

STUDY OF THE SURFACTANT PROPERTIES OF ALIPHATIC AMINE SYNTHESIZED ON THE BASIS OF FAT AND OIL PRODUCTION WASTES

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Abstract: *the surface properties of aliphatic amines synthesized on the basis of fat and oil production wastes have been investigated. For their solutions, the CMC values were determined in the temperature range 10–45 °C. According to the data obtained, the values of equilibrium adsorption at research temperatures, which have values at CMC, which is approximately $1.68 \cdot 10^{-2}$ mol/cm², have been calculated. Therefore, for the flotation of sylvinite ores with a mass content of the main required component of more than 20%, the required amount of this amine is more than 10 g per ton of ore (this amount is calculated using the CMC value). As shown by the research results, the optimal temperature for extracting KCl from model solutions using the developed amine fluctuates in the temperature range $22 < 35$ °C. It was found that at 30 °C the CMC value is 145 mg / l, and at 35; 40 and 45 °C the values of this indicator are 201; 342 and 376 mg / l.*

Keywords: *aliphatic amine, critical micelle concentration, Kraft point, flotation, collector, surfactant, conductometry, surface tension.*

ИЗУЧЕНИЕ ПОВЕРХНОСТНО-АКТИВНЫХ СВОЙСТВ АЛИФАТИЧЕСКОГО АМИНА, СИНТЕЗИРОВАННЫХ НА ОСНОВЕ ОТХОДОВ МАСЛОЖИРОВОГО ПРОИЗВОДСТВА

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Аннотация: исследованы поверхностные свойства алифатических аминов, синтезированных на основе отходов масложирового производства. Для их растворов определены значения ККМ в интервале температур 10–45 °С. По полученным данным рассчитаны значения равновесной адсорбции при температурах исследований, имеющие значения при ККМ, которая составляет примерно $1,68 \cdot 10^{-2}$ моль/см². Следовательно, для флотации сильвинитовых руд с массовым содержанием основного необходимого компонента более 20% необходимое количество данного амина составляет более 10 г на тонну руды (данное количество рассчитано с использованием значений ККМ). Как показали результаты исследований, оптимальная температура извлечения КСI из модельных растворов с использованием разработанного амина колеблется в диапазоне температур 22 < 35 °С. Установлено, что при 30 °С значение ККМ составляет 145 мг/л, а при 35; 40 и 45 °С значения этого показателя составляют 201; 342 и 376 мг/л.

Ключевые слова: алифатический амин, критическая концентрация мицеллообразования, точка Крафта, флотация, собиратель, ПАВ, кондуктометрия, поверхностное натяжение.

Early works reported on the synthesis of aliphatic amines based on oil and fat production waste. [1]. The study of the composition of these amines showed that this product is a mixture consisting mainly of saturated amines with more than 17 carbon atoms. The study of some colloidal-chemical characteristics of this raw material predetermines the possibility of their use as a cationic collector of mineral ores. Therefore, this work presents the results of studying the surface characteristics of the synthesized mixture of aliphatic amines (AA) and its flotation activity in relation to KCl.

The flotation activity of amines is indirectly characterized by the amount of adsorption of their molecules on mineral crystals and the turbidity of its aqueous solution, which depends on the solubility, as well as the critical micelle concentration (CMC).

In aqueous solutions of aliphatic amines at very low concentrations corresponding to the critical micelle concentration (CMC), spherical micelles are formed containing from 20 to 100 molecules and characterized by a narrow

particle size distribution. Micelle formation occurs within a certain temperature range for each surfactant, the most important characteristics of which are the Kraft point and the cloud point [2].

The Kraft point is the lower temperature limit of micelle formation of ionic surfactants, in most cases it has values within the temperature range of 10-20°C. It is known that at low temperatures of the Kraft point, the solubility of surfactants is insufficient for the formation of micelles.

The cloud point is the upper temperature limit of micelle formation, usually having values within the temperature range of 50-60°C, and at higher temperatures, the system consisting of surfactant molecules and a solvent loses its stability and stratifies into two macrophases. It is known that at concentrations below the CMC, the amount of surfactant is insufficient for the formation of stable adsorption layers on the surface of minerals, and in the opposite case, the adsorption layers are characterized by low mobility, fragility and instability due to the transition of a micelle from one form to another (cylindrical, disk-shaped).

With a change in temperature, for solutions of aliphatic amines, a shift in CMC is characteristic, respectively, an urgent task was to determine this point for the synthesized amines in the temperature range of 10–45 ° C.

