Corresponding Member of the Academy of Sciences of the USSR A. V. NIKOLAEV and M. P. MIKHAILOVA

1961

SovietRxiv

Fig. 1. Extraction rays in the system $FeCl_3$–HCl–H_2O–$(C_2H_5)_2O$

Figure 1: Fig. 1. Extraction rays in the system $FeCl_3$–HCl–H_2O–$(C_2H_5)_2O$

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR A. V. NIKOLAEV and M. P. MIKHAILOVA

A METHOD FOR DETERMINING THE COMPOSITION OF AN EXTRACTED COMPLEX

In studies of diagrams of multicomponent extraction systems ([1–3]), the concept of the extraction ray has been introduced—a line along which the composition of the aqueous phase changes in the course of the extraction process. The extraction ray begins at the composition point corresponding to the concentration of the initial solution, and ends at the point corresponding to one of the compositions of the equilibrium aqueous phase.

Fig. 1. Extraction rays in the system $FeCl_3$–HCl–H_2O–$(C_2H_5)_2O$

When considering the question of the form of the extraction ray in four-component systems of the type extracted substance—salting-out agent—water—extractant, we make the following assumptions:

1) The organic extractant is practically insoluble in the aqueous phase, whose composition is therefore described within the limits of a three-component system.

2) In some region of the diagram (in our case, in part of the stratification region), only one compound of definite composition is extracted into the organic phase (the number of extractant molecules entering into the extracted complex is not taken into consideration).

Then it is easy to show that, when the composition of the aqueous phase is expressed in weight (or molecular) percent, the extraction rays will be straight lines intersecting at the point corresponding to the composition of the extracted complex. Thus, radiation of the extraction rays is one of the methods for establishing the composition of the extracted form. The method proposed here for determining the composition of the extracted form is essentially analogous to the well-known Schreinemakers "residue" method, used in determining the composition of a solid phase in three-component systems, and therefore possesses all the generally recognized advantages of that method.

This method was used by us to determine the composition of the extracted form in the previously studied [4] system $FeCl_3$–HCl–H_2O–$(C_2H_5)_2O$.

The second of the assumptions made above means that the extraction proper of water, hydrochloric acid, and ferric chloride into the ether phase in the region of applicability of this method must be small in comparison with their extraction

in the form of the complex $mFeCl_3 \cdot n HCl \cdot pH_2O$. Obviously, this occurs only in extraction from solutions that are comparatively concentrated both in hydrochloric acid and in ferric chloride. At the origin of the coordinates (where the proper extraction of water is large), and near both coordinate axes (where the proper extraction of $FeCl_3$ and HCl cannot be neglected), curvature of the extraction rays must therefore occur. When working in the region of concentrated solutions, the proper extraction of water and HCl can be reduced by preliminary saturation of the ether with a hydrochloric-acid solution of the corresponding concentration. The extraction rays obtained in this way are shown in Fig. 1.

As can be seen from Fig. 1, a considerable portion of the extraction rays is straight and intersects at a single point corresponding to the composition of the extractable complex $HFeCl_4 \cdot 6H_2O$. Curvature of the extraction rays is also noticeable in the regions adjoining the coordinate axes. Thus, $HFeCl_4 \cdot 6H_2O$ is only the dominant form of transfer of ferric chloride into the ether phase over a considerable range of compositions. When the concentration of any component in the aqueous phase is insufficient, the ether phase is likewise depleted in the corresponding component.

We have established the preferential extraction of ferric chloride into diethyl ether in the form $HFeCl_4 \cdot 6H_2O$, which agrees with data obtained by other authors by different methods. The proposition that ferric chloride is extracted from hydrochloric-acid solutions in the form of the complex acid $HFeCl_4$ is generally accepted [5]. The ratio $FeCl_3 : H_2O$ in the organic phase, according to data from various authors, is $1 : 4.5$–6 [4–6].

We believe that the method described here for determining the composition of the extractable form is associated with a minimal number of arbitrary assumptions and, as a result, may find broad application in the study of extraction equilibria.

Institute of Inorganic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

Received
14 XI 1960

CITED LITERATURE

1. A. V. Nikolaev, A. G. Kurnakova, *ZhNKh*, **3**, 1037 (1958).

2. A. V. Nikolaev, *DAN*, **129**, 582 (1959).

3. A. V. Nikolaev, A. G. Kurnakova, I. I. Yakovlev, *ZhNKh*, **8**, 1832 (1960).

4. N. H. Nachtrieb, J. G. Conway, *J. Am. Chem. Soc.*, **70**, 3547 (1948).

5. J. Axelrod, E. H. Swift, *J. Am. Chem. Soc.*, **62**, 33 (1940).

6. R. J. Myers, D. E. Metzler, *J. Am. Chem. Soc.*, **72**, 3767 (1950).

Note: Figure translations are in progress. See original paper for figures.