

## Precipitation Potentials of Sodium, Potassium & Ammonium Chlorides, Bromides & Iodides

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Precipitation and phase potentials of chlorides, bromides and iodides of sodium, potassium and ammonium have been measured in water. The build-up and decay of precipitation potentials is also observed. The temperature dependence of precipitation and phase potentials of the halides of sodium have been studied. True precipitation potentials have been plotted against (i) percentage covalent character, (ii) lattice energy, (iii) ratio of ionic radii of cation and anion, (iv) ratio of ionic mobilities of cation and anion, (v) ratio of heats of ion-water interaction of cation and anion and (vi) ratio of real hydration energies of cation and anion. Except for ionic mobilities, the potentials show linear relationship with these properties for each set of halides having a common cation. The sign and magnitude of true precipitation potential has been explained on the basis of unequal rate of removal of the cation and anion from the solution phase due to their different hydration energies.

THE electrochemical aspect of crystal growth is of great interest and some investigations have been reported with reference to the potential differences that developed during (i) solidification of dielectrics<sup>1-4</sup>, (ii) freezing of aqueous solutions of electrolytes<sup>5-7</sup>, (iii) precipitation from molten electrolytes<sup>8-11</sup> and (iv) precipitation of electrolytes from saturated solutions<sup>12</sup>. When an ionic crystal grows in an aqueous solution cations and anions are transferred from solution phase to solid phase. Thus crystallization of ionic salts can be regarded as an electrochemical process. Rastogi *et al.*<sup>13</sup> have recently defined the precipitation potential as the potential difference arising from the electrical double layer developed at crystal/saturated solution interface by the ionic migration from the liquid phase.

However, the previously arrived conclusion could not be generalized because these were based upon very limited experimental data. Keeping this in view the authors in the present paper report on precipitation potentials of nine uni-univalent electrolytes and their correlations with some properties of the electrolytes and the constituent ions.

### Materials and Methods

AR grade (BDH) chemicals were used as such and LR quality chemicals were purified by crystallization from their saturated solutions. Deionized water prepared using Elgastat B105 was used.

Platinum (99.99% purity) electrodes were cleaned with boiling nitric acid and then washed with water. These were kept always in water when not in use. By doing so the asymmetry potential was found to be negligible. This asymmetry potential was also measured before each run.

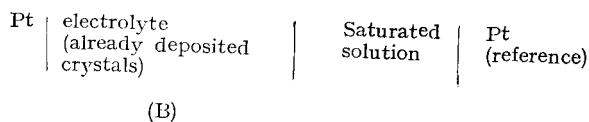
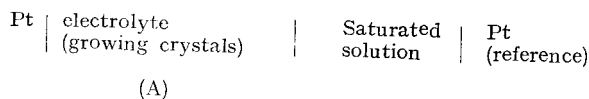
Vacuum tube voltmeter (Philips GM 6001/90) which could read with an accuracy of 2 mV was used for the measurement of potentials. In order

to protect the apparatus from the effects of stray external fields, the coaxial wires with earthed screens were used for the connections. The reproducibility of the data was checked by repeating the experiment several times.

*Measurement of precipitation potential* — Since the potential at the electrolyte/solution interface cannot be measured directly, the voltage of the cell of the type (A) was measured. A sintered disc is fitted such that no solid electrolyte, if any, comes directly in contact with the electrodes during filling the cell with the saturated solution prepared at 40°. The cell was kept in a water-bath having initial temperature of about 45°. The reference platinum electrode being very small gets completely immersed by just dipping at the surface of saturated solution. This was done in order to keep it free from the growing crystals. The water bath was then allowed to cool slowly and the potential that developed due to crystal deposition on the spiral electrode was recorded as a function of time. The cooling rate was controlled to ensure smooth formation of crystals. Moreover, special care was taken to avoid slight shocks being transmitted to the solution during crystallization. The build-up and decay of these potentials was also investigated.

*Measurement of phase potential* — The phase potential was measured using the cell (B).

The crystals of electrolyte were deposited on the electrode by controlled cooling of saturated solution



prepared at about 85° in a separate bath. The electrode loaded with deposited crystals was then transferred to the experimental cell in which the saturated solution was kept separated from the excess solute by sintered disc fitted at the bottom of the cell. The potential measured by adopting this procedure is only due to the crystal/saturated solution interface because all other processes such as dissolution, precipitation and diffusion are not operating.

