ALKYLPHENOL REAGENTS FOR THE OIL AND GAS INDUSTRY

K. D. Korenev and V. A. Zavorotnyi UDC 622.276.65:661.185.004

The efficiency of well drilling, oil and gas production, industrial refining of the feedstock produced, inhibition of corrosion of the equipment, etc., is determined to a significant degree by regulation of phase and energy interactions when they are conducted with chemical reagents having the properties of surfactants (SF) [1, 2]. Hydrocarbon (lipophilic) and highly polar (hydrophilic) groups are combined in SF molecules and their competition is characterized by the value of the hydrophilic-lipophilic balance (HLB) [3].

Many types of SF (Table 1) are synthesized from alkylphenols with an alkyl group of 6 – 20 carbon atoms; the proportion of these SF is ~40%. Their properties and efficiency are a function of both the nature of the highly polar groups (ethoxy, sulfo groups, amino groups, etc.) and the structure of the hydrocarbon part of the molecules. When an alkyl group in the aromatic ring of the alkylphenol molecule is in the *para* position, the degree of symmetry of the molecules and their tendency to aggregate into micelles increase (the bulk properties of solutions of SF improve); on the other hand, in the *ortho* position, micellization of the molecules is slowed so that the surface activity of the SF solutions is intensified [3].

We found that the predominant position of the alkyl group is determined by the structure of the olefin and the reaction conditions in alkylphenols obtained by the reaction of olefins with phenol in the presence of an acid catalyst — KU-2 sulfonic cation-exchanger or *p*-toluenesulfonic acid (TSA) (Table 2). KU-2 sulfonic cation-exchanger, a solid sulfonic acid polymer in comparison to TSA, which is soluble in the reaction mixture, favors formation of *p*-alkylphenols from olefins of both linear and branched structure to a greater degree, although with a lower total yield. However, this catalyst, in contrast to TSA, allows easily organizing production of alkylphenols in continuous flow conditions with the total yield increased to 80% and higher. In organizing production of alkylphenols based on isobutene and its dimers in domestic refineries with this technology, its
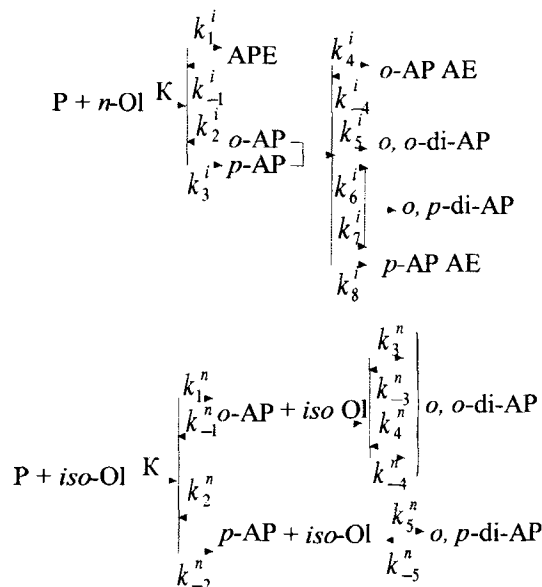
TABLE 1

SF based on alkylphenols	Type	Area of application
Ethoxylates (polyethylene glycol esters)	I	Emulsifiers, demulsifiers, reagents for increasing recoverable petroleum, removal of ARWD*, etc
Na, NH4 alkylphenol sulfoethoxylates	II	Same
Na, Ca, Mg alkylphenolsulfonates	III	Dispersants, corrosion inhibitors, reagents for removal of ARWD,* oil detergent additives
Na, Ca, Mg alkylsalicylates	IV	Same
Aminomethylenealkylphenols (Mannich bases)	V	Corrosion inhibitors, antioxidants, antiseptics
Ca, Ba and other metal di(alkylphenol dithiophosphates)	VI	Antioxidants, metal corrosion and wear inhibitors
Ca, Ba di(alkylphenol)sulfides	VII	Same
Note. *ARWD: asphalt—resin—wax deposits.		

developers — V. I. Isagulyanets, Academician of the Academy of Sciences of the Armenian SSR and Professor P. S. Belov, deserve great credit.

As a result of further refinements of synthesis of alkylphenols, kinetic schemes were created for the parallel-consecutive reactions of olefins of linear and branched structure with phenol [4], yielding products of different composition (see Table 2):

$$
P + n\text{-Ol} \xrightarrow{K}
\begin{cases}
\xrightarrow{k_1^i} \text{APE} & \xrightarrow{k_4^i} o\text{-AP AE} \\
\xleftarrow{k_{-1}^i} & \xleftarrow{k_{-4}^i} \\
\xrightarrow{k_2^i} o\text{-AP} & \xrightarrow{k_5^i} o, o\text{-di-AP} \\
\xrightarrow{k_3^i} p\text{-AP} & \xrightarrow{k_6^i} o, p\text{-di-AP} \\
& \xleftarrow{k_7^i} \\
& \xrightarrow{k_8^i} p\text{-AP AE}
\end{cases}
$$

