The Impact of Water and Some Salt Solutions on Some Properties of Hydrophilic Acrylamide Copolymeric Hydrogels

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***Abstract*-A series of polyelectrolyte hydrogels ranging from 92-98wt% were synthesized by copolymerization of acrylamide, AAM with 2-acrylamido-2-methyl propane sulphonic acid, AMPS using 0.001g APS as initiator in the presence of 30wt% H_2O and 1.0wt% ethylene glycol dimethacrylate,EDMA as cross-linking agent. The final copolymers was obtained in the form of glassy and transparent roads at room temperature, these roads were soaked in water for two days to remove unreacted monomers. The swelling behavior of the hydrogels was studied in distilled water and salt solutions of 1.5 mol/l each of NaCl and KCl. The Swelling in water shows decreasing values of q, LE, $Ø_1$, EWC% and increasing polymer volume fraction, $Ø_2$ by increasing acrylamide, due to increasing hydrophobicity and decreasing the hydrophilicity. The swelling in salt solutions shows a decreasing in the values of ESSNa%, WCNa%, SCNa%, ESSK%, WCK% and SCK% by increasing acrylamid monomer in the feed due to increasing the hydrophobicity and decreasing the ionized ionic groups (SO_3H). The increasing values of ESSNa%, WCNa% and SCNa% compared with the values of ESSK%, WCK% and SCK% respectively, is due to the higher charge density of sodium ion than that of potassium ion.**

Key words, hydrogels, swelling, charge density, polyelectrolyte

I. INTRODUCTION

Hydrophilic gels called hydrogels are cross-linked materials absorbing large quantities of water or biological fluids. Due to their high water content, porosity and soft consistency, they closely simulate natural living tissue, more than any other class of synthetic biomaterials [1].These 3D structures can absorb large amounts of water or aqueous fluids in relatively short periods of time, as compared to conventional hydrogels, and generally absorb an amount of water that can reach 1000 times (or more) their dry weight material [2].Furthermore hydrogels can be formulated in a variety of physical forms, including slabs, microparticals, nanoparticals, coatings and films. As a result, hydrogels are commonly used in clinical practice and medicine, with a wide range of applications, including tissue engineering and regenerative medicine, diagnostic, separation of bimoleculis, and barrier materials to regulate biological adhesions [3]. The equilibrium swelling degree of hydrogels depends on the cross-linking and charge density of the network. The hydrogel materials have good properties in terms of physical, water content and rubber consistency. The above mentioned properties and the possibility of preparing different forms such as blocks, microparticle, nanoparticle, paint and films that qualify for use in an important and different areas, such as biotechnology, pharmaceutical, agricultural, oil and industry [4-7]. As well as other uses such as extraction of metals, waste water treatment, wound dressings, diapers and others. This has led to an increased global production of hydrogels of 6000 tons in 1983 to 450,000 tons in 1996 [8]. Of important applications that brought attention of scientists at the present time as an area of research and study, is the use of hydrogels as tools for the distribution of drugs where a hydrogel provides protection of drug from the impact of the surrounding effects such as enzymes and low pH in the stomach.

