

Interphase Distribution of Triflic Acid and Acid-Soluble Oil in the Isobutane Alkylation with Olefins

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Abstract—The interphase distribution of trifluoromethanesulfonic acid (TfOH) and acid-soluble oil (ASO) in a two-phase liquid mixture of these components and hexane was studied at 25°C. This system is a model for isobutane alkylation reactions with olefins in the presence of liquid acid catalyst partially soluble in hydrocarbons. UV spectrophotometry and acid–base titration were used to measure the total equilibrium concentrations of free and combined TfOH and ASO depending on the molar ratio of ASO to TfOH. The obtained data on the interphase distribution of TfOH and the ASO were explained assuming three equilibria: (1) TfOH interphase distribution (solubility); (2) ASO · 2TfOH complex formation; and (3) ASO · 2TfOH interphase distribution (solubility). An adequate mathematical model was developed on this basis. The equilibrium constant values were determined and the TfOH interphase distribution constant dependence on the phase composition was expressed in analytical form. The mathematical description developed is intended for the calculations of the amounts and compositions of phases and is necessary for the kinetic model design of isobutane alkylation with butenes.

INTRODUCTION

Liquid-phase alkylation is an important process for the production of valuable high-octane alkylates from light olefins and isobutane [1–4].

The so-called acid-soluble oil (ASO) is formed in noticeable quantities as a reaction by-product [5–7].

Previously, it was shown by us that ASO is a mixture of unsaturated oligomers of which the main fragment is a substituted five-member cycle of an approximate general formula $C_{20}H_{36}$ and containing conjugated double bonds [8]. In the presence of the alkylation catalyst, trifluoromethanesulfonic acid (TfOH), ASO forms a complex with the composition ASO · 2TfOH in acid phase and hydrocarbon phase. This complex is very stable in the acid phase and moderately stable in the hydrocarbon phase (the stability constant is equal to $4.35 \times 10^5 \text{ l}^2/\text{mol}^2$ at 25°C).

It is known from the literature that ASO strongly influences the alkylation chemistry and, among other factors, has a noticeable poisoning effect [5–7].

Although the alkylation has already been studied for many years [2], no reliable data on the kinetics and mechanism of this reaction taking into account the ASO influence are practically available from the literature.

It is known that alkylation occurs in a liquid system including two phases: hydrocarbon and acid. Therefore, the mechanistic study and kinetic model development for this reaction requires not only a knowledge of the chemical interaction of ASO with the catalyst but also a taking into account of quantitative data on ASO distribution between acid and organic phases.

Thus, the aim of the present work is to study the interphase distribution equilibrium in the TfOH–ASO–hydrocarbon liquid system at a temperature of 25°C.

EXPERIMENTAL

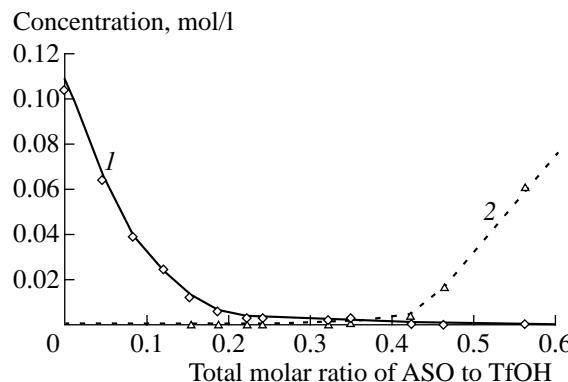
In the course of alkylation, the hydrocarbon phase mainly contains isobutane. Because of the experimental difficulties associated with the high vapor pressure of isobutane, a less volatile hydrocarbon was chosen for the study. Hexane was selected for two reasons: it is substantially less volatile than isobutane, and resistant enough to the TfOH action [8].

The sources, quality, and preparation (when needed) of TfOH, ASO, and hexane were described in [8].

Hexane was purified by treatment with TfOH for 20–30 min before use. Then the acid was separated the hexane was washed with water until it reached a neutral pH, separated again, and distilled over sodium metal in an argon atmosphere.

The total TfOH content (free and complex-bound) in the hydrocarbon phase was determined by common acid–base titration procedure, using a color pH indicator. An appropriate amount of the hydrocarbon phase was mixed with an equal volume of water and titrated with a standard 0.1 M NaOH solution using phenolphthalein as an indicator.

