

# Colloid stability and Schulze – Hardy rule: Its origin and new inputs

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## ABSTRACT

The Schulze - Hardy (S-H) rule, which deals with coagulation of colloid particles, is a late nineteenth century salt induced colloid coagulation rule that stood the test of time. However, it does not consider the effects of co-ions, ionic strength, charge density, solvent character etc. We have attempted to consider effects of some of these variables on the coagulation process. In this article, we summarize the modifications of the S-H rule in a broader perspective based on recent publications in research journals.

## 1. Perspective

Colloid particles are known for time immemorial. These are very small particles, and have interesting relationship with the solvent: in our discussion most often water. With reference to water they can be divided into two groups, (i) hydrophilic i.e. those which have a liking for water e.g. gum, starch etc., which interact with water, and (ii) hydrophobic, which do not interact with water e.g. AgI, Ag, Au, CdS etc. This second group substances are basically small particles which are suspended in water, and cannot be filtered out through ordinary filter paper; they actually pass through it. Researches on the behavior of the hydrophobic colloids were not much until the second decade of the twentieth century which leads W. Ostwald [1] to term them as the "World of neglected dimension". However, today we may say that it is not true. Colloids have earned reputations of numerous applications in the domains of physical, chemical, and biological science. Quite often it is necessary to separate out the colloid particles from their dispersions in solution, and for that one needs to get them precipitated. This can be done by (a) nucleation process, and (b) by destabilizing the colloidal dispersion or the sol. Of course we can isolate the dispersed parts by ultracentrifugation method, and also by membrane filtration.

## 2. Nucleation process

The nucleation process is one where ions, atoms or molecules get arranged in a pattern characteristic of a crystalline solid on

which further deposition occurs, and thereby form a new thermodynamic phase [2]. It is a physical process. There are two types of nucleation process: (i) homogeneous nucleation, and (ii) heterogeneous nucleation. Homogeneous nucleation occurs from a supersaturated solution away from the surface of the container. Here, a few particles get into a required arrangement(s) randomly on their own during their random motion in the medium. Other particles then get deposited over these arranged structures to form crystals. This automatically means that there is formation of an interface between the "required arrangement" in one side, and "the medium" in the other side inside the medium. The heterogeneous nucleation occurs at the surface of the container or it may happen by the addition of foreign small crystals, which work as seeds, on which the crystallization occurs. Formation of rain drops in the presence of small dust particles is a good example of "heterogeneous nucleation". In group IV of qualitative inorganic analysis, scratching of inner surface of test tube is suggested to precipitate BaSO<sub>4</sub>: it is another interesting example of heterogeneous nucleation. Crystallization of ice from a supercooled water, can be an example of "homogeneous nucleation". The water can get supercooled to about -42°C without getting frozen though its freezing point is at 0°C.

## 3. Destabilization of colloid particles

Colloid particles can grow and be destabilized (1) by the

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phenomenon of “Ostwald Ripening”, and (2) by precipitation (flocculation) being destabilized by addition of electrolyte solution.

The prepared or formed colloid particles are heterogeneous in nature. In the Ostwald Ripening process, the small particles get dissolved, diffuse, and deposit on bigger particles. For thermodynamic reason the process spontaneously continues, and eventually causes destabilization (precipitation) of the grown fractions of the colloid. IUPAC defined Ostwald ripening as “dissolution of small crystals or sol particles, and re-deposition of the dissolved species on the surfaces of larger crystals or sol particles” [3]. There is a natural tendency to minimize the surface area to volume ratio of dispersed sol particles which for spherical particles of radius  $r$  is equal to  $3/r$ . When  $r$  increases  $3/r$  decreases, and the system becomes stable. This spontaneous process was first described by Wilhelm Ostwald [4,5] in 1896. From Kelvin equation [6] and definition of chemical potential it can be shown that equilibrium concentration  $C_{eq}(r) > C_{eq}(R)$  where  $r$  and  $R$  are radii of colloid particles in original dispersion, and after growth, respectively; obviously,  $R > r$ . Some examples of Ostwald ripening are (i) water re-crystallization within ice-cream giving old ice cream a gritty, crunchy texture (here smaller water crystals are sacrificed and larger crystals grow providing a crunchy texture), and (ii) in the clouds small drops of water slowly disappear and larger drops of water are formed due to diffusional growth. To initiate the stability of the tiny water droplets surface bearing materials like dust, AgI, solid floating pollutants, etc. are required, and used in practice for making artificial rains, particularly in the arid region. The ripening process can also happen in emulsion, and vesicular systems [7].

