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Abstract

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POTENTIOMETRIC METHOD OF DIFFERENTIATED TITRATION OF ORGANIC BASES IN METHYL ETHYL KETONE MEDIUM

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Methods of analysis in nonaqueous media have their own essential features and are distinguished by many advantages in comparison with the analysis of aqueous solutions ([1]). Thus, for example, many monomeric and polymeric organic compounds are insoluble in water or are hydrolytically decomposed by water. Those water-soluble organic compounds that are not affected by water are weak electrolytes. In particular, organic bases, as a rule, exhibit very weak basic properties; the numerical values of their $pK > 10$. Therefore, the titration of organic bases in most cases cannot be carried out in aqueous solutions and is usually performed in nonaqueous media.

As solvents for the titration of organic bases, protogenic solvents are usually used: acetic ([1]), formic ([2]), propionic ([3]), butyric ([4]), and chloroacetic ([5]) acids, as well as mixtures of these acids with acetic anhydride ([6]). In doing so, the premise is that protogenic solvents enhance ionization of the base type. Thus, for example, titration of an organic base in anhydrous formic acid medium with perchloric acid dissolved in acetic acid may be represented by the following equations:

$$\mathrm{HCOOH + R(Ar)NH_2 \rightleftharpoons HCOO^- + R(Ar)NH_3^+;}$$

$$\mathrm{HClO_4 + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + ClO_4^-;}$$

$$\mathrm{R(Ar)NH_3^+ + ClO_4^- \rightarrow [R(Ar)NH_3]^+ClO_4^-;}$$

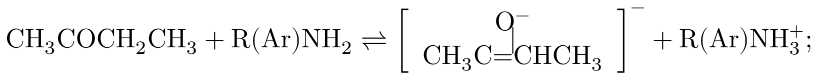
$$\frac{\mathrm{CH_3COOH_2^+ + HCOO^- \rightleftharpoons CH_3COOH + HCOOH}}{\mathrm{R(Ar)NH_2 + HClO_4 \rightarrow R(Ar)NH_3ClO_4}}$$

However, protogenic solvents, along with this, exert a leveling effect on bases, which makes it impossible to carry out differentiated titration of mixtures of bases in their medium. Meanwhile, as our investigations have shown, in ketone media it is possible to carry out differentiated determination of multicomponent mixtures of bases, which is of the greatest theoretical and practical interest. For differentiated titration of two-component mixtures of bases, acetonitrile (^{7}), chloroform (^{8}), and methyl isobutyl ketone (^{9}) have been used.

For the titration of bases in nonaqueous solutions, a solution of perchloric acid in acetic acid or dioxane is usually used. As a titrant we propose, for the first time, a solution of perchloric acid in methyl ethyl ketone medium, which has significant advantages over all previously used titrants.

Experimental Part

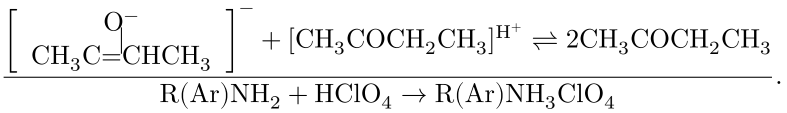
The objects of our investigation were various organic bases, including aliphatic and aromatic primary, secondary, and tertiary amines, quaternary ammonium bases, and their mixtures. The titration of bases was carried out in a medium of anhydrous organic acids, nitriles, ketones, etc. The best results were obtained when titrating in a ketone medium, which has a differentiating effect. Our investigations showed that one of the best differentiating solvents is methyl ethyl ketone. The titration of bases in a methyl ethyl ketone medium with perchloric acid dissolved in methyl ethyl ketone may be represented by the following equations:



$$CH_3COCH_2CH_3 + R(Ar)NH_2 \rightleftharpoons \left[CH_3\overset{O^-}{C}{=}CHCH_3 \right]^- + R(Ar)NH_3^+;$$

$$HClO_4 + CH_3COCH_2CH_3 \rightleftharpoons [CH_3COCH_2CH_3]^{H^+} + ClO_4^-;$$

$$R(Ar)NH_3^+ + ClO_4^- \rightarrow [R(Ar)NH_3]^+ClO_4^-;$$



$$\frac{\left[CH_3\overset{O^-}{C}{=}CHCH_3 \right]^- + [CH_3COCH_2CH_3]^{H^+} \rightleftharpoons 2CH_3COCH_2CH_3}{R(Ar)NH_2 + HClO_4 \rightarrow R(Ar)NH_3ClO_4}.$$

A 0.1 N solution of the titrant is prepared by dissolving 8.5 ml of 72% $HClO_4$ in one liter of purified and dried methyl ethyl ketone and saturating it with dry nitrogen for 5 min.

Fig. 1. Curves of potentiometric titration of organic bases and their mixtures in a methyl ethyl ketone medium. **A** –tetraethylammonium hydroxide –hydrochloric acid, prepared: 1 –in a methyl ethyl ketone medium; 2 –in a dioxane medium; 3 –in an acetic acid medium. **B** –tetraethylammonium hydroxide + piperidine –hydrochloric acid, prepared: 1 –in a methyl ethyl ketone medium; 2 –in a dioxane medium; 3 –in an acetic acid medium. **C** –piperidine + acridine

—hydrochloric acid, prepared: 1 —in a methyl ethyl ketone medium; 2 —in a dioxane medium; 3 —in an acetic acid medium.