The determination of the total content of ASO (free and complex-bound) was carried out using UV spectrophotometry at 250 nm (in the organic phase) and at 300 nm (in the acid phase) [8]. Based on measurements performed using samples containing a weighed amount



Total TfOH and total ASO content in hydrocarbon phase—measurements and modeling data at 25°C: (1) TfOH total content, (2) TfOH total content by model, (3) ASO total content, and (4) ASO total content by model.

of isolated ASO, the extinction coefficients were determined experimentally [8]. The values are $37.51 \text{ g}^{-1} \text{ cm}^{-1}$ at 250 nm and $42.31 \text{ g}^{-1} \text{ cm}^{-1}$ at 300 nm. The aliquots were diluted to a measurable absorbance level using hexane or TfOH, respectively. A quartz cell of 2 mm optical length was used for the measurements.

Results of experimental runs for equilibrium study of the TfOH–ASO–hexane system (25°C)

| Initial quantities, g | | Found (in hexane) | |
|-----------------------|--------|--------------------------------|------------------------------|
| ASO | TfOH | [TfOH] _{total} , wt % | [ASO] _{total} , g/l |
| 0 | 3.2800 | 2.33 | — |
| 0.2710 | 3.2530 | 1.45 | — |
| 0.4997 | 3.2573 | 0.89 | — |
| 0.7234 | 3.2840 | 0.556 | — |
| 0.9209 | 3.2902 | 0.295 | 0.10 |
| 1.1268 | 3.2660 | 0.161 | 0.15 |
| 1.3457 | 3.2818 | 0.0940 | 0.14 |
| 1.4582 | 3.2729 | 0.102 | 0.15 |
| 1.9499 | 3.2893 | 0.0824 | 0.36 |
| 2.1285 | 3.3135 | 0.0585 | 0.37 |
| 2.5083 | 3.2323 | 0.0496 | 1.5 |
| 2.7901 | 3.2770 | 0.0505 | 5.0 |
| 3.3617 | 3.2550 | 0.0510 | 17.3 |

Note: 50 ml of purified hexane was used in each experiment.

The procedure of establishing equilibrium was carried out as follows. A flask was purged with an argon stream and loaded with an appropriate amount of TfOH, hexane, and ASO (the hexane/TfOH volume ratio was 20 : 1). To prevent the system from moistening, the flask was hermetically sealed, placed in the thermostat at 25°C, and shaken for 30 min. Afterwards, the mixture was left for 15–20 min at 25°C to allow the phases to separate. Longer (>30 min) shaking time did not change the total TfOH and total ASO content in the hydrocarbon phase.

Primary analytical data on the total TfOH content were obtained in weight percents and recalculated into mol/l. This value was assumed to be the sum of free and complex-bound TfOH concentrations [8]

$$[\text{TfOH}]_{\text{total}} = [\text{TfOH}]_{\text{free}} + 2[\text{ASO} \cdot 2\text{TfOH}].$$

Primary analytical data on the total ASO content were obtained in the units of g/l and recalculated into mol/l using 276 as a molar weight value (corresponding to the molecular formula $\text{C}_{20}\text{H}_{36}$) [8]. This value was assumed to be the sum of free and complex-bound ASO concentrations:

$$[\text{ASO}]_{\text{total}} = [\text{ASO}]_{\text{free}} + [\text{ASO} \cdot 2\text{TfOH}].$$

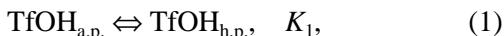
RESULTS AND DISCUSSION

The table summarizes the experimental data obtained in the study of the equilibrium in the TfOH–ASO–hexane system.

By way of primary data processing, the dependences of total TfOH and ASO concentrations in hexane on the ASO/TfOH molar ratio in the starting mixture of ASO and TfOH were determined (see points in the figure). It is seen that TfOH and ASO suppress the solubility of each other. In other words, the presence of ASO strongly decreases the TfOH solubility in hexane and TfOH does the same with respect to ASO. This fact can be a consequence of a low $\text{ASO} \cdot 2\text{TfOH}$ solubility in the hydrocarbon phase. It is interesting that the ASO concentration in the hydrocarbon phase begins to increase somewhat before the ASO/TfOH molar ratio reaches a value of 0.5 corresponding to the complex composition: $\text{ASO} \cdot 2\text{TfOH}$ (see figure).

Based on these results and previous data on TfOH and ASO interaction in the hydrocarbon phase [8], the scheme of equilibrium reactions in this system was proposed and the reactions' constants were calculated [9]. The important feature of an algorithm used is the possibility of handling the so-called observation models. This approach consists in expressing measurable experimental data through the modeled values [9]. In our case, this means the use of the total TfOH and the total ASO concentrations instead of free and complex-bound concentrations separately. In addition, the program takes into account the material balance for all components.

