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Abstract

Full Text

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ANALYSIS OF DIAMINES AND THEIR MIXTURES BY TITRATION IN NONAQUEOUS SOLUTIONS

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Diamines are used as monomers for the production of heterochain polyamides ([1]). Although many articles and monographs ([2,3]) have been published on the synthesis of polyamides, insufficient attention has so far been given to the analysis of polyamides, as well as of the starting diamines. Recently, methods for titrating monomeric and polymeric organic compounds in nonaqueous solutions ([4,5]) have been finding increasingly wide application. However, methods for titrating mixtures of diamines in nonaqueous solutions have still not been developed. Volumetric methods for the analysis of diamines in nonaqueous solutions are the most promising, since many diamines are either poorly soluble in water or are very weak electrolytes and therefore are not titrated in aqueous solution. The use of nonaqueous solvents as the medium for titration has a number of substantial advantages ([6]). The chief of these is that in nonaqueous solutions it is possible to determine differentially mixtures of diamines whose dissociation constants are very close.

Fig. 1. Curves of potentiometric titration of individual diamines with 0.1 *N* $HClO_4$ solution in a chloroform–acetonitrile medium (4 : 1); 1 – hexamethylenediamine; 2 –*o*-phenylenediamine; 3 –*m*-phenylenediamine; 4 – *p*-phenylenediamine; 5 –*m*-tolylenediamine; 6 –4,4′-diaminodiphenylmethane; 7 –4,4′-diamino-3,3′-dimethyldiphenylmethane; 8 –*o*-tolidine; 9 –benzidine.

We have developed a potentiometric method for titrating diamines and their

Fig. 2. Potentiometric titration curves of two-component mixtures of diamines in 0.1 N $HClO_4$ solution in a chloroform–acetonitrile medium (4:1); 1 – 4,4′-diaminodiphenylmethane + p-phenylenediamine; 2 – 4,4′-diamino-3,3′-dimethyldiphenylmethane + p-phenylenediamine; 3 – p-phenylenediamine + o-tolidine; 4 –m-toluylenediamine + o-tolidine; 5 – o-phenylenediamine + p-phenylenediamine; 6 –o-phenylenediamine + m-phenylenediamine; 7 –m-phenylenediamine + p-phenylenediamine

Figure 2: Fig. 2. Potentiometric titration curves of two-component mixtures of diamines in 0.1 N $HClO_4$ solution in a chloroform–acetonitrile medium (4:1); 1 –4,4′-diaminodiphenylmethane + p-phenylenediamine; 2 –4,4′-diamino-3,3′-dimethyldiphenylmethane + p-phenylenediamine; 3 –p-phenylenediamine + o-tolidine; 4 –m-toluylenediamine + o-tolidine; 5 –o-phenylenediamine + p-phenylenediamine; 6 –o-phenylenediamine + m-phenylenediamine; 7 –m-phenylenediamine + p-phenylenediamine

mixtures in a medium of nonaqueous solvents.

Experimental Part

The objects of our investigation were hexamethylenediamine, *o,m,p*-phenylenediamines, *m*-tolylenediamine, 4,4′-diamino-diphenylmethane, 4,4′-diamino-3,3′-dimethyldiphenylmethane, *o*-tolidine, benzidine, and others. The titration of diamines was carried out by the potentiometric method with glass and calomel electrodes according to the previously described procedure ([7]). As the titrant acid solution, a solution of hydrochloric acid prepared in methyl ethyl ketone was used ([8]). The following solvents were investigated: acetone, methyl ethyl ketone, acetonitrile, acetic acid esters, chloroform, and also some mixtures of these solvents. The investigations carried out showed that the best medium for titrating diamines is the mixed solvent chloroform–acetonitrile (4 : 1). The combination of chloroform, distinguished by a low dielectric permeability (DP = 4.806), with acetonitrile, characterized by pronounced amphoteric properties, made it possible to obtain a solvent with high differentiating properties. As our experiments showed, in the chloroform –acetonitrile medium it is possible to determine not only individual diamines, but also to titrate mixtures of diamines differentially.

Figure 1 presents titration curves for individual diamines. Analysis of the titration curves shows that, in a chloroform–acetonitrile medium, *m*- and *p*-phenylenediamine, *m*-toluylenediamine, and benzidine (curves 3, 4, 5, 9) are titrated as diacid bases; the titration curves are characterized by two titration jumps, corresponding to separate neutralization of the two amino groups of the diamine molecule.

Fig. 2. Potentiometric titration curves of two-component mixtures of diamines with 0.1 N $HClO_4$ solution in a chloroform–acetonitrile medium (4:1); 1

−4,4′-diaminodiphenylmethane + *p*-phenylenediamine; 2 −4,4′-diamino-3,3′-dimethyldiphenylmethane + *p*-phenylenediamine; 3 −*p*-phenylenediamine + *o*-tolidine; 4 −*m*-toluylenediamine + *o*-tolidine; 5 −*o*-phenylenediamine + *p*-phenylenediamine; 6 −*o*-phenylenediamine + *m*-phenylenediamine; 7 − *m*-phenylenediamine + *p*-phenylenediamine.

Hexamethylenediamine, 4,4′-diaminodiphenylmethane, 4,4′-diamino-3,3′-dimethyldiphenylmethane, and *o*-tolidine are titrated (curves 1, 6, 7, 8) as diacid bases, with simultaneous neutralization of the two amino groups of the diamine occurring. On the titration curves of these diamines, one titration jump is observed, corresponding to the total basicity of the diamine. During titration of *o*-phenylenediamine (curve 2) in a chloroform–acetonitrile medium, only one amino group is neutralized; the second amino group exhibits such weak basic properties that it is not titrated at all.

