and modification of carbon nanostructures(Barkauskas et al., 2007), synthesis of sulfur nanowires with carbon to form hybrid materials with useful properties for gas sensor and catalytic applications (Santiago et al., 2006; Cooper et al., 2004).

Although various sulfur nanoparticle products had been developed in the past and even showed some promising results in biomedicine and agriculture, the mechanism of a surfactant wetting on the sulfur surface remains poorly studied.

In recent years, the main research results have been as follows: (Chaudhuri et al., 2006) studied dynamic advancing (θ_A) and receding (θ_R) contact angles as well as made some measurements for the aqueous solution of three different surfactants (TX-100, SDBS, and CTAB) using the Wilhelmy plate technique. He also showed that in the presence of both ionic surfactants and nonionic surfactants a linear relationship with different slope and intercept forms between the adhesion and surface tensions at an air-water interface. Diez S et al., 2017) studied the surface chemical structure, surface electrical properties, and surface wetting ability of sulfur via electrophoresis, infrared spectroscopy, and further penetration experiments. Results revealed that the wetting ability of a surfactant solution on the sulfur surface not only depended on the gas-liquid surface tension of the solution but also on the solid-liquid interfacial tension between the solution and sulfur surface. The interfacial tension between the solution and sulfur surface was closely related to the hydrophobicity, electricity of the dust, and structural properties of the surfactant. Bera et al., (2018) studied counteracting interfacial energetics for the wetting of hydrophobic surfaces in the presence of surfactants and proposed an improved Zisman method for quantifying the wetting behavior of surfactants at the solid surface. This method allowed us to show that many highly common surfactants do not alter the wetting ability of a solid. In other words, they produce the same contact angle as a simple liquid with the same liquid-vapor surface tension. A surfactant increases the interaction between water and surface of sulfur, reduces the surface tension of water and interfacial tension between the surface of sulfur and water, and reduces the free energy of the system, thereby improving the ability of sulfur crystals to transform into sulfur nanoparticles. (Jean Berthier et al.,2013; Xu et al., 2007) found that there is a linear relationship between $\gamma_{LG} \cos\theta$ (adhesion tension) and surface tension of the aqueous solution, γ_{LG}, for hydrophobic solids (Zhu et al., 2019; Zdziennicka et al., 2018; Wang, et al., 2019). They also found that the slope of the straight line equals -1, which implies a similar adsorption density at both solid-liquid and air-liquid interfaces (Shaoxian et al., 2019).

Three types of surfactants: CTAB, SDBS, and TX-100 were used in this work. Parameters such as surface tension and the contact angle on the flat hydrophobic sulfur surface were established for each compound. Their wetting ability along with adhesion for a sulfur surface and mechanism of adsorption for wetting sulfur surface are discussed further in the study.

Materials and basic methods. The surfactants CTAB and TX-100 were acquired from Loba Chemie Pvt. Ltd., India, with 98 % and 99.5 % purity, respectively. SDBS was taken from Sigma Aldrich, Germany (Technical grade, Cat no. 28995-7). All surfactants were used as received without any further purification. Ultrapure water with a resistivity of *18.2* MΩ.cm (at 25°C) and pH 6.4–6.5 was used in the experiments (Sartorius, Germany). The DCAT-11EC surface tensiometer (Data Physics, Germany) was used for measuring the surface tension and dynamic contact angle at room temperature (28 ±0.5 0C).

Basic theory. Wetting is the ability of liquids to form interfaces with solid surfaces. A wetting process is actually a process in which a liquid and gas compete for the surface of particles. It can be regarded as the disappearance of the solid–vapor interface and formation of a solid–liquid interface (Yuan et al.,2013). A wetting process is related to the surface tension of the system. When a drop of liquid falls on a horizontal solid surface and reaches equilibrium (Figure 1), the relationship between the contact angle and surface tension conforms to the following equation (Young's equation) (Yuan et al.,2013):

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} * \cos\theta, \qquad (1)$$

where c is the solid–gas surface tension (mN/m), is the solid–liquid interfacial tension (mN/m), is the liquid–vapor surface tension (mN/m), and θ is the contact angle at the solution interface (°).