$$
P + iso\text{-Ol} \xrightarrow{K}
\begin{cases}
\xrightarrow{k_1^n} o\text{-AP} + iso\text{ Ol}
\begin{cases}
\xrightarrow{k_1^n} \\
\xrightarrow{k_{-3}^n} o, o\text{-di-AP} \\
\xrightarrow{k_4^n} \\
\xleftarrow{k_{-4}^n}
\end{cases} \\
\xleftarrow{k_{-1}^n} \\
\xrightarrow{k_2^n} \\
\xleftarrow{k_{-2}^n} p\text{-AP} + iso\text{-Ol} \xrightarrow{k_5^n} o, p\text{-di-AP} \\
\xleftarrow{k_{-5}^n}
\end{cases}
$$

where P is phenol; n-Ol, iso-Ol are respectively normal and isoolefin; K is catalyst; APE are alkylphenol esters; o-AP, p-AP are respectively ortho- and para-alkylphenols; o-AP AE, p-AP AE are o- and p-alkylphenol alkyl esters; $k_1^i - k_8^i$, $k_1^n - k_8^n$ are respectively the effective rate constants of conversion of the initial and intermediate substances.

These schemes are described by a system of differential equations, and constants $k_1 - k_8$ were calculated for the first time with their solution using a computer. The values of the constants for reactions of n-1-decene with phenol in the presence of different catalysts — TSA, KU-2, and a porous sulfonic cation-exchanger KSM-2, are

TABLE 2

Products of reaction	Content in mixture (wt. %) in catalyst	
	TSA	KU-2
Reaction* of n-octene with phenol (1:1 mol.)		
Mono-p-alkylphenols	17.2	26.9
Mono-o-alkylphenols	55.3	52.3
Alkylphenol esters	2.2	15.5
Dialkylphenols	15.3	5.3
Total yield of alkylphenols, %	23.5	18.3
Reaction* of isooctene with phenol (1:1 mol.)		
Mono-p-alkylphenols	93.1	98.1
Mono-o-alkylphenols	6.1	1.8
Alkylphenol esters	0.0	0.0
Dialkylphenols	0.8	0.1
Total yield of alkylphenols, %	66.5	53.5
Note. * At 110°C for 2 h.		

TABLE 3

Reaction of n-1-decene with phenol at 80°C	Rate constant, $k_j^i \cdot 10^4$						
	k_{-1}, sec^{-1}	k_1	k_2	k_3	k_5	k_6	k_7
		liter/(mole·sec)					
In a mixture reactor in the presence of TSA	0.377	0.093	0.185	0.0377	0.0691	0.0325	0.0718
In a continuous flow reactor in the presence of							
KU-2	3.72	2.03	1.41	0.960	0.0741	0.0544	0.0850
KSM-2	90.6	61.4	31.4	19.3	2.21	1.68	2.66
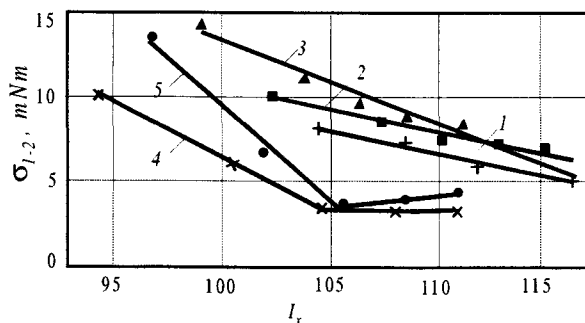
Fig. 1. Interfacial tension σ_{1-2} on the water—kerosene interface in the presence of alkylphenol ethoxylates vs. index I_x of their relative polarity: 1) p-$tert$-octylphenol; 2) p-isononylphenol; 3) p-sec-octyl-o-o-dimethylphenol; 4) o-$tert$-octyl-p-methylphenol; 5) o-sec-octyl-p-methylphenol. The values of I_x increase with an increase in the average number (7, 10, 13, 16, 19) of ethoxyl groups added to the alkylphenol.

reported in Table 3.

When TSA is replaced by sulfonic cation-exchangers, especially porous KSM-2 and the reaction conditions are changed, the values of k_1^i increase significantly. This is due to the creation of flow of the reacting molecules through the polymeric granules of catalyst in one direction, which first causes conversion of these molecules to approach the thermodynamically equilibrium conversion and second, involvement of an additional amount of sulfo groups difficultly accessible for contact in random diffusion of the reagents in a mixture reactor. In addition, diffusion inhibition of the reactions decreases sharply in the granules of porous KSM-2 [5]. This highly active catalyst introduced at Nizhnekamskneftekhim Industrial Association allowed intensifying production of isononylphenols and their ethoxylates (type I, see Table 1).

When TSA is replaced by KU-2 and KSM-2, the ratio of k_j^i also changes (see Table 3): dissociation of phenol alkyl esters (k_{-1}/k_1 decreases from 4.05 to 1.48) and formation of dialkylphenols slow (ratio of $k_1 + k_2 + k_3$ and $k_5 + k_6 + k_7$ increases from 1.82 for TSA to 20.6 for KU-2 and decreases to 17.1 for KSM-2); the proportion of alkylphenol esters in the total monodecylphenols formed increases (from 29.5 to 54.8%). As a consequence, the selectivity of formation of alkylphenol isomers can be varied by appropriate selection of the catalysts and reaction conditions.