Currently, there are numerous measurement methods for determining the CMC, which were determined using the conductometric method and the maximum pressure method. The conductometric method is based on measuring the concentration dependence of the electrical conductivity of solutions. Based on the obtained research results, isotherms of electrical conductivity were constructed, which served as the basis for establishing the amounts of adsorption of the studied samples of aliphatic amines at the S: L interface. The electrical conductivity of the solutions was measured on an FE-30 conductometer (Mettler Toledo). Aqueous solutions of the amine were prepared using a bidistillate obtained by distilling the distillate in a quartz apparatus with the addition of potassium permanganate.

From the original amine solution, 8 solutions with different concentrations were prepared by successive doubling of the previous solutions. An initial solution of a colloidal surfactant with a concentration of 50 g/l in an amount of 25 cm³ was introduced into a volumetric flask with a volume of 50 cm³, and its volume with the addition of distilled water was brought to 50 cm³. From the prepared solution, 25 cm³ of the solution was taken, transferred to a 50 cm³ volumetric flask, brought to 50 cm³ with water, and the remaining solution was poured into a conductometric cell and the electrical conductivity was measured. In this sequence, the remaining solutions were prepared and the values of electrical conductivity were measured. All solutions (12.5; 6.25; 3.125; 1.5625; 0.78125; 0.39; 0.195 and 0.0975 g/l) were prepared immediately before measurement. After each dilution and thorough mixing, the contents of the vessel were kept for 8-10 minutes in a thermostat to establish thermal

equilibrium. After the end of the measurement, the cell and electrodes were thoroughly washed. To determine the constant of the conductometric cell, a resistance of 0.1 N was measured. KCl solution prepared from twice recrystallized salt sample.

The dependence of the equivalent electrical conductivity on concentration to CMC obeys the Onsager equation:

$$\lambda = \lambda_{\infty} - A\sqrt{C}, \quad (1)$$

where, λ_0 is the equivalent electrical conductivity at infinite dilution; A-constant, depending on temperature, dielectric constant, viscosity of the medium.

Cell constant k was calculated by the formula:

$$k = \lambda_0 R_0, \quad (2)$$

where, R_0 is the resistance of 0.1 n KCl solution; λ_0 - specific conductivity of 0.1 n KCl solution, reference data.

The specific electrical conductivity of solutions (S/m) was calculated by the formula:

$$\lambda = \frac{k}{R_x}, \quad (3)$$

where, R_x is the resistance of the surfactant solution.

The equivalent electrical conductivity of solutions was calculated as the ratio of specific electrical conductivity to concentration ($\text{dm}_2\text{cm/g}$), where the concentration is expressed in g/dm^3 .

The obtained data were used to plot the curves of the dependence $\lambda = f(C)$, which is shown in Fig. 1.

A break in the slope of the curve at a concentration of 130 mg/l corresponds to the formation of ionic micelles, i.e. KKM. The relatively low CMC values are probably associated with the presence of branched hydrocarbon radicals and double bonds close to the functional group.

The effect of temperature on the CMC values is investigated. The temperature was maintained with an accuracy of ± 0.05 °C using a water thermostat and controlled by two thermometers. The measurements were carried out at temperatures of 30, 35, 40 and 45°C.

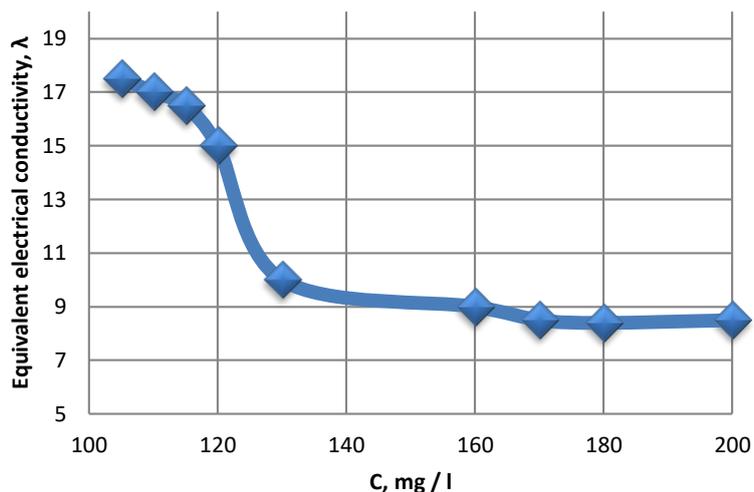


Fig. 1. Dependence of the equivalent electrical conductivity of the synthesized amine solutions at a system temperature of 25 °C

In the process of measuring the surface tension, the CMC value was determined. At 30 °C, the CMC value is 145 mg/l, and at 35; 40 and 45 °C the values of this indicator are 201; 342 and 376 mg / l (Fig. 2).

