BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2638—2639 (1970)

Mutual and Acid Distribution in Methyl Isobutyl Ketone-Water System

Tatsuya SEKINE, Toshio FUKUSHIMA and Yuko HASEGAWA

Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

(Received March 4, 1970)

Many authors have reported on the mutual and acid distribution equilibria in extraction systems containing carbon-bonded oxygen-type solvents.[1] However, this kind of knowledge about the MIBK (methyl isobutyl ketone)-water system seems to be rather limited. In order to obtain further information on the system, the present authors have carried out the following measurements.

Experimental

Reagents. The MIBK was washed with 0.1 M perchloric acid, water, and 0.1 M sodium hydroxide respectively, and then several times with water. It was dried with anhydrous sodium sulfate and distilled. The distillate at 116°C was used for the experiments. All of the other reagents were of an analytical grade and were used without further purification.

Procedure. All of the procedures were carried out in a thermostatted room at 25°C. Stoppered glass tubes (volume, 20 m*l*) were used to equilibrate the two phases. Organic and aqueous solutions were placed in the tubes and agitated mechanically for one hour. They were then centrifuged at 1000 rpm for 3 min, with some portion being pipetted from each phase. The content of the material in these samples were determined as follows: the MIBK in an aqueous phase was determined by spectrophotometry at 273 mμ. The molar extinction coefficient of MIBK in water at this wavelength was 20, and the absorption obeyed Lambert-Beer's law, at least between 8.5×10^{-3} and 5.0×10^{-2} M. The concentration in the organic phase was calculated from the initial concentration and the aqueous concentration at the equilibrium. The water content was determined by Karl-Fischer titration. The acid concentrations in the organic and aqueous phases were determined by titration with standard barium hydroxide solutions.

Results

The distribution ratio of a material, M, is defined as;

$$D = [\mathrm{M}]_{\mathrm{org,total}}/[\mathrm{M}]_{\mathrm{total}}$$

The percentage concentration is given by the volume percentage. The density of water-saturated MIBK at 25°C is 0.793 g/m*l*; thus, the molar concentration is 7.8 M.

Mutual Distribution. The mutual solubility is 1.8×10^{-1} mol/*l* (18 g/*l*) for MIBK in water and 8.5×10^{-1} mol/*l* (15.3 g/*l*) for water in MIBK. The mutual distribution ratios of these materials have been calculated to be as is shown in Table 1.

Acid Distribution. The distribution ratios of five mineral acids are given in Fig. 1 as a function of the queous acid concentration. The results shown in Fig. 1 agree with the general tendency

---

[1] Y. Marcus and A. S. Kertes, "Ion Exchange and Solvent Extraction of Metal Complexes," Wiley-Interscience, New York (1969), pp. 575, 617.

Table 1. Distribution of materials and effect of dilution with hexane

The figures show the distribution ratio of the materials ($D=[\mathrm{M}]_{org}/[\mathrm{M}]$).

Material	Organic phase		
	MIBK	50% MIBK*	Hexane
MIBK	4.3×10	3.3×10	1.0×10
Water	1.5×10^{-2}	3.1×10^{-3}	7×10^{-6}
$HClO_4$**	1.4×10^{-1}	5.2×10^{-4}	very low

* by the volume percent

** Values obtained when the aqueous concentration is 1.0 M.

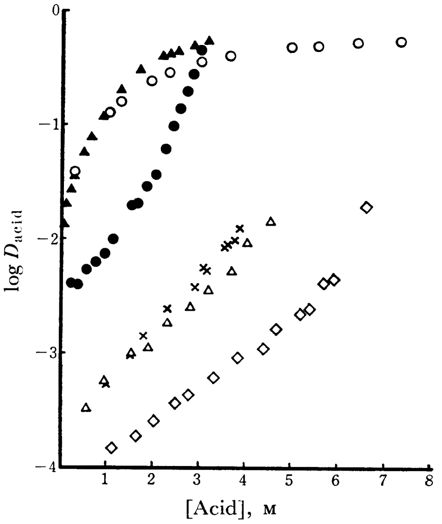

Fig. 1. Distribution of mineral acids as a function of the aqueous acid concentration. The organic phase is undiluted MIBK except the data given by ×.

▲: $HClO_4$, ○: HNO_3, ●: HI, △: HBr, ◇: HCl, ×: $HClO_4$ distributed between 50% MIBK (diluted with hexane) and water

of the distribution of mineral acids, that is, the extraction grows larger in this order; $HClO_4 > HNO_3 > HI > HBr > HCl$.[2]

It was observed that the mutual solubility of the organic and the aqueous phases increases with the increase in the acid concentration; the contact of the same volume of MIBK and the aqueous solution formed a single layer when the initial acid concentration was above 8 M (hydrochloric acid), 5 M (hydrobromic acid), or 3.5 M (perchloric acid and hydroiodic acid), but two immiscible layers were always observed in the nitric acid system, even when the initial acid concentration was 13 M.

Effect of Dilution with *n*-Hexane. The dilution of MIBK with an "inert diluent" changes the distribution of the materials. Figure 2 shows the effect of the dilution with *n*-hexane on the distribution of MIBK and water. The distribution of perchloric acid between 50% (*v*/*v*) MIBK and water is also shown in Fig. 1.

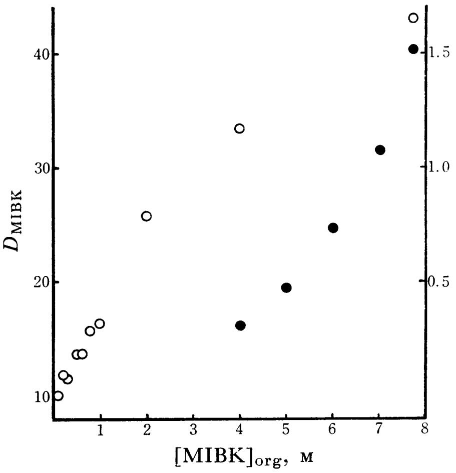

Fig. 2. Effect of the dilution with hexane on the distribution of MIBK (○) and water (●).

The effect of the dilution with *n*-hexane can be summarized as is shown in Table 1. It may be seen from Table 1 that the effect of the dilution can be quite different for different materials. MIBK has been used very often without any dilution. However, the results seem to indicate that dilution with an inert solvent could improve the efficiency of the separation of materials or that of back-extraction in MIBK-water systems.

---

[2] R. M. Diamond and D. G. Tuck, *Progress in Inorganic Chemistry*, **2**, 109 (1960).