Pores in the gel matrix which allows to download and distribute the drug at a predesigned processes is possible to control the distribution of drug bychanging the gel composition to suit the environmental influences such as pH, temperature [9] and ionic strength [10]. The hydrophilicity of the network is due to the Presence of the amide ($-CONH_2$) and sulphonic ($-SO_3H$) groups in the copolymer matrix. The hydrogels can be synthesized by using thermal initiators such as azoisobutyronitrile, Photoinitiators such as benzoin, benzile and other sources such as Gama-ray. In high pH solutions, the $-CONH_2$ groups become hydrolyzed, causing repulsion between the resulting charged carboxylate groups, which will extend the polymer chains. This creates large spaces within the gel to absorb water molecules and increase swelling [11]. Solvent molecules penetrate through the polymer chains leading to an increase of volume of the polymer as a result of two phases. The sheath of swollen polymer is formed, and water then passing through the sheath to reach the interior of the hydrogel. Water inside the hydrogel allows free diffusion of some solute molecules, while the polymer serves as a matrix to hold water together. Increasing number of ionic groups in the hydrogels increases their swelling capacity, this is mainly due to simultaneous increase of the number of counter ions inside the gel. Sulfonic acid containing hydrogels repre-sent a class of strong polyelectrolyte gels with a high degree of ionization. It was shown that the linear polymers with sulfonate groups derived from 2-acrylamido-2-methylpropanesulfonic acid (AMPS) exhibit extensive coil expansion in aqueous solutions, even in 5 M NaCl solution, the expansion of polymer coils due to charge repulsion cannot be totally screened [12].The amount of water that a hydrogel can hold at equilibrium depends on the number and type of hydrophilic groups in the network. The degree of swelling of hydrogels depends on the temperature, pressure, pH and the nature of solution, when all this variables were constant, the volume that gel access at equilibrium is known as equilibrium swelling [13, 14]. A polymer or copolymer carrying ionic charges along the back bone of skeletal chains that causes the polymer dissolving, if the charges is negative the polymer is an ionic and cationic if it is positive. The negative charges along the chains cause an intra and inter chain repulsion, leading to an extension of the chain. Increasing the amide groups increases the rate of solubility of the polymer. The negative charged ions along the polymer chains, causes repulsion leading to an extension of the chain, when some electrolyte (salt) is added, the chains is contracted [15]. The hydrophilic polymers are categorizes to two kinds according to its behavior in the salt solutions [16].

1- Non isolated polymers in water: salt ions may enhance polymer and water mixing (salting in) or impair them. Increasing salt concentration leads to an attraction of water molecules by salt ions as result of decreasing water molecules required to attract to a charged part of gel that leads to more water needed. The attraction between gel molecules is higher than that between solvent and solute as result of gel precipitation (salting out).

2- An isolated polymers in water: possesses the behavior of polyelectrolyte characterized by unnoticeable swelling in salt solutions [17].The net polymer matrix ended by ionizable groups and in the presence of solvent this net becomes an ionic net work and counter ions moves easily in the solvent, and the molecules of the solvent exchanges between the solvent and gel until reach equilibrium. The addition of salt to the solvent, leads to migration of salt ions to the gel until donnan equilibrium is established. Increasing salt concentration leads to shrinking the gel [18]. In the present work, we describe the preparation and characterization of acrylamide copolymers based hydrogel. The effect of reaction variables affecting the swelling capacity of the hydrogel and swelling behavior in various salt solutions was investigated.

II. EXPERIMENTAL

A. Materials

Acrylamide (AAm, Merck) was crystallized from an acetone/ethanol mixture (70/30 by volume) below 303K, 2-acrylamido-2-methylpropane sulfonic acid (AMPS, Merck) was crystallized from boiling methanol. The purity of the monomers was checked by IR and NMR. Ethylene glycol dimethacrylate (EGDM) cross-linker was purchased from Fluka and used as received as cross linking agent, ammonium persulfate (98%) (APS) were purchased from Aldrich Company, USA and KCl and NaCl (Merck) were used as received. Double distilled and deionized water was used in the hydrogel preparation and in the swelling measurements.

B. Hydrogel synthesis

The hydrogels were prepared by free radical cross-linking copolymerization of AAm with AMPS in presence of fixed amounts of 1.0wt%, 0.001g of EDMA as cross-linker and APS initiator respectively. The reactions were carried out at 353K. The monomers were quoted according to the weight percentage in the presence of 30 wt% water .(AMPS + AAm + EDMA).The ratio by weight of AMPS to AAm remains 2/98.The components were weighed and mixed in a small clean vial, and transferred to the test tube 125 × 25 mm by a long syringe needle. The monomer mixture was outgased by bubbling nitrogen gas for 3 minutes through each mixture by using a glass pipette connected with rubber tube. The glass tubes were covered and placed in thermostated water bath at 353± 1K for one hour. After polymerization, the tubes were broken up to obtain the polymer rods. The rods were swollen in deionised water for two days to remove unreacted monomers and dried in to constant weight in a vacuum oven at 308K. The degree of swelling refers to the percentage increase of the volume of hydrogels;

$$\mathrm{EWC\%} = \frac{\mathrm{Ww} - \mathrm{W0}}{\mathrm{Ww}} \times 100 \qquad (1)$$

