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# Topological transformation of phase diagrams water – ethoxylated nonylphenols – sodium chloride systems

In this work phase equilibria in water – ethoxylated nonylphenol (Neonol) – sodium chloride systems was investigated, and temperature ranges of two-phase liquid and monotectic equilibrium region existence were established. These regions exist at temperature of more than 23 ºC in system with Neonol AF-9-12 and more than 42 ºC in system with Neonol AF-9-25. A feature of water – Neonol AF-9-12 – sodium chloride system is the salting-out of double water – Neonol AF-9-12 subsystem at the temperature of more than 84 ºC. A scheme of phase diagrams of topological transformation of water – ethoxylated surfactant – inorganic salt systems for cases, when salt has only salting-out effect and water – surfactant subsystem is characterized by a lower critical solubility temperature (Neonol AF-9-12) or homogeneous throughout liquid state interval was developed. The correspondence of developed schemes to generalized scheme for the salt — binary solvent systems was shown. The data obtained allow evaluating surfactant ethoxylation degree effect to sodium chloride salting-out ability. It was found that ethoxylation degree increase is accompanied by increase in surfactant micelles hydration, which leads to decrease in the salting-out ability of sodium chloride. The obtained data can be used to optimize the temperature and concentration extraction parameters.

*Keywords*: surfactants, ethoxylated nonylphenol, sodium chloride, stratifying systems, salting-out, phase diagrams, solubility, topological transformation.

## *Introduction*

Surfactant based optimization of temperature-concentration parameters for extraction in the systems can be done with the methods of physical chemical analysis. Typically, the first stage is aimed to decide on a salting-out agent and temperature of the process for a particular surfactant or to choose a surfactant for extraction with a particular salting-out agent. Many published works consider the impact of surfactant structure on stratifying temperature for its water solutions [1–3], as well as the impact of non-organic salt nature on a salting-out capacity of ethoxylated surfactant [4–6], with surfactant structure during its formation and temperature transformation in the stratifying area in water – ethoxylated surfactant – inorganic salt systems being hardly examined.

Earlier, a scheme of topological transformation for phase diagrams of water – ethoxylated surfactant – inorganic salt systems has been proposed in cases when a water – surfactant subsystem remains homogeneous in all temperature intervals, while salt salts out, and in case of a water – surfactant system with the lower critical solubility point (LCSP) and salting-in – salting-out effect of salt [7]. The present paper is aimed to identify the schemes of topological transformation for phase diagrams of water – ethoxylated surfactant – inorganic salt for the salt with salting-out effect only with regard to ethoxylated nonylphenols with different – ethoxylation degree.

Sodium chloride which was extensively used in surfactant-based extraction systems was chosen to be a salting-out agent [8, 9]. Some papers give the information about the impact of sodium chloride on the stratifying temperature of water solutions of ethoxylated octylphenols [4, 10], ethoxylated dodecanols [11], and polyethyleneglycols [12]; although no regularities in transformations of phase areas are looked at.

