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TECHNICAL NOTE

Interfacial Activity of 2-Hydroxy-5-*tert*-butylbenzaldehyde Oxime in Systems Containing Mixed Diluents

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ABSTRACT

The interfacial activity of 2-hydroxy-5-*tert*-butylbenzaldehyde oxime was studied in systems containing toluene, octane, and mixtures of these diluents containing up to 20% toluene. A significant change in the interface character of the system containing 20% toluene is observed. The interface, however, is still not fully aromatic. For a system containing 1% toluene, the interface seems to have an aliphatic character.

INTRODUCTION

Diluents used in solvent extraction significantly affect the extractant properties, changing both their extraction strength and kinetics (1–19). Due to this, an appropriate choice of diluent can have an important effect upon an extraction process and its economics.

High boiling hydrocarbon fractions are used in commercial processes. In the case of hydroxyoximes, the presence of large amounts of aromatics in commercial diluents negatively affects both the equilibrium extraction and the kinetics. However, some percentage of aromatics is necessary to avoid precipitation of metal complex during extraction. As a result, commercial diluents contain some amount of aromatics, e.g., commercial Escaid 100 contains about 56.5% aliphatic hydrocarbons, 23.5% cyclic hydrocarbons, and 20% aromatics. This amount of aromatics still does

not affect the extraction properties of commercial hydroxyoxime extractants but it is sufficient to prevent any precipitation.

The diluent type can significantly affect the interfacial properties of hydroxyoxime extractants. The interfacial activity of commercial LIX 65N in various extraction systems was discussed using different literature data. It was found that in an extraction system containing Escaid 100, the interface seems to have the aromatic character (20). This was not, however, confirmed by more recent studies in which the interfacial activity of 1-(2'-hydroxy-5'-methyl-phenyl)-1-decanone oxime was studied (21).

The aim of this work is to study the interfacial properties of pure 2-hydroxy-5-*tert*-butylbenzaldehyde oxime in systems containing toluene, octane, and mixtures of these diluents containing up to 20% toluene. This compound can be considered as the model for ACORGA and LIX-type extractants containing 2-hydroxy-5-nonylbenzaldehyde oxime or 2-hydroxy-5-dodecyl-benzaldehyde oxime as the active substance. The use of such a model is very convenient because it exists only in the form of an (E)-isomer (*anti*).

EXPERIMENTAL

Pure 2-hydroxy-5-*tert*-butylbenzaldehyde oxime was used. Its synthesis and analytical data, extraction, and other properties were described previously (22–25).

The interfacial tension was measured by the ring method at 20°C. The time of surface aging was ~24 hours. Redistilled water was used as the water phase. Octane, toluene, and their mixtures containing up to 20% toluene were used as model organic diluents. They were redistilled over sodium before use with a Vigreux distillation column. Mutually presaturated phases were used. Equal volumes (25 cm^3) of both phases were automatically shaken at room temperature for 6 hours and then left for 24 hours for full separation. They were separated, disregarding layers near the interface of 1 cm depth each.

RESULTS AND DISCUSSION

The interfacial tension isotherms for systems containing octane, toluene, and their mixtures are shown in Fig. 1. In the last case, taking into account the composition of commercial diluents used in extraction installations containing hydroxyoxime extractants, only toluene concentrations up to 20% v/v were used.

The interfacial activity of hydroxyoxime is significantly different in systems containing toluene and octane. In the first system considered the

