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Determination of individual stability constants of coexisting molecular complexes formed by unresolvable isomers

Motomichi Inoue[a], Claudia Virués[b] and Inocencio Higuera-Ciapara[c]

[a]Departamento de Investigación en Polímeros y Materiales, Universidad de Sonora, Hermosillo, México; [b]Centro de Investigación y Asistencia en Tecnología y Diseño del Estado de Jalisco, A.C., Clúster Científico y Tecnológico Biomimic®, Xalapa, México; [c]Centro de Investigación y Asistencia en Tecnología y Diseño del Estado de Jalisco, A.C., Guadalajara, México
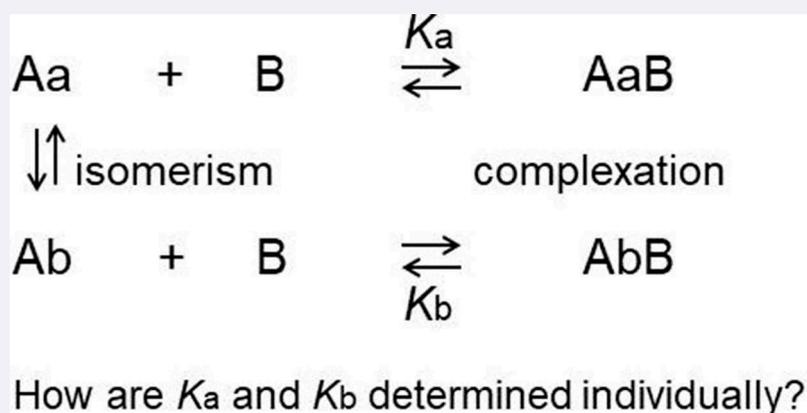
ABSTRACT

Some biogenic substances undergo steric isomerism or tautomerism in which the isomers are unresolvable. Naturally, the isomers are expected to form molecular complexes with distinct stabilities. This paper proposes the method of determining individually the stability constants of complexes formed under isomerisation and complexation equilibria: the NMR titration curves are modelled and formulated for fast and slow isomeric equilibria, the process of least-squares fittings is explained, and the application to supramolecular complexation of unresolvable isomers is discussed as compared with NMR titration data reported for α- and β-D-glucosamine anomers.

Introduction

Competitive complexation proceeds in a solution that involves multiple metal ions together with a ligand. The species distribution in such a system can be calculated when the proper stability constant is known for each of the metal complexes (1). This principle holds for supramolecular complexes as well. In the complexation of isomers, the mole fractions of their complexes can be calculated for the coexisting systems, if the isomers can be separated so that the stability constant of each complex can be determined independently. In certain steric isomerism or tautomerism, isomers cannot be resolved even when they are detected separately by NMR. For the complexation of such an unresolvable isomeric pair, the stability constants should be determined under the competitive equilibria that are illustrated in Figure 1: compound A undergoes isomerism to exist as isomers Aa and Ab, which react with compound B to yield complexes AaB and AbB, respectively. An experimental example has been presented by our previous study of the complexation of α- and β-D-glucosamine anomers with capsaicin (2). The ¹H NMR signals of the two anomers are detected separately, and are shifted with increasing capsaicin concentration, as represented in Figure 2. From the titration curves, the stability constants of the complexes have been determined individually on the basis of an assumed model, demonstrating that the complex of α-glucosamine is more stable than the β-anomer complex. As exemplified by this NMR study, the molecular