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ORIGINAL ARTICLE

Investigating the parameters affecting the adsorption of amino acids onto AgCl nanoparticles with different surface charges

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Abstract In this paper, adsorption behaviors of typical neutral (alanine), acidic (glutamic acid) and basic (lysine) amino acids onto the surfaces of neutral as well as positively and negatively charged silver chloride nanoparticles were examined. Silver chloride nanoparticles with different charges and different water content were synthesized by reverse micelle method. The adsorptions of the above mentioned amino acids onto the surfaces of differently charged silver chloride nanoparticles were found to depend strongly on various parameters including pH of the aqueous solution, type of amino acid, water to surfactant mole ratio, and type of charges on the surfaces of silver chloride nanoparticles. It was found that the interaction of $-NH_3^+$ groups of the amino acids with silver ion could be a driving force for adsorption of amino acids. Alanine and Glutamic acid showed almost similar trend for being adsorbed on the surface of silver chloride nanoparticles. Electrostatic interaction, hydrophobicity of both nanoparticle and amino acid, complex formation between amine group and silver ion, interaction between protonated amine and silver ion as well as the number of nanoparticles per unit volume of solution were considered for interpreting the observed results.

Keywords Amino acid · AgCl nanoparticle · Microemulsion · Alanine · Glutamic acid · Lysine

Introduction

Amino acids are amphoteric compounds that can exist in cationic, anionic, and zwitterionic forms depending on the pH of the aqueous solution. The α-amino acids are known to be the basic building blocks of peptides and proteins as well as the biosynthetic precursors of many biologically relevant molecules and metabolic fuels (Horton et al. 2002). Amino acids are of great importance in many fields, including solid-phase peptide synthesis (Meng et al. 2004) and production of pharmaceutical as well as agrochemical compounds and biomedical sensors (Vinu et al. 2006). These applications generally require amino acids to be adsorbed in the form of well-ordered layers onto a solid surface (Vinu et al. 2006). Understanding the mechanism by which proteins or amino acids adsorb onto an inorganic surface is a major concern in manufacturing of bioproducts and in various biotechnological fields, such as the preparation of biocompatible materials and biosensors (Nakanishi et al. 2001). Moreover, the adsorption of amino acids on mineral surfaces may have played an important role in understanding the origin of life (Lambert 2008; Churchill et al. 2004). Therefore, various researches have been carried out in different disciplines to investigate their adsorptions on various materials including mesoporous materials (Qiang et al. 2008); minerals (Ikahsan et al. 2004); activated carbon (Vinu et al. 2006); TiO_2 (Roddick-Lanzilotta and McQuillan 2000) and gold nanoparticles (Hoefling et al. 2010; Sethi and Marc 2010). On the other hand, elucidating the adsorption mechanisms of amino acids can not only contribute to a better understanding for the adsorption of proteins or enzymes on solid materials but also provide sufficient theoretical guides for the practical processes such as separation or purification of amino acids (Krohn and Tsapatsis 2005, 2006). In this regard,

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partitioning of amino acids into various phases including ionic liquids and reverse micelles has also been studied (Absalan et al. 2010; Wang et al. 2004).

The abilities of engineered peptides and antibodies for recognizing specific inorganic surfaces have attracted attentions of researchers to the interaction of proteins with inorganic surfaces which promise their applications in nanobiotechnology, biomedicine and other related scientific fields (Schnirman et al. 2006; Sarikaya et al. 2003). However, the adsorption mechanism has not yet been clarified mainly due to the large three-dimensional structure of polypeptide chains with various amino acid residues. Generally, depending on the degree of protonation of amine group, $-NH_2$, and deprotonation of either carboxylic, $-COOH$, or protonated amine groups, $-NH_3{}^+$, amino acids show different adsorption behaviors such as electrostatic attraction, covalent bonding, hydrogen bonding, and hydrophobic interactions (Krohn and Tsapatsis 2005, 2006; Lambert 2008; Kitadai et al. 2009). This behavior often makes data interpretation difficult, and in some cases inconsistent conditions have been reported (Kitadai et al. 2009). At present, limited analytical techniques are available to probe these interactions, especially for materials dispersed in solution (Sethi and Marc 2010; Imamura et al. 2007). About two decades ago, some researchers reported that nanoparticles are technologically important in satisfying the need for materials with specific chemical, physical, and electronic properties (Pileni 1988; Switzer 1988). Biologically active molecules such as amino acids, peptides and proteins are usually attached to nanoparticles to improve their bio-specificity and to expand application potentialities of these types of systems in biological and medical sciences. Understanding the surface orientation and interactions between biomolecules and nanoparticles is an important concern in order to determine their effects on the final structure and activity. Considering this, investigating the interaction of nanoparticles with amino acids has been thought to provide interesting information as it is of concern in biology, biochemistry and medicine. The increase in the surface area-to-volume ratio, as the particle gets smaller, leads to an increasing dominance of the properties of the particle. These properties provide unique application for the particle in both science and technology. In this regard, a decade ago, nanoparticles were studied because of their size-dependent physical and chemical properties. Nanoparticles are generally defined as discrete particles between 1 and 100 nm in size. The properties of nanoparticles are significantly different from those of atoms or bulk materials so that the controlling of these properties can lead to new science as well as new products, devices and technologies. In this regard, the design, synthesis, and application of biocompatible nanoparticles provide enormous improvement in the biological and biomedical applications. The adsorption of proteins, for example, on a particle surface is of particular importance in many industries including bio-separation processes. Despite the protein-surface interactions (Gray 2004), the underlying chemical principles are still not fully understood. Also, there is a significant interest in the development of antimicrobial materials and surfaces for applications in the health and biomedical device industry, food industry, and personal hygiene industry. Among inorganic nanoparticles, silver halide nanoparticles have attracted considerable attention because of the relative ease of synthesis and their strong antimicrobial activity (Zachariadis et al. 2004; Sambhy et al. 2006) as well as providing constant concentration of biocidal Ag^+ ions in aqueous environments (Lide 2002). Most silver-containing antimicrobial polymers consist of highly water-soluble silver salts or silver (I) complexes (McDonnell et al. 2005; Melaiye et al. 2005). Substitution by a sparingly soluble silver salt in place of elemental silver should significantly increase the rate of generation of biocidal Ag^+ ion over that from elemental silver, while it should be possible to control the rate of release of Ag^+ ion into the liquid phase by size of the embedded silver halide particles.