### Results and Discussion

The observed precipitation potential (maximum value) and the phase potential of nine uni-univalent electrolytes at 25° are given in Table 1. The build-up and decay of observed precipitation potentials of the chlorides is shown in Fig. 1. Similar curves were obtained for bromides and iodides.

True value of precipitation potential is given by the relation<sup>13</sup>.

True precipitation potential = Obs. precipitation potential - (phase potential + diffusion potential + Nernst potential + thermodiffusion potential)

It was further reported by the authors that thermodiffusion and Nernst potentials have a much smaller magnitude. The diffusion potentials of the nine electrolytes used in this investigation, calculated using Eq. (1), were found to be negligible.

$$\text{Diffusion potential} = (2t_+ - 1) \frac{RT}{F} \ln \frac{C}{\bar{C}} \quad \dots(1)$$

In Eq. (1),  $t_+$  is the transport number of cation and  $C_1$  and  $C_2$  refer to the concentrations of the two solutions of the electrolyte. Hence, neglecting the diffusion, thermodiffusion and Nernst potentials, the true precipitation potential can be written as:

True precipitation potential = Obs. precipitation potential - phase potential

The true precipitation potentials thus calculated are given in Table 1.

It was difficult for Rastogi *et al.*<sup>11</sup> to say whether the potential develops just when a tiny crystal forms on the electrode or when it grows to a certain dimensions. However, it can be seen from the decay curves (Fig. 2) that the development of

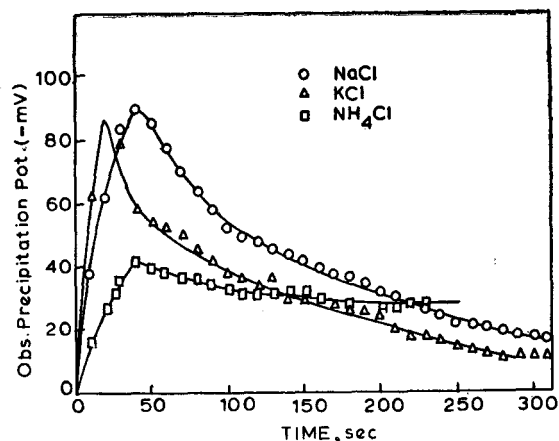


Fig. 1 — Decay of observed precipitation potential for sodium, potassium and ammonium chlorides

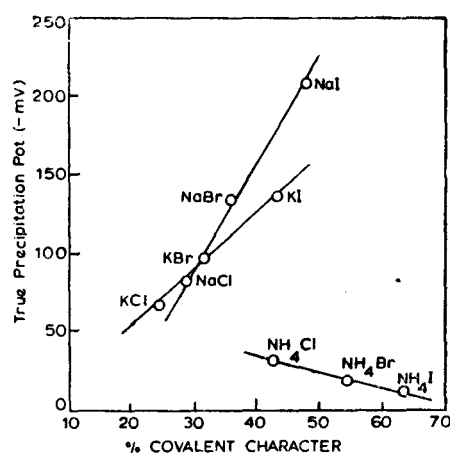


Fig. 2 — True precipitation potential versus percentage covalent character [Data taken from ref. 9b]

TABLE 1 — PRECIPITATION POTENTIALS OF THE ELECTROLYTES AT 25°C

| Electrolyte        | Obs. pptn pot. (mV) | Phase pot. (mV) | Phase pot. from decay curves (mV) | True pptn pot. (mV) | True dissoln pot. (a) (mV) |
|--------------------|---------------------|-----------------|-----------------------------------|---------------------|----------------------------|
| NaCl               | -90                 | -8              | -10                               | -82                 | -72                        |
| NaBr               | -152                | -18             | -16                               | -134                | -150                       |
| NaI                | -238                | -30             | -25                               | -208                | -238                       |
| KCl                | -86                 | -20             | -20                               | -66                 | -18                        |
| KBr                | -122                | -26             | -12                               | -96                 | -62                        |
| KI                 | -170                | -34             | -32                               | -136                | -124                       |
| NH <sub>4</sub> Cl | -42                 | -30             | -32                               | -12                 | +120                       |
| NH <sub>4</sub> Br | -70                 | -50             | -34                               | -20                 | +66                        |
| NH <sub>4</sub> I  | -106                | -74             | -50                               | -32                 | -8                         |

(a) Values taken from reference 15 were modified taking into account the contribution of phase potentials.

potential to a maximum value takes some time, probably due to nucleation process. The maximum value may then correspond to the formation of a perfect crystal. After attaining the maximum value it then falls exponentially to a steady value which in fact should correspond to a situation where the supersaturated solution approaches the concentration of the saturated solution at the temperature of observation and no more precipitation is occurring. Thus such limiting potential is due to the presence of a crystal/saturated solution interface. The phase potentials obtained from the decay curves are also recorded in Table 1 and these are found to be in approximate agreement with those measured by direct experiments.

