Dissolution Potentials of Sodium & Potassium Chlorides, Bromides & Iodides & of Ammonium Halides

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Dissolution potentials of nine uni-univalent electrolytes, i.e. NaCl, NaBr, NaI, KCl, KBr, KI, NH_4Cl, NH_4Br and NH_4I have been measured in water at $25° \pm 0.1°$ with the maximum inaccuracy of $\pm 2.5\%$ using a vacuum tube voltmeter. The decay of the observed potentials as a function of time has also been investigated. In order to find out the contribution of the diffusion potentials these were measured from separate experiments. True dissolution potentials of all these electrolytes have negative sign with the exception of NH_4Cl and NH_4Br which show positive signs. The magnitude of true dissolution potentials has been interpreted in terms of heat of ion-water interaction and real hydration energies of ions.

RECENTLY a good deal of interest has been evinced in the study of electrical effects during phase transformations. Potential differences have been observed to develop during (i) solidification and melting of dielectrics[1-4], (ii) freezing of aqueous solutions of electrolytes[5], (iii) precipitation from molten electrolytes[6-8], (iv) precipitation of electrolytes from saturated solutions[9,10] and (v) dissolution of electrolytes[9-12]. In spite of these extensive studies the origin of such potentials is not yet clear.

Srivastava and coworkers[11] measured the dissolution potential of some uni-univalent electrolytes. Since they have not taken into account diffusion potential, therefore, the measured dissolution potential could not represent the true value. Rastogi *et al.*[10] have computed the true dissolution potential from their experimental data but the study is limited to only three uni-univalent electrolytes. Therefore, no generalized relation of these potentials with properties of the electrolytes could be made. With this background, it was considered desirable to determine the values of true dissolution potentials of some simple systems. Such as the chlorides, bromides and iodides of sodium, potassium and ammonium cation the detailed data of which on ionic properties are available so that some relationship could be built up.

Materials and Methods

Analytical reagent grade (BDH) chemicals were used as such and LR quality chemicals were purified by crystallization from their saturated solutions. The deionized water prepared using Elgastat B105 deionizer was used throughout this investigation.

Every time before use, the platinum electrodes (99.99% purity) were cleaned with boiling nitric acid and finally washed with deionized water. These cleaned electrodes were always kept in deionized water when not in use. By adopting this procedure the asymmetry potentials of electrodes were found to be considerably reduced. The asymmetry correc-

tion of various electrodes was in the range 0-12 mV. The potentials were measured using vacuum tube voltmeter (Philips model GM 60001/90) having least count of 2 mV. Fluctuations in potentials due to stray external fields were avoided by earthing (i) the thermostat, (ii) the voltmeter, and (iii) coaxial cables connecting the experimental cell and voltmeter. All the potentials were measured at $25° + 0.1°$.

Measurement of dissolution potential — The reference electrode was kept dipping in deionized water in the experimental cell. A thin layer of crystals of electrolyte was deposited on other electrodes by controlled cooling of saturated solution prepared at about 85°. The smoothness of the crystals was seen by observing under a microscope. The electrode loaded with crystals, immediately after removing from the crystallization bath was dipped in the cell and the maximum potential developed was measured instantaneously. The experiments were repeated several times to check the reproducibility of the results. The decay of observed potential as a function of time was investigated. The above experiments were also performed with the electrode on which the deposited crystals were completely dried but the results obtained were not reproducible.

Measurement of diffusion potential — The reference electrode was kept dipping in deionized water in the cell. The second electrode was immersed in a saturated solution maintained at 25°. Immediately after withdrawing the second electrode loaded with a thin layer of saturated solution it was dipped into the cell and the maximum value of potential was measured instantaneously. Since the potential measured by adopting this technique is due to the diffusion of adhering solution layer on the electrode, therefore, it is being called as diffusion potential.