Regarding the above demands, the adsorption characteristics of acidic (glutamic acid), basic (lysine) and neutral (alanine) amino acids while adsorbed onto differently charged AgCl nanoparticle surfaces have been investigated as models because amino acids are the building blocks of proteins and peptides so their interactions with nanoparticles that consist of the same chemical constituents but different charges may help researchers not only to elucidate the possible mechanism of adsorption of proteins and peptides but also to provide new approaches for their separation or purification. The AgCl nanoparticles were synthesized in microemulsion systems composed of AOT/*n*-heptane/water. Water-in-oil microemulsions (reverse micelles) provide a convenient medium for the preparation of nanoparticles. They have the advantage of easy manipulation of the particle size (Pillai et al. 1995) and provide a highly homogeneous product due to efficient mixing at the molecular level (Vaucher et al. 2002) and wide applications in semiconductors technology, photographic industry, drug delivery and separation science (Pramanik et al. 2007; Jeunieau et al. 2000; Jeunieau and Nagy 1999a, b).

Materials and methods

Instruments

Ultraviolet absorption spectra were recorded against the solvent blank at room temperature using Ultrospec 4000 spectrophotometer (Pharmacia Biotech) operated in double-beam mode. The pH measurements were made with a Metrohm 780 pH meter using a combined glass electrode. Transmission electron microscope (Philips CM 10TEM) was used for recording of TEM images. An ultrasonic cleaner model CD-4800 (China) was used to achieve the stable state of the microemulsion.

Reagents

Sodium bis-2-ethylhexylsulfosuccinate (AOT) with a purity of 99 % and hydrindantin dehydrate were purchased from Sigma Company. Alanine, glutamic acid, lysine dihydrate, ninhydrin, *n*-heptane, hydrindantin dehydrate, silver nitrate, potassium chloride, potassium nitrate, potassium hydroxide, and nitric acid used in this study were of the highest purity available from Merck Chemical Company and were used without further purification. Doubly distilled deionized water (0.5 µS cm^{-1}) was used throughout the work.

Procedure

The AgCl nanoparticles were synthesized in microemulsion systems composed of AOT/*n*-heptane/water (Cabos and Delord 1979). Two microemulsions were prepared, one with a mixture of 15 mL of 0.12 M AOT in *n*-heptane and 100 µL of 0.063 M silver nitrate. The second microemulsion was prepared with a mixture of 15 mL of 0.12 M AOT in *n*-heptane and 100 µL of 0.063 M potassium chloride. The microemulsions were mixed to prepare the neutral silver chloride nanoparticles (denoted as [NanoAgCl]). Considering a density of 1.0 g/mL for each microemulsion, the $[H_2O]/[AOT]$ ratio (denoted as W in the text) was calculated and found to be 3.1 for each microemulsion solution. Using 200 and 300 µL of either silver nitrate or potassium chloride, microemulsions with W values of 6.1 and 9.1 were also prepared to synthesis nanoparticles with larger sizes.

The same procedure as above was used for the synthesis of charged AgCl nanoparticles but 0.094 M silver nitrate (containing 50 % excess silver ion than its 0.063 M solution) was used for preparing positively charged silver chloride nanoparticles (denoted as $[NanoAgCl]^+$). For negatively charged nanoparticles (denoted as $[NanoAgCl]^-$), 0.094 M potassium chloride (containing 50 % excess chloride ion than its 0.063 M solution) was used. Charged nanoparticles with different particle sizes were prepared by solutions having different values of W as explained in the previous paragraph. Figure 1 shows a typical TEM photographs of the AgCl nanoparticles with different charges for $W = 6.1$. All procedures were performed in dark from the time that the nanoparticles were produced till measuring the adsorption of amino acids on

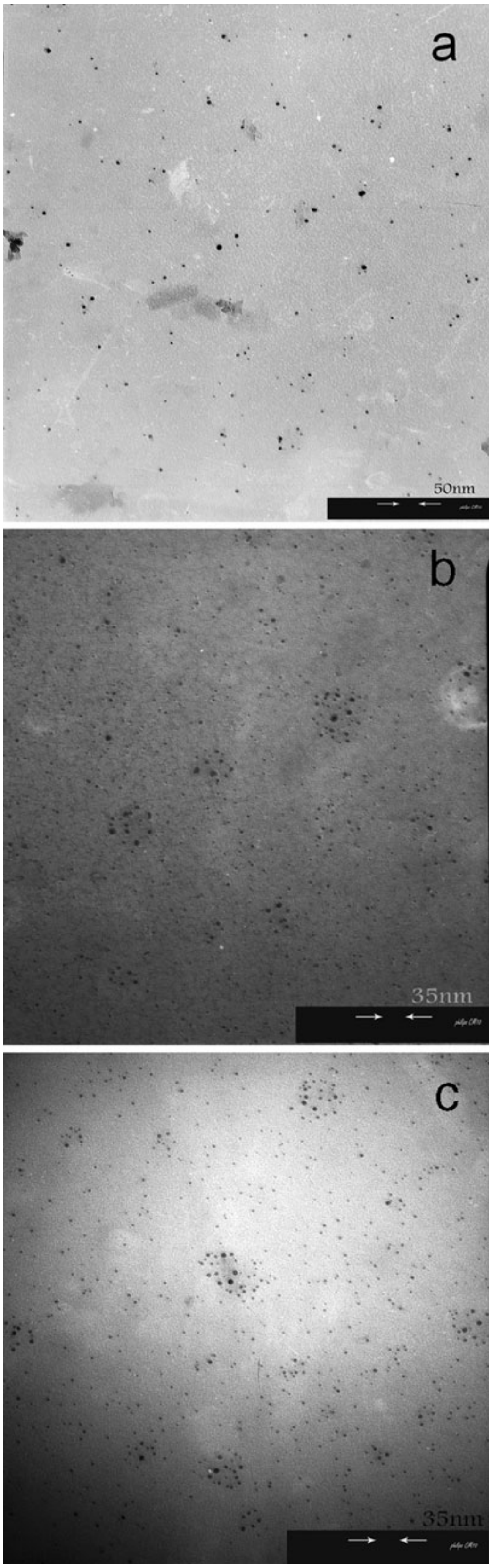


Fig. 1 TEM photographs ($W = 6.1$) for: negatively charged silver chloride nanoparticles (**a**), positively charged silver chloride nanoparticles (**b**), and neutral silver chloride nanoparticles, (**c**)

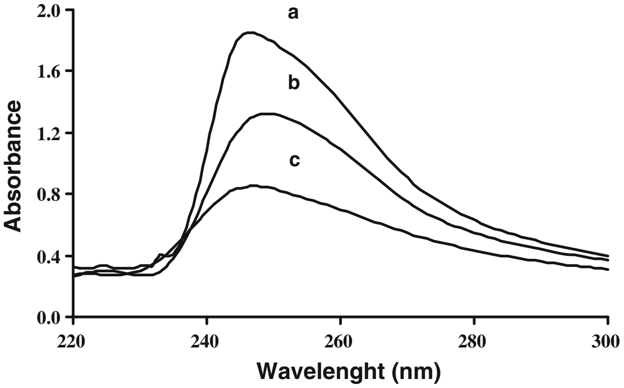


Fig. 2 The UV–Vis absorption spectra of positively charged silver chloride nanoparticles with *W* values of: 3.1 (**a**), 6.1 (**b**), and 9.1 (**c**)

the surface of the nanoparticles to avoid decomposition of silver salt. Moreover, Fig. 2 presents a typical UV–Vis spectrum of AgCl nanoparticles. As no peaks appeared around 400 nm wavelength, it is concluded that no Ag formed by the reduction of Ag^+ in these systems.

