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Substituted phenols are highly efficient for extracting alkali elements from aqueous alkali solutions [1]. However, there is a dearth of information for extracting alkali elements from strongly alkaline media ( $\text{pH} > 13$ ). The process itself varies, depending on the nature of the phenolic extractant. In some cases water is very soluble in the organic phase, or the extractant is highly soluble in the aqueous phase; in others, these phenomena is completely absent. The causes of such behavior of phenolic reagents in the extraction of alkali elements from strongly alkaline solutions are not clear.

It has been reported [2,3] that substituted alkali metal phenolates are surface-active colloidal substances capable of forming in aqueous and nonaqueous solutions lyotropic liquid crystals and micelles. In this work it is shown that the extraction of potassium, rubidium, and cesium with phenolic reagents in hydrocarbon solvents under strongly alkaline conditions is determined by the tendency of alkali metal phenolates produced during the extraction to form micelles in the aqueous and organic phases. And the tendency of the phenolate to form micelles is determined mainly by the size and position of the hydrocarbon substituent group in the molecule.

Micelle formation in the aqueous phase of the extraction system was detected with the aid of additions of a color indicator. As the latter we used a pinacyanol chloride or sudan III. Besides, the detection of the micelle formation in the aqueous phase was based on the inflection of the curve obtained by plotting the surface tension of the aqueous phase as the function of the concentration of alkali metal hydroxide in the aqueous phase. Micelle formation in the organic phase was indicated by a sharp rise in the extractability of water. This was determined on the basis of the magnitude of the relative volume of organic phase,  $V_o$ , at equilibrium (relative to the total volume of aqueous and organic phases). In addition, micelle formation in the organic phase was determined by the extraction by the phenolic reagent of the inorganic salt, alkali metal carbonate or alkali metal sulfate. The anion of the salt was detected in aqueous phase after stripping of extract by hydrochloric acid followed by chemical analysis. Also, the analysis of the anion was carried out directly in the extract with the aid of infrared spectroscopy.

It was found that alkali metal phenolates of p-alkylphenols with small hydrocarbon substituents form micelles more readily in aqueous than in hydrocarbon solutions. Similar behavior was observed for

o-substituted phenols with different molecular mass. When the extraction was carried out with p-alkyl- or p-arylphenols having a small substituent groups (e.g., 4-t-butylphenol) and with o-substituted phenols (e.g. 2-benzylphenol, 4-methyl-2-t-butylphenol), micelles form only in the aqueous phase,  $L_w$ , and not in the organic phase,  $L_o$  (Fig. 1). Micelles form only when the concentration of alkali metal

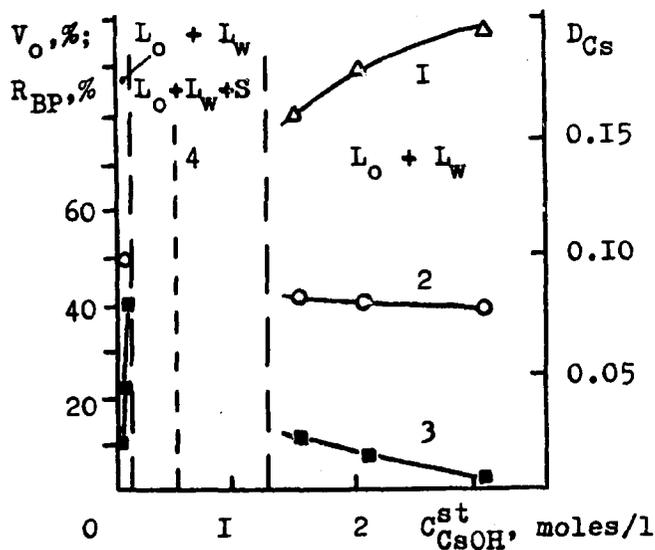


Fig. 1. Extraction of cesium by IN toluene solution of 2-benzylphenol from water solutions of  $CsOH + Cs_2SO_4$ . (Concentration of  $Cs_2SO_4$  in the starting aqueous phase - 0.25 mole/l). 1 -  $R_{BP}$ ; 2 -  $V_o$ ; 3 -  $D_{Cs}$ ; 4 - boundary for micelle formation in the aqueous phase

hydroxide in the extraction system is sufficiently high. Upon a further increase in alkali metal hydroxide concentration, the solid precipitate of alkali metal phenolate (S) which has formed becomes fully dissolved. And practically all of the extraction reagent passes into the aqueous phase (the extraction efficiency of 2-benzylphenol into the aqueous phase,  $R_{BP}$ , approaches 100%). At the same time extraction of alkali metal stops (the distribution coefficient for cesium,  $D_{Cs}$ , approaches zero).