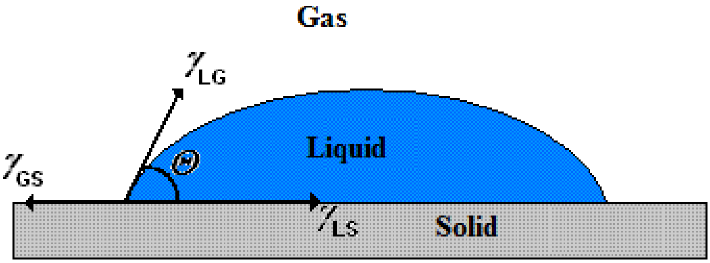

Fig.1. The relationship between the contact angle and solid– liquid, solid–gas, and liquid–gas surface tension.

Contact angle measurements. Contact angle measurements for aqueous solutions of CTAB, SDBS, and Triton X-100 on sulfur plates were carried out via the sessile drop method using the telescope-goniometer system at 25x in a thermostated measuring chamber at 28 °C (Marmur et al.,2017). After settling a drop of the aqueous solution of the surfactant at a given concentration on a sulfur plate, the contact angle on both sides of the drop was read immediately. The measurements were repeated several times by settling other drops on the same plate. A new plate was further placed in the chamber and the above procedure was repeated. For each solution, at least 30 independent drops were used to determine the average values of the contact angles which were obtained with good reproducibility. The standard deviation for each set of values was less than ±1.1.

RESULTS AND DISCUSSION

Surface tension and molecular density at the air-water interface

The surface tension of all the surfactants with varying concentrations was measured to determine the critical micelle concentration (CMC) and molecular density at the air-water interface (Fig. 2.) The values of CMC and surface tension at the air-water interface along with the literature values are given in Table 1. The minimum surface tension values, γCMC, for CTAB, SDBS, and Triton X 100 are: 32.75, 33.75, and 31.5 mN m-1, respectively, and corresponding CMC values are: 0.93, 1.20 and 0.15 mM, respectively.

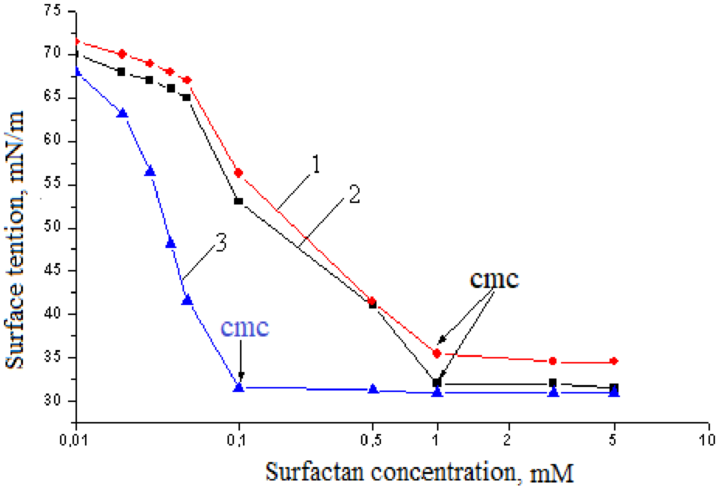

Fig.2. Surface tension of surfactants at different concentrations

Surface excess is a useful measure of adsorption effectiveness at the interface. The adsorption effectiveness is an important factor in determining the properties of surfactants such as wetting, contact angle, etc. Surface excess (Γ / mol m^{-2}) and surface area ($A_{\min}$ / nm^2) for each surfactant can be calculated using the following equations:

