Abstract

A series of polymeric ionic liquids (PILs) possessing varied chemical makeup and composition were applied as selective solid-phase microextraction (SPME) sorbent coatings for the analysis of genotoxic impurities (GTIs) and related structurally alerting compounds, namely, alkyl halides and aromatics. In addition to exploiting two previously synthesized PILs as selective coatings, two new PILs, namely, N,N-didecyl-N-methyl-D-glucaminium poly(2-methyl-acrylic acid 2-[1-(3-{2-[2-(3-trifluoromethanesulfonylamino-propoxy)-ethoxy]-ethoxy}-propylamino)-vinylamino]-ethyl ester) (poly([DDMGlu][MTFSI])), and poly(1-vinyl-3-propylphenylimidazolium) chloride (poly([VPPIM][Cl])), were designed, synthesized, and their selectivity examined in the extraction of the selected analytes. The glucaminium-based coating was developed to exploit the hydrogen bond-acidic hydroxyl groups within the carbohydrate moiety of the PIL in addition to dispersive capabilities resulting from the cation and anion. The poly([VPPIM][Cl]) coating was tailored to possess π-π interaction capabilities through the phenyl functionality while also containing the hydrogen bond-basic chloride anion. Calibration studies were performed via headspace extraction to determine the sensitivity and limit of detection (LOD) for all analytes with respect to each PIL-based sorbent coating and compared to the polyacrylate (PA) and polydimethylsiloxane (PDMS) sorbent coatings. PILs containing the chloride anion exhibited high selectivity for aniline-based compounds. The glucaminium-based PIL exhibited good sensitivity for larger aliphatic alkyl halides. The poly(1-4-vinylbenzyl-3-hexadecylimidazolium) bis[(trifluoromethyl)sulfonyl] imide (poly([VBHDIM][NTf_2])) PIL coating demonstrated superior selectivity for larger aliphatic/aromatic analytes. The LODs of both commercial and PIL-based coatings for the two classes of GTIs ranged from low part-per-billion (ppb) to mid part-per-trillion (ppt) levels. Recovery studies were performed at two concentration levels within the linear range in order to validate the accuracy of the technique. Scanning electron micrographs were obtained for three PIL-based coatings following approximately 70 extraction/desorption steps, wherein the fiber coatings were observed to be largely smooth and intact.