The linear expansion, LE and the polymer volume fraction, $Ø_2$ are calculated as follows;

$$\%\mathrm{LE} = \text{hydrogel diaminsion} - \text{diamension} / \text{hydrogel diamension} \times 100 \qquad (2)$$

$$Ø_2 = (\text{xerogel diamension})3/(\text{hydrogel diamension})3 \qquad (3)$$

$$Ø_{2 = 1 - Ø_1} \qquad (4)$$

Where, $Ø_1$ is the volume fraction of water in the hydrogel

The soluble fraction is the fraction loss in the weight of xerogel;

$$\% \mathrm{S} = (\mathrm{Wb} - \mathrm{Wa})/(\mathrm{Wb}) \times 100 \qquad (5)$$

Where W_b andW_a are weights of the rods before and after extraction respectively.

C. Swelling in water and salt solutions

A sharp plade was used to cut the discs from the rods for measurement of swelling in water and salt solutions, in order to reach the equilibrium degree of swelling,the swelling of discs were carried out at room temperature, 298 K. The known weights (W_o) and diameters (d_o) of dried discs were immersed in clean sample vials andcoveredwithdistilled

water for eight days, during which water was replaced everyotherday.Theirweights were taken at regular time intervals until constant weight was achieved and the swellingtime was counted from the moment of addition of solvent to the vial. The diameters of dried and swollen discs at equilibrium were measured by using a vernier caliper, a millimeter chart paper and microscope respectively. The extension ratio, ER is calculated as;

$$ER = (d)/(do) \quad (6)$$

Were d and d_o are the diameters of swollen and dried discs respectively. The swelling measurements of NaCl and KCl solutions were carried out at room temperature, 298 K, were dried discs of known weights are immersed in a clean sample vials, and completely covered with a 1.5 M solution of sodium chloride, while the other dried discs of known weights and same compositions are placed in another vials and covered with a 1.5 M solution of potassium chloride. The swelling time was extended to eight days, and theweights were taken at regular time intervals until constant weight was achieved. The swollen discs at equilibrium were removed and first dried at room temperature and finally in a vacuum oven at 308K to constant weight. The equilibrium salt solution content, water content and salt content of all hydrogels in salt solutions respectively, were calculated as follows;

$$ESSC\ \% = (W_2 - W_O)/(W_2) \times 100 \quad (7)$$

$$WC\ \% = (W2 - Ws)/(W2) \times 100 \quad (8)$$

$$SC\ \% = (W2 - Ww)/(W2) \times 100 \quad (9)$$

While the expression on an ion charge density, σ is as follows;

$$\sigma = Q/v \quad (10)$$

Where:

W_2 is theweight of dry xerogel + salt + water, Wo is the weight of dry xerogel, Ws is the weight of dry xerogel + salt, W_w is the weight of dry xerogel + water, Qand v is the charge and volume of the ion respectively.

III. RESULTS AND DISCUSSION

A. Swelling in water

The hydration curves of water content versus time for different compositions of AAM/AMPS/EDMA ranging from 92 to 98wt% of AAM are shown in "Fig. 1,". The time of swelling was extended to eight days. The highest amount of water was absorbed during the first two days, and then the curves leveled off to a constant value, indicating the true value of equilibrium water content. The EWC decreases by increasing acrylamide content in the copolymer. The acrylamide monomerrepresents the undisociated groups while AMPS represents the dissociated hydrophilic groups. When they were swollen in water, the hydrophobic part of the chains tended to aggregate avoiding contact with water, whilst the water formed hydrogen bonding to the polar groups in the AAM and AMPSunits. The rate of dissolution in water increases as the level of ionic charges increases [18]. Increasing AAM units in the net work decrease the degree of ionization and consequently decreasing hydrogen ions that moves freely inside the gel, creating an osmotic pressure. The decreasing of ions leads to a weak expansion of xerogels in water and decreasing water uptake. The equilibrium water

content, EWC of the hydrogels in water was calculated by using "Equation (1)". The volume fraction, $Ø_1$and linear expansion, LE, was illustrated in "Fig. 2," and "Fig. 3," respectively, this values were decreased by increasing AAM and decreasing AMPS units, as a result of increasing the hydrophobicity and then decreases degree of swelling, the other factor is due to the cross linking density of the copolymer matrix. "Fig. 2," and "Fig. 4," shows an increasing of, $Ø_2$ and decreasing of an equilibrium swelling content, EWC by increasing AAm units in the xerogel respectively, as a result of increasing hydrophopicity.