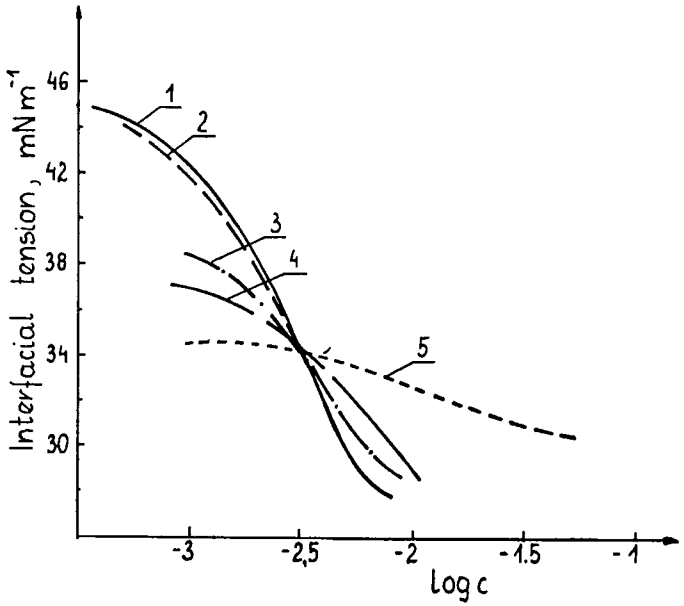

FIG. 1 Interfacial tension isotherms: (1) octane, (2) 1% toluene, (3) 5% toluene, (4) 20% toluene, and (5) toluene.

interfacial activity was small and the oxime used decreased the interfacial tension by only ~3 $mN \cdot m^{-1}$. A much larger decrease of the interfacial tension was observed in a system containing octane as the organic phase: ~17 $mN \cdot m^{-1}$ (Fig. 2).

The effect of toluene content upon the interfacial tension was observed for systems containing at least 5% toluene in the organic phase. The isotherm obtained for a system containing 1% toluene in the organic phase is almost the same as that for a system with pure octane.

The surface activity of surfactants/extractants may be characterized by the concentration, $-\log c_0$, obtained from the intercept of the asymptotes of interfacial tension isotherm γ vs $\log c$ at its beginning and in the linear part of the isotherm, where the interfacial tension is almost constant and then drops rapidly, respectively. Thus, it characterizes the efficiency of adsorption and determines the concentration at which a significant decrease in interfacial tension is observed. The following values of $-\log c_0$ were obtained: 2.9, 2.8, 2.64, 2.50, and 2.44 for systems containing octane, 1, 5, and 20% toluene, and toluene, respectively. Thus, almost the same values were obtained for systems containing octane and 1% toluene. The

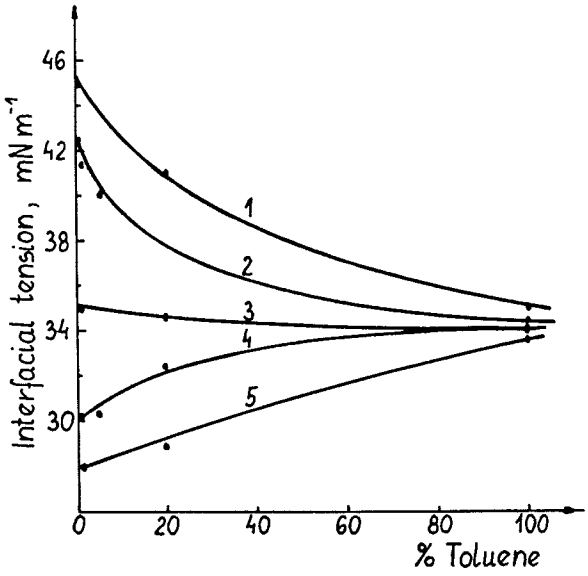

FIG. 2 Effect of toluene upon interfacial tension for various oxime concentrations: (1) 0; (2) 1×10^{-3}, (3) 3×10^{-3}, (4) 5×10^{-3}, and (5) 7×10^{-3} mol·dm^{-3}.

value obtained for the system containing 20% toluene is close to that obtained for the system containing toluene.