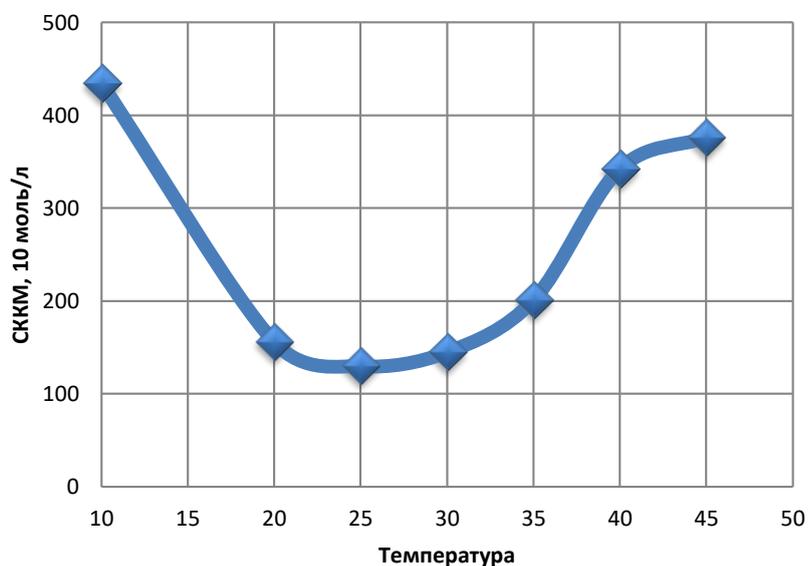


Fig. 2. Dependence of the critical concentration of micelle formation on the temperature of the system

Fig. 2 clearly shows a minimum in the range of 20–30°C, therefore, the Kraft point for this substance in aqueous solutions lies in the range of these temperatures. A similar character of the temperature dependence of CMC was

observed for anion-active [3] and for cation-active surfactants in [4, 5]. The U-shaped curve with a minimum can be explained by a change in the structure of water and the nature of hydration of surface-active ions with a change in temperature [6]. Thus, there is a temperature of $\approx 27^\circ\text{C}$, which corresponds to the minimum CMC value. At higher and lower temperatures, a high concentration of surfactant molecules is required to form micelles.

Numerous existing literature data show that the CMC of one surfactant, determined by different methods, has different meanings. Therefore, to verify the above data, the CMC values were calculated by changing the surface tension of surfactant solutions using a laboratory stalagmometer ST-2 (maximum pressure method). The surface tension of solutions was calculated by the formula:

$$\sigma = \frac{P}{P_0} \sigma_0, \quad (4)$$

where, σ and σ_0 - surface tension of amine and distilled water, mN/m; P and P_0 are the pressure of the bubble when it rushes through the amine solution and distilled water. The results of determining the CMC by this method are shown in table. 1.

Table 1. CMC values of aliphatic amine in aqueous solutions at different temperatures

Method of measurement	CMC, mg/l		
	20	30	40
conductometric method	156	150	350
maximum pressure method	149	146	339

The detection of a minimum in the CMC region on the isotherms indicates a mixed composition of the studied surfactants. The obtained values of surface tension were used to calculate the amount of adsorption A (mol/m²):

$$A = - \frac{1}{2RT} \cdot \frac{d\gamma}{d \ln \alpha'} \quad (5)$$

where, R is the universal gas constant; T is the absolute temperature, K; α - activity.

The calculated values of adsorption depending on concentration and temperature are presented in table. 2.

Table 2. Values of equilibrium surface tension (γ), and adsorption (A) of aqueous solutions of an aliphatic amine at $T = 35^\circ\text{C}$

C, mg/l	γ , mN/m	A, mol/cm ²
90	74,6	$4,0 \cdot 10^{-3}$
110	73,5	$5,8 \cdot 10^{-3}$
130	68,4	$1,04 \cdot 10^{-2}$
150	56,7	$1,24 \cdot 10^{-2}$

170	43,1	$1,58 \cdot 10^{-2}$
200	31,2	$1,68 \cdot 10^{-2}$
250	76,5	$1,71 \cdot 10^{-2}$
300	78,2	$1,78 \cdot 10^{-2}$

As shown in table. 2, with an increase in concentration, the adsorption values increase and after reaching the CMC it has a stable value. This character of the dependence is due to the spatial structure of the surface-active ion and the limiting amount of surfactant particles adsorbed per unit surface area [7].