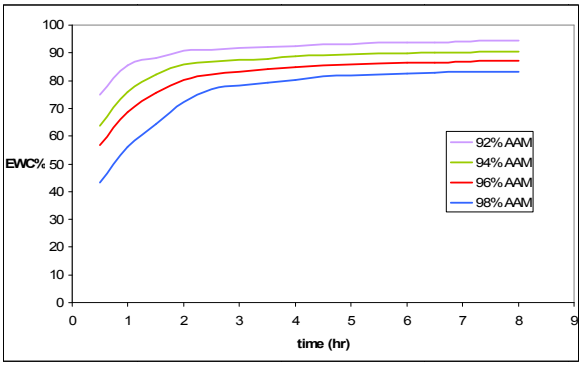

Figure 1.EWC% vs. time at 298 K

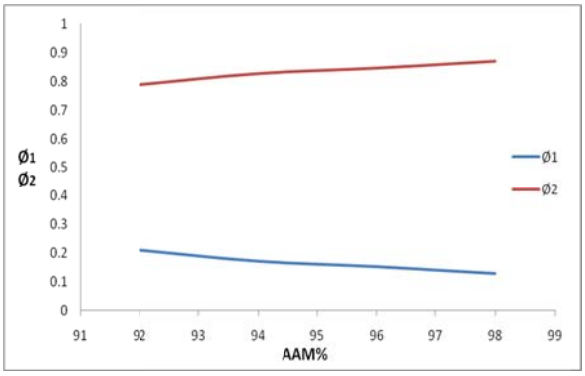

Figure 2. Volume fractions vs. AAM wt% at 298 K

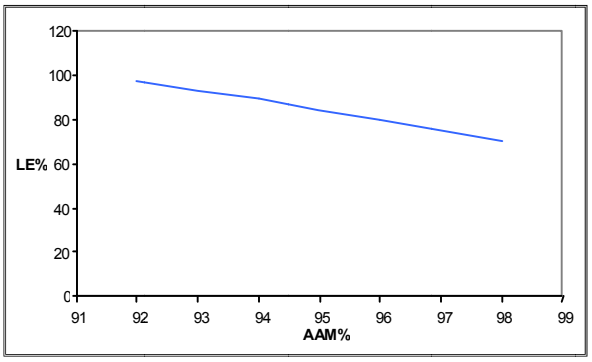

Figure 3.LE% vs.AAMwt% at 298 K

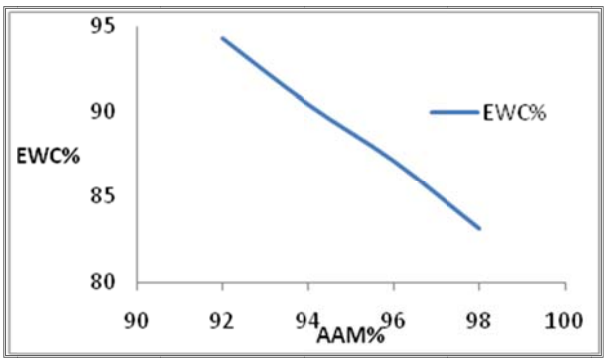

Figure 4.EWC% vs. AAM wt% at 298 K

B. Swelling in salt solutions

The swelling time was also extended to eight days. The equilibrium salt solution content ESSCNa%, water content WCNa% and salt content SCNa% in 1.5 Mol/l NaCl solution at 298K was shown in figures "Fig. 5," , "Fig. 6," and "Fig. 7," respectively.

