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 °C in system with Neonol AF-9-12 and more than 42 °C 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 °C. A scheme of phase diagrams of topological transformation of water – ethoxylated surfactant – inorganic salt systems for cases, when salt only has 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 ethoxylate 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 (nD^25 = 1.3325).

Visual-polythermal method identified the stratifying area boundaries. Sections method was used to obtain solubility isotherms at temperatures below 75 °C. 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 °C (3.0 mas.% neonol AF-9-12). Stratifying area in the system is within the temperature interval — from 84 °C 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.

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

\[ a \rightarrow 10 \, ^\circ \text{C}; \ b \rightarrow 23 \, ^\circ \text{C}; \ c \rightarrow 60 \, ^\circ \text{C}; \ d \rightarrow 84 \, ^\circ \text{C}; \ e \rightarrow 90 \, ^\circ \text{C} \]
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 °C in the system (Fig. 1a) 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 °C, NaCl solubility line is characterized by a critical point KS and a critical node of monotectonic equilibrium KS-NaCl (Fig. 1b). 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 (L1+L2) together with its neighboring monotectonic equilibrium area (L1+L2+NaCl). Phase diagram is characterized by five areas, namely, unsaturated solutions, stratification, monotectonic equilibrium and sodium chloride crystallization (Fig. 1c).

At 84 °C, 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 homogenous area being divided into two fields (Fig. 1d). Further temperature increase expands stratifying area and salts out the heterogeneous system of water — surfactant (Fig. 1e). 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.

\[ a \rightarrow 25 \, ^\circ C; \quad b \rightarrow 42 \, ^\circ C; \quad c \rightarrow 60 \, ^\circ C; \quad d \rightarrow 90 \, ^\circ C \]

Figure 2. Phase equilibrium 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 °C 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. 2a).

At 42 °C, NaCl solubility line is characterized by a critical point KS and a critical node of monotectonic equilibrium KS-NaCl (Fig. 2b). 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 (L1+L2) together with its neighboring monotectonic equilibrium area (L1+L2+NaCl). Phase diagram is characterized by five areas, namely, unsaturated solutions, stratification, monotectonic equilibrium and sodium chloride crystallization (Fig. 2c). 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 °C and higher than neonol AF-9-12, therefore its salting-out capacity is significantly lower than the one for neonol AF-9-12.

**Table**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>HLB</th>
<th>LCSP, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neonol AF-9-12</td>
<td>6.93</td>
<td>84</td>
</tr>
<tr>
<td>Neonol AF-9-25</td>
<td>11.22</td>
<td>&gt; 100</td>
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</tbody>
</table>

**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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**References**

А.М. Елохов, А.В. Станкова, О.С. Кудряшова, А.Е. Леснов

Су – окситилендеген нонилфенол – NaCl жуйелерінің топологиялық трансформациялары

Макалада су – окситилендеген нонилфенол (неонол) – натрий хлорид жуйелерінің фазалық диаграммаларының топологиялық трансформациялары анықталған. Көрсетілген схема акустар АФ-9-12 неонолмен жүйесіндегі 9–12 °С астында жататын температуралық интервалдарының өзгертілігіне, параметрлердің өзгеруіне, концентрациялық айырмашылықтарға әсер етеді.

А.М. Елохов, А.В. Станкова, О.С. Кудряшова, А.Е. Леснов

Топологическая трансформация фазовых диаграмм системы вода – окситилендированный нонилфенол – NaCl

В статье исследованы фазовые равновесия в системах вода – окситилендированный нонилфенол (неонол) – хлорид натрия, установлены температурные интервалы существования области двухфазного жидкого и монотектического равновесий. Указанные области существуют при температуре более 23 °C в системе с неонолом АФ-9-12 и более 42 °C 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 °C. Разработана схема топологической трансформации фазовых диаграмм систем воды – окситилендированный 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 общениной схеме для систем соль – бинарный растворитель. Полученные данные позволили оценить влияние степени окситилендирования ПАВ на высаливающую способность хлорида натрия. Установлено, что рост степе-
ни оксиэтилирования сопровождается увеличением гидратации мицелл ПАВ, что приводит к снижению высылающей способности вводимого хлорида натрия. Полученные данные могут использоваться для оптимизации температурно-концентрационных параметров экстракции в системах на основе оксиэтилированных ПАВ в присутствии высылающего.

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

References