The extraction procedure was carried out by mixing equal volumes of AgCl nanoparticles with individual aqueous amino acid solutions (2.0×10^{-3} M) in a glass test tube at 24 ± 1 °C. The ionic strengths of the aqueous solutions were kept constant using 0.10 M potassium nitrate for all pH values. The carefully stoppered glass test tube was vigorously stirred with magnetic stirrer for 30 min and then two phases were carefully separated using a centrifuge device. The partition coefficients of amino acids between nanoparticle phase and the aqueous solution were calculated as: $P_{\mathrm{N/W}} = (C_{\mathrm{i}} - C_{\mathrm{f}})\ V_{\mathrm{aq}}/C_{\mathrm{f}}V_{\mathrm{n}}$ where C_{i} and C_{f} refer to the initial and final concentrations of the amino acid in aqueous phase; V_{aq} refers to the volume of the aqueous phase containing amino acid and V_{n} shows the volume of the nanoparticle phase. The final concentration of amino acids in aqueous phase was measured in duplicate by ninhydrin method (Sun et al. 2006). According to this method, the amino acid solution is mixed with a solution prepared by dissolving 2.0 g ninhydrin and 0.30 g hydrindantin in 75 ml DMSO and 25 ml of sodium acetate buffer in pH 6.4. The mixture is heated up in a boiling water bath for a period of 5 min, and then it is immediately cooled in an ice-bath. The absorbance of the reaction mixture is measured with spectrophotometer at 575 nm. It should be mentioned that the order of reagent addition has no effect on the result of this experiment as was tested.

It should be mentioned that upon addition of amino acid to the aqueous solution containing any of AgCl nanoparticles, i.e. charged or neutral nanoparticles, a hazy solution produced. The nanoparticles were separated through centrifugation and the aqueous solution was tested for the residual amino acid. So, the data obtained for residual AA in liquid phase were sufficient for calculating the partition coefficient of amino acid between phases, i.e. aqueous and nanoparticle phases. Consequently, the fate of the nanoparticle phase was not our concern.

Results and discussion

Determination of hydrophobicity of differently charged AgCl nanoparticles by Rose Bengal method

The Rose Bengal method (Mielke and Zimehl 2001) is a procedure for finding the relative hydrophobicity of substances. Standard Rose Bengal solutions (1.0–14.0 mg/l) were used to prepare a calibration curve. Aliquot of 6.0 ml of the Rose Bengal dye was mixed with a known amount of nanoparticle and the mixture was stand for 3 h and then centrifuged. The residual concentration of the Rose Bengal dye in the liquid phase (C_{eq}, mg/l) was determined using UV–Vis spectrophotometer adjusted at 542 nm. Based on the initial concentration and volume of the dye and the weight of the nanoparticles, the amount of the dye adsorbed by nanoparticles, q_{e} (mg/g), was calculated. A similar procedure was performed for the blank sample, i.e. dye solution in the absence of nanoparticles. Maximum adsorption capacities ($q_{\max}$) of differently charged AgCl nanoparticles for adsorption of Rose Bengal solution are presented in Table 1. The value of $q_{\max}$ is a measure of the relative hydrophobicity of the nanoparticles; the higher $q_{\max}$ represents a higher hydrophobicity. According to this experiment, the hydrophobicity of AgCl nanoparticles is in the following order: $[\mathrm{NanoAgCl}]^+ > [\mathrm{NanoAgCl}]^0 > [\mathrm{NanoAgCl}]^-$. The hydrophobicity of all amino acids (Black and Mould 1991) studied in this work are provided in Table 2 to follow the discussion.

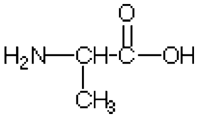
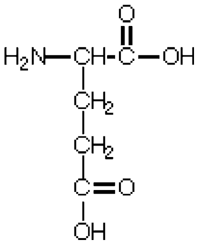
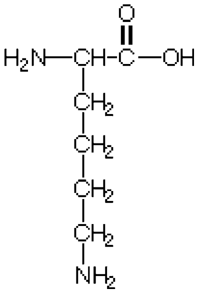
Adsorption of amino acids onto the surfaces of charged AgCl nanoparticles at different pH

Adsorption of amino acids onto the surface of AgCl nanoparticles strongly depends on the pH of the aqueous solution. The pH of aqueous solution provides condition for a special chemical (ionic) form of an amino acid to exist in the dominant form, i.e. with a fraction of 0.9 or more. Generally, amino acids in $\mathrm{pH_s}$ less than $\mathrm{pK_a}$ values

Table 1 $q_{\max}$ values for adsorption of Rose Bengal onto different charged silver chloride nanoparticles surfaces

	$[\mathrm{NanoAgCl}]^+$	$[\mathrm{NanoAgCl}]^0$	$[\mathrm{NanoAgCl}]^-$
$q_{\max}$(mg/g)	0.386	0.200	0.129

Table 2 Chemical structure of the amino acids and their dissociation constants at 25 °C

Amino acid	Chemical structure	Carboxylic acid pK_a	Ammonium pK_a	Substituent pK_a	pI[a]	Hydrophobicity index
Alanine		2.35	9.87		6.10	0.616
Glutamic acid		2.23	9.95	4.42	3.32	0.043
Lysine		2.04	9.08	10.69	9.88	0.283

[a] pI is the pH of isoelectric point

(Table 2) of their carboxylic acid groups are present in the cationic forms due to the protonation of the ammonium groups. Moreover, carboxylic acid and ammonium groups of amino acids dissociate in order with increasing pH and consequently different ionic forms are expected to produce. Since various chemical forms of an amino acid exist in aqueous solution, therefore, different interactions must be taken into consideration when the partitioning of an amino acid between AgCl nanoparticles solution and aqueous solution is studied.