Colloid destabilization can also be done by the addition of electrolyte solution in the dispersion or sol. This was independently observed by Schulze [8] and Hardy [9]. Salt effects are associated with hydrophobic colloids such as Au,  $As_2S_3$ , AgI, CdS etc. The free energy of formation of such colloids is positive, and hence they are unstable. The minimum concentration of the completely dissociated neutral electrolyte at which the coagulation (flocculation) of a colloid starts is called the “critical coagulation concentration” (CCC). The phenomenon of coagulation may be fast and slow: the rapid coagulation can occur by adding large amount of electrolyte in solution whereas small amount of electrolyte addition causes slow coagulation. The CCC is also defined as the intersection point of the two lines (i) rate of fast coagulation, and (ii) rate of slow coagulation vs the concentration of the electrolyte plots. According to Schulze - Hardy rule, the critical coagulation concentration (CCC) is proportional to  $Z^{-6}$ , where  $Z$  is the charge of the counter ion, without sign. It is known that every colloid is charged, may be positive or negative, and hence  $Z$  is the charge of the counter ion i.e. negative or positive,

respectively. Before discussing the Schulze - Hardy rule, let us discuss in short two important concepts; the double layer theory (DL theory), and the DLVO theory.

#### 4. Double layer (DL) theory

It was Hermann von Helmholtz who in 1853 suggested that a particle or an insoluble matter in contact with an electrolyte solution gives rise to a double layer. The formed interface will automatically acquire a charge (positive or negative), depending upon the nature of the colloid particle/or emulsion droplet on an imaginary plane at the interface. Automatically, following the natural law, a plane bearing opposite charges also forms face to face. These two planes, combined together is called Helmholtz's double layer. However, with time new ideas came and Helmholtz's double layer was termed electrical double layer. Most important of them are Gouy and Chapman (in 1910), and Stern's modifications (in 1924). Essentially, Stern's modification is a combination of Helmholtz and Gouy - Chapman models: a) compact layer, akin to Helmholtz's double layer, and b) diffuse double layer, which is the Gouy - Chapman model [10]. To explain let us assume that some negative charges are formed on the surface of the colloid surface plane. Consequently, as stated above positive ions are accumulated in another plane at a short distance away toward the solution. The total amount of negative charges on the colloid is higher than the total amount of positive charges on the second plane and the charges there after exponentially decrease until they match with the bulk neutral condition. In Fig. 1, a schematic diagram of the double layer is shown.

