

Nitromethane as solvent in capillary electrophoresis

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Available online 16 March 2005

Abstract

Nitromethane has several properties that make it an interesting solvent for capillary electrophoresis especially for lipophilic analytes that are not sufficiently soluble in water: freezing and boiling points are suitable for laboratory conditions, low viscosity leads to favourable electrophoretic mobilities, or an intermediate dielectric constant enables dissolution of electrolytes. In the present work we investigate the change of electrophoretically relevant analyte properties – mobilities and pK_a values – in nitromethane in dependence on the most important experimental conditions determined by the background electrolyte: the ionic strength, I , and the pH. It was found that the mobility decreases with increasing ionic strength (by, e.g. up to 30% from $I=0$ to 50 mmol/L) according to theory. An appropriate pH scale is established by the aid of applying different concentration ratios of a buffer acid with known pK_a and its conjugate base. The mobility of the anionic analytes (from weak neutral acids) depends on the pH with the typical sigmoidal curve in accordance with theory. The pK_a of neutral acids derived from these curves is shifted by as much as 14 pK units in nitromethane compared to water. Both findings confirm the agreement of the electrophoretic behaviour of the analytes with theories of electrolyte solutions. Separation of several neutral analytes was demonstrated upon formation of charged complexes due to heteroconjugation with chloride as ionic constituent of the background electrolyte.

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Keywords: Capillary electrophoresis; Nitromethane; Organic solvent; Contactless conductivity detection; Non-aqueous; UV detection; Heteroconjugation; pK_a shift; Mobility

1. Introduction

Although water is by far the most common solvent in capillary electrophoresis (CE), it has the disadvantage that lipophilic compounds may exhibit a low solubility in it, and the amount of analytes dissolved often does not reach the limit of detection. In such cases it is favourable to substitute water by aqueous–organic mixtures or organic solvents. It is obvious that in some cases these solvent systems might also improve the separation selectivity (though the case can be vice versa as well). Most probably the effect of organic solvents on separation efficiency is overestimated, as has been discussed in detail in a previous paper [1]. Methanol and acetonitrile are certainly the most common members of

the class of organic solvents for solutions of analytes and of the constituents of the background electrolyte (BGE). However, not only are these two solvents used in CE, but also a number of other protic or dipolar aprotic solvents (see, e.g. ref. [2]).

Nitromethane (NM) has not been applied as solvent to CE so far; only one recent application dealt with the separation of chlorophenols in binary mixtures of water with NM [3]. However, NM is widely used, e.g. as extraction solvent or as a reaction medium. It has a broad application range in organic synthesis (e.g. pharmaceuticals, pesticides, fibres, etc.) and as stabilisation agent, e.g. for halogenated hydrocarbons. It is also used as a fuel for high performance engines (e.g. in drag racing) because of the low amount of air it needs to burn. In addition, NM is also used for cleaning electronic circuit boards and in explosive industry. It should be noted, however, that NM itself is not classified as an explosive, but an explosive is formed only when it is mixed together with inorganic nitrite [4].

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