ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 9, pp. 1522–1527. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © L.V. Dikhtievskaya, A.D. Markin, L.F. Shlomina, V.V. Shevchuk, F.F. Mozheiko, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 9, pp. 1425–1430.

Study of the Interfacial Tension in Model and Technical Emulsions in the Presence of Surfactants and Inorganic Electrolytes

L. V. Dikhtievskaya, A. D. Markin, L. F. Shlomina, V. V. Shevchuk, and F. F. Mozheiko

Institute of General and Inorganic Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus

Received March 10, 2009

Abstract—Interfacial tension in the oil/water system in the presence of various ionic surfactants and inorganic electrolytes was studied. Special features of the effect of the surfactant and oil phase natures, of the structure of their molecules, and also of the electrolytes containing ions with various radii, valences, and hydratabilities on the value of the interfacial tension were studied. The criteria and conditions of obtaining model emulsions based on paraffin hydrocarbons and technical emulsions based on vegetable oils were determined.

DOI: 10.1134/S1070427209090043

Various emulsions find wide application in many technological processes. Stability of emulsions, which represent microheterogeneous systems consisting of two or more immiscible liquids, is defined by a free energy excess on an interface. Therefore a necessary condition of obtaining emulsions of any type is a decrease in the interfacial tension between liquids contained in the emulsion system. To stabilize emulsions, most often various surfactants are applied which are capable of effective reducing the interfacial tension by forming a strong adsorption layer representing a structurally-mechanical barrier hindering a coalescence of disperse phase drops. The determination of the interrelation between interphase $\sigma_{o/w}$ (oil/water) and surface $\sigma_{l/g}$ (liquid/gas) tensions of surfactant solutions is of a considerable practical value.

Inorganic electrolytes are also among agents stabilizing the formation of emulsions. However these compounds are ineffective at the individual application, as they can ensure obtaining only dilute emulsions of the o/w type with short life times [1]. The study of the effect of various electrolytes on the state of emulsion systems is of interest mainly from the viewpoint of their action on colloid-chemical properties of emulsifiers, first of all of the ionic type.

For this purpose we have fulfilled comparative anchor-ring measurements of the surface tension on the aqueous and water-salt surfactant solution/air interface and of the interfacial tension on the aqueous and water-salt surfactant solution/oil interface in the presence of various surfactants and electrolytes. Model and technical emulsion systems were studied. Typical cationic (salts of aliphatic amines) and anionic (sodium alkyl sulfates and alkyl carbonates) surfactants served as emulsifiers; hexane, octane, decane, dodecane, rapeseed and olive oils, as oil phases; sodium, calcium, and aluminum chlorides and sodium carbonate and hydroxide, as electrolytes.

EXPERIMENTAL

It was found that the interfacial tension on the water–hydrocarbon boundary weakly depends on the hydrocarbon chain length in the emulsifier absence. In the presence of a surfactant the interfacial tension increases as the number of carbon atoms in a hydrocarbon molecule increases and decreases as the concentration and length of a surfactant hydrophobic radical increase (Fig. 1a). For a fixed length of a surfactant hydrocarbon radical with various polar groups the interfacial tension decreases in the series –COONa, $-NH_3Cl$, $-SO_4Na$ (Fig. 1b), which is determined by the values of their critical concentration of micelle formation c_c and surface activity G_m. Thus, c_c in the specified series decreases, being 2.3×10^{-2},