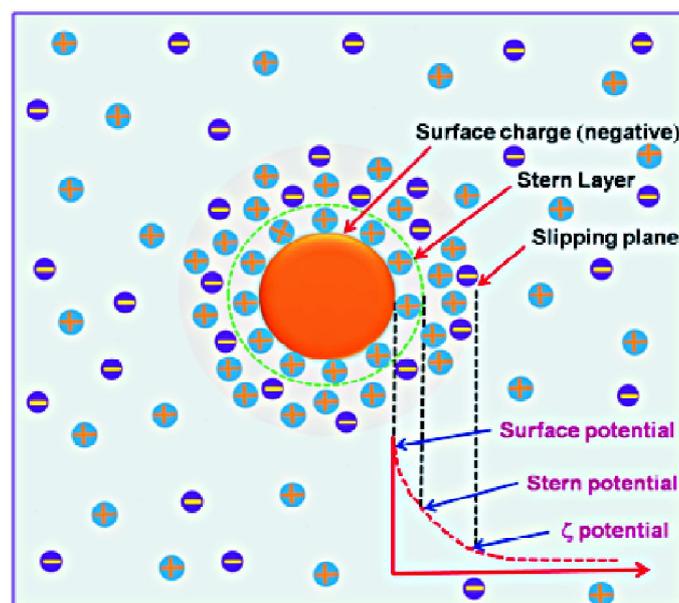


Fig. 1. A schematic diagram of electrical double layer of a colloid, and its different sections.

## 5. DLVO theory

In colloidal dispersion as well as in many other situations a balancing act between the van der Waal's attractive force, and the electrical double layer repulsion happens; and this in gist is the basis of DLVO (Derjaguin, Landau, Verwey and Overbeek) theory. B. Derjaguin and L. Landau in 1941, and independently E. J. W. Verwey and J. Th. G. Overbeek in 1948 discussed about the stability of the colloids. The theory known as DLVO theory [6] explains the aggregation of aqueous dispersions, quantitatively. In a colloidal dispersion, due to random Brownian motion, two colloidal particles will have possibility to come near each other, and then the van der Waal's attractive force steps in. For neutral particles only attractive force prevails. For charged colloid particles, the electrical double layer of both particles will repulsively interact with each other. Qualitatively, there will be simultaneous presence of attractive and repulsive forces. If the attractive force is stronger, agglomeration/ coagulation/ flocculation of the colloidal particles will occur (Fig. 2). For stronger repulsive force destabilization/ coagulation etc. will not happen. The repulsive force is a function of charge density, and lower the charge density, lower the repulsive force. At high  $\xi$ -potential repulsion is stronger which reverses at low  $\xi$ -potential. It is defined as the potential difference in an otherwise uniform medium between the particle surface and the plane of shear (slipping plane). The  $\xi$ -potential for a large number of hydrophobic colloids was obtained from various electrokinetic measurements (like electroosmosis, electrophoresis, streaming potential and sedimentation potential). It gives a practicable idea about the stability of the colloids. For  $\xi \geq \pm 60$  mV, flocculation is

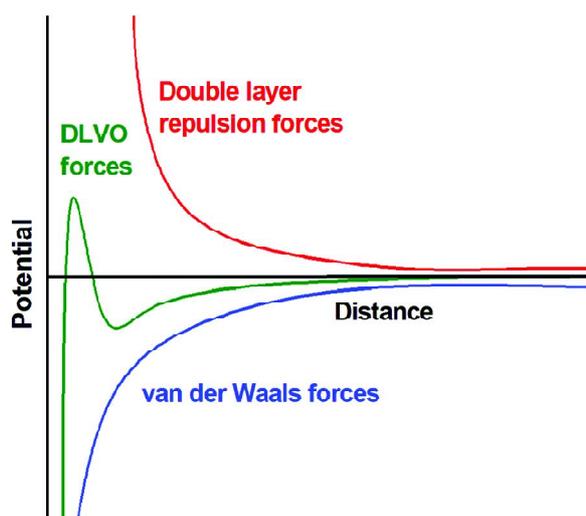


Fig. 2. Variation of van der Waals forces, Double layer repulsion forces and DLVO forces (a combination of the above two) as a function of distance between the two colloid particles.

uncertain; for  $\xi \approx \pm 10$  mV, flocculation is a certainty.