Results

The observed dissolution potentials and the diffusion potentials of uni-univalent electrolytes measured with respect to the reference electrode are given in

Table 1. These data have been corrected for asymmetry potential of the electrodes. The decay of the observed potentials for these electrolytes as a function of time were also plotted. For the sake of economizing the space the decay curves for the chlorides of sodium, potassium and ammonium ion are shown in Fig. 1.

Discussion

Since the dissolution potential is identified as an instantaneous potential which is developed as soon as a tiny crystal starts dissolving in water, its value would be a sum of the potentials developed due to various parallel factors which lead to the initiation of dissolution process. Keeping in view the limitations of our present day knowledge regarding the mechanism of dissolution process we should there-
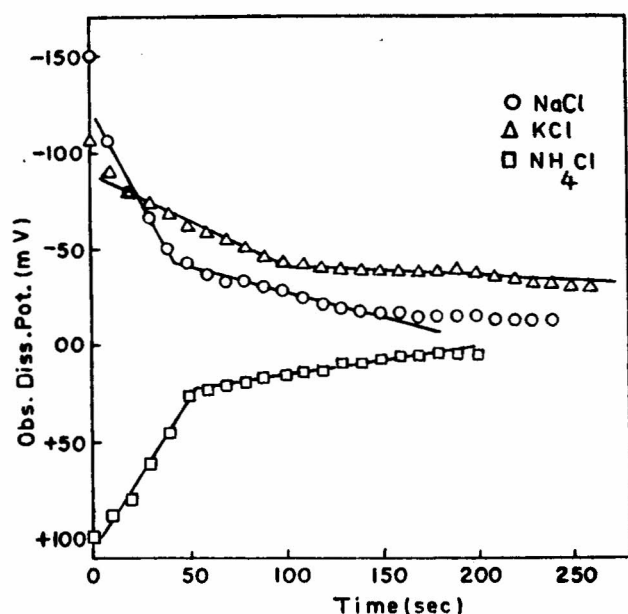

Fig. 1 — Decay of observed potential with time of sodium chloride, potassium chloride and ammonium chloride

fore, probe into the mechanism for the development of this potential as a combined effect of several parallel processes. Thus when the experiment is carried out with completely dried crystals the instantaneous observed potential will be the true value of dissolution potential. But the results obtained using dried crystals are not reproducible. This is probably due to some vital factors which could not be controlled during the process of drying the crystals, e.g. the rate of drying and the formation of cracks on crystals surface are found to have a tremendous influence on dissolution potential. That is why, in the present investigation all the measurements were carried out with the freshly deposited wet crystals. This would imply that the electrode is loaded not only with crystals but with their saturated solution also. Accordingly when the electrode is immersed in water, firstly diffusion between saturated solution and water occurs which will be followed by the dissolution of crystals and simultaneous diffusion due to the creation of concentration gradient. Thus the maximum value of observed potential would include both the true dissolution potential and the diffusion potential.

Since diffusion potential arises when the mobilities of the diffusing ions of the electrolyte are different, therefore, one may expect some relationship of the diffusion potential with ionic mobilities. However, the experimental values of diffusion potential are found to show no correlation with either I_+/I_-, (I_+-I_-) or $(I_++I_-)/(I_+-I_-)$ where I_+ and I_- are mobilities of cation and anion respectively.

Rastogi and Shukla[10] have qualitatively explained the mechanism of dissolution potential of four electrolytes on the basis of unequal ionic mobilities of the ions being detached from the crystal lattice. However, the process of dissolution initially involves breaking of the crystal lattice and then the interaction of anions and cations with the solvent. Depending upon the magnitude of the ion-solvent interaction, the rate of removal of cation and anion from the crystal lattice will be different. This unequal rate of removal will thus lead to the formation of an