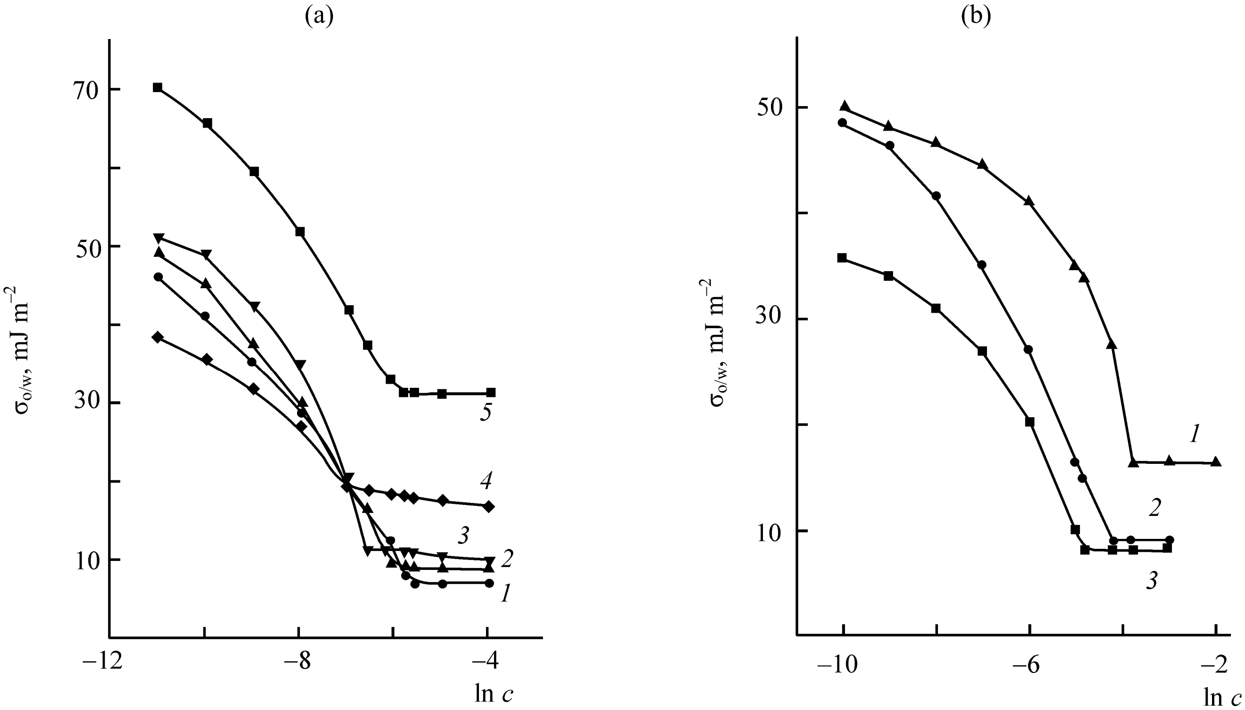

Fig. 1. Surface tension isotherms of (a) tetradecylammonium acetate solutions on the boundary with (*1*) hexane, (*2*) octane, (*3*) decane, (*4*) dodecane, (*5*) air and (b) of (*1*) sodium laurate, (*2*) dodecylammonium acetate, (*3*) sodium dodecyl sulfate on the boundary with dodecane; $\sigma_{o/w}$ is interfacial tension and *c* is surfactant concentration, M.

1.3×10^{-2}, and 8.0×10^{-3} M, and surface activity increases, being 1.8, 3.0, and 4.3 J m kmol^{-1}, respectively.

It is seen from Fig. 1 that characteristic concentration points are clearly pronounced both in the surface tension isotherms and in the interfacial tension isotherms in aqueous and salt solutions. One of them c_{sat} is connected with the saturation of an adsorption layer and reflects the surfactant concentration in a membrane. This concentration is determined graphically in the $\sigma(\ln c)$ isotherms as a point of transition of the isotherm curvilinear section to the rectilinear section, i.e. it is the concentration at which the derivative $d\sigma/d\ln c$ reaches a maximal value. The second concentration point c_{c} is connected with the micelle formation and reflects surfactant changes in bulk solution. It is a concentration at which minimal $\sigma_{l/g}$ and $\sigma_{o/w}$ values are reached.

To make clear the role of the specified characteristics in the formation mechanism and in the stability of the microemulsions, we have constructed the $\sigma_{o/w}$–$\sigma_{l/g}$ dependence for the studied series of amine salts according to the data of [3], Fig. 1. Figure 2a illustrates the interrelation between the surface and interfacial tension for solutions of alkylamine acetates. Analogous dependences were obtained also for anion-active surfactant–sodium alkyl sulfates. Sharp bends in the points corresponding to the concentration of the adsorbed layer or membrane saturation in the field of dilute solutions are clearly seen, as well as those in the field of high concentrations corresponding to the association in bulk solutions.