$$\Gamma = -\frac{1}{n \times 2.303RT} \times \frac{d\gamma}{d\log c} \tag{2}$$

$$A_{\min} = \frac{1}{N_A \times \Gamma_{\max}} \tag{3}$$

where *T* is an absolute temperature, *R* is the gas constant (8.314 J K^{-1} mol^{-1}), and N_A is Avogadro number (6.022×10^{23} mol^{-1}). A_{min} is a minimum surface area of a molecule occupied at the surface in nm^2. The value of n is 1 for nonionic surfactants and 2 for 1:1 ionic surfactants. Normally, Γ is considered as Γ_{max} if there is a linear dependence between surface tension and log *c*, from which A_{min} for surfactant molecule can be obtained. The value *d/dlog c* can be obtained from the slope of the plot of surface tension () against log *c* at a constant temperature of 28 °C The experimental values of the surface excess and molecular area of the three surfactants can be found in Table 1 along with the literature values. The table demonstrates that final experimental values correspond to those found in the literature.

Table 1. The comparison between experimental and literature values of CMC, surface tension at CMC, surface excess, and molecular area for three different surfactant solutions

Surfactant	*CMC* / mM	Exp. / mN m^{-1}	Exp. Γ_{max} / mol m^{-2} 10^6	Exp. A_{min} / nm^2	Lit. / mN m^{-1}	Lit. Γ_{max} / mol $m^{-2}10^6$	Lit. A_{min} / nm^2
CTAB	0.93	32.75	1.074	0.96	1.00[c]	1.80[a]	0.91[a]
SDBS	1.20	33.75	2.305	0.69	1.15[c]	2.41[b]	0.69[b]
TX-100	0.15	31.50	2.423	0.68	0.12[c]	2.60[a]	0.61[a]

[a] Ref. [23]; [b] Ref. [24]; [c] Ref. [25]

Effect of surfactant concentration on contact angle

The change in contact angle with varying surfactant concentrations on the sulfur surface is shown in Fig. 3, a, b, c for CTAB, SDBS, and TX-100, respectively. The experimental contact angle of 115.7° was measured on the sulfur surface in the presence of pure water, corresponding to the range of 108-116° reported in the literature. In the presence of CTAB and SDBS, the contact angle was gradually decreasing until it finally reached a value of 48.31° and 34.42°, respectively, at 1.0 mM surfactant concentration. The line corresponding to TX-100 shows that the contact angle value was rapidly dropping until 0.05 mM surfactant concentration was used. The contact angle value was reduced from 33.25° at 0.1 mM to 11.23° at 1.0 mM. For all three surfactant solutions, there was no significant change in contact angle at a concentration above 1.0 mM.

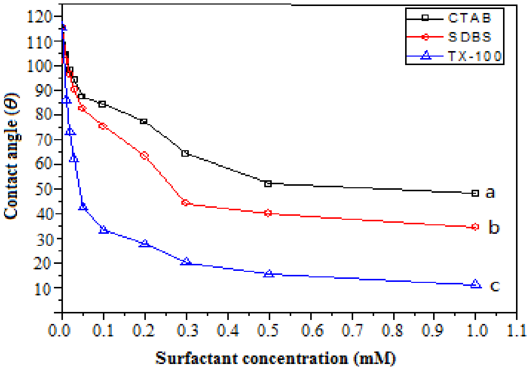

Fig. 3. Contact angles of CTAB, SDBS, and TX-100 solutions on the sulfur surface.

The wetting of water and surfactants (CTAB, SDBS, and TX-100) on the sulfur surface at the CMC concentration (a, b, c, d stand for water, CTAB, SDBS, and, respectively) is demonstrated in Fig. 4. It also shows that among all four solutions at 0.1 mM concentration, the best wetting is observed in the presence of TX-100 as it has the smallest contact angle. Thus, the wetting ability was improving in the following order: Water<CTAB<SDBS<TX-100.

All surfactants have distinct head and tail groups. This implies that adsorption densities on the solid surface as well as the resulting contact angle of surfactants on the sulfur surface would be different for each surfactant. In addition, the contact angle is affected by the surface tension at the air-water interface (low surface tension leads to a small contact angle).