TABLE 1 — DISSOLUTION AND DIFFUSION POTENTIALS OF UNI-UNIVALENT ELECTROLYTES AT 25°

Electrolyte	Obs. dissolution potential (mV)	Diffusion potential (exp) (mV)	True dissolution potential (mV)	Diffusion potential (graphical) (mV)	Ionic mobilities* (cm²/sec volt) × 10⁵		$\dfrac{\Delta H_{cation-H_2O}}{\Delta H_{anion-H_2O}}$ (ref. 14)	$\dfrac{Uh_{cation}}{Uh_{anion}}$ (ref. 16)
					Cation	Anion		
NaCl	−120	−40	−80	−42	51·9235	79·0788	1·832	1·389
NaBr	−238	−70	−168	−76	51·9235	81·1516	2·035	1·513
NaI	−380	−112	−268	−109	51·9235	79·5970	2·446	1·717
KCl	−80	−48	−38	−42	76·1768	79·0788	1·523	1·140
KBr	−140	−52	−88	−49	76·1768	81·1516	1·693	1·242
KI	−230	−80	−158	−84	76·1768	79·5970	2·034	1·409
NH₄Cl	+114	+24	+90	+24	76·3841	79·0788	1·340 (ref. 15)*	0·905
NH₄Br	+36	+20	+16	+22	76·3841	81·1516	1·489 (ref. 15)	0·896
NH₄I	−282	−200	−82	−200	76·3841	79·5970	1·790 (ref. 15)	1·119

*Ionic mobility calculated from limiting ionic conductance data[13].
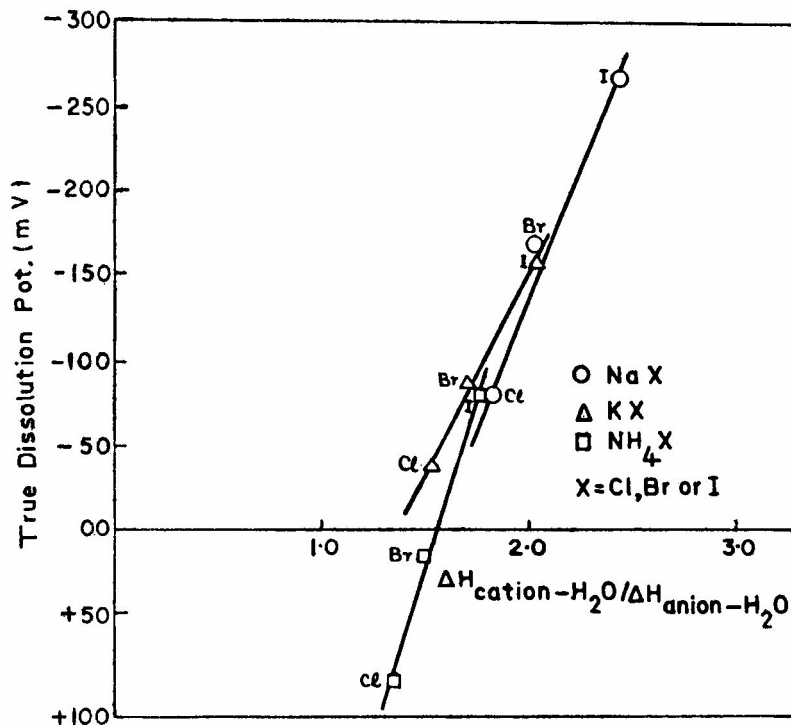ΔH = heat of ion-water interaction; Uh = real hydration energy.