To investigate the adsorption behaviors of amino acid molecules onto the surfaces of charged nano-adsorbent, AgCl nanoparticles with different surface charges were used. The "neutral" AgCl nanoparticles synthesized with equimolar quantity of chloride and silver ions; the "positively charged" AgCl nanoparticles prepared with an excess of 50 % (mole/mole) in silver ion; and the "negatively charged" AgCl nanoparticles obtained with an excess of 50 % (mole/mole) in chloride ion were used as three different charged nanoparticles in this study.

It should be mentioned that because surface charge density of silver chloride is determined by the concentration of either Ag^+ or Cl^- and that of the amino acid depends only on pH, hence, the charge densities of AgCl and amino acids can be controlled independently.

Adsorption of alanine onto the surface of AgCl nanoparticles with different charges

Alanine (Ala) is a hydrophobic neutral amino acid (Black and Mould 1991) that exists in its cationic form (Ala^+) at pHs <2.35 because of the protonated amine group, $-NH_3^+$. As it is seen in Tables 3, 4 and 5, partition coefficient of Ala on all silver chloride nanoparticles is high at lower pH values and its adsorption at any pH, considering the charges of nanoparticles, is in the order of $[NanoAgCl]^+ > [NanoAgCl]^0 > [NanoAgCl]^-$. One may expect that the adsorption of Ala^+ on the surface of $[NanoAgCl]^+$ must be the lowest due to the electrostatic repulsion. But, the higher adsorption of amino acid on $[NanoAgCl]^+$ could be explained due to complex formation between amine group of Ala and more Ag^+ available at the surface of $[NanoAgCl]^+$. It should be mentioned that at pHs <2.35, Ala^+ predominates because of the protonation of the amine group of the amino acid but it can still interacts with silver ion as it is also reported in a paper published by Singha et al. (2006). In this paper, the authors used the surface enhanced Raman scattering (SERS) for studying the adsorption of phenylalanine and tyrosine on the surface of silver colloids and reported the observation of relatively strong bonds at 1,582 and 1,036 cm^{-1} due to asymmetrical deformation of $–NH_3^+$ and νCN, respectively. They explained this by assuming the proximity of $–NH_3^+$ group to the silver surface. In another study for protein adsorption at AgI-water interface (Galisteo and Norde 1995), it is reported that 70–80 % of protein is adsorbed with a high affinity character even when the net electrostatic charges on the surface of AgI and the protein were of the same sign. Furthermore, alanine which is a hydrophobic amino acid could be better adsorbed on the surface of a hydrophobic AgCl nanoparticles and that is why its adsorption on $[NanoAgCl]^0$ is higher than $[NanoAgCl]^-$. Between $[NanoAgCl]^-$ and $[NanoAgCl]^0$ nanoparticles, the later is more hydrophobic (Table 1) in nature, so its higher adsorption property toward Ala at $pH < pK_{a1}$ could be explained due to its interaction with the hydrophobic side of Ala. The solubility of AgCl in the presence of excess chloride ion occurs due to complex formation (i.e. formation of $AgCl_2^-$), the result is decrease in the number of nanoparticles per unit volume and consequently the total surfaces (Kolthoff and Yutzy 1937) available for adsorption of amino acid decreases. In the other words, the number of $[NanoAgCl]^-$ particles in comparison to the number of $[NanoAgCl]^+$ particles, in the unit volume of their solutions, would be less available for adsorption of the amino acid and consequently less amount of Ala would be adsorbed when $[NanoAgCl]^-$ is used.

As a complimentary discussion for the above results, the following words are also included. Before the isoelectric point, pH 6.10, with pH increasing, zwitterionic form of alanine ($Ala^\pm$) produces as soon as the carboxylic acid group dissociates; consequently the adsorption of amino acid onto the surfaces of AgCl nanoparticles probably decreases as a result of diminishing the hydrophobic character of amino acid. Also, after the isoelectric point, pH 6.10, ammonium group of alanine dissociates and its anionic form (Ala^-) produces which predominates at $pH > pK_{a2}$ (=9.87). At higher pH values due to the hydrolysis of silver ion, the AgCl nanoparticles collapse and consequently the study of adsorption process is not applicable. A similar situation has been reported when AgCl nanoparticles were used (Zhu et al. 2000).

Generally, the data shown in Tables 3, 4 and 5 indicate that the adsorption of alanine on the surface of AgCl nanoparticles could be interpreted on the basis of proximity of $–NH_3^+$ group to the silver surface and hydrophobic characters (Gao et al. 2008). Order of nanoparticles for adsorption of Ala follows the same order as their hydrophobic characters reported in Table 1.

Adsorption of glutamic acid onto the surface of AgCl nanoparticles with different charges

As it is shown in Tables 6, 7 and 8, for glutamic acid (Glu), an amino acid with a substituted acidic group, the partition coefficient in the presence of differently charged AgCl nanoparticles at all pH values is in the order of: $[NanoAgCl]^+ > [NanoAgCl]^0 > [NanoAgCl]^-$. This observation is in agreement with the findings of some researchers

Table 3 Partition coefficients of alanine between aqueous solutions, with different pH values and diverse silver chloride nanoparticles at water content ($W = 3.1$)

AgCl nanoparticles	pH						
	1.39	2.35	3.50	4.50	5.50	6.10	7.50≤
Positively charged	0.086	0.072	0.061	0.035	0.013	0.008	Nd
Neutral	0.074	0.067	0.055	0.022	0.007	0.002	Nd
Negatively charged	0.037	0.024	0.012	0.007	0.00	Nd	Nd

Experimental conditions: aqueous solution, 1.0 ml of 2.0×10^{-3} M alanine solution with different pH values; nanoparticle phase volume, 1 ml; extraction period, 30 min; KNO_3, 0.1 M

Table 4 Partition coefficients of alanine between aqueous solutions, with different pH values and diverse silver chloride nanoparticles at water content ($W = 6.1$)

AgCl nanoparticles	pH							
	1.39	2.35	3.50	4.50	5.50	6.10	7.50	8.50≤
Positively charged	0.10	0.091	0.072	0.043	0.013	0.008	0.003	Nd
Neutral	0.086	0.080	0.061	0.030	0.009	0.004	Nd	Nd
Negatively charged	0.048	0.036	0.026	0.010	0.005	0.002	Nd	Nd

Experimental conditions: aqueous solution, 1.0 ml of 2.0×10^{-3} M alanine solution with different pH values; nanoparticle phase volume, 1 ml; extraction period, 30 min; KNO_3, 0.1 M

Table 5 Partition coefficients of alanine between aqueous solutions, with different pH values and diverse silver chloride nanoparticles at water content ($W = 9.1$)

