EFFECTS OF COUNTERIONS ON SOLID SUPPORTED ANALYTICAL DERIVATIZATIONS

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Solid phase analytical derivatization reduces the duty cycle of sample preparation by combining the extraction and derivatization steps. These reactions are applicable to combinations of acidic, basic or neutral analytes and reagents. Based on the hypothesis that the reaction occurs on the solid phase, we investigated the effects of counter-ions to enhance the sorption of the ionized species. Addition of heptane sulfonic acid to the reaction mixture for derivatization of malonyldialdehyde with DANSYLhydrazine increased the reaction rate. The proposed mechanism was that the formation of an ion-pair between the hydrazine and the sulfonic acid enhanced the sorption of the reagent, which allowed the derivatization of this polar, water-soluble analyte on the surface. We also investigated the converse situation with a lipophilic reagent, PFBBr and hydrophilic analyte. Addition of ammonium cations enhanced the reaction rate for derivatization of phenols and carboxylic acids relative to reaction with NaOH as the base. For instance, in this condition there was no detectable recovery of the PFBether of phenol but with ammonium hydroxide the ether was detected in high yield. To the best of our knowledge this is the first report of direct a simultaneous extraction and derivatization of this polar analyte from water. Studies on the combination of lipophilic analytes (ketosteroids) and hydrophilic reagent (pentafluorobenzylhydroxylamine hydrochloride) produced an unexpected relationship between the molecular weight of the alkylsulphonic acid counter ion and the reaction rate for oximation of the keto groups. A mechanism based on the hypothesis of reactions on the surface is proposed to explain these results.