Fig. 2 — Plots of true dissolution potential versus ratio of heat of ion-water interaction
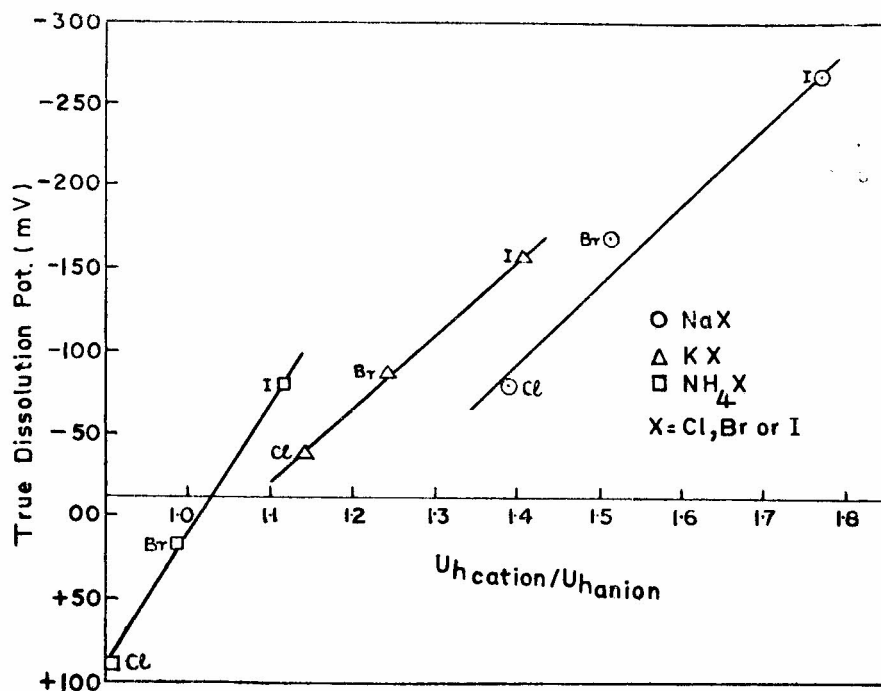

Fig. 3 — Plots of true dissolution potential versus ratio of real hydration energies

electrical double layer in the vicinity of solid electrolyte. Therefore, true dissolution potential should be related to the heats of hydration and real hydration energies of various ions because these properties are the ture measure of ion-water interactions. The plots of true dissolution potential against ratio of (i) heats of ion-water interactions, and (ii) real hydration energies of cation and anion are shown in Figs. 2 and 3 respectively. There is a linear relationship of true dissolution potential for each set of halides with both these ionic properties. It is of interest to mention that when the ratio of real hydration energies of cation and anion is less than unity the sign of dissolution potential is positive such as in the case of NH_4Cl and NH_4Br. However, when this ratio is greater than unity the

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sign of potential is negative. This is explainable on the unequal rate of removal of cation and anion from the crystal lattice.

Decay of observed potential — Recently Rastogi and Shukla[10] have reported that the observed dissolution potential of KCl, NaCl, NH$_4$Cl and BaCl$_2$ decays exponentially. However, the present data of decay of observed potential show a pair of intersecting straight lines (Fig. 1). Unless a quantitative theory of the phenomenon is available, it will be difficult to say that the curves have some discontinuity or are exponential. When the electrode loaded with crystals and the saturated solution is dipped in water the following three processes are likely to occur: (i) the diffusion between saturated solution on crystals and water, (ii) the dissolution of the crystals and simultaneous diffusion of saturated solution and (iii) only diffusion when all the crystals on the electrode are dissolved. Since the first process is of very short duration, the diffusion potential would immediately be superimposed by the build up of dissolution potential. Though we had some indications of such a rise in potential but it could not be recorded accurately as a function of time. Furthermore, the potential due to first process may also include asymmetry potential due to the electrodes. Now the second process will give potential both due to dissolution and simultaneous diffusion. When all the crystals have dissolved, the potential will be due to only the third process and the decay curve should have a trend to approach zero potential with passage of time. This is what one should expect when the system achieves equilibrium. If we ignore the built-up stage of potential the decay curve will consist of two

straight lines instead of three and the potential at the point of intersection will correspond to the maximum value of diffusion potential. The average values of diffusion potential calculated from a number of decay curves for each electrolyte are in accord with the experimental values as shown in Table 1.

Acknowledgement

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