The effect of toluene content upon the interfacial tension depends upon the hydroxyoxime concentration. The interfacial tension decreases and rises at hydroxyoxime concentrations below and above $\sim 3 \times 10^{-3}$ mol·dm^{-3}, respectively. In these two regions of hydroxyoxime concentration, the decrease of the interfacial tension is, respectively, stronger and weaker in comparison to the one predicted from the additive rule, i.e., in comparison to the additive values calculated from the appropriate interfacial tensions determined for systems containing only toluene and octane as organic diluents. As a result of this, the surface pressure, $\Pi = \gamma - \gamma_0$, falls when the toluene concentration increases (Fig. 3). Thus, the effect of toluene concentration upon the interfacial tension in the system now being considered is different than that described previously for the less surface active 1-(2′-hydroxy-5′-methylphenyl)-1-decanone oxime.

The interfacial tension isotherms in the system now being considered can be well matched by the Szyszkowski and Temkin equations, the logarithmic polynomial, and the spline function discussed in a previous paper (21). The errors of approximation are low and similar to those previously reported.

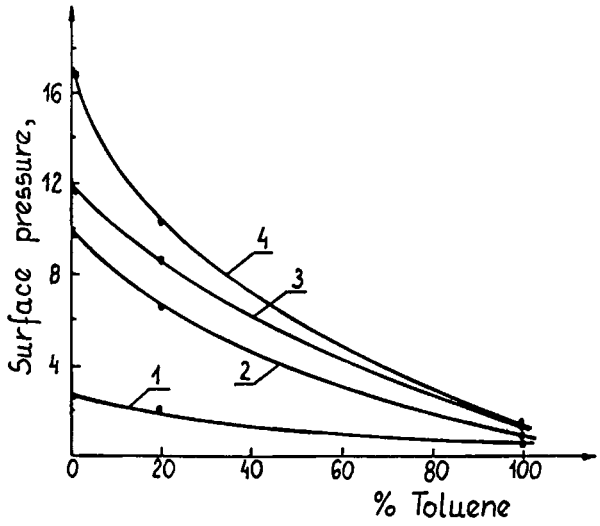

FIG. 3 Effect of toluene upon surface pressure for various oxime concentrations: (1) 1×10^{-3}, (2) 3×10^{-3}, (3) 5×10^{-3}, and (4) 7×10^{-3} mol·dm^{-3}.

The surface excess isotherms are also similar to those reported previously (21). The maximum values of the surface excess, i.e., at the saturated interface, are given in Table 1. Somewhat different values were obtained by using various isotherms. The deviations, however, are typical for such calculations.

Figure 4 demonstrates the effect of toluene concentration upon the surface excess calculated with the use of the Szyszkowski isotherm. For all four cases the surface excess drops sharply when the toluene concentra-

TABLE 1
Surface Excess at the Saturated Interface as Calculated Using Various Equations/Isotherms for the Matching of the Interfacial Tension

	Surface excess (mol·m^2 × 10^6)			
Diluent	Gibbs	Spline	Szyszkowski	Temkin
Octane	3.56	3.17	5.22	4.82
1% Toluene	3.50	3.04	4.24	4.36
5% Toluene	2.96	2.34	3.05	3.68
20% Toluene	2.10	1.62	1.93	2.08
Toluene	0.62	0.59	0.75	0.85