The phase potential was found to be independent of temperature but the true precipitation potentials decreased linearly with increasing temperature.

Before probing into the mechanism of the development of the precipitation potential it would be worth while to correlate it with some of the properties of electrolytes and their constituent ions. Such relationships are expected because the precipitation of electrolytes is an ionic phenomenon. This was achieved by plotting the true precipitation potentials

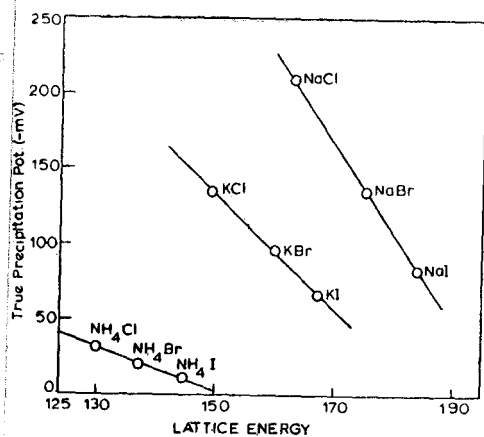


Fig. 3 — True precipitation potential versus lattice energy [Data taken from ref. 19a]

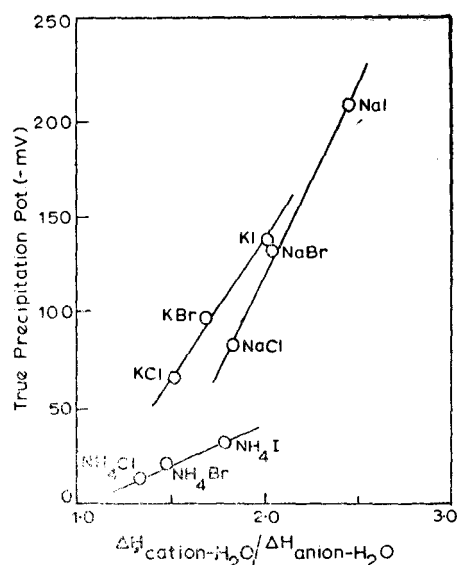


Fig. 6 — True precipitation potential versus ratio of heats of ion-water interaction of cation and anion [Data taken from references 20 and 21]

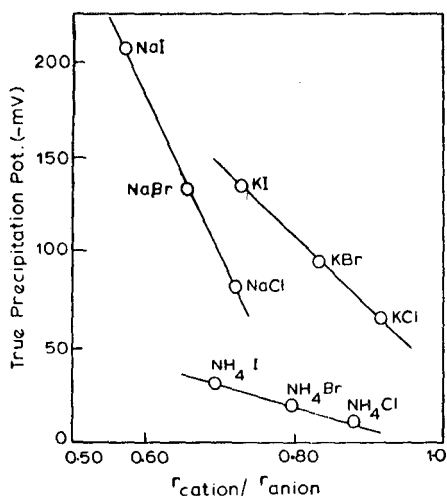


Fig. 4 — True precipitation potential versus ratio of ionic radii of cation and anion [Data taken from references 16 and 17]

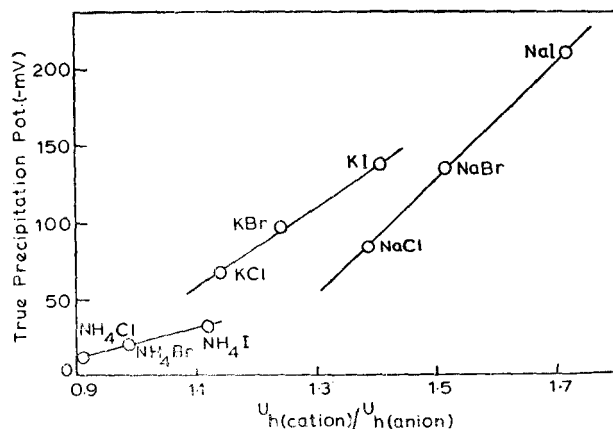


Fig. 7 — True precipitation potential versus ratio of real hydration energies of cation and anion [Data taken from ref. 18]