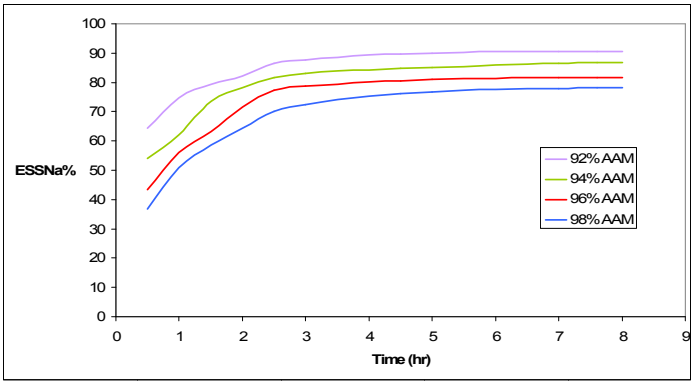

Figure 5.ESSCNa % vs. swelling time at 298K

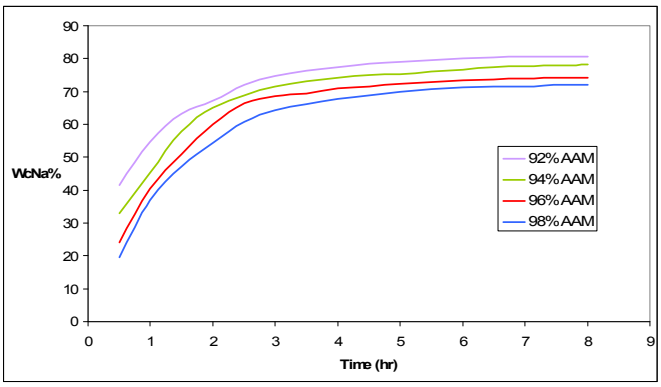

Figure 6.WCNa% vs. swelling time at 298K

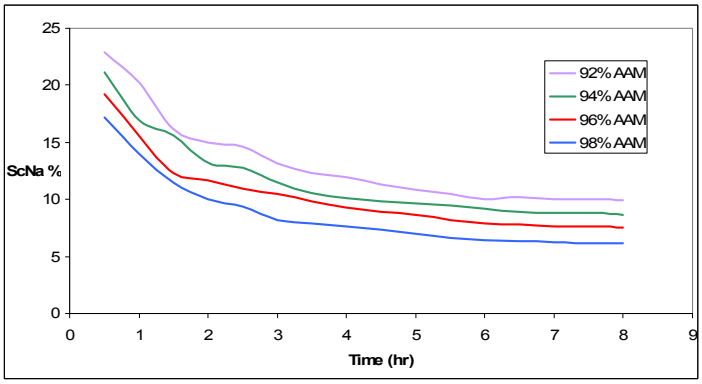

Figure 7.SCNa% vs. swelling time at 298K

The equilibrium salt solution content ESSCK%, water content WCK% and salt content SCK% in 1.5 mol/l KCl solution at the same temperature for other hydrogels of the same composition were shown in figures "Fig. 8," , "Fig. 9," and "Fig. 10," respectively.