Besides the above discussed DLVO forces, two other forces (“hydration force” and “hydrophobic interaction force”) are also considered in relation to colloid stability. In general, ‘**hydration force**’ is a repulsive force acting up to a distance of  $\sim 5$  nm from the surface, and thereby prevents the coagulation of the colloid particles. The hydration force arises when adsorbed hydrated ions are prevented from desorbing as two interacting ions approach each other. This is found to be important in case of stability of sols and soap films, biomembrane interactions etc.[11]. When hydrocarbon molecules come in contact with water molecules, they are found to separate away from each other. Consequence to this water molecules come together to form stronger hydrogen bonded structure, and the hydrocarbon molecules also assemble together. This is known as ‘**hydrophobic interaction**’, and is also considered responsible for colloid stability/ instability. Besides, in some cases ‘**steric force**’ may also assist colloid stability e.g. in presence of polymers that get adsorbed on the surfaces of the colloid particles and thereby preventing coagulation. The steric repulsion essentially arises from entropic factors; polymers also support flocculation by bridging the colloid particles. The steric stabilization is dependent on temperature and independent of ionic strength [12–14].

Guerrero-Garcia [15,16] spoke about “**capacitive compactness**” which means charge neutralization capacity of charged fluid at a microscopic level, and stated that in presence of symmetric 1:1 electrolyte, the capacitive compactness decreases as a function of electrical charge. But for multivalent co-ions, the electrical double layer may expand or shrink. We suggested [17] that this may be one of the reasons that some systems follow Schulze - Hardy (S-H) rule and some do not. A fairly detail discussion on the rule is presented below.

## 6. Schulze - Hardy Rule

H. Schulze [8] and W.B. Hardy [9], independent of each other, found that addition of electrolyte solutions to a colloidal dispersion can destabilize the dispersion, and help them to coagulate (flocculate). They observed that

$$CCC \propto Z^{-n} \quad (1)$$

where,  $n > 1$  (generally taken as 6), and  $Z$  is the charge on the counter ion. This rule is known as Schulze - Hardy (S-H) rule in honour of the discoverers.

The S-H rule has the promise to explore the role of the valence of the multivalent ions (including the complex ions) toward coagulation. The rule considers only the charge-charge interaction, and not the charge density of the ion. The charge

density represents polarising power, and S-H rule has been modified to state “the greater the polarising power of the flocculating ion, the greater is its power to cause coagulation” [18]. Experiments have shown that the value of the exponent  $n$  can be any value between 2 and 6, and in some cases higher. Actually, the coagulation process is a function of many variables like polarizing power, time, and concentration of the salt as well as the amount of colloid present. Temperature is also an important factor. It was found that coagulation process is made up of two distinct rates, fast and slow. The intersection point of these two linear rate courses is also termed CCC. It has been found valid in practice.

The CCC of monovalent, bivalent and trivalent counter ions on coagulation of oppositely charged colloids ought to be in the order [monovalent] or  $C_1 >$  [bivalent] or  $C_2 >$  [trivalent] or  $C_3$ . From experimental findings the S-H rule (the CCC concentration ratios with respect to the trivalent counter ion) on the average follows the relation below [19,14]

$$C_1:C_2:C_3 = 3^6:(1.5)^6:1^6 = 729:11.4:1 \quad (2)$$

Various attempts have been made to explain the S-H rule. It was suggested that the colloid stability is due to the chemical interaction with the counter ions, and the linear relation is

$$\log CCC = -BZ + \log C_{ref} \quad (3)$$

where both  $B$  and  $C_{ref}$  are constants [20,21].