It was of interest to consider the dependence of the interfacial tension on these concentrations for homologous series of surfactants, especially as these concentrations can be used as the basis for the calculation of free energies of adsorption and micelle formation [4]. It has appeared that the dependence of the interfacial tension on the adsorption and micelle-formation energies precisely keeps within the linear form. Furthermore we have considered the slopes of the curves presented in Fig. 2a as distribution constants $K = \sigma_{o/w}/\sigma_{l/g}$ for all members of the homologous series of amine salts (Fig. 2b). Here again the *K*(*n*) dependence is linear.

It follows from Fig. 2 that there is a close connection between interphase and surface tensions, their ratio *K*, and also the concentrations describing surfactant behavior in a membrane and in a bulk solution. It suggests that any of the considered characteristics can serve as a criterion of a possibility

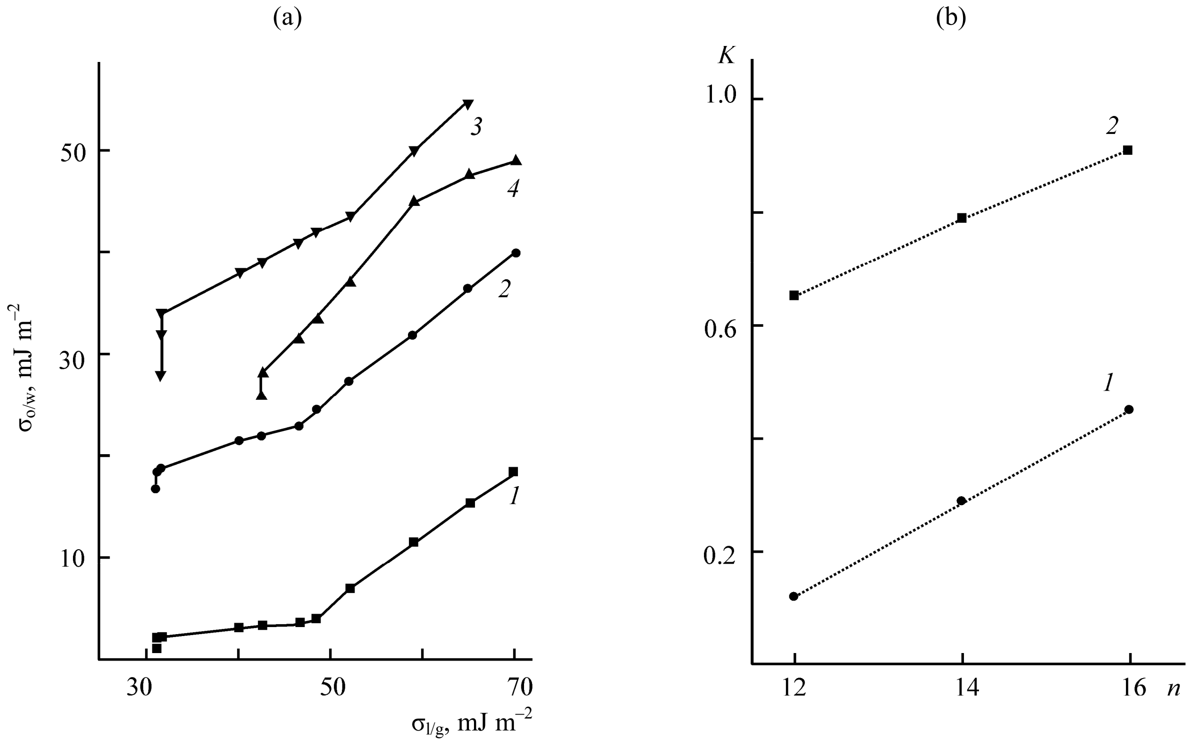

Fig. 2. (a) Correlation of interphase $\sigma_{o/w}$ and surface $\sigma_{l/g}$ tensions of acetic-acid amines (*1*) $C_{12}H_{25}NH_2\cdot CH_3COOH$, (*2*) $C_{14}H_{29}NH_2\cdot CH_3COOH$, (*3*) $C_{16}H_{33}NH_2\cdot CH_3COOH$, (*4*) $C_{18}H_{37}NH_2\cdot CH_3COOH$ and (b) dependence of the constant $K = \sigma_{o/w}/\sigma_{l/g}$ on the length (n) of chain of acetic-acid amines in the concentration ranges (*1*) c_0–c_{sat} and (*2*) c_{sat}–c_{cr}.

to obtain an emulsion and also as a criterion of its kinetic and aggregate stability.