Drying and purification of methyl ethyl ketone from acidic impurities are carried out by shaking with anhydrous potassium carbonate and then distilling. The titer of the solution is established with potassium hydrogen phthalate by potentiometric and visual methods in the presence of crystal violet indicator. The titer of the solution remains practically unchanged for a month.

The titration of organic bases and their mixtures was carried out potentiometrically with glass and calomel electrodes. Into a 100-ml titration beaker, 30 ml of methyl ethyl ketone are poured and a stream of dry nitrogen is passed through. A sample of the substance within the range 0.02–0.05 g, weighed on an analytical balance, is transferred to the titration beaker. Stirring is carried out with a magnetic stirrer. The titrated solution is added in 0.1-ml portions, and near the equivalence point in 0.02-ml portions. The titration is continued—

continue until the potential reaches a maximum and remains relatively constant upon further addition of titrant. The equivalence point is determined from the titration curve.

For comparison, simultaneously with the hydrochloric acid solution prepared in methyl ethyl ketone, titration was carried out with acetic-acid and dioxane solutions of hydrochloric acid, which were prepared by methods known from the literature (10).

Comparison of the titration curves of individual bases with hydrochloric acid solutions prepared in methyl ethyl ketone, dioxane, and acetic acid showed that, when titrating with an $HClO_4$ solution prepared in methyl ethyl ketone, larger titration jumps are obtained than in the case of dioxane and, especially, acetic-acid solutions of $HClO_4$. Thus, the titration jump of tetraethylammonium hydroxide with an $HClO_4$ solution prepared in methyl ethyl ketone is 1150 mV (Fig. 1 A, 1), whereas when a dioxane solution is used it is 500 mV (Fig. 1 A, 2), and with the acetic-acid solution only 300 mV (Fig. 1 A, 3). The increase in the titration jumps expands the possibilities for the differentiated determination of mixtures of organic bases.

Fig. 2. Curves of potentiometric titration of multicomponent mixtures of bases in methyl ethyl ketone with hydrochloric acid prepared in methyl ethyl ketone:
1 —tetraethylammonium hydroxide + triethylamine + pyridine;
2 —tetraethylammonium hydroxide + triethylamine + *m*-toluylenediamine;
3 —tetraethylammonium hydroxide + triethylamine + pyridine + *m*-toluylenediamine

With a hydrochloric acid solution prepared in methyl ethyl ketone, various multicomponent mixtures of organic bases were titrated. The titration was carried out in methyl ethyl ketone. In Figs. 1 and 2, titration curves of several mixtures of bases are given as examples. As a result of titration of a mixture of tetraethylammonium hydroxide and piperidine, a curve was obtained (Fig. 1 B, 1) with two sharp titration jumps corresponding to the separate determination of tetraethylammonium hydroxide and piperidine. When this mixture was titrated with a dioxane solution (Fig. 1 B, 2) and with an acetic-acid solution (Fig. 1 B, 3) of hydrochloric acid, curves characterized by a single titration jump were obtained. Analysis of the titration curves shows that when a hydrochloric acid solution prepared in methyl ethyl ketone is used, differentiated determination of the mixture of tetraethylammonium hydroxide with piperidine is achieved, whereas in the case of dioxane and acetic-acid solutions both bases are titrated together. When a mixture of piperidine and acridine was titrated (Fig. 1 C), both with a hydrochloric acid solution in methyl ethyl ketone (Fig. 1 C, 1) and with a dioxane solution of hydrochloric acid (Fig. 1 C, 2), curves with two sharp titration jumps were obtained. The first jump corresponds to neutralization of piperidine, and the second to acridine. Titration with an acetic-acid solution of hydrochloric acid gives a curve (Fig. 1 C, 3) on which the first jump, corresponding to neutralization of piperidine, is only weakly noticeable.

The results of titration in methyl ethyl ketone of three- and four-component mixtures of bases are given in Fig. 2. In titrating a mixture of tetraethylammonium hydroxide, triethylamine, and pyridine, curve 1 was obtained, with three sharp titration jumps; the first jump corresponds to neutralization of tetraethylammonium hydroxide, the second to triethylamine, and the third to pyridine. Curve 2 is the result of titrating a mixture of tetraethylammonium hydroxide, triethylamine, and *m*-toluylenediamine. Four titration jumps are visible on the curve, corresponding to the separate determination of tetraethylammonium hydroxide, triethylamine, and the two amino groups of the diamine molecule.

When pyridine is added to this mixture, we obtain a curve with four titration jumps (3). The first jump corresponds to neutralization of tetraethylammonium hydroxide, the second to triethylamine, and the third to simultaneous neutralization of pyridine and the first amino group of *m*-toluylenediamine; the fourth jump corresponds to neutralization of the second amino group of the diamine.

Analysis of the titration curves shows that, in methyl ethyl ketone, differentiated titration of multicomponent mixtures of organic bases can be carried out. In this case curves with sharp titration jumps are obtained. Thus, the investigation carried out showed that the system methyl ethyl ketone–solution of $HClO_4$ in methyl ethyl ketone can be successfully used for the differentiated determination of organic bases. The error in determining individual compounds is $±$1%, and for individual components of a mixture $±$2%. The indicated method may find broad practical application in various research and industrial laboratories.

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

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