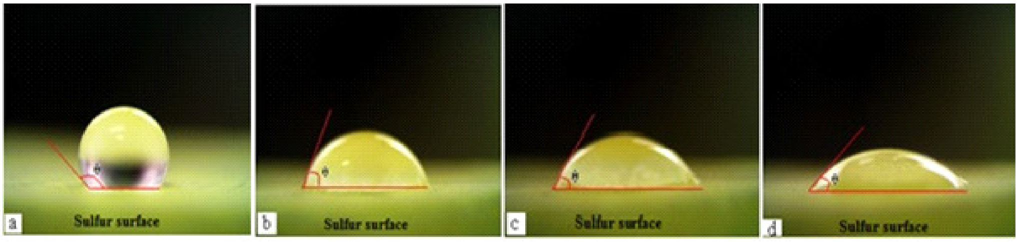

Fig. 4. Wetting effect of drops of surfactant solutions on the sulfur surface at CMC

Effect of surfactant concentration on the work of adhesion

At an instant when surfactant touches sulfur, the surfactant–air interface and sulfur-air interface become a sulfur-surfactant interface in a process known as adhesion. The adhesion work is used to characterize the binding ability of a surfactant to sulfur and the interaction force between the molecules of the two phases. The work of adhesion (W_a) for the contact angle was calculated and plotted against the surfactant concentration in Figure 4 using the following equation:

$$W_a = \gamma_{SG} - \gamma_{SL} + \gamma_{LG} = \gamma_{LG} \times (1 + \cos\theta) \qquad (4)$$

where, $\gamma_{SG} - \gamma_{Sl} = \gamma_{LG} \cos\theta$. For all examined surfactants, the sharp increasing of the adhesion work with increasing of surfactant concentration in the surfactants low-concentration range (Fig.5) is obtained. Here, as the contact angle decreases in the presence of surfactants, the work of adhesion is increased reaching its maximal value. After that, Wa suddenly decreases with increasing of surfactant concentration and becomes almost constant at higher surfactant concentration. Nonetheless, the initial contact angle on the sulfur surface in water and slightly concentrated surfactants exceeds 90^o, meaning cos θ values are negative, so (1+cos θ) term increases gradually, whereas surface tension value steadily declines with decreasing contact angle. As a result, Wa values become smaller at higher surfactants concentrations. Figure 4 shows that the adhesion of CTAB and SDBS on sulfur is better than that of TX-100.

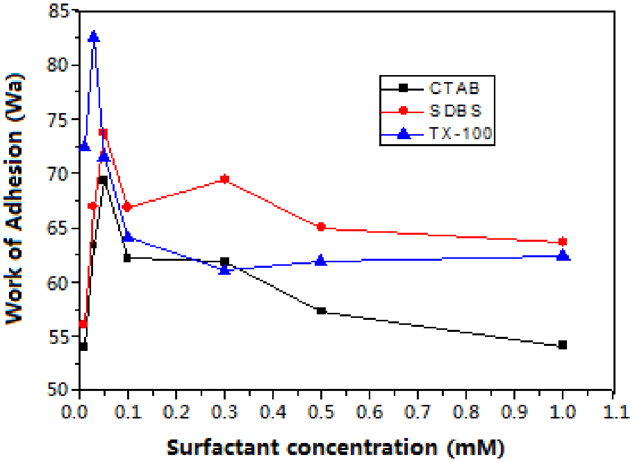

Fig. 5. Adhesion work of surfactant solutions on the sulfur surface at different concentrations

The sulfur surface has a hydrophobic character (Walker et al.,1986). Electrophoresis experiments revealed that the sulfur surface is negatively charged (Turganbay et al.,2013). Sulfur collides with the surfactants due to Van der Waals forces (Moldoveanu et al.,2022) so that the hydrophobic groups of the surfactants are adsorbed onto the surface of the sulfur.