To summarize the obtained experimental data, we conclude that $\sigma_{o/w}$ depends only slightly on the length of the oil phase hydrocarbon chain. When diphyl molecules surfactants are introduced into an emulsion system the $\sigma_{o/w}$ value is determined by the length of a hydrocarbon hydrophobic radical, by the saturation of hydrocarbon bonds in it, by the surfactant polar group, and by the length of a hydrocarbon of the oil phase.

Inorganic electrolytes correspond to the agents stabilizing and controlling properties of emulsions. It was revealed that there is a concentration limit providing aggregative stability for each electrolyte. The interfacial tensions of sodium dodecyl sulfate and sodium oleate solutions on the boundary with hexane as functions of the concentrations of sodium, calcium, and aluminum chlorides are presented in Fig. 3. These data illustrate different character of the action of electrolytes on alkyl sulfates and salts of carboxylic acids. The decrease in the interfacial tension of the sodium dodecyl sulfate solution on the boundary with an oil phase under the action of electrolytes is limited by the value of the salt concentration corresponding to the coagulation threshold, and at higher concentrations the system is destroyed, i.e. the surfactant is salted out from the aqueous phase. In the case of sodium oleate the interfacial tension variation in the electrolyte presence passes through a clearly pronounced minimum that seems to be connected with the latent coagulation phenomenon accompanied by a disturbance of integrity of the surfactant adsorption layer on the oil/water boundary due to penetration of coions in it, i.e. of ions charged similarly to the surfactant ion [5]. In the case of anionic surfactants the concentration of electrolyte providing the maximal decrease in the interfacial tension depends on the cation valence and is the greatest for single-charged cations.

Effect of electrolytes on the interfacial tension on the boundary of surfactant solutions with oil is defined not only by the electrolyte and surfactant nature, but also by the hydrophylicity degree of the surfactant molecules belonging to one homologous series. Thus, sodium octyl sulfate, which is a more hydrophylic and resistant to salting out action of strong electrolytes than sodium dodecyl sulfate, provides a greater decrease in