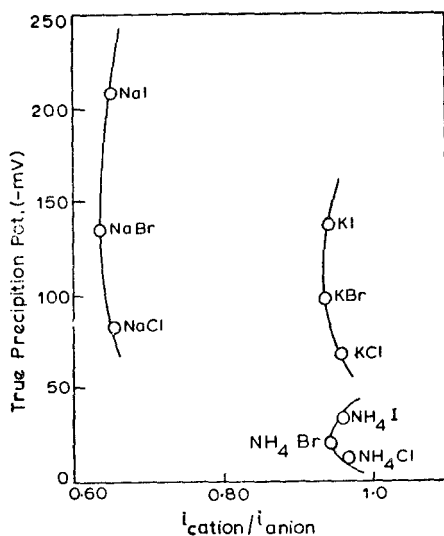


Fig. 5 — True precipitation potential versus ratio of ionic mobilities of cation and anion [Data taken from ref. 22]

against (i) percentage covalent character (Fig. 2), (ii) lattice energy (Fig. 3), (iii) ratio of ionic radii of cation and anion (Fig. 4), (iv) ratio of ionic mobilities of cation and anion (Fig. 5), (v) ratio of heats of ion-water interaction of cation and anion (Fig. 6) and (vi) ratio of real hydration energies of cation and anion (Fig. 7). The true precipitation potential has been found to decrease linearly with properties at serial numbers (ii) and (iii) for each set of halides while reverse is the case with the properties (i), (v) and (vi). Though there is no direct relationship of the precipitation potential with the ratio of ionic mobilities yet some regularity is there. Further, it can be seen that the magnitude of true precipitation potential is in the order  $\text{Na}(\text{K}, \text{NH}_4) \text{I} > \text{Na}(\text{K}, \text{NH}_4) \text{Br} > \text{Na}(\text{K}, \text{NH}_4) \text{Cl}$  and  $\text{NaCl}(\text{Br}, \text{I}) > \text{KCl}(\text{Br}, \text{I}) > \text{NH}_4\text{Cl}(\text{Br}, \text{I})$ .

*Mechanism and sign of precipitation potential* — Rastogi *et al.*<sup>11,12</sup> have explained the sign of precipitation potentials on the basis of the difference in mobilities of the ions moving to the crystal lattice.

Accordingly when the mobility of the anion is greater than that of the cation the electrode on which precipitation is taking place would become negative with respect to the reference electrode dipped in solution. The development of dissolution potential which arises when the crystal of electrolyte embedded on the electrode goes into solution was also explained on similar basis by these workers. Again when the mobility of the anion is greater than that of the cation, the anion would leave the lattice faster than the cation, thus the electrode on which dissolution is occurring would become positive. In other words the sign of the potential developed both during the precipitation and the dissolution processes should be opposite for the same electrolyte. However, in contrast, the experimental data of Rastogi *et al.*<sup>12,13</sup> for a few electrolytes in water and in other solvents have revealed that both the dissolution and precipitation potentials have the same sign for each electrolyte. Rastogi *et al.* could explain their results qualitatively on the basis of combined effect of relative tendency of hydration of ions and mobilities.

Recently<sup>15</sup> we could correctly predict the sign and relative magnitude of dissolution potential from the point of view of solvation mechanism which is as follows. Since the transfer of ions from the crystal into water is due to their interactions with water molecules which will pull these ions away from the lattice, the rate of removal of cation and anion would be proportional to their hydration energies which are the true measure of ion-water interaction. Thus, an unequal rate of removal of cations and anions from the crystal lattice will form an electrical double layer in the immediate vicinity of the solid electrolyte. Obviously, when the ratio of hydration energies of cation and anion is greater than unity, the cation will be removed faster than anion and the electrode on which dissolution is taking place would become negative. But in precipitation process, the ion before entering the crystal lattice sheds the hydration sheath at the crystal/solution interface. Thus, ion with higher hydration energy will get detached from its hydration sheath with difficulty as compared to an ion with lower hydration energy. Accordingly when the ratio of hydration energies of cation and anion is greater than unity, the cation will be removed from the solution phase and will enter the crystal lattice slowly than the anion. In this case also the electrode on which precipitation is occurring would become negative. Table 1 reveals that for all the electrolytes the observed sign of both the precipi-

tation potential (except  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$ ) and dissolution potential is correctly predicted. Moreover, the above mentioned mechanism based on solvation process predicts that the sign of both the dissolution and precipitation potentials should be same which is also evident from Table 1.

It can be further seen from Table 1 that for each set of halides having a common cation, the order of magnitude of precipitation potential is reverse to that of the hydration energy, i.e. chloride > bromide > iodide. This is also explicable from the ion-water interaction consideration.

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