In the case of alkali metal phenolates of p-alkylphenols and p-arylphenols

with a large hydrocarbon group (e.g., 1,1,3,3-tetramethylbutylphenol, p-alkylphenol with  $C_4$ - $C_8$ -alkyl groups), micelles form only in the organic phase, and not in the aqueous phase of the extraction system (Fig. 2). Owing to the solubilization in reverse micelles, the extraction of water sharply increases. This is shown in Fig. 2 by hydration number  $y_{H_2O}/y_{Cs_2}$  and leads to an increase in the volume of the organic phase at the expense of the aqueous phase until the aqueous phase completely passes into the organic phase. Our results show that when micelles form in the organic phase the alkali elements can be extracted not only via the cation-exchange mechanism but also via the micellar mechanism. The latter process is discovered when the alkali elements pass into the organic phase together with their inorganic anion (Fig. 2, curve 5) owing to the secondary solubilization in reverse micelles [4]. The micellar mechanism makes it possible to extract alkali elements above the stoichiometric level (Fig. 2, cur-

ve 3). The formation of micelles in the organic phase begins only when the concentration of the alkali metal phenolate is sufficiently high; this concentration is characterized by a molar ratio, alkali metal:phenolic reagent,  $N$ , in the organic phase. A further increase in the concentration of the alkali component results in the formation of the lyotropic liquid crystal phase followed by the precipitation of solid alkali metal alkylphenolate.

As a rule, micelles form only in one of the phases

of the extraction system. However, when the extraction of alkali elements is carried out with a toluene solution of 4-( $\alpha, \alpha$ -dimethylbenzyl)phenol micelles form in both the organic and aqueous phase practically at the same concentration of the alkali. At the beginning the process of aggregation predominates in the organic phase. A further increase in the concentration of the alkali metal hydroxide in the original aqueous phase results in micelle formation predominantly in the aqueous phase.

Alkali metal disubstituted phenolates with a large hydrocarbon groups in the o- and p-positions (e.g., 2-( $\alpha$ -methylbenzyl)-4-(1,1,3,3-tetramethyl)phenolate), do not, owing to the steric effect, form micelles either in aqueous or organic solutions. And consequently no micelle formation takes place when extraction is carried out with such phenolic reagents.

The formation of micelles in the organic phase also occurs when the alkali elements are extracted by phenolic oligomers (e.g., p-al-

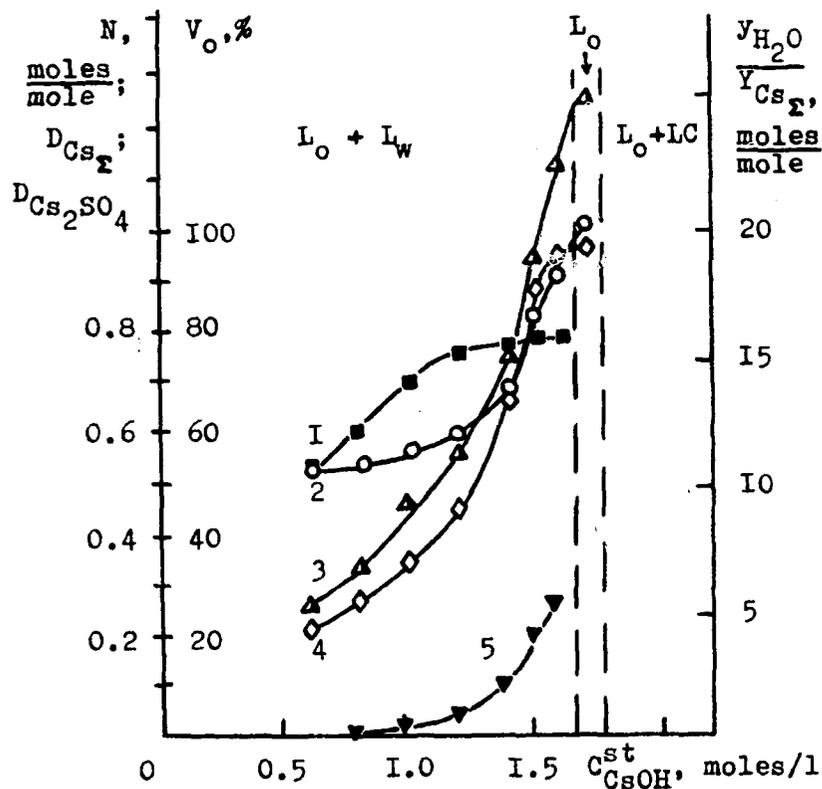


Fig. 2. Extraction of cesium by 2N n-octane solution of p-alkyl( $C_4-C_8$ )phenol from water solutions of  $CsOH + Cs_2SO_4$ . (Concentration of  $Cs_2SO_4$  in the starting aqueous phase - 0.4 mole/l).