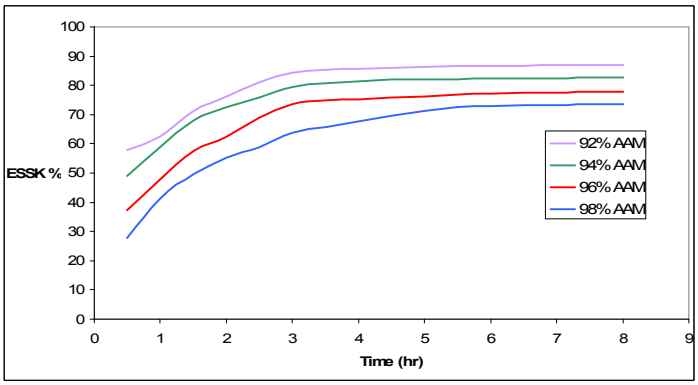

Figure 8. ESSCK% vs. swelling time at 298K

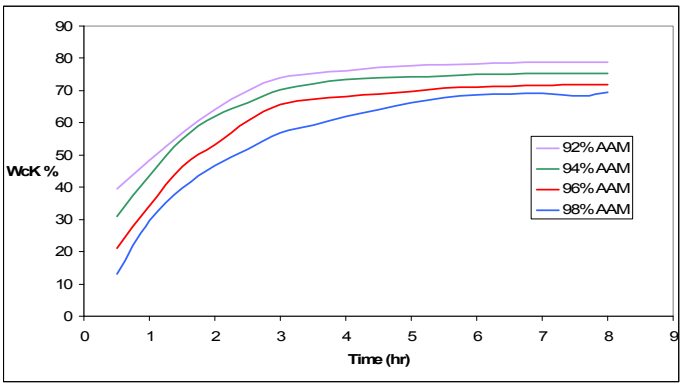

Figure 9. WCK% vs. swelling time at 298K

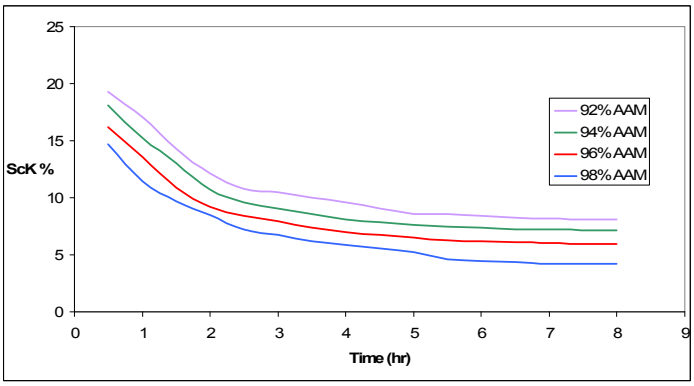

Figure 10. SCK% vs. swelling time at 298K

The above mentioned figures showing that the equilibrium in both salt solutions was increases with time, while the salt content decreases. “Fig. 11,” illustrates that ESSK <ESSNa< EWC, were decreases with increasing acrylamide monomer for the same compositions. The presence of salt affects the swelling values of this hydrogels. It was found that the salt decreases the swelling of cellulose gel [19]. The decrease of swelling in salt solutions means that the salt is able to reduce the water (salting-out). Increasing AAm monomer in gel matrix decreases the ionizing groups and increases the hydrophobicity, which is contribute in the decreasing of equilibrium content, water content and salt content both in 1.5 mol/l solutions each of NaCl and KCl.“Fig. 12,” shows that both water content of WCNa, and WCK in salt solutions decrease with increasing AAm content in the xerogel. The values of WCNa are higher than that of WCK. The salt contents of both SCNa and SCK decreases with increasing AAm content and the SCNa is higher than that SCK as shown in “Fig. 13,”.