The conducted studies of the surface tension of aliphatic amine at temperatures from 10 to 45 °C in the concentration range from 0.09 to 12.5 g/l made it possible to determine the minimum values of the critical concentration of micelle formation in the temperature range 25-30 °C. According to the data obtained, the values of equilibrium adsorption at research temperatures, which have values at CMC, which is approximately $1.68 \cdot 10^{-2}$ mol/cm², have been calculated.

The nature of the interaction of the collecting reagents with minerals and the form of their adsorption depend on the state of the mineral surface and the reagent in the pulp. Sorption phenomena on the surface of sylvinite minerals, which are heteropolar crystals, have both a chemical nature and a physical form of adsorption of ions and molecules [8]. However, in real processes it is impossible to clearly define the boundary between physical sorption and chemisorption.

The hydrophobicity of the surface of mineral particles is the thermodynamic condition for their flotation. Hydrophobization of a mineral surface is possible when the energy of interaction of water molecules with each other is greater than their energy of interaction with the mineral surface.

The results of modern studies using modern instrumentation confirm that the main forms of sorption of a collector on a mineral surface are: chemisorptions, the formation of valence-saturated products of a heterogeneous chemical reaction, and physical sorption of ions and molecules. At the same time, there are conflicting scientific opinions. For example, Sutherland and Wark, 1958; Bachmann, 1955; De Bruyn, 1955; Fuerstenau и Fuerstenau, 1956 and others determined that hydrophobization and flotation of minerals are due to the fixation of amine ions and vice versa Arbiter other 1943; Heil, 1961 fixing not ions but molecules.

At the present time, a theory has been created that probably quite adequately describes the processes of hydrophobization and flotation of mineral ores [8]. According to which, for the effective flotation of minerals that do not have natural hydrophobicity, both a chemically fixed and physically adsorbed collector must be present on the surface. The absence of one of the forms of sorption of the collector on the surface will lead to depression of the mineral flotation.

Thus, in order to ensure the maximum recovery of insoluble impurities into

the flotation sludge product, the determining factor is the choice of the optimal flocculant flow rate at the base flow rate of the sludge collector.

References / Список литературы

1. *Qodirov O.Sh., Qurbanov Z.Ch., Ikramov A.* Methods for producing amines of aliphatic fatty acids. *chemistry and chemical technology*, 2018. № 1. С. 35-38.
2. Micelle formation. [Electronic resource]. URL: <http://www.cnshb.ru/AKDiL/0048/base/RM/280002.shtm>. Title from the screen/ (date of the application: 03.08.2020).
3. *Shah S.S., Jamroz N.U., Sharif Q.M.* Micellization parameter and electrostatic interactions in micelles solution of sodium dodecyl sulfate (SDS) at different temperatures // *Colloids and Surfaces A: Physicochemical and Eng. Aspects*, 2001. Vol. 178. P. 199–206.
4. *Korotkin O.P., Kochurova N.N., Hong Po-Da.* Investigation of aggregation of the aqueous solutions of alkylpyridinium chlorides by conductivity method // *Journal of Mendeleev Communications*, 2008. № 18. P. 347–349.
5. *Kochunova N.N., Ayropetova Y.P., Medvedev I.A., Abdulin N.G.* Investigation of the viscosity of micelles solutions of a cationic surfactant (DAEDMBAX) // *St. Petersburg University Bulletin. Ser.4: Physics chemistry*, 2006. Vol. 2. P. 78-82.
6. *Sarkisov G.N.* Structural models of water // *Advances in physical sciences*, 2006. T. 176. № 8. P. 833-845.
7. *Korotkih O.P.* Influence of concentration and temperature on aggregation in aqueous solutions of N-alkyl pyridine surfactants: author. dis. cand. chem. sciences: 02.00.11., St. Petersburg, 2007. 18 p.
8. *Abramov A.A.* Collected works. Flotation. Collector reagents. M.: MMGU «Mountain Book», 2012. 656 p.