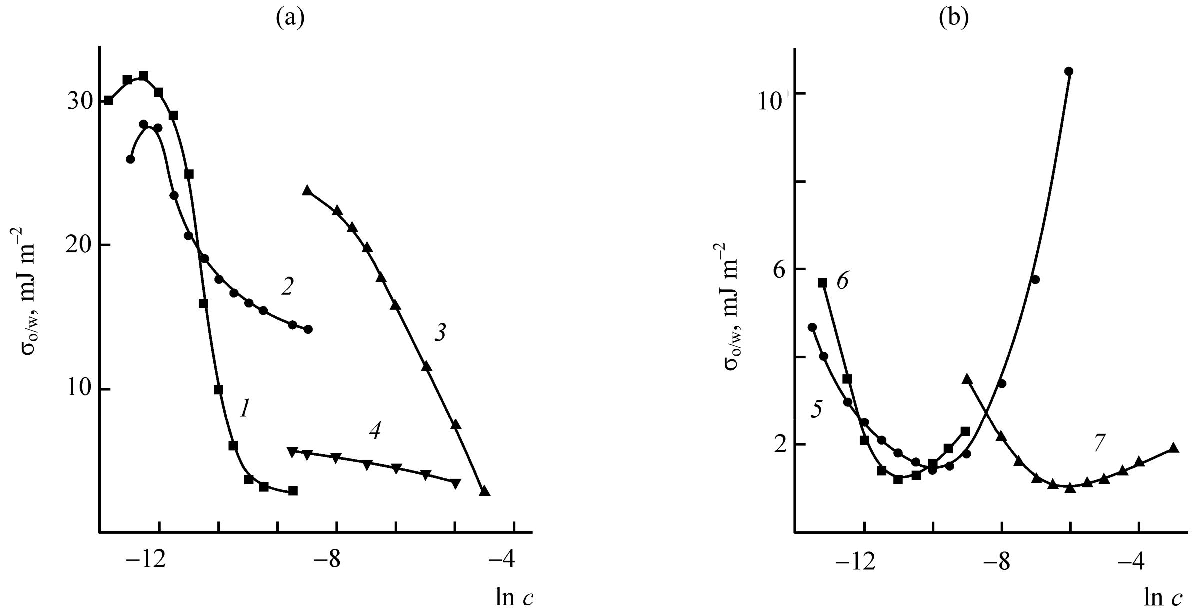

Fig. 3. Effect of electrolyte concentration c on the interfacial tension $\sigma_{o/w}$ of solutions of (*1*) sodium dodecyl sulfate and (b) sodium oleate on the boundary with hexane. (*1, 5*) $AlCl_3$; (*2, 6*) $CaCl_2$; (*3, 4, 7*) NaCl. Surfactant concentration in aqueous phase, M: (*1–3*) 1×10^{-3}; (*4*) 1×10^{-2}; (*5–7*) 6.6×10^{-4}.

the interfacial tension at concentrations of inorganic salts considerably exceeding its coagulation threshold.

The addition of inorganic salts to a surfactant solution promotes a rather sharp decrease in the interfacial tension. When dilute surfactant solutions, more stable to the salting out action of an electrolyte, are used, the addition of an inorganic salt provides a greater $\sigma_{o/w}$ decrease as compared to more concentrated solutions characterized by a low coagulation threshold. This fact can be used for reducing emulsifier expenditure while obtaining emulsions.

Thus, the introduction of various electrolytes in an emulsion system makes it possible to regulate the interfacial tension value, which is one of the most important characteristics defining the emulsification process.

Dependences characteristic of model emulsion systems are observed also on technical emulsions. Technical oils, in particular rapeseed oil, contain a certain quantity of various surfactants. It is seen from Fig. 4a that the introduction of electrolytes into the aqueous phase promotes essential decrease in an interfacial tension on the oil/water boundary. The action of alkaline electrolytes is the most effective. Thus, when rapeseed oil is used as an oil phase, the introduction of sodium carbonate into the emulsion system causes a sharp decrease in the interfacial tension up to a value close to zero (~0.3 mJ m^{-2}) that points to a possibility of obtaining a stable emulsion by simple combining technical rapeseed oil and an alkaline electrolyte. It is obviously connected with the process of the vegetable oil saponification in the alkaline medium.

The study of stabilization of emulsions based on vegetable oils by surfactants, in particular of sodium dodecyl sulfate, (Fig. 4b) has shown that the interfacial tension on the boundary of their solutions with olive and rapeseed oils sharply decreases as a surfactant content in an aqueous phase increases. In the field of dilute solutions of the stabilizer the interfacial tension on their boundary with rapeseed oil has a much lower value as compared to olive oil that also can be connected with the presence of surfactant admixtures in rapeseed oil. Even higher decrease in the interfacial tension on the boundary of sodium dodecyl sulfate solutions with rapeseed oil can be reached by introducing capronic acid as a co-surfactant in an emulsifier solution (Fig. 4b). Thus, the variation of the disperse medium composition makes it possible to regulate the value of interfacial tension on the boundary with various oils that provides preparation of emulsions with predetermined properties.

We have carried out the study on the development of aqueous emulsions based on rapeseed oil and on their use in production of potash fertilizers as modificators of the dehydration in filtration processes