Alkylphenol isomers are distinguished not only by the reactivity but also the polarity, which can be measured chromatographically [6], particularly with the retained volume on a type SE-30 low-polarity stationary phase in gas-liquid chromatography. We found that this volume is due to the inverse linear dependence (in logarithmic coordinates) with relative polarity index I_x determined by inverse chromatography. Indexes I_x for alkylphenol ethoxylates, which are proportional to the value of their HLB as indicated in [7], are determined by the same method.

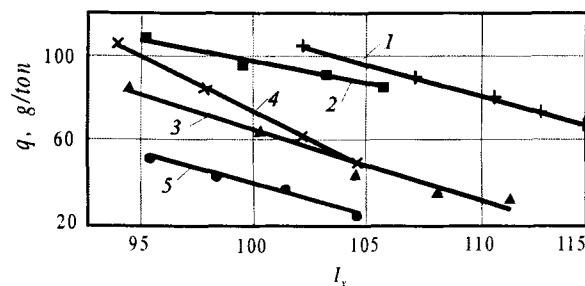Quantitative correlations between index I_x and the colloid chemical properties of solutions of their

Fig. 2. Flow q of alkylphenol ethoxylates vs. their relative polarity index I_x in demulsification of water—oil emulsions: 1) p-isononylphenol; 2) o-sec-decyl-p-methylphenol; 3) o-$tert$-octyl-p-methylphenol; 4) o,p-di-$tert$-octylphenol; 5) o,o-di-sec-octylphenol. The values of Ix increase with an increase in the average number (7, 10, 13, 16, 19) of ethoxyl groups added to the alkylphenol.

surface-active derivatives were found for the *ortho*- and *para*-isomers: surface and interfacial tension, wetting, emulsifying, and other powers. For example, for the same I_x (Fig. 1), o-alkylphenols with both branched and linear C_8 groups (curves 4, 5) are characterized by higher interfacial activity in comparison to p-alkylphenol derivatives (curves 1, 3) (the value of σ_{1-2}, determined stalagmometrically, are minimum). As a consequence, solutions of o-alkylphenol ethoxylates can exhibit elevated petroleum displacement activity.

The consumption of isomeric alkylphenol ethoxylates — emulsifiers in treatment of fresh industrial water—oil emulsions to reduce the residual water content — as a function of their index I_x is shown in Fig. 2. For SF with linear alkyl groups, the curves (2 and 5) are characterized by a smaller slope than for SF with branched alkyl groups (1, 3, and 4). o- and p-alkylphenol ethoxylates differ in effectiveness even more markedly (for example, curves 1 and 3). The lowest demulsifier consumption (27 – 41 g per ton of crude oil) is attained when o-$tert$-octyl-p-methylphenol ethoxylates (curve 3) and o,o-di-sec-octylphenol (curve 5) with 16 – 19 ethoxyl groups (on average) are used.

A quantitative correlation between Ix and the wetting, foaming, and detergent powers of aqueous solutions was also established for alkylphenol ethoxylates. Similar dependences were also found for aqueous solutions of anionic SF: isomeric alkylphenol Na sulfoethoxylates (type II, see Table 1), Na alkylphenolsulfonates (type III), and cationic SF aminomethylenealkylphenols (Mannich bases, type V). A linear correlation was found between index I_x for Ca phenolsulfonates (type III), Ca alkylsalicylates (type IV), and their detergent potential at 250°C in a solution of M-11 mineral oil.

The scientific principles for regulation of the colloid chemical and performance properties of alkylphenol chemical reagents obtained by directed synthesis of their isomers and surface-active derivatives were thus elaborated.

REFERENCES

1. G. Z. Ibragimov, K. S. Fazlutdinov, and N. I. Khisamutdinov, *Use of Chemical Reagents for Boosting Oil Production* [in Russian], Nedra, Moscow (1991).
2. L. M. Gurvich and N. M. Sherstnev, *Multifunctional SF Compounds in Industrial Oil Production Operations* [in Russian], VNIIOENG, Moscow (1994).
3. A. A. Abramzon, *Surfactants: Properties and Use* [in Russian], Khimiya, Moscow-Leningrad (1981).
4. V. A. Zavorotnyi, V. I. Neizvestnyi, and K. D. Korenev, *Neftekhimiya*, **36**, No. 3, 227 – 236 (1996).
5. V. I. Neizvestnyi, V. A. Zavorotnyi, K. D. Korenev, et al., *Ibid.*, No. 4, 336 – 343.
6. E. Tesarova and V. Pacakova, *Chromatographia*, **17**, No. 5, 269 – 284 (1983).
7. N. Schoenfeld, *Ethylene Oxide Surfactants* [Russian translation], Khimiya, Moscow (1982).