

INFLUENCE OF COMPOSITION OF REACTION MEDIUM OF PROCESS SULPHURIC ACID ALKYLATION OF ISOALKANES BY ALKENES ON ISOBUTANE SOLUBILITY AND ALKYLATE OCTANE NUMBER

A.I. Lutsyk, E.S. Rudakov and G.G. Gundilovich
Institute of Physical-Organic Chemistry and Coal Chemistry
of National Academy Science of Ukraine. Donetsk

Introduction

The process of a sulphuric acid alkylation isoalkanes by the alkenes is one of the main ways of obtaining of the high-octane benzene. The important role in it belongs so-called «red oil» - products of alkenes oligomerization and polymerization which is accumulating during process. The «red oil» is known to play a key role in chemical mechanism of all process, as the tank of hydrogen-ions; and it influences also on viscosity and surface tension of a sulphuric acid, promotes solubility in the sulphuric acid of the isobutane and other isoalkanes.

We investigated the influence of the additions of «red oil» and acid concentration on isobutane solubility and found that the changes of solubility and octane number (ON) of alkylbenzene at modification of reaction medium composition are symbate.

Experimental

The isobutane solubilities was obtained as limiting distribution coefficients between the gas and solution $\alpha = C_{\text{gas}}/C_{\text{sol}}$ at $C_{\text{gas}} \rightarrow 0$ at 284 K. The value α^{-1} is equal to solubility at given isobutane concentration in the gas phase and coincides with the Ostwald coefficient, which is widely used measure of volatile substrates solubility. Measurements were performed by gas-liquid chromatography method. The concentration of isobutane in equal volumes of gas and liquid phases was analysed at condition of equilibrium distribution of substrate between two phases. In each case it was made 5-7 measurements. The reproducibility of results was within $\pm 7-10\%$. «Red oil» was received from the spent sulphuric acid of industrial plants Scientific Industrial Association «Grozneftekhim» and Industrial Association «Permnefteorgsintez» by it water dilution and following benzene extraction.

Results and Discussion

When going from 86 to 98% sulphuric acid the solubility of isobutane increase (value α decrease) 16 time (Fig. 1, Line 4). The introduction of 1-2% «red oil» in the acid produces a sharp, 8-10 times, decrease of α

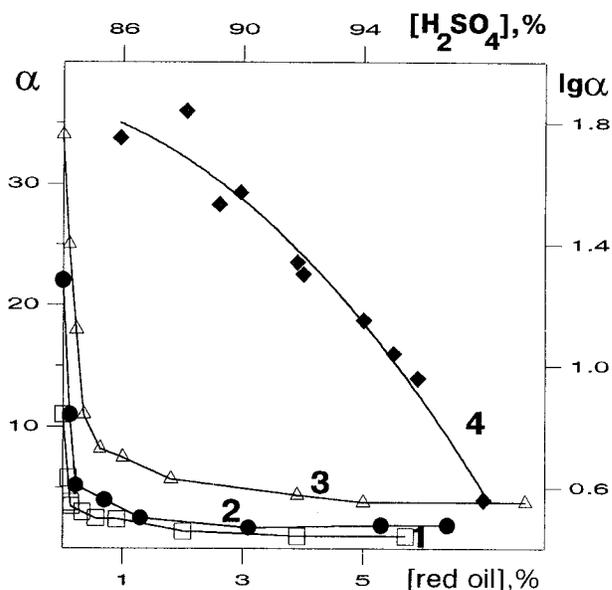
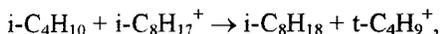


Figure 1. The influence on isobutane solubility at 284 K the concentration of sulphuric acid (line 4) and red oil concentration of in $[\text{H}_2\text{SO}_4] = 95\%$ (1), 91.8% (2) and 89% (3).

(growth solubility) of isobutane and solubility unchanged at the higher «red oil» concentrations (Fig. 1, Lines 1-3).

In accordance with [1-3] reaction of alkylation is induced by the additions of «red oil», and increase of its quantity in reaction medium to 3-3,5% as well as acid concentration to 96-97% induces growing alkylate ON. Taking into account, that for exclusion of induction period a very small quantities «red oil» is enough, it is

possible to assume, that the main reason of «red oil» positive influence in investigated concentration range is salting-in of isobutane. Because this the contribution in general rate of alkylation process of reaction of hydrogen-ion abstraction from isobutane is increased:



and selectivity of process on isooctane increase. At decreasing of isobutane concentration in a solution isooctane cation under oligomerization, cracking and the process becomes less selective.

In Fig.2 there are compared influence of isobutane solubility on ON of alkylation products depending on concentration of a sulphuric acid and «red oil». Value of solubilities in Fig. 2 are received by interpolation of data in Fig. 1, and ON - of data [3]. In case of the «red oil» additions values ON are corrected with respect of the acid dilution.

Linear dependence between of the isobutane solubility and alkylbenzene ON takes place in the "red oil" presence: the increasing of isobutane solubility 2 times cause growing ON by 4 units. In concentration range 89-94% of a sulphuric acid ON increases with growth of H_2SO_4 concentration as well as isobutane solubility. However at further increasing of acid concentration the increase ON is slowed down on comparison with growth of isobutane solubility that, probably, is connected with increase of the contribution of isomerization, oligomerization, cracking and so on.

Conclusions

Thus, salting-in of isobutane plays an essential role in influence of reaction medium composition on process. Results obtained by us are also argument, that

alkylation reaction takes place in reaction medium, instead of on a surface between phases.

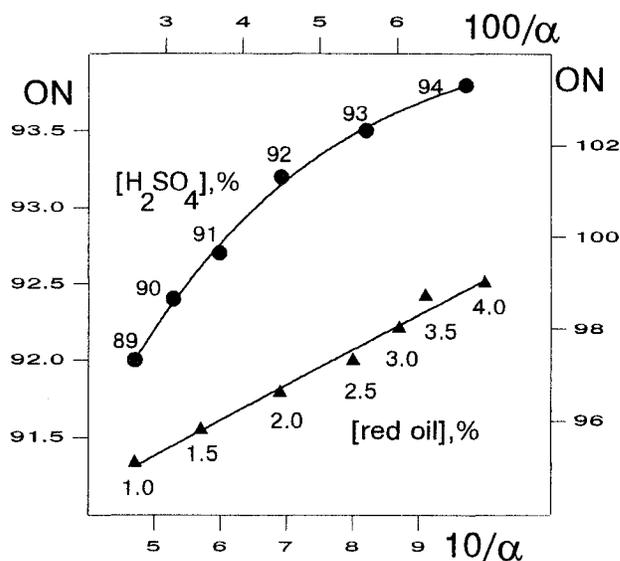


Figure 2. The influence of sulphuric acid concentration and «red oil» additions at $[H_2SO_4] = 95\%$ on isobutane solubility at 284 K and on alkylate octane number.

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