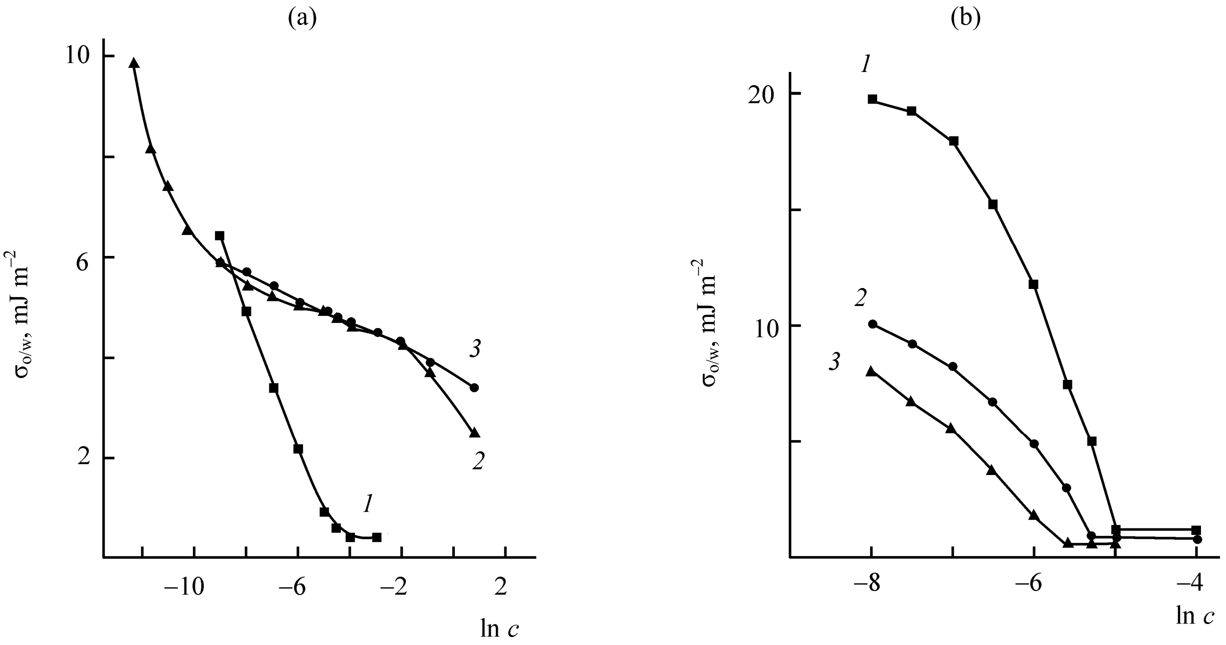

Fig. 4. Isotherms of the interfacial tension on the boundary of (a) solutions of (*1*) sodium carbonate, (*2*) calcium chloride, (*3*) sodium chloride with rapeseed oil and (b) solutions of (*1, 2*) sodium dodecyl sulfate and its mixtures with (*3*) capronic acid on boundary with (*1*) olive and (*2*) rapeseed oil; $\sigma_{o/w}$ is an interfacial tension; *c* is a concentration, M.

for water-salt suspensions of sodium chloride with water-insoluble residual of potassium ore of Starobinsk deposit and for potassium ore flotation tailings.

The flotation of potassium ore gives rise to a significant amount of wastage in the form of suspensions (flotation tailings) with a solid phase consisting mainly of sodium chloride with admixtures of potassium chloride and argillo-carbonate minerals (a water-insoluble residual). The suspension of flotation tailings is subjected to the filtration on drum-type vacuum filters. A liquid phase (an aqueous solution saturated with respect to sodium and potassium chlorides) is returned into the enrichment process, and a solid phase (filter cake) with a humidity of×10–12% is stored in salt piles. The liquid phase of the tailing cake in salt piles is wringed out under the pressure of overlying layers and is diluted by atmospheric precipitations. Partially these dilute aqueous solutions come back in the process, and partially are lost, being filtrated in underground horizons. It results in considerable losses of potassium chloride and a salinization of the environment. Therefore it is an urgent problem to develop procedures for filtering sodium chloride suspensions providing a decrease in the humidity of a filter cake during the filtration of

Effect of rapeseed oil emulsions with soda ash on the filtration of potassium ore flotation tailings

Specific emulsion consumption, g t^{-1}	Amount of filtered liquid phase, cm^3, within filtration time, s								Residual cake humidity, %
	20	40	60	80	100	120	140	160	
0	15	22	29	36	43	49	55	59	12.5
500	16	23	30	37	45	51	57	61	11.2
1000	18	24	32	39	47	53	59	62	10.2
2000	20	25	33	40	48	54	60	63	9.2
3000	20	26	34	40	47	54	60	63	9.1

potassium ore flotation tailings. It can be reached by the application of modificators during the filtration of such suspensions [6, 7].