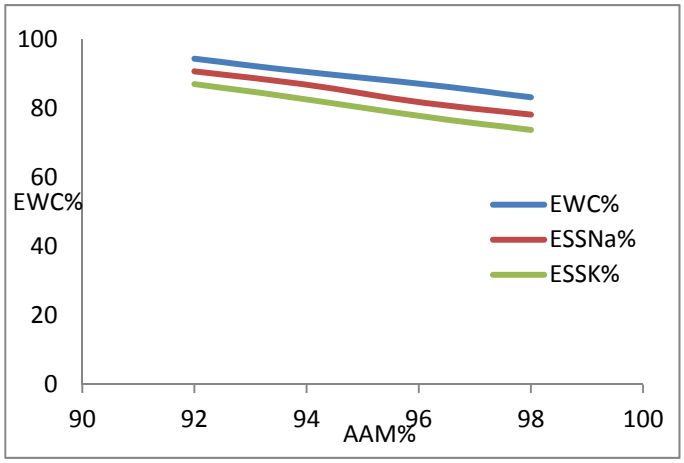

Figure 11. EWC% vs .AAM wt% at 298 K

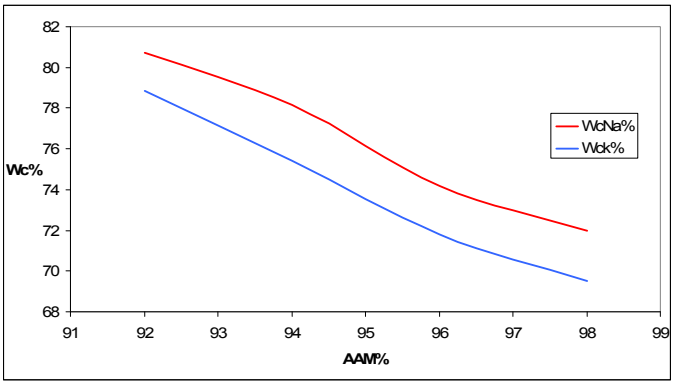

Figure12. WC% vs.AAMwt% at 298K

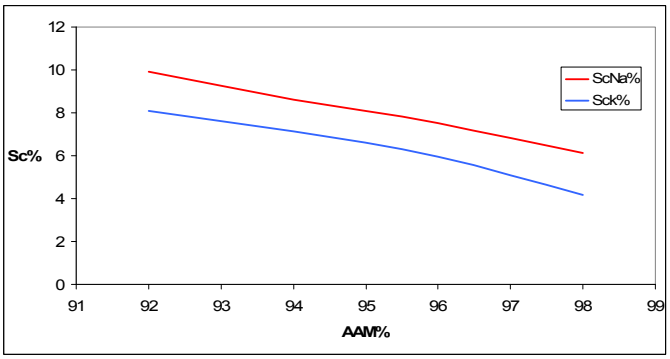

Figure 13. SC% vs .AAMwt% at 298K

One of the properties that characterize the strength of the ions is the charge and volume. The charge density of the ion, σ is directly proportional to its charge, Q and inversely with its volume, table 3.1. As the charge density increases the strength of the ion increases. This leads to,

1. the rate of diffusion of small volume ions in to the gel is higher than that of ions of larger volume.
2. Increasing hydration of outer orbital of the small volume ions inside the network of the gel.

The small volume ions of higher charge density were capable of connecting with water molecules more than that of large volumes, (the hydration number of small volume ions is higher than that of large one [20].

The volume of sodium ion is less than that of potassium ion, and the volume is directly proportional to the radiusTable 3.1.

Table 3.1 some properties of sodium and potassium ions

Ion	Diameter(r) pm	Hydration radius, pm	Hydration No	Charge of the ion
Na^+	102	276	17	+1
K^+	138	232	11	+1

Some mono and heteroatom's ions of higher volume and low charge density,

(Cl^- ,NO_3^- ,NH_4^+,Cs^+ ,K^+ , SCN^-,()$N^+CH_3)_4$

($H_2PO_4^-$, $HSO4^-$,HCO_3 ,I^-)

Possesses interactions with water less than the interactions between the water molecules itself and have a little effect in the hydrogen bonds of the surrounded water. The small volume ions of high charge density,

(Ca^{+2} , Na^+ , Li^+ , H^+ , OH^-,HPO_4^{-2} ,$SO_4^{-2}Mg^{+2}$) [21].,

have strong interactions with the water molecules higher than that between water molecules itself. This ion becomes more hydrated than the ions of low charge density. The interactions between Na^+ ions and negative charged polyelectrolyte groups is higher than that with K^+ as a result of increasing values of ESSCNa% , WCNa% and SCNa% comparing with the values in the potassium chloride solution.

IV. CONCLUSION

The degree of swelling decreases with increasing AAM content in the xerogel as a result of decreasing water uptake**.** The decreasing ionization of the polyelectrolyte decreases the release of positive charged hydrogen ions as a result of decreasing gel expansion and less water uptake**.** The decreasing values of ($Ø_1$, EWC, LE, and q) and increases of $Ø_2$ with increasing AAM content is due to its lower hydrophilicity and the effective cross-linking density. ESSC% in salt solutions is less than EWC% in water as evidence of salting- out effect and less swollen hydrogels. Decreasing AMPS content decreases EWC, ESSC and salt content, SC, both inwater and salt solutions. ESSCNa, WCNa, SCNa is higher than the corresponding values of ESSCK, WCK and SCK respectively, due to the higher charge density of Na than that of K ion.

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