The results of the quantitative determination of individual diamines are given in Table 1. As can be seen from the data in Table 1, the relative error of determination generally does not exceed $±$1%.

Table 1

Results of the quantitative determination of individual diamines

Substance determined	Chemical formula	Taken, g	Found, g	Relative error, %
Hexamethylenediamine	$H_2N-(CH_2)_6-NH_2$	0.0392	0.0388	−1.0
o-Phenylenediamine	$H_2N-C_6H_4-NH_2$ (*o*)	0.0388	0.0391	+0.8
m-Phenylenediamine	$H_2N-C_6H_4-NH_2$ (*m*)	0.0266	0.0263	−1.1
p-Phenylenediamine	$H_2N-C_6H_4-NH_2$ (*p*)	0.0377	0.0376	−0.2
m-Toluylenediamine	$CH_3-C_6H_3(NH_2)_2$ (*m*)	0.0296	0.0299	+1.0
4,4′-Diaminodiphenylmethane	$H_2N-C_6H_4-CH_2-C_6H_4-NH_2$	0.0415	0.0418	+0.8

Substance determined	Chemical formula	Taken, g	Found, g	Relative error, %
4,4′-Diamino-3,3′-dimethyldiphenylmethane	$H_2N-C_6H_3(CH_3)-CH_2-C_6H_3(CH_3)-NH_2$	0.0409	0.0410	+0.2
o-Tolidine	$H_3C-C_6H_3(NH_2)-C_6H_3(NH_2)-CH_3$	0.0312	0.0315	+1.0
Benzidine	$H_2N-C_6H_4-C_6H_4-NH_2$	0.0293	0.0295	+0.7

The titration curves of two-component mixtures of diamines in a chloroform–acetonitrile medium are presented in Fig. 2. Curves 1 and 2 were obtained with

in the titration of two-component mixtures of *p*-phenylenediamine with 4,4′-diaminodiphenylmethane and 4,4′-diamino-3,3′-dimethyldiphenylmethane. Analysis of the titration curves of the mixtures and their comparison with the titration curves of the individual compounds shows that the first titration jump corresponds to the joint neutralization of the first amino group of *p*-phenylenediamine and the two amino groups of the second component; the second titration jump corresponds to neutralization of the second amino group of *p*-phenylenediamine.

When titrating a mixture of *p*-phenylenediamine and *o*-tolidine, three jumps are visible on the titration curve of the mixture (Fig. 2, 3), corresponding to separate neutralization of the amino groups of *p*-phenylenediamine (the 1st and 2nd jumps) and to joint neutralization of the two amino groups of *o*-tolidine (the 3rd jump). A titration curve of the same character was obtained for a mixture of *m*-toluylenediamine and *o*-tolidine (Fig. 2, 4).

In the chloroform–acetonitrile medium we were able to carry out differential determination of mixtures of phenylenediamine isomers. When titrating a mixture of the *o*- and *p*-isomers of phenylenediamine, joint neutralization first occurs of one amino group of the *o*-isomer and one amino group of the *p*-isomer (the first titration jump on curve 5), and then the second amino group of the *p*-isomer is titrated (the second titration jump on curve 5). The same curve was obtained when titrating a mixture of the *o*- and *m*-isomers (curve 6).

The titration curve of a mixture of the *m*- and *p*-isomers (curve 7) is characterized by two titration jumps, of which the first jump corresponds to joint

neutralization of the first amino groups of both isomers, and the next jump to the second amino groups of these isomers.

The results of the quantitative determination of two-component mixtures of diamines are presented in Table 2. Thus, the investigations carried out showed that in nonaqueous solutions it is possible to titrate mixtures of diamines differentially, which is not feasible in an aqueous medium.

Table 2

Results of the quantitative determination of mixtures of diamines

Substance determined	Taken, g	Found, g	Relative error
4,4′-Diaminodiphenylmethane + *p*-phenylenediamine	0.0211	0.0205	−2.8
4,4′-Diaminodiphenylmethane + *p*-phenylenediamine	0.0299	0.0235	+2.9
4,4′-Diamino-3,3′-dimethyldiphenylmethane + *p*-phenylenediamine	0.0263	0.0258	−1.9
4,4′-Diamino-3,3′-dimethyldiphenylmethane + *p*-phenylenediamine	0.0237	0.0241	+1.6
p-Phenylenediamine + *o*-tolidine	0.0253	0.0245	−3.1
p-Phenylenediamine + *o*-tolidine	0.0234	0.0229	−2.1
m-Toluylenediamine + *o*-tolidine	0.0238	0.0246	+3.3
m-Toluylenediamine + *o*-tolidine	0.0274	0.0277	+1.1

Substance determined	Taken, g	Found, g	Relative error
o-Phenylenediamine + *p*-phenylenediamine	0.0246	0.0245	−0.4
o-Phenylenediamine + *p*-phenylenediamine	0.0258	0.0256	−1.0
o-Phenylenediamine + *m*-phenylenediamine	0.0212	0.0206	−2.8
o-Phenylenediamine + *m*-phenylenediamine	0.0259	0.0255	−2.3

Thus, in a chloroform–acetonitrile (4 : 1) medium, it is possible to quantitatively determine not only individual diamines but also their mixtures. The method developed may find application in research and industrial laboratories.

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