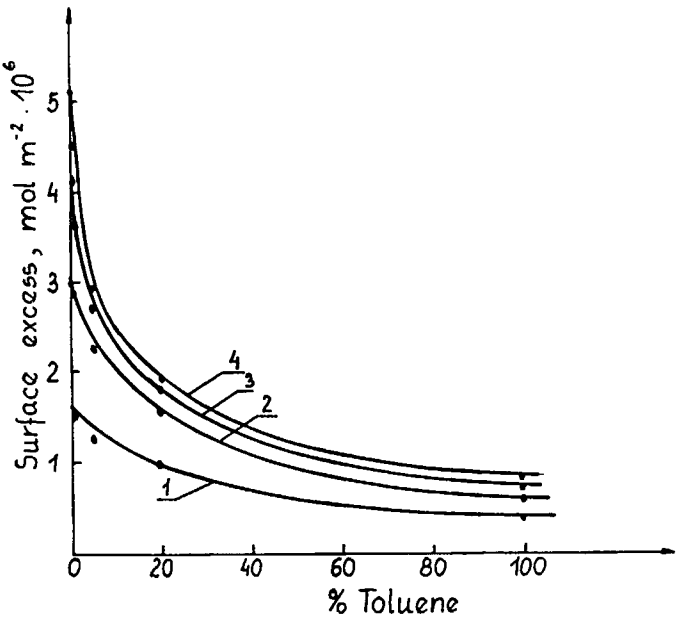

FIG. 4 Effect of toluene upon surface excess computed with the use of the Szyszkowski equation for various oxime concentrations: (1) 1×10^{-3}, (2) 3×10^{-3}, (3) 5×10^{-3}, and (4) 7×10^{-3} mol·dm^{-3}.

tion rises to 20–30%, especially at higher hydroxyoxime concentrations. This means that the interfacial region seems to contain sufficient amounts of toluene molecules which are polar enough to penetrate the adsorption layer and to decrease the interfacial concentration of hydroxyoxime. This conclusion is supported by the data given in Fig. 5.

The same conclusion is reached when other equations/isotherms are used. However, depending upon the isotherm considered, the decrease of the surface excess in the system containing 20% toluene, defined by the relation

$$\Delta\Gamma = \frac{\Gamma_{\text{octane}} - \Gamma_{20\%\text{ toluene}}}{\Gamma_{\text{octane}} - \Gamma_{\text{toluene}}} \times 100\%$$

amounts to 49.7, 60.1, 73.6, and 69.0% for the Gibbs isotherm, the spline function, and the Szyszkowski and Temkin equations, respectively. Thus, the presence of 20% toluene in the organic phase changes the character of the interface probably significantly but is still not fully aromatic. The observed effect is stronger than in the case of systems previously dis-

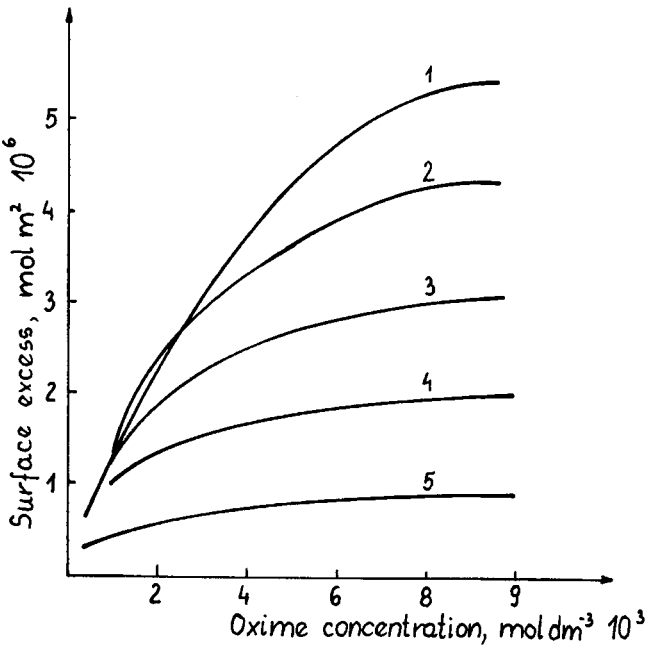

FIG. 5 Surface excess isotherms as computed with the use of the Szyszkowski equation: (1) octane, (2) 1% toluene, (3) 5% toluene, (4) 20% toluene, and (5) toluene.

cussed (21) which contained the less surface active 1-(2′-hydroxy-5′-methylphenyl)-1-decanone oxime.

The results obtained also indicate that it is impossible to predict quantitatively the effect of diluents upon the adsorption characteristics of extractants. Each system must be studied separately.

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