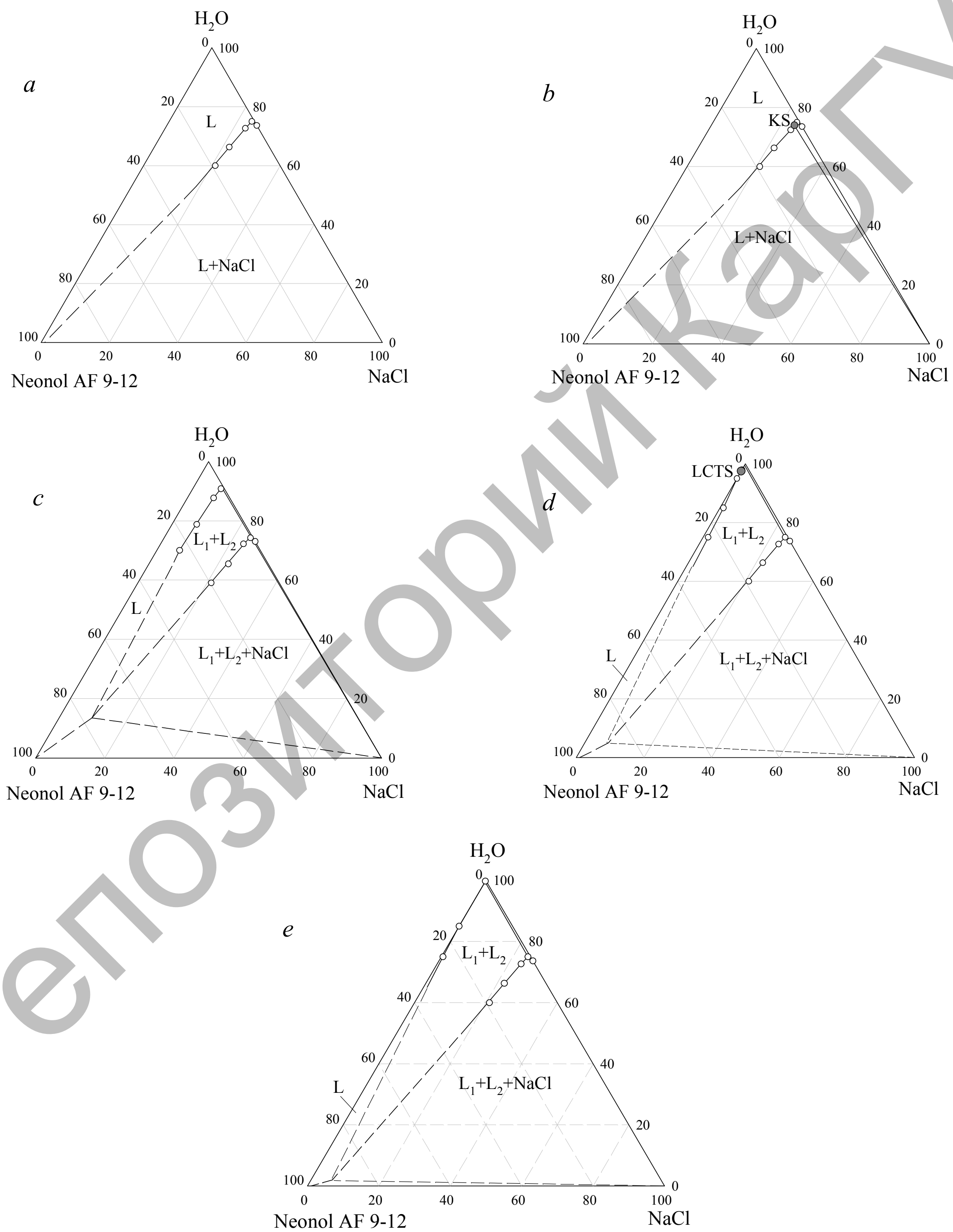
## *Experimental*

The paper uses ethoxylated nonylphenols ($C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$, n = 12 for neonol AF-9-12, n = 25 for neonol AF-9-25, TU 2483-077-05766801-98), analytic grade sodium chloride, distilled water ($n_D^{25}$ = 1.3325).

Visual-polythermal method identified the stratifying area boundaries. Sections method was used to obtain solubility isotherms at temperatures below 75 ºC. The paper [7] examines the methodology of the experiment in detail.

*Results and discussion*

Sodium chloride crystallizes into waterless salt in the specified temperature range and has positive solubility temperature index. Water – neonol AF-9-12 system is characterized by the lower critical solubility point (LCSP), namely, 84 ºC (3.0 mas. % neonol AF-9-12). Stratifying area in the system is within the temperature interval — from 84 ºC to the boiling temperature. Water – neonol AF-9-25 double system is homogeneous within the whole interval of liquid state. Experiments showed that sodium chloride was practically insoluble in surfactant under question.