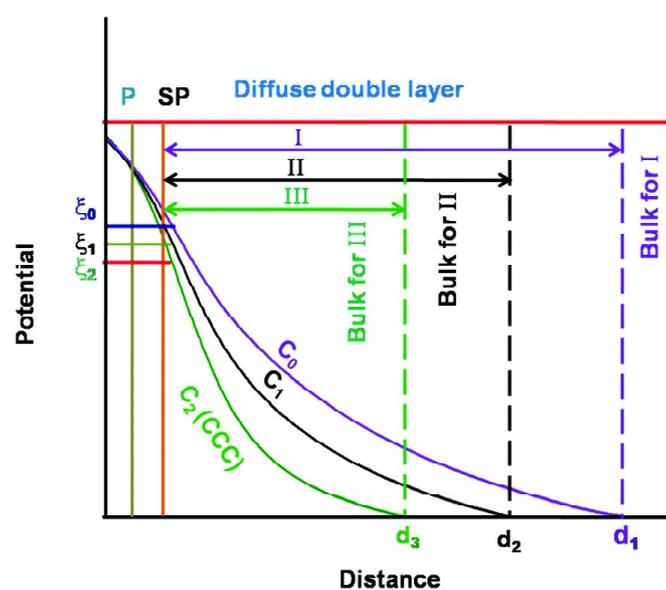
$B$  is the ratio of the critical distance for 1:1 ion pair formation using Bjerrum equation.  $C_{ref}$  denotes the concentration of an uncharged species of particles which would exert the same amount of effect as the charged ions in the region of CCC. Further, the critical distance of 1:2, 1:3 ion pair formations are different from the critical distance of 1:1 ion pair formation, and hence the slope and the intercept values will be different in these cases. It should be mentioned here that adsorption – desorption process also has a say on the phenomenon of coagulation.

In the S-H rule discussed above, it is obvious that the effect of only the counter ions are taken into account. However, no mention has been made on the effect of co-ions though it is known that both positive and negative ions of an electrolyte do have effects on the structure of water, and on the Gouy – Chapman diffuse double layer (GCL) as well. Recently, it has been proposed that co-ions have a say on CCC [18] presented in the relation below,

$$CCC \propto 1/z \quad (4)$$

where  $z$  is the charge of the co-ion. This has been termed as “Inverse Schulze - Hardy Rule (i S-H rule)”. Experimentally, it has been shown that co-ions also can affect  $\xi$ -potential due to

their adsorption at the glass-solution interface. They thus may affect CCC because Gouy – Chapman layer (GCL) controls  $\xi$ -potential, and GCL thickness changes on addition of electrolytes. A pictorial representation of the events is illustrated in Fig. 3. It should also be noted that deviation from S-H rule is not uncommon.



**Fig. 3.** Salt effect and the role of the electrical double layer in the process of coagulation of hydrophobic colloids: A pictorial summary. Double layer potential-distance profiles (scale arbitrary). S: Stern potential; PS: plane of slip or shear;  $C_0$ : aqueous medium without salt;  $C_1$ : salt added;  $C_2$ : at CCC. The zeta potentials at  $C_0$ ,  $C_1$ , and  $C_2$  are  $\xi_0$ ,  $\xi_1$ , and  $\xi_2$ , respectively;  $d_1$ ,  $d_2$ , and  $d_3$  represent the corresponding end-distances of the diffuse double layers, that is, the beginning of the bulk regions I, II, and III, respectively.

We suggested that these deviations may be due to non-consideration of the above mentioned non DLVO forces (“hydration force,” “hydrophobic force,” “steric factors,” etc.) in propounding the DLVO theory, and in the proposition of equation (1). In view of this, we modified S-H rule combining both co and counter ion effects in the following equations.

$$CCC \propto 1/z Z^n \quad (5)$$

Or,

$$CCC = K/zZ^n \quad (6)$$

where  $K$  is the proportionality constant [17,22].

Based on ion-valence consideration, the equation is then modified to

$$CCC \propto 1/(xz^1 \cdot yZ^n),$$

Or,

$$CCC = k/(xz^1 \cdot yZ^n) \quad (7)$$

where  $k$  is the proportionality constant,  $x$  and  $y$  can be obtained from electrolytes of general type  $(M^+)x(N^-)y$ , both  $x$  and  $y$  may have values 1, 2, 3, etc. Nature of the electrolytes determine the magnitudes of  $x$  and  $y$  depending on the valence of the cations and anions, respectively. Generally, exponents of  $z$  and  $Z$  are considered to be 1 and 6, respectively. However, for generalization we write them to be  $m$  and  $n$ , respectively; thereby eq. 7 becomes

$$CCC = k/(x y z^m Z^n) \quad (8)$$

It is known that CCC is a function of pH, ionic strength of the solution, size of the counter-ions etc. It also depends upon the nature of the solvent. Hence eq. 8 was further modified by us as described below [22].