Adsorption of Surfactant Molecules on Sulfur Surface Schematic presentation of adsorption of the examined surfactants (CTAB, SDBS and TX-100) on the sulfur surface is shown in Figure 6. Fig. 6 (a) demonstrates that in the process of adsorption of cationic surfactant CTAB and sulfur, a negative charge on the hydrophobic surface of sulfur attracts the cationic hydrophilic groups of the surfactants. An outer hydrophilic adsorption layer, therefore, forms on the surface of sulfur, and the surface property changes from hydrophobic to hydrophilic. When the concentration of the surfactant solution increases, the adsorption continues, until the sulfur surface charge becomes positive. Now, the polar heads of the adsorbed surface-active ions point towards the aqueous solution, which leads to higher hydrophilicity of the sulfur surface and smaller contact angle (Turganbay et al., 2012). Cationic surfactants' ability to frequently form such adsorbed layers on the surface of the sulfur makes them suitable wetting agents for it (Ansari et al., 2013).

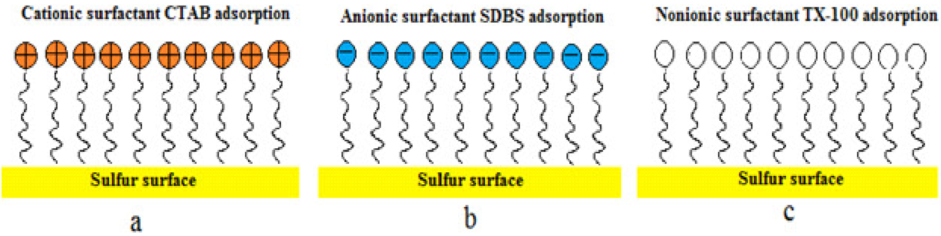

Fig. 6. Adsorption of different surfactants: CTAB (a), SDBS (b) and TX-100 (c) on the sulfur surface.

As shown in Fig. 5 (b), during the adsorption process of anionic surfactant SDBS and sulfur, the hydrophobic surface of sulfur interacts strongly with the hydrophobic groups of the surfactant. They, therefore, absorb the sulfur surface as the tail hydrophobic group becomes directed towards the sulfur surface and the head anionic hydrophilic group - towards the solution. As the hydrophilic group of the surfactant extends towards the solution after adsorption, the hydrophilicity of sulfur is enhanced and the wetting ability of the solution for sulfur is significantly improved.

As shown in Fig.5 (c), the adsorption of nonionic surfactant TX 100 and sulfur neither depends on the ion exchange nor the ion pair but rather on the hydrogen bonds and intermolecular force. The hydrophilic group of nonionic surfactant is oriented towards the water solution. This increases the hydrophilicity of the sulfur surface, simplifying its wetting with water and dispersion in the aqueous phase.

Overall, it is clear that different adsorption modes are responsible for anionic and nonionic surfactants being more effective at wetting sulfur as opposed to cationic surfactants.

Conclusions.

The surface tension of CTAB, SDBS, and TX-100 was found to decrease with increasing concentration. When the concentration is higher than CMC, the surface tension tends to stabilize and the changing trend in the plot of contact angle against concentration is similar to that for surface tension. The surface tension and contact angle of TX-100 and SDBS were found to be smaller than those of CTAB. Their work of adhesion, on the other hand, was actually higher than that of CTAB. This indicates that TX-100 and SDBS solutions are better at wetting the sulfur surface compared to CTAB. The wetting ability of the TX-100 and SDBS aqueous solutions on the sulfur surface is stronger than that of CTAB because of the different adsorption forms of the surfactant molecules on the surface of sulfur. The tail hydrophobic group of the TX-100 and SDBS surfactant molecules tends to point towards the surface of sulfur, whereas the head hydrophilic group is usually directed towards the solution. Anionic and nonionic surfactant solutions can significantly improve the wetting ability of the sulfur surface.

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