*a* — 10 ºC; *b* — 23 ºC; *c* — 60 ºC; *d* — 84 ºC; *e* — 90 ºC

Figure 1. Phase equilibriun in the water – Neonol AF-9-12 – NaCl system

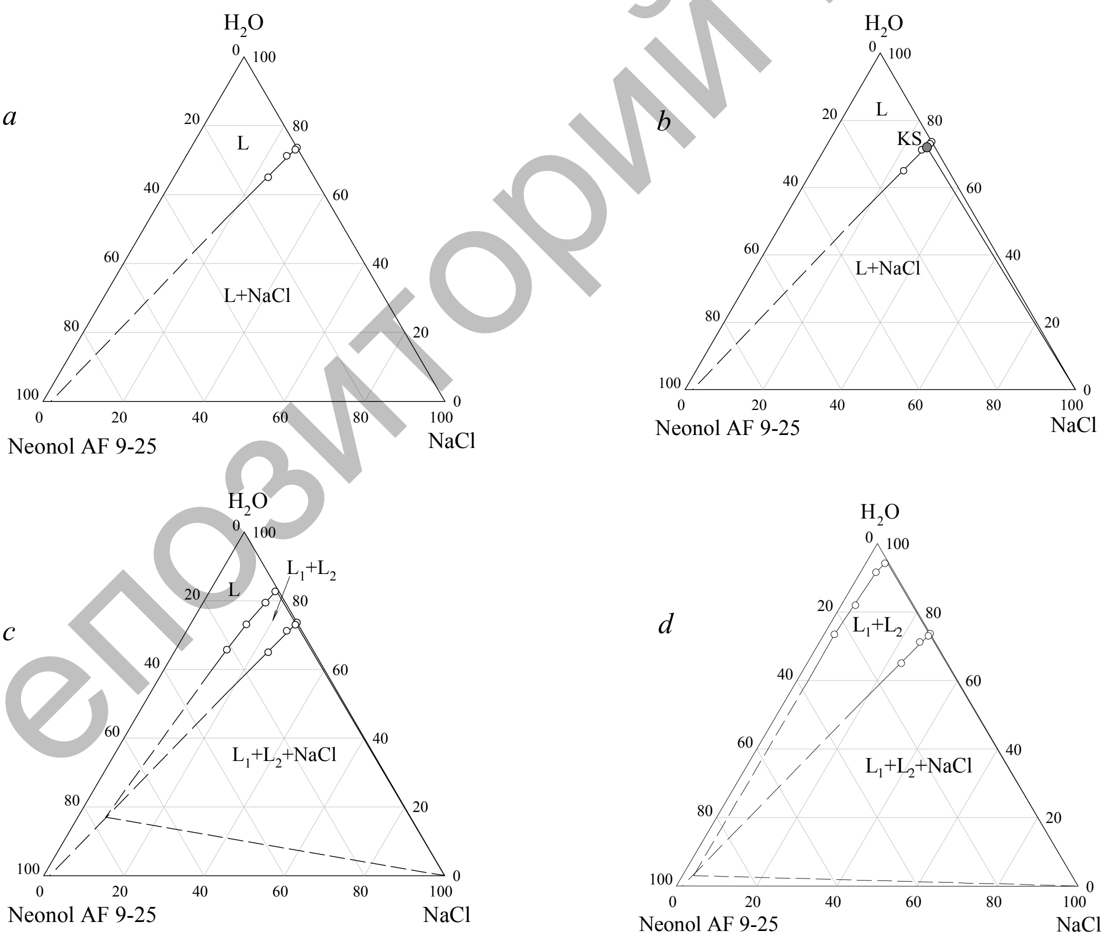
Solubility in a water – neonol AF-9-12 – NaCl system, which fits the case when water – surfactant binary subsystem is characterized by LCSP, while the salt is a salting-out agent, has been analyzed in five sections.

Four sections connect the solutions of neonol AF-9-12 with different concentration and the sodium chloride peak; the fifth section connecting the peak of neonol AF-9-12 and a heterogeneous mixture of water and sodium chloride with the mass content of 40.0 % were used to identify the critical point (KS).

The temperature range of 10–23 ºC in the system (Fig. 1*a*) is known to have two areas: unsaturated solutions (L) and crystallization of sodium chloride (L+S). Salt solubility slightly increases with temperature in the solutions of neonol AF-9-12.