If it is assumed that both the positive and negative ions of the electrolytes are hydrated and spherical then  $z$  and  $Z$  terms in eq. 8 can be replaced by  $(z/4\pi r_h)^2$  and  $(Z/4\pi R_h)^2$ , respectively (where  $r_h$  and  $R_h$  are the respective radii of the hydrated co-ion and counter-ion), and consideration of charge densities are inclusive. Further, it has been experimentally observed that coagulation is a function of the size (diameter) of the ions i.e., higher the diameter of the ion greater is the critical coagulation concentration or CCC.

Therefore, eq. 8 becomes

$$CCC = K/[x \cdot y (z \cdot d/4\pi r_h^2)^m (ZD/4\pi R_h^2)^n] \quad (9)$$

where,  $d (=2r_h)$ , and  $D (=2R_h)$ , are the diameters of the hydrated co-ion and counter-ion, respectively;  $4\pi r_h^2$  and  $4\pi R_h^2$  are the surface areas of the hydrated co-ion and counter-ion, respectively. By simplification, we get eq. 10

$$CCC = K/[x \cdot y (z/2\pi r_h)^m (Z/2\pi R_h)^n] \quad (10)$$

$$\text{Or, } X_{CCC} \cdot x \cdot y (z/2\pi r_h)^m = K' / (Z/2\pi R_h)^n \quad (11)$$

where,  $X_{CCC}$  is CCC in unit less mole fraction scale and  $K'$  is the corresponding proportionality constant. Taking logarithm of both sides and,  $m = 1$  (i S-H rule) we get,

$$\log(X_{CCC} \cdot x \cdot y) + m \log(z/2\pi r_h) = \log K' - n \log(Z/2\pi R_h) \quad (12)$$

The above equation which may be termed as Rakshit-Naskar-Moulik (RNM) equation may be used by plotting LHS [ $\log(X_{CCC} \cdot x \cdot y) + m \log(z/2\pi r_h)$ ] vs RHS [ $\log(Z/2\pi R_h)$ ], and getting a straight line with intercept  $\log K'$  and slope  $-n$ .

In Fig. 4, straight line plots for a few systems are shown. In Table 1 computed values of RNM equation are presented and compared them with those which can be obtained from original S-H equation (eq. 1) in terms of mole fraction scale. The comparative form of eq. 1 in mole fraction scale in logarithm form looks as

$$\log X_{ccc} = \log K_{SH} - n_{SH} \log Z \quad (13)$$

The difference between eq. 12, and eq. 13 becomes obvious.