The model is based on three reversible reactions, which are so fast that equilibrium is quickly established:



where the subscripts a.p. and h.p. denote the acid phase and the hydrocarbon phase, respectively.

The concentration equilibrium constants are defined as follows:

$$K_1 = [\text{TfOH}_{\text{h.p.}}]/[\text{TfOH}_{\text{a.p.}}],$$

$$K_2 = [\text{ASO} \cdot 2\text{TfOH}_{\text{h.p.}}]/([\text{ASO}_{\text{h.p.}}][\text{TfOH}_{\text{h.p.}}]^2),$$

$$K_3 = [\text{ASO} \cdot 2\text{TfOH}_{\text{h.p.}}]/[\text{ASO} \cdot 2\text{TfOH}_{\text{a.p.}}],$$

where $[\text{TfOH}_{\text{a.p.}}]$ denotes the concentration of free TfOH in the acid phase (excluding the amount present as ASO \cdot 2TfOH complex).

We found that the simple empirical model designed by us gives a good fit of experimental data and the possibility of calculating the equilibrium compositions at any specified total TfOH and ASO quantities.

In the model proposed, the constant K_1 depends on the medium composition and is empirically described by the equation

$$K_1 = P/1025,$$

$$P = (1 + aX + bX^2) \times 10^{(cY + dY^2)},$$

$$X = \log([\text{TfOH}_{\text{h.p.}}]/0.001674),$$

where

$$0.001674 \leq [\text{TfOH}_{\text{h.p.}}] \leq 0.1 \text{ mol/l},$$

$$Y = [\text{ASO}_{\text{h.p.}}] \text{ at } 0 \leq [\text{ASO}_{\text{h.p.}}] \leq 0.03 \text{ mol/l}.$$

Outside of the specified intervals, X and Y are constant,

$$a = -0.8074,$$

$$b = +3.223,$$

$$c = -10.60 \text{ l/mol},$$

$$d = -257.7 \text{ (l/mol)}^2.$$

In this model, K_2 and K_3 , unlike K_1 , are independent of the medium composition and have the following values:

$$K_2 = 4.35 \times 10^5 \text{ (mol/l)}^{-2},$$

$$K_3 = 1/2013.$$

The figure shows how the model simulates the experimental measurements in the graphical form, and it is seen that the model fits well with available experimental data.

It can be easily seen that K_1 monotonically decreases with an increase in the ASO fraction. The whole composition range must be examined as two intervals. The first one (shown on the left part in the figure) corresponds to the hydrocarbon phase containing undissociated TfOH in solution with very low total ASO content. The TfOH activity coefficient in the hydrocarbon solution in this interval is only affected by the TfOH concentration. In the acid phase, the situation is much more complicated since the TfOH activity depends not only on the concentration but also on the acid–base equilibrium. It is known that TfOH dilution with water is followed by an increase in TfOH dissociation, thereby decreasing the concentration of undissociated TfOH [10]. ASO may be assumed to cause an analogous effect. So the observed dependence of the TfOH interphase distribution constant on the system composition is the result of the interaction of the above conditions.

The second interval (the right part in the figure) corresponds to the ASO solution in the hydrocarbon phase with an insignificant total acid content. Therefore, ASO concentration becomes the main factor affecting the TfOH interphase distribution through the TfOH activity coefficient. For the acid phase, the main factors remain the same: a decrease in the undissociated acid concentration (due to the ASO effect on the acid dissociation degree) and its activity coefficient dependence on the phase composition.

The observed independence of K_3 on the ASO fraction is not surprising. However, it is interesting to note that the solubility of ASO \cdot 2TfOH in the hydrocarbon phase is very low and, consequently, the TfOH content of the hydrocarbon phase is very low as long as there is excess ASO.

More surprising is the independence of K_2 on the phase composition (one should keep in mind that the acid and hydrocarbon phase compositions are functionally related through equilibrium) since TfOH is a reagent for the ASO \cdot 2TfOH complex formation. However, it becomes understandable when taking into account that this equilibrium is only significant for a narrow region of ASO fractions (near the central part in the figure).

Thus, ASO formed as a by-product during alkylation reaction not only causes binding of the acid catalyst [8], but considerably affects the ratio and the composition of the hydrocarbon and acid phases in the TfOH–ASO–hydrocarbon system.

The mathematical description developed by us makes it possible to calculate the phase quantities and compositions depending on variable total amounts of TfOH, ASO, and saturated hydrocarbons. This description is a necessary part of the general alkylation reaction kinetic model.

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