At 23 ºC, NaCl solubility line is characterized by a critical point KS and a critical node of monotectonic equilibrium KS-NaCl (Fig. 1*b*). Composition of a critical point is as follows: 24.0 % NaCl, 3.0 % neonol AF-9-12, 73.0 % water. Further temperature increase results in the formation of stratifying area ($L_1$+$L_2$) together with its neighboring monotectonic equilibrium area ($L_1$+$L_2$+NaCl). Phase diagram is characterized by five areas, namely, unsaturated solutions, stratification, monotectonic equilibrium and sodium chloride crystallization (Fig. 1*c*).

At 84 ºC, the area of critical point stratification is connected with the lower critical solubility point (LCSP) of water — neonol AF-9-12 binary subsystem with the homogenious area being divided into two fields (Fig. 1*d*). Further temperature increase expands stratifying area and salts out the heterogeneous system of water — surfactant (Fig. 1*e*). Further temperature increase does not change significantly the solubility diagram; one can only observe the expansion of stratifying area and the decrease of the unsaturated solution area.




*a* — 25 ºC; *b* — 42 ºC; *c* — 60 ºC; *d* — 90 ºC

Figure 2. Phase equilibriun in the water – Neonol AF-9-25 – NaCl system

Solubility in water – neonol AF-9-25 – NaCl system, which fits the case when water – surfactant binary subsystem is homogeneous in the whole interval of liquid state and the salt serves as a salting-out agent, has been analyzed in the same sections described for neonol AF-9-12. The temperature range of 25–42 ºC in the system is known to have two areas: unsaturated solutions (L) and crystallization of sodium chloride (L+S). Temperature growth leads to a slight increase in sodium chloride solubility in surfactant solutions, with the salting-out effect of neonol AF-9-25 in relation to sodium chloride being minimal (Fig. 2*a*).

At 42 ºC, NaCl solubility line is characterized by a critical point KS and a critical node of monotectonic equilibrium KS-NaCl (Fig. 2*b*). Composition of a critical point is 26.0 % NaCl, 3.0 % neonol AF-9-12, 71.0 % water. Further temperature increase results in the formation of stratifying area ($L_1$+$L_2$) together with its neighboring monotectonic equilibrium area ($L_1$+$L_2$+NaCl). Phase diagram is characterized by five areas, namely, unsaturated solutions, stratification, monotectonic equilibrium and sodium chloride crystallization (Fig. 2*c*). Further temperature increase does not change the phase diagram significantly; one can only observe the expansion of stratifying and monotectonic equilibrium areas. Data obtained supports previously published scheme for water – synthanol DS-10 – KBr system [7].

It is relevant to see the impact of surfactant ethoxylation on temperature dependent changes in salting-out capacity of sodium chloride. Ethoxylation degree increase raises the temperature to form both stratifying and monotectonic equilibrium areas. Observed regularities are determined by greater salting-out capacity of salt and a drop in micelle hydration degree with temperature growth. Temperature dehydration of micelles with their further aggregation depends on surfactant molecule hydrophility which can be expressed in hydrophilic-lipophilic balance (HLB) or water – surfactant system LCSP. The Table gives the calculated values for HLB by Davis [13] and LCSPs for water – surfactant binary systems. Neonol AF-9-25 is even more hydrated at 60 ºC and higher than neonol AF-9-12, therefore its salting-out capacity is significantly lower than the one for neonol AF-9-12.

T a b l e

**Main characteristics determining the salting-out ability NaCl to neonols**

| Surfactant | HLB | LCSP, ºC |
|---|---|---|
| Neonol AF-9-12 | 6.93 | 84 |
| Neonol AF-9-25 | 11.22 | > 100 |

*Conclusion*

Thus, the obtained data from the experiments proved the possibility for two summarized schemes of topological transformation of phase diagrams for water – ethoxylated surfactant – inorganic salt systems, when salt serves as a salting-out agent only, while water — surfactant binary system is characterized by LCSP (water – neonol AF-9-12 – NaCl system) or is homogeneous in the whole interval of liquid state (water – neonol AF-9-25 – NaCl system). These schemes perfectly fit the summarized scheme of topological transformation of phase diagrams for triple stratifying systems of salt — binary solvent [14].

