

and dimethylaminoethyl methacrylate are synthetic cationic monomers with basicity due to amino groups (Koetting et al. 2015). The importance of carboxylic acids and amino functional groups in determining swelling/deswelling and overall charge (pK_a) of the molecule lead scientists to hypothesizing a role for amino acid molecules in hydrogel applications.

Amino acids are excellent monomers for controlling pH dependent self-assembly and hydrogelation. Comprising of at least one amino group and one acid functionality as a minimum, a variety of properties and charge/ pK_a are endowed by variation in respective R-groups. The naturally occurring amino acids aspartic acid and glutamic acid become ionized in solutions with a pH greater than their respective pK_a . Basic amino acids, for example histidine, arginine and lysine, provide the potential for cationic behaviour. Charged amino acids are utilized to create highly specific charge-charge interactions to drive (opposing charges) or prevent (equal charge) self-assembly and hydrogel formation (Fig. 1) (McCloskey et al. 2014). The influence of the amino acid R-group is increased further when respective amino and carboxylic acid groups (attached to the α -carbon) covalently attach via a condensation reaction forming an amide bond and the peptide chain.

Biomolecules are also able to self-organize and assemble into nanostructures. The formation of a nanofibrous architecture can allow supramolecular hydrogel formation. The Schneider group demonstrated that pH could be utilized as a trigger for the self-assembly of β -hairpin peptides forming a cytocompatible, mechanically

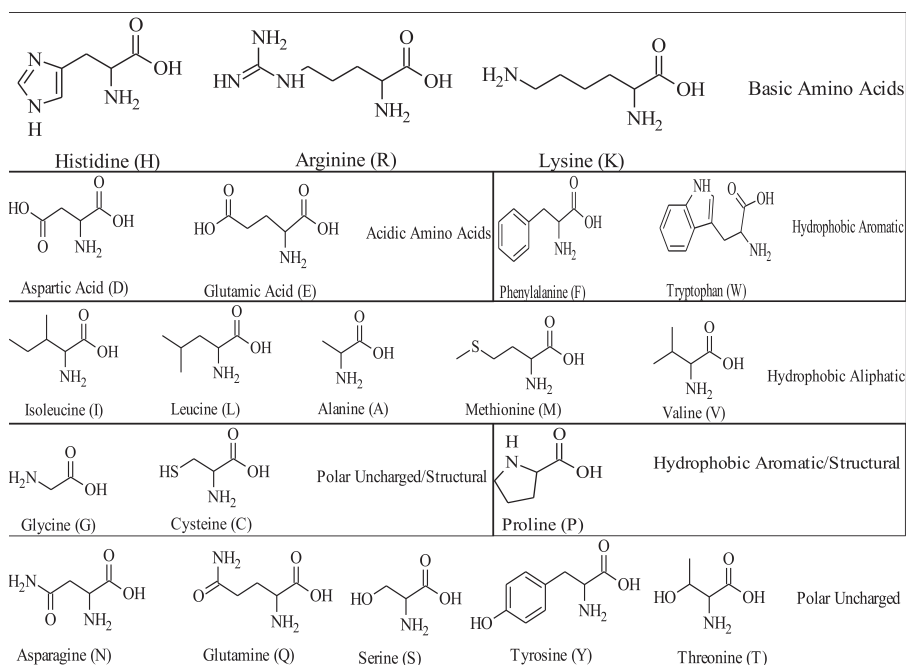


Fig. 1. The structures and codes for the 20 naturally occurring amino acids. Each amino acid shares a carboxylic acid ($-\text{COOH}$) and a primary amine group ($-\text{NH}_2$). The properties of the individual amino acids are governed by the nature and functionality of the R-group attached to the α -carbon. Adapted from (McCloskey et al. 2014).