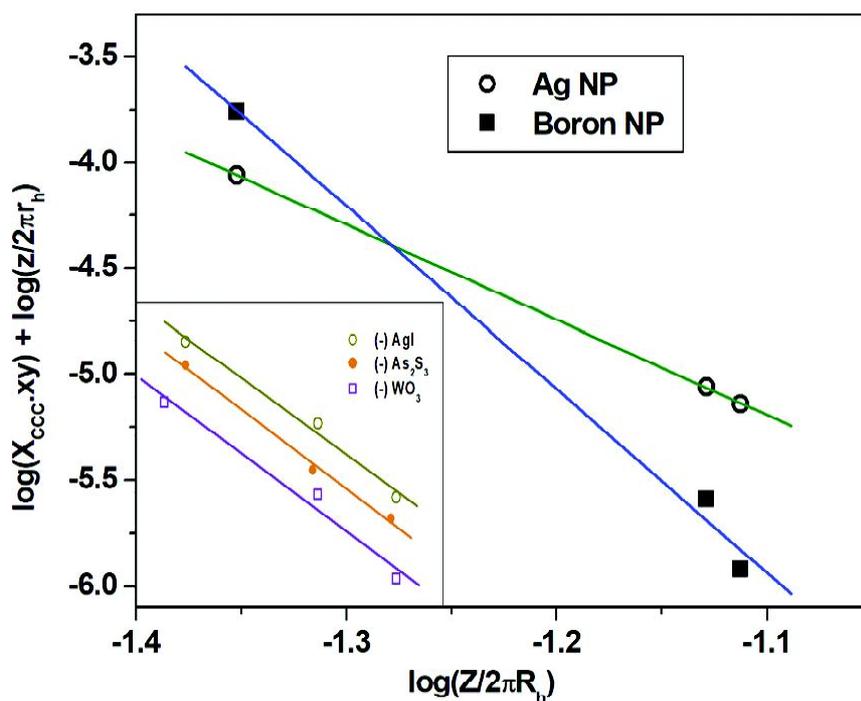


Fig. 4. Plots of  $\log(X_{CCC} \cdot xy) + \log(z/2\pi r_h)$  vs  $\log(Z/2\pi R_h)$  for AgNP and BNP. Inset: same plots for AgI, As<sub>2</sub>S<sub>3</sub>, and WO<sub>3</sub>.

**Table 1**

Correlation coefficients (corr. coeff.),  $\log K'$ ,  $\log K_{SH}$ ,  $n$  and  $n_{SH}$  found for several colloidal systems from the plots in terms of eqs. 12 and 13.

System	Eq. 12 (RNM)			Eq. 13 (S-H)		
	Correlation coefficient	$\log K'$	$n$	Correlation coefficient	$\log K_{SH}$	$n_{SH}$
(-) AgI	0.995	-13.31	7.28	0.996	-2.39	6.21
(-) As <sub>2</sub> S <sub>3</sub>	0.998	-11.96	5.96	0.999	-2.77	5.25
(-) WO <sub>3</sub>	0.987	-12.59	5.99	0.994	-3.17	5.77
(-) AgNP	0.999	-10.13	4.49	0.999	-2.74	4.45
(-) BNP	0.996	-15.44	8.64	0.992	-2.44	7.60

Results in Table 1 comprise two nanocolloidal systems (AgNP and BNP); it is shown that the exponent values from both eq. 12 and eq. 13 are though different, the correlation coefficients are nearly similar. The variations of the exponent values indicate that these are not really constant. The upper range may be larger than 6, and on the whole the modified S-H rule (eq. 12) produces values two units more than that proposed by S-H rule (eq. 3) for colloidal systems (-) AgI and (-) BNP (interestingly first is a classical system and the second is a modern nanoparticle system). With reference to the science and technology of nanocolloids, we may add that in solution, nanoparticles are stabilized by capping with thiols, surfactants, polymeric materials etc. [23,24]. Such nanocolloids obviously have electrical double layers and zeta potentials which need adequate investigations in terms of their preparation, stabilization and application.

## 7. Summary

The text of the article may be summarised as follows:

1) The charge densities of the colloid, the co- and counterions are important criteria for broader understanding of the salt induced colloid coagulation.

2) The power on the charge of counter-ions range around 2-8. For macro-colloidal systems it is lower, 2-4. For the nano-, and micro-colloids it is ~ 6.

3) The  $\log K'$  value depends on the surface charge of the colloid, and related to the  $\zeta$  potential at CCC.

4) "Capacitive compactness" may be one of the reasons for non-obeying of the Schulze - Hardy rule or its modification by some systems.

5) The variables which should affect the coagulation of colloids e.g. co-ions, charge densities, hydrated radius etc. have been taken into consideration in our method which was not considered in the more than hundred year old Schulze - Hardy rule.

6) It is interesting that nano-colloids also follow the extended Schulze-Hardy rule; more studies are required.

7) Interested readers may consult both the papers of Rakshit et al. [17,22] for references as well as for incisive discussion on the topic.

## Conflict of interest

We declare no conflict of interest as well as no funding source for this work.

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