AgCl nanoparticles	pH							
	1.39	2.35	3.50	4.50	5.50	6.10	7.50	8.50≤
Positively charged	0.16	0.12	0.092	0.075	0.064	0.020	0.009	Nd
Neutral	0.096	0.090	0.081	0.052	0.011	0.008	0.002	Nd
Negatively charged	0.056	0.044	0.032	0.018	0.007	0.002	Nd	Nd

Experimental conditions: aqueous solution, 1.0 ml of 2.0×10^{-3} M alanine solution with different pH values; nanoparticle phase volume, 1 ml; extraction period, 30 min; KNO_3, 0.1 M

Table 6 Partition coefficients of glutamic acid between aqueous solutions, with different pH values and diverse silver chloride nanoparticles at water content ($W = 3.1$)

AgCl nanoparticles	pH							
	1.27	1.50	2.23	2.50	3.32	4.50	5.36	6.50≤
Positively charged	0.30	0.23	0.15	0.09	0.03	0.009	0.003	Nd
Neutral	0.21	0.16	0.09	0.02	0.007	Nd	Nd	Nd
Negatively charged	0.15	0.10	0.05	0.01	0.005	Nd	Nd	Nd

Experimental conditions: aqueous solution, 1.0 ml of 2.0×10^{-3} M glutamic acid solution with different pH values; nanoparticle phase volume, 1 ml; extraction period, 30 min; KNO_3, 0.1 M

Table 7 Partition coefficients of glutamic acid between aqueous solutions, with different pH values and diverse silver chloride nanoparticles at water content ($W = 6.1$)

AgCl nanoparticles	pH								
	1.27	1.50	2.23	2.50	3.32	4.50	5.36	6.50	7.50≤
Positively charged	0.38	0.30	0.24	0.18	0.03	0.02	0.01	0.006	Nd
Neutral	0.27	0.20	0.11	0.08	0.01	0.005	Nd	Nd	Nd
Negatively charged	0.19	0.13	0.09	0.07	0.008	0.002	Nd	Nd	Nd

Experimental conditions: aqueous solution, 1.0 ml of 2.0×10^{-3} M glutamic acid solution with different pH values; nanoparticle phase volume, 1 ml; extraction period, 30 min; KNO_3, 0.1 M

Table 8 Partition coefficients of glutamic acid between aqueous solutions, with different pH values and diverse silver chloride nanoparticles at water content ($W = 9.1$)

AgCl nanoparticles	pH										
	1.27	1.50	2.23	2.50	3.32	4.50	5.36	6.50	7.50	8.50	9.50≤
Positively charged	0.50	0.40	0.33	0.25	0.05	0.036	0.023	0.014	0.008	0.003	Nd
Neutral	0.35	0.26	0.19	0.10	0.03	0.012	0.003	Nd	Nd	Nd	Nd
Negatively charged	0.26	0.19	0.12	0.09	0.01	0.007	0.004	Nd	Nd	Nd	Nd

Experimental conditions: aqueous solution, 1.0 ml of 2.0×10^{-3} M glutamic acid solution with different pH values; nanoparticle phase volume, 1 ml; extraction period, 30 min; KNO_3, 0.1 M

showing that hydrophilic amino acids, such as Glu, could highly adsorb on hydrophobic inorganic surfaces than hydrophilic ones (Trudeau and Hore 2010; Aladdine and Nygren 1996; Gregorczyk and Carta 1996). This indicates that mechanisms other than hydrophobic interaction must be taken into consideration for interpreting the results as discussed below.

At lower pHs, the dominant form of glutamic acid is its cationic form, (Glu^+), with one $–NH_3^+$ and two undissociated carboxylic acid, –COOH, groups, so that interaction between Ag^+ and amine group is the driving force for more adsorption of Glu^+ on $[NanoAgCl]^+$ with respect to either $[NanoAgCl]^0$ or $[NanoAgCl]^-$. As the results show, in spite of electrostatic repulsion with

$[NanoAgCl]^+$, the adsorption of Glu^+ is higher on the surface of these particles in comparison with $[NanoAgCl]^-$. With the same reason as discussed for Ala^+, the higher adsorption of amino acid on $[NanoAgCl]^+$ could be explained due to interaction between $–NH_3^+$ group of Glu^+ and Ag^+ ions available at the surface of $[NanoAgCl]^+$. It should be mentioned that one expects unprotonated amine, i.e. $–NH_2$, group to complex silver ion and extract it from the bulk of $[NanoAgCl]^+$ into the liquid phase; in this case, less adsorption of amino acid occurs on the surface of nanoparticles. This situation was also observed for lysine with two amine group as will be discussed later.

As it was explained for Ala^+, the solubility of AgCl in the presence of the excess of chloride ion occurs due to formation of $AgCl_2^-$ complex, the result of which is the reduction of the number of nanoparticles and consequently the reduction of the total surfaces (Kolthoff and Yutzy 1937) available for adsorption of amino acid.

Before the isoelectric point, pH 3.32, the stronger carboxylic acid group dissociates by increasing pH and the zwitterionic form of glutamic acid ($Glu^\pm$) generates. It seems that the electrostatic interaction of $Glu^\pm$ with all types of nanoparticles is weak due to its net charge of zero resulting in its lower adsorption.

The dissociation of the substituted carboxylic acid group (pK_{a2} 4.42) results in the formation of Glu^- with two negative carboxylic and one positive ammonium groups. Consequently, a higher adsorption of glutamic acid (Tables 6, 7, 8) on the surface of $[NanoAgCl]^+$, in contrast to $[NanoAgCl]^-$ and $[NanoAgCl]^0$, is expected due to electrostatic interaction. Furthermore, the number of $[NanoAgCl]^+$ in comparison to the number of $[NanoAgCl]^-$ per unit volume of their solutions is higher as discussed before, so a higher adsorption of amino acid on the surface of positively charged nanoparticles was observed. The results show that the electrostatic interaction, not interaction between silver ions with amino acid (through $–NH_3^+$ group), must be considered as a driving force for adsorption process of amino acid onto the surface of nanoparticles.

At pH 6.50 and higher, the partition coefficients of glutamic acid onto the surfaces of both $[NanoAgCl]^0$ and $[NanoAgCl]^-$ were low or could not be measured and are reported as "not detected" in Tables 6, 7 and 8, therefore, they considered to be almost the same at the performed experimental condition. At higher pH values due to the hydrolysis of silver ion (Zhu et al. 2000), the AgCl nanoparticles collapse and consequently the adsorption process on AgCl nanoparticle is not applicable in these pH values. It should be mentioned that the value of W is another factor that must be considered for interpreting the observed data. This will be discussed later.

