

On the Effect of Organic Solvent Composition on the pH of Buffered HPLC Mobile Phases and the pK_a of Analytes—A Review

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Abstract: A review about the analyte pK_a and buffer pH variations in RP-HPLC mobile phases with the changes in the organic modifier content (acetonitrile or methanol) is presented. A model to accurately predict the pH of particular mobile phases for several commonly used buffers (acetic, citric and phosphoric acid and ammonia systems) in acetonitrile-water and methanol-water mixtures is described. Linear relationships are also presented for several families of acid-base compounds (aromatic and aliphatic carboxylic acids, phenols, amines and pyridines) to estimate pK_a values of analytes in methanol-water and acetonitrile-water from their corresponding aqueous pK_a . From both, the estimated pH of the mobile phase and the estimated pK_a of acid-base analytes, it is possible to predict their degree of ionization and, therefore, the analyte chromatographic retention.

Keywords: Mobile phase composition, methanol–water mixtures, acetonitrile–water mixtures, pH, pK_a , buffers, chromatographic retention, ionization degree

INTRODUCTION

The use of buffered mobile phases in liquid chromatography is very common for separation of analytes with acid-base properties. For monoprotic acids

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