



Application of Electrochemistry to Determination of Transfer Gibbs Energies and Autoprotolysis Constants for Aqueous Mixtures of Dimethyl Sulfoxide

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Abstract

A practical potentiometric method was applied successfully to experimental electrochemical data in order to determine the autoprotolysis constants (pK_{ap}) of water + dimethyl sulfoxide mixtures containing 0-90 % of DMSO by volume at 25° C and 0.1 M ionic strength was maintained in each mixture by NaClO₄ solution. The results indicated that water-DMSO mixtures are more basic media than pure water and the pK_{ap} value of media increases with addition of DMSO. The variation of pK_{ap} value over the media composition range was explained by a linear solvation energy relationship. Thus the correlations between pK_{ap} values and the Kamlet-Taft parameters were analyzed by means of multiple linear regressions. The equations obtained can be used to estimate the autoprotolysis constants in a water-DMSO solvent from the relationship between the pK_{ap} values and the Kamlet-Taft parameters of the solvent. The literature values of transfer Gibbs free energies of H⁺, $\Delta_t G^0(H^+)$, have been applied successfully to quantify the activity of hydroxide ion ($\Delta_t G^0(H^-)$) from the pure water solvent to any binary mixtures which is critical in understanding the organic reactivity in solution.

Keywords: water-DMSO mixture solvent, autoprotolysis constant, Gibbs Energies of Transfer.

Introduction

The aqueous organic solvent mixtures such as water-DMSO mixtures are appropriate reaction media in different area of chemistry due to specific properties and better ability to dissolve more compounds than pure solvents [1]. The availability and diversity of these reaction media powerfully increase from

the combination of pure water and organic solvents in binary mixtures. DMSO is highly polar, very weakly acidic and fairly basic, but while water is also highly polar but acidic and negligibly basic. DMSO can interact strongly and specifically with water through hydrogen bonds. So DMSO is miscible like alcohol with water in all proportions. Aqueous mixtures

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