For this purpose we used emulsions based on technical rapeseed oil. The composition of rapeseed oil includes preferentially esters of glycerol with fatty acids of various lengths and structure of a hydrocarbon chain. When rapeseed oil is added to alkaline aqueous solutions of caustic soda or soda ash fatty glycerides of rapeseed oil are hydrolyzed, partially or completely depending on conditions, to form aqueous emulsions. Stability and efficiency of the action of these emulsions as dehydration modificators depends on the weight ratio of the specified components and concentration and temperature of the emulsions. At the weight ratios of alkaline reagents and rapeseed oil 1:2 and less the hydrolysis of rapeseed oil proceeds rather deeply to form sodium salts of fatty acids and glycerol. The increase in the rapeseed oil fraction above 2:1 only partial hydrolysis of esters occurs to form sodium salts of carboxylic acids and mono- and twice-substituted esters of glycerol containing free hydroxy groups. These emulsions are slightly less stable, and in the absence of stirring within 1–3 h they are gradually separated into layers without coalescence of drops. Therefore even a weak shaking or stirring provides recovery of the homogeneity of the investigated emulsions. The increase in the temperature of emulsions above 30°C promotes the acceleration of the separation into layers and coalescence of emulsion drops.

The study of the effect of emulsions based on rapeseed oil on the filtration of flotation tailings has shown (see the Table) that these emulsions with an optimal composition provide the 1.2–1.5-fold acceleration of the filtration and reduce residual humidity of a solid phase by 1.3–3.4%

The mechanism of the action of the developed modificators consists in the adsorption of their molecules on the surface of solid phase particles and in its hydrophobization, which promotes a decrease in the resistance to the motion of liquid in precipitate capillaries during filtration. Furthermore the addition of surfactants to aqueous suspensions promotes reduction in the surface tension and viscosity of a liquid phase. As a result the filtration is accelerated and the residual humidity of the dehydrated solid phase decreases.

CONCLUSIONS

(1) The interfacial tension value, which is one of the major characteristics defining the emulsification process, can be regulated by varying such factors as the nature of surfactants and oil phase, the structure of their molecules, and the introduction of various electrolytes in the emulsion system.

(2) The criteria and conditions were determined for obtaining model emulsions based on paraffin hydrocarbons and technical emulsions of vegetable oils. Emulsions based on rapeseed oil with alkaline reagents (caustic soda and soda ash) were shown to be effective modificators of the filtration of water-salt suspensions of sodium chloride and potassium ore flotation tailings.

REFERENCES

1. *Emulsion Science*, Sherman, P., Ed., London and New York: Academic Press, 1968.
2. *Poverkhnostno-akivnye veshchestva: Spravochnik* (Surfactants: Handbook), Abramzon, A.A. and Gaevoi, G.M., Eds., Leningrad: Khimiya, 1979.
3. Dikhtievskaya, L.V., Markin, A.D., Shevchuk, V.V., and Krut'ko, N.P., *Dokl. Akad. Nauk Belarusi*, 2004, vol. 48, no. 6, pp. 53–56.
4. Shchukin, E.D., Pertsov, A.V., and Amelina, E.A., *Kolloidnaya khimiya* (Colloid Chemistry), Moscow: Mosk. Gos. Univ., 1982.
5. Dikhtievskaya, L.V. and Mozheiko, F.F., *Dokl. Akad. Nauk Belarusi*, 1999, vol. 43, no. 5, pp. 58–61.
6. Kaminskii, V.S., Barbin, M.B., and Dolina, L.F., *Intensifikatsiya protsessov obezvozhivaniya* (Intensification of Deaquation Processes), Moscow: Nedra, 1982.
7. Zhuzhikov, V.A., *Fil'trovanie: Teoriya i praktika razdeleniya suspenzii* (Filtration: Theory and Practice of Separation of Suspensions), Moscow: Khimiya, 1971.