Adsorption of lysine onto the surface of AgCl nanoparticles with different charges

As it is shown in Tables 9, 10 and 11, adsorption of lysine on the nanoparticle phase is significantly higher in pH values of 1.08 and 1.50 (note that these values are less than pK_{a1} 2.04 of carboxylic acid group of lysine) and also adsorption is more favored in the case of $[NanoAgCl]^-$ in comparison with either $[NanoAgCl]^+$ or $[NanoAgCl]^0$. In these pH values, dicationic form of lysine (Lys^{2+}) with undissociated carboxylic acid group is dominant, therefore, the electrostatic interaction of Lys^{2+} with $[NanoAgCl]^-$ is expected to be higher. Though, it is not expected that Lys^{2+} with a charge of 2+ be adsorbed on the surface of $[NanoAgCl]^+$ but interaction of both $–NH_3^+$ and Ag^+, as discussed for glutamic acid and alanine, could be the driving forces for adsorption of amino acid. The situation is completely different for $[NanoAgCl]^0$ with lower silver ion available for interaction with amine groups; that is why the adsorption of amino acid on the surface of this nanoparticles is less than that on the surface of $[NanoAgCl]^+$.

At pH 2.04, Lys^{2+} loses one of its protons on the carboxylic group and converts to a species, denoted as Lys^+, with two $–NH_3^+$ and one $–COO^-$ groups. In this situation, dipole–dipole interaction between Lys^+ molecules in the liquid phase could prevent their adsorption on the surface of all three types of silver chloride nanoparticles. Decrease in adsorption of Lys^+, in contrast to Lys^{2+}, on the surface of $[NanoAgCl]^-$ could also be interpreted due to decrease of the electrostatic interaction as a negatively charged group, i.e. $–COO^-$, is developed on the molecule.

It should be mentioned that adsorption of lysine is mainly driven by electrostatic interaction between nitrogen and chloride ions in the case of $[NanoAgCl]^-$ due to hard–hard interaction as reported (Jeunieau and Nagy 1999a, b). Interaction between Ag^+ and amino acid could be considered as driving forces for adsorption of amino acid on the surface of either $[NanoAgCl]^+$ or $[NanoAgCl]^0$.

At pH, pI = 9.88, zwitterionic form of lysine ($Lys^\pm$) predominates. In this chemical form, lysine has a deprotonated α-amino group ($–NH_2$), a deprotonated α-carboxyl group ($–COO^-$), and a protonated side chain-amino group ($–NH_3^+$). This charge distribution in zwitterionic lysine could provide dipole–dipole interactions between $Lys^\pm$ molecules in the liquid phase that consequently could prevents their adsorption on the surface of all three types of silver chloride nanoparticles. Furthermore, adsorption of $Lys^\pm$ on the surface of $[NanoAgCl]^-$ is expected to decrease in contrast to Lys^+ due to decrease of the electrostatic interaction. Also, because of losing one of the protonated amine group, interaction of $Lys^\pm$ with silver ions at the surface of $[NanoAgCl]^+$ decreases and the

Table 9 Partition coefficients of lysine between aqueous solutions, with different pH values and diverse silver chloride nanoparticles at water content ($W = 3.1$)

AgCl nanoparticles	pH										
	1.08	1.50	2.50	3.00	3.50	4.50	5.50	6.50	7.50	8.50	9.88≤
Negatively charged	2.96	2.00	0.85	0.19	0.11	0.078	0.063	0.015	0.006	0.003	Nd
Positively charged	1.08	0.87	0.46	0.11	0.093	0.062	0.045	0.00	Nd	Nd	Nd
Neutral	0.90	0.73	0.37	0.026	0.019	0.010	0.008	0.004	Nd	Nd	Nd

Experimental conditions: aqueous solution, 1.0 ml of 2.0×10^{-3} M lysine solution with different pH values; nanoparticle phase volume, 1 ml; extraction period, 30 min; KNO_3, 0.1 M

Table 10 Partition coefficients of lysine between aqueous solutions, with different pH values and diverse silver chloride nanoparticles at water content ($W = 6.1$)

AgCl nanoparticles	pH										
	1.08	1.50	2.50	3.00	3.50	4.50	5.50	6.50	7.50	8.50	9.88≤
Negatively charged	3.12	2.50	1.32	0.26	0.20	0.12	0.088	0.062	0.053	0.020	Nd
Positively charged	1.66	1.05	0.43	0.16	0.11	0.092	0.078	0.057	0.042	0.033	Nd
Neutral	1.05	0.89	0.20	0.091	0.081	0.072	0.056	0.040	0.031	0.023	Nd

Experimental conditions: aqueous solution, 1.0 ml of 2.0×10^{-3} M lysine solution with different pH values; nanoparticle phase volume, 1 ml; extraction period, 30 min; KNO_3, 0.1 M

Table 11 Partition coefficients of lysine between aqueous solutions, with different pH values and diverse silver chloride nanoparticles at water content ($W = 9.1$)

AgCl nanoparticles	pH											
	1.08	1.50	2.50	3.00	3.50	4.50	5.50	6.50	7.50	8.50	9.88	10.50≤
Negatively charged	3.77	2.63	1.15	0.36	0.33	0.25	0.17	0.090	0.064	0.045	0.003	Nd
Positively charged	2.17	1.81	0.99	0.26	0.21	0.12	0.091	0.0670	049	0.033	0.002	Nd
Neutral	1.35	1.10	0.43	0.12	0.10	0.080	0.053	0.046	0.037	0.02	0.002	Nd

Experimental conditions: aqueous solution, 1.0 ml of 2.0×10^{-3} M lysine solution with different pH values; nanoparticle phase volume, 1 ml; extraction period, 30 min; KNO_3, 0.1 M

produced unprotonated amine, $–NH_2$, group is able to make complex with silver ion and extract it from the bulk of solid $[NanoAgCl]^+$ into the liquid phase, the result of which is less adsorption of amino acid on the surface of nanoparticles.