1 -  $D_{Cs_2}$ ; 2 -  $V_o$ ; 3 -  $N$ ; 4 -  $\frac{Y_{H_2O}}{Y_{Cs_2}}$ ; 5 -  $D_{Cs_2SO_4}$

kyl- and arylphenol disulfides and polysulfides), the phenolates of which are capable of forming micelles in an organic medium but not in aqueous solutions. In the oligomer systems the alkali elements can pass into the organic phase via the micellar mechanism and through super-stoichiometric extraction (Fig. 3). Under conditions of micelle

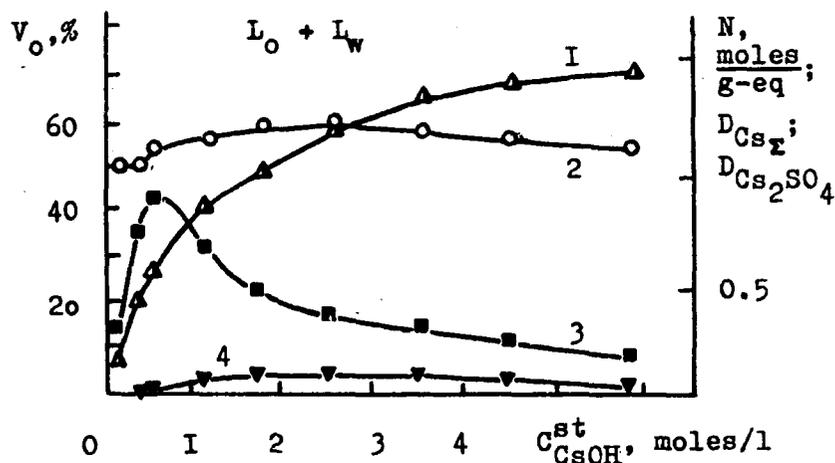


Fig. 3. Extraction of cesium by IN toluene solution of p-alkylphenol disulfide from water solutions of  $\text{CsOH} + \text{Cs}_2\text{SO}_4$ . (Concentration of  $\text{Cs}_2\text{SO}_4$  in the starting aqueous phase - 0.25 mole/l).

I - N; 2 -  $V_o$ ; 3 -  $D_{\text{CsX}}$ ; 4 -  $D_{\text{Cs}_2\text{SO}_4}$

formation in the organic phase in a region of relatively low alkali concentration, the extraction of alkali elements by phenolic oligomers proceeds in a similar way as the extraction by monomeric p-alkylphenols containing large alkyl groups (Fig. 2). However, when extracting alkali elements by phenolic oligomers, an increase in the concentration of the alkali metal hydroxides in the starting aqueous phase leads not to the formation of solid phenolate but to an increase in the volume of the aqueous phase. The extractability of water in the region of high alkali concentrations of aqueous phase decreases when there is an increase in the concentration of alkali (Fig. 3, curve 2) or when there is an increase in inorganic salt (alkali metal sulfate or alkali metal carbonate). These processes result from the competition for water between the aqueous and organic phases: at higher concentrations of alkali metal derivatives water is held more strongly in the aqueous phase owing to hydration. Our experiments show that the tendency of oligomer phenolates to form reversible micelles decreases with an increase in molecular weight of the oligomer.

The considerable losses of the phenolic reagent, which is soluble in the aqueous phase, are caused by the formation of micelles from the corresponding phenolate in the aqueous phase. Also the diluent can transit into the aqueous phase owing to the solubilization effect of the direct micelles of the phenolate. At the same time there is a decrease in the extraction of alkali elements. Therefore, the extraction of alkali elements from strongly alkaline media requires a correct choice of the extracting agent: the phenolate of the alkali me-

formation in the organic phase in a region of relatively low alkali concentration, the extraction of alkali elements by phenolic oligomers proceeds in a similar way as the extraction by monomeric p-alkylphenols containing large alkyl groups (Fig. 2). However, when extracting alkali elements by phenolic oligomers, an increase in the

tal being extracted should be free of the tendency to form micelles in aqueous solutions. Consequently, o- and p-substituted phenols with small hydrocarbon substituents are unfit for extracting alkali elements from strongly alkali aqueous solutions. Our experiments with 4-( $\alpha, \alpha$ -dimethylbenzyl)phenol and 4-t-butylphenol have shown that the increase in the size of the hydrocarbon substituent in the molecule of the phenolic reagent does not result in the decrease in its solubility in strongly alkaline aqueous solutions, if the resulting, in the extraction system, phenolates tend to form micelles mainly in the aqueous phase. On the contrary, the increase in the hydrophobic part of the extracting agent leads to the increase of the ability of the alkali phenolate to the micelle formation and apparition of micelles at lower concentration of alkali in the aqueous phase. However, the growth of the size of the hydrocarbon substituent in case of p-alkyl- or p-arylphenols can lead to fact, that micelles will start in the organic phase and not in the aqueous phase. It decreases considerably the solubility of the phenolic reagent in the aqueous phase.

The employment of phenols with hydrocarbon substituents in p-position for extracting alkali elements from strongly alkaline mediums is not the best variant. The micelle formation in the organic phase increases noticeably the alkali metal capacity of the organic phase due to the micellar mechanism of extraction. However, the aggregation in the organic phase, going rather deeply, makes more difficult and even impossible the extraction process. If the formation of micelles in the organic phase is limited, then the aggregation does not breach the extraction process and the characteristic advantages of the micelle formation are preserved. Therefore, the phenolic oligomers are more preferable for extracting alkali metals from strongly alkaline mediums if chosen among the above reviewed compounds.

#### References

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