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## Су – оксиэтилденген нонилфенол – NaCl жүйелері фазалық диаграммаларының топологиялық трансформациялануы

Мақалада су – оксиэтилденген нонилфенол (неонол) – натрий хлориді жүйелеріндегі фазалық тепе-теңдіктер зерттелген, екіфазалық сұйық және монотектикалық тепе-теңдіктердің мүмкін болу аумақтарының температуралық интервалдары анықталған. Көрсетілген аумақтар АФ-9-12 неонолмен жүйесінде 23 ºС астам, ал АФ-9-25 неонолмен жүйесінде 42 ºС астам температурада бола алады. Су – неонол АФ-9-12 – натрий хлориді жүйесінің ерекшелігі болып 84 ºС асқан температурада екі қабатқа бөлінетін су-неонол АФ-9-12 жүйешесінің тұзсыздануы табылады. Су – оксиэтилденген ББЗ – бейорганикалық тұз жүйелері жағдайлары үшін, тұз тек тұзсыздану әрекетіне ие болатын, ал су – ББЗ (неонол АФ-9-12) жүйешесі төменгі шекті еру температурасымен сипатталатын немесе сұйық жағдайдың барлық интервалдарында гомогенді болатын жағдайлары үшін фазалық диаграммалардың топологиялық трансформациялануының сызбасы өңделген. Ол сызбаның тұз – бинарлы еріткіш жүйелері үшін біріктірілген сызбаларына сәйкестігі көрсетілген. Алынған мағлұматтар ББЗ оксиэтилдену деңгейі натрий хлоридінің тұзсыздандыру қабілетіне қалай әсер ететінін бағалауға мүмкіндік берді. Оксиэтилден деңгейінің өсуі ББЗ мицеллаларының гидратациялануы артуымен қатар жүретіні анықталды, бұл енгізілетін натрий хлоридінің тұзсыздандыру қабілетінің төмендеуіне әкеледі. Алынған мәліметтерді тұзсыздандыратын заттар қатысында оксиэтилденген ББЗ негізінде экстракцияның температуралық-концентрациялық параметрлерін оңтайландыруға қолдануға болады.

*Кілт сөздер:* беттік-белсенді заттар, оксиэтилденген нонилфенолдар, натрий хлориді, қабаттарға бөлінетін жүйелер, тұзсыздандыру, фазалық диаграммалар, ерігіштік, топологиялық трансформациялану.

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## Топологическая трансформация фазовых диаграмм систем вода – оксиэтилированный нонилфенол – NaCl

В статье исследованы фазовые равновесия в системах вода – оксиэтилированный нонилфенол (неонол) – хлорид натрия, установлены температурные интервалы существования области двухфазного жидкого и монотектического равновесий. Указанные области существуют при температуре более 23 ºС в системе с неонолом АФ-9-12 и более 42 ºС в системе с неонолом АФ-9-25. Особенностью системы вода – неонол АФ-9-12 – хлорид натрия является высаливание двойной расслаивающейся подсистемы вода – неонол АФ-9-12 при температуре более 84 ºС. Разработана схема топологической трансформации фазовых диаграмм систем вода – оксиэтилированное ПАВ – неорганическая соль для случаев, когда соль обладает только высаливающим действием, а подсистема вода – ПАВ характеризуется нижней критической температурой растворения (неонол АФ-9-12) или является гомогенной во всем интервале жидкого состояния. Показано соответствие разработанных схем обобщенной схеме для систем соль – бинарный растворитель. Полученные данные позволили оценить влияние степени оксиэтилирования ПАВ на высаливающую способность хлорида натрия. Установлено, что рост степени оксиэтилирования сопровождается увеличением гидратации мицелл ПАВ, что приводит к снижению высаливающей способности вводимого хлорида натрия. Полученные данные могут использоваться для оптимизации температурно-концентрационных параметров экстракции в системах на основе оксиэтилированных ПАВ в присутствии высаливателя.

*Ключевые слова*: поверхностно-активные вещества, оксиэтилированные нонилфенолы, хлорид натрия, расслаивающиеся системы, высаливание, фазовые диаграммы, растворимость, топологическая трансформация.

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