Adsorption isotherms

Successful application of the adsorption technique demands studies based on various adsorptions isotherm models (Mittal et al. 2007) as the right model reveals the relationship between amount adsorbate per gram of adsorbent at the equilibrium condition. Concerning this, two well-known isotherm models, the Freundlich and Langmuir models, have been applied for interpretation of the adsorption data obtained in this study (Figs. 3, 4, 5). The adsorption equilibrium data were applied to Langmuir model which is described as follows (Langmuir 1918):

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}}$$

where C_e shows the equilibrium concentration of amino acid (mmol/L) and q_e is the amount of the amino acid adsorbed (mmol) per gram different charged AgCl nanoparticles. The $q_{\max}$ is the surface concentration at monolayer coverage in mmol/g and illustrates the maximum value of q_e that can be attained as C_e is increased. The b parameter is a coefficient related to the energy of adsorption and increases with increasing strength of the adsorption bond. Values of $q_{\max}$ and b are determined from the linear regression plot of (C_e/q_e) versus C_e. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by:

$$R_L = 1/(1 + bC_0)$$

where C_0 is the initial amino acid concentration (mmol/L). The parameter $R_L > 1$; $R_L = 1$; $0 < R_L < 1$; $R_L < 0$ indicates the isotherm shape according to unfavorable, linear, favorable and irreversible, respectively (Tony and Pant 2004). The results in Tables 12, 13 and 14 show that favorable adsorption of three amino acids on adsorbents takes place. The adsorption equilibrium data were also applied to the Freundlich model (Freundlich 1906):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where K_F and n are the constants from the Freundlich equation representing the capacity of the adsorbent for the adsorbate and the reaction order, respectively. The reciprocal reaction order, $1/n$, is a function of the strength of adsorption.

The calculated parameters of the Langmuir and Freundlich models are given in Tables 12, 13 and 14. The comparison of correlation coefficients (R^2) of the linearized form of both equations indicates that the Langmuir model yields a better fit for the experimental equilibrium adsorption data than the Freundlich model. This suggests the monolayer coverage of the surface of different charged AgCl nanoparticles by Lys, Glu and Ala molecules.

Effect of water to surfactant mole ratio, *W*

The effect of water-to-surfactant mole ratio (*W*) on the adsorption of amino acids was studied in $W = 3.1$, 6.1 and 9.1. It is well known (Bagwe and Khilar 1997) that the particle size produced in a reverse micelle system usually increases with increasing *W* at a constant concentration of the surfactant. It should be mentioned that each microemulsion was prepared with a constant concentration (0.12 M) of AOT in heptane, and the aqueous solutions of $AgNO_3$ and KCl were added in such amounts to have $W = [H_2O]/[AOT]$ with specific values of 3.1, 6.1 and 9.1. This has conventionally been explained in terms of the size increase of the water pool of a reversed micelle as a nanotemplate of the particles. Increasing the water to surfactant mole ratio induces a dilution effect as a result of either the formation of larger water pools or the formation of more reverse micelles. Hence the concentration of AgCl monomers in the water pools falls to below the critical nucleation concentration, and nucleation become more dependent on the intermicellar exchange of solubilizate. Moreover, increasing *W* reduces the surface rigidity and the interaction between the surfactant protective layer and the nanoparticles inside the water pool. This result in higher

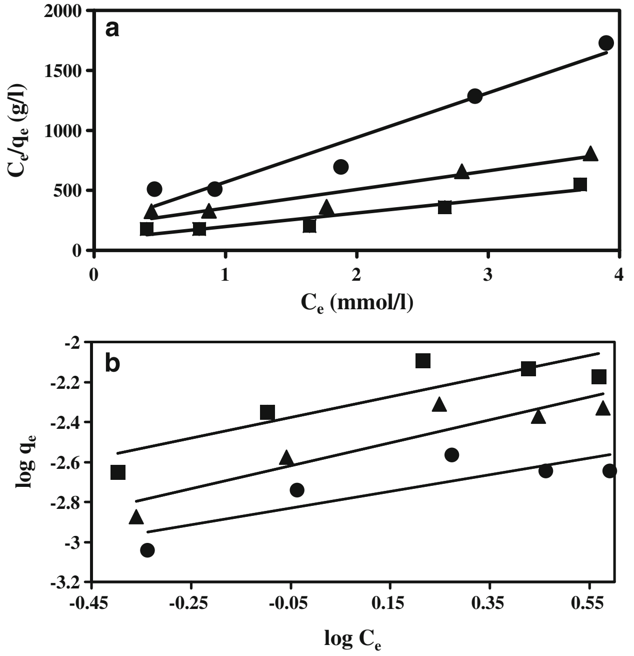


Fig. 3 **a** Langmuir isotherm plots, **b** Freundlich isotherm plots for adsorption of alanine onto negatively charged silver chloride nanoparticles (*filled circle*) and positively charged silver chloride nanoparticles (*filled square*) and neutral silver chloride nanoparticles (*filled triangle*)

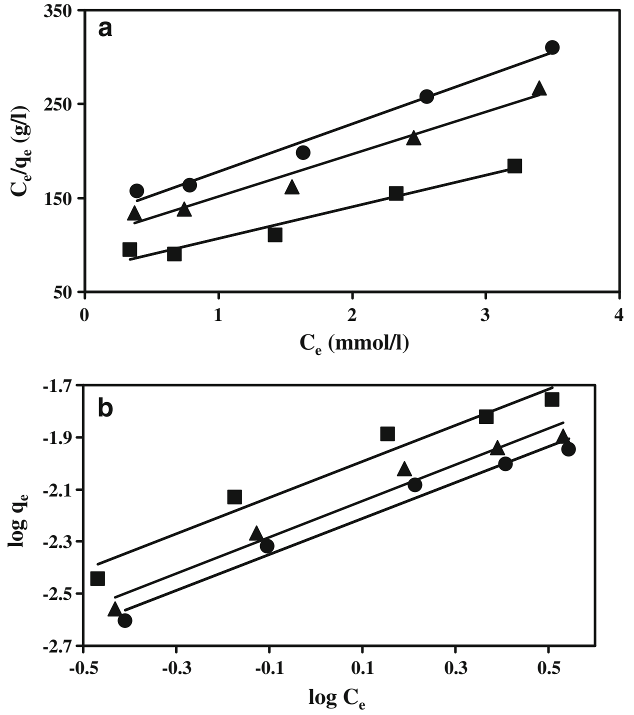


Fig. 4 **a** Langmuir isotherm plots, **b** Freundlich isotherm plots for adsorption of glutamic acid onto negatively charged silver chloride nanoparticles (*filled circle*) and positively charged silver chloride nanoparticles (*filled square*) and neutral silver chloride nanoparticles (*filled triangle*)

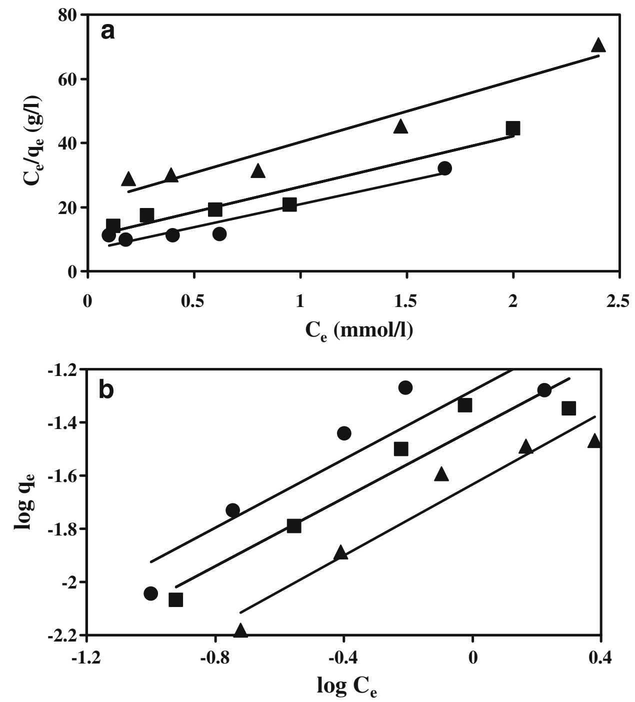


Fig. 5 **a** Langmuir isotherm plots, **b** Freundlich isotherm plots for adsorption of lysine onto negatively charged silver chloride nanoparticles (*filled circle*) and positively charged silver chloride nanoparticles (*filled square*) and neutral silver chloride nanoparticles (*filled triangle*)

Table 12 Adsorption isotherm parameters for adsorption of alanine onto different charged silver chloride nanoparticles surfaces at water content ($W = 9.1$)

AgCl nanoparticles	Langmuir model			Freundlich model	
	$q_{\max}$	R_L	R^2	$1/n$	R^2
Positively charged	0.0088	0.270	0.908	0.515	0.780
Neutral	0.0064	0.389	0.913	0.575	0.852
Negatively charged	0.0027	0.209	0.942	0.418	0.715

Table 13 Adsorption isotherm parameters for adsorption of glutamic acid onto different charged silver chloride nanoparticles surfaces at water content ($W = 9.1$)

AgCl nanoparticles	Langmuir model			Freundlich model	
	$q_{\max}$	R_L	R^2	$1/n$	R^2
Positively charged	0.0297	0.520	0.962	0.691	0.958
Neutral	0.0222	0.542	0.970	0.696	0.961
Negatively charged	0.0196	0.555	0.983	0.690	0.975

Table 14 Adsorption isotherm parameters for adsorption of lysine onto different charged silver chloride nanoparticles surfaces at water content ($W = 9.1$)

AgCl nanoparticles	Langmuir model			Freundlich model	
	$q_{\max}$	R_L	R^2	$1/n$	R^2
Positively charged	0.0633	0.252	0.935	0.642	0.922
Neutral	0.0523	0.311	0.941	0.670	0.933
Negatively charged	0.0670	0.187	0.921	0.643	0.850

interaction between the water droplets and induces particle aggregation (Chew et al. 1990; Husein et al. 2003). As it is observed in Fig. 2, the UV absorption spectra of $[\text{Nano-AgCl}]^+$ depends on the value of W due to the change in the size of the nanoparticle. Similar UV absorption spectra were observed for neutral and negatively charged silver chloride nanoparticles. As the size of the particles increases, the larger particles can accommodate a large number of amino acid molecules and therefore partition coefficient increases. Moreover, in the present system, both amino acid and nanoparticle resided in the interior of the water pool of the microemulsion, so that the interaction property was essentially guided by the fluidity of the core water which increases with increasing W, resulting in a concomitant increase in partition coefficient. At low W, the solution of interfacially adsorbed sodium bis-2-ethylhexylsulfosuccinate molecule in the water pool fairly decreased the pool fluidity and hence partition coefficient (Tables 3, 4, 5, 6, 7, 8, 9, 10, 11).

Application of the method for separation of amino acids

To demonstrate the applicability of the finding results for separation of the amino acids, some data are presented in a figurative format in Fig. 6. This figure which shows the typical partition coefficients of the studied amino acids at different pH values is depicted for $W = 6.1$, when positively charged AgCl nanoparticles were used. It seems that

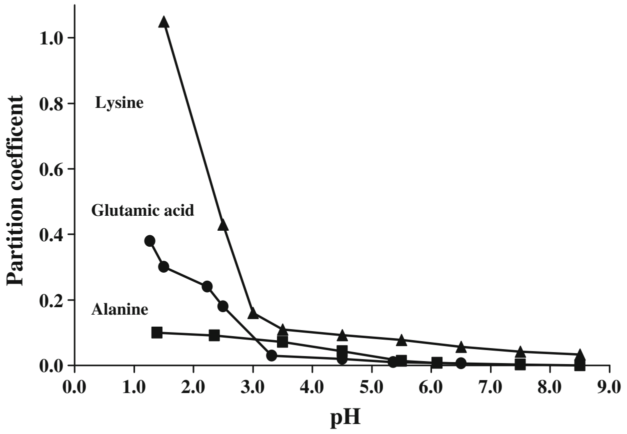


Fig. 6 Partition coefficients of the studied amino acids at different pH values, with $W = 6.1$ on the surface of positively charged silver chloride nanoparticles

at pHs lower than 3.0, the studied amino acids could be easily separated from each other by applying the proposed procedure, when positively charged silver chloride nanoparticles were used as adsorbent. However, similar figures could be presented for different *W* values with differently charged nanoparticles to show that AgCl nanoparticles with different charges provide suitable adsorption media for separation of amino acids as well as elucidating the mechanisms of their adsorption on the surface of solid materials which is the concern of many researchers (Sethi and Marc 2010) in manufacturing of bioproducts and in various biotechnological fields, such as the preparation of biocompatible materials and biosensors.

Conclusions

The results of this study revealed that the interaction of $-NH_3^+$ groups of the amino acids with silver ion could be a driving force for adsorption of amino acids even on the surface of positively charged nanoparticles. Adsorption of amino acid on the surface of the nanoparticles reduced at pHs when $-NH_2$ group is present. Alanine and glutamic acid with one amine group showed almost similar trend for being adsorbed on the surface of silver chloride nanoparticles; the situation is different for lysine with two amine groups. In some cases, hydrophobicity rather than electrostatic interaction could be considered as a criterion for interpreting the adsorption processes in the studied systems. Adsorption of amino acids on the surface of nanoparticles is also increased by *W*. Experimental results revealed that the size of AgCl nanoparticles and also fluidity of the core water increase with increase in the content of water to surfactant (W) resulting in a concomitant increase in partition coefficient.

Generally, it is concluded that adsorption or unadsorption of acidic, basic, and neutral amino acids on the surfaces of differently charged silver chloride nanoparticles could be explained by different mechanism such as electrostatic interaction, hydrophobicity of both nanoparticle and amino acid, complex formation between amine group and silver ion, interaction between protonated amine and silver ion as well as the number of nanoparticles per unit volume of solution.

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