Dissolution Potentials of Nitrates of Sodium, Potassium & Ammonium

H. L. GIRDHAR & R. P. MATTA

Department of Chemistry, University of Kashmir, Srinagar

Dissolution potential and diffusion potential of $NaNO_3$, KNO_3 and NH_4NO_3 have been measured at 25° with an accuracy of $\pm 2.5\%$. The experimental values of diffusion potential are in good accord with those computed from the decay curves. True dissolution potentials of nitrates of sodium and potassium show negative signs but for ammonium nitrate its sign has been found to be positive.

IN spite of a large amount of work on dissolution potential of electrolytes[1-5], the mechanism of such potential is still not clear. Girdhar et al.[6] have correlated the true dissolution potentials and diffusion potentials of nine uni-univalent electrolytes with some properties of the electrolyte and its constituent ions. They could also predict the sign and order of these potentials in terms of the real ionic hydration energies which seem to play an important role in the development of such potentials. As a part of continuing investigation of these potentials of uni-univalent electrolytes we have now measured the true dissolution potential and diffusion potential of $NaNO_3$, KNO_3 and NH_4NO_3.

Materials and Methods

Ammonium nitrate and potassium nitrate both LR grade (BDH) were purified from their saturated solutions. Sodium nitrate double refined grade (Schmidt & Berg, Germany) was used as such. All the measurements were made in deionized water (using Elgastat B 105 deionizer) which was also used for preparing saturated solutions of electrolytes. The experimental procedure for measurement of dissolution potential and diffusion potential is the same as described by Girdhar et al.[5] Before each measurement the platinum electrodes were cleaned with boiling nitric acid and finally washed with deionized water. This brings down the asymmetry potential of the electrodes to the lowest possible value. A uniform layer of the electrolyte was deposited on a cleaned platinum electrode by controlled crystallization from solution of electrolyte saturated at 85°C. The reproducibility of data was checked by repeating the experiments several times.

Results and Discussion

The observed dissolution potential and the diffusion potential of these electrolytes at 25°C with respect to the clean platinum electrode dipping in water as reference electrode are given in Table 1. These data have been corrected for asymmetry potentials of the electrodes used. The decay of the observed dissolution potentials for these electrolytes is shown in Fig. 1.

The first one or two points in each of these decay curves were ignored while drawing the straight lines because these points correspond to the sum of the actual observed dissolution potential and the asymmetry potential of the electrode. However, the rest of the points represent the actual values of the observed dissolution potentials as the asymmetry effect has been found to vanish within a few seconds after the electrode is dipped in water.

As reported in our earlier communication[5], this observed dissolution potential is the sum of the true dissolution potential and the diffusion potential because the dissolution of crystals and the diffusion of preexisting saturated solution on the crystals start simultaneously when the electrode loaded with wet crystals is immersed in water. Thus subtracting diffusion potential from the observed dissolution potential would yield the values of true dissolution potentials which are also given in Table 1. It is

TABLE 1 — POTENTIALS AND SOME PROPERTIES OF ELECTROLYTES AT 25°C

Electrolyte	Obs. dissolution potential (mV)	Diffusion potential (mV)	True dissolution potential (mV)	Diffusion potential (graphical) (mV)	Solubility[7] (mole/1000 g H_2O)	$\dfrac{u_{cation}}{u_{anion}}$ (ref 8)	$U^*_{h_{cation}}$ (kcal/g ion)
$NaNO_3$	−204	−86	−118	−88	10·823	0·70	97·0(9)
KNO_3	−140	−52	−88	−51	3·827	1·02	77·0(9)
NH_4NO_3	+74	+40	+34	+42	27·112	1·03	69·5(10)

(a) The solubility at 25° is taken as the mean of the values given at 20° and 30°, the literature values given in g/100 g H_2O were converted into mole/1000 g H_2O.
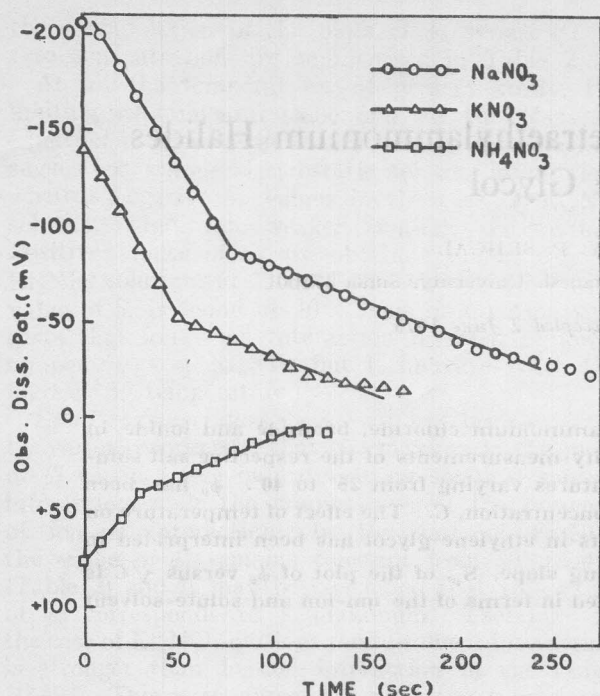
*u = ionic mobility; U_h = real hydration energy.

Fig. 1 — Decay of observed dissolution potential

experimental studies of diffusion potential were carried out under standard condition, i.e. when saturated solution is in contact with pure solvent. However, as is evident from Table 1, the solubilities reveal no correlation with diffusion potentials. Further, diffusion potential does not appear to be related to the ratio of ionic mobilities.

Girdhar et al.[6] have explained the mechanism of development of dissolution potential on the basis of solvation phenomenon. The molecules of the solvent being absorbed at the interface interacts with ions of electrolyte and pull them out of its lattice. Since hydration energy is a true measure of water-ion interaction, therefore, the rate of removal of the ions will depend on their respective hydration energies. Thus unequal rates of removal of anions and cations from the lattice will lead to the formation of electrical double layer. Since hydration energy of nitrate ion is not available in the literature therefore no direct comparison of the hydration energies of Na^+, K^+ and NH_4^+ ions could be made with NO_3^- ion and that is why the sign of dissolution potential can not be predicted. Nevertheless, it appears from Table 1 that the true dissolution potentials of electrolytes are in the order of real hydration energies of their respective cations.

Acknowledgement

References

1. Rastogi, R. P., Batra, B. P. & Dass, R. K., Nature, Lond., 191 (1961), 764.
2. Shukla, R. D. & Rastogi, P., Indian J. Chem., 8 (1970), 192.
3. Srivastava, R. C. & Khurana, O. P., J. Indian chem. Soc., 48 (1971), 1151.
4. Rastogi, R. P. & Shukla, R. D., J. appl. Phys., 41 (1970), 2787.
5. Girdhar, H. L., Arora, A. J. & Matta, R. P., Indian J. Chem., (1976), in press.
6. Girdhar, H. L., Arora, A. J. & Matta, R. P., Indian J. Chem., 13 (1975), 1047.
7. Lange, J. O., Handbook of chemistry (McGraw-Hill, New York), 1967, 184.
8. Antropov, L., Theoretical electrochemistry (Mir Publisher, Moscow), 1970, 113.
9. Antropov, L., Theoretical electrochemistry (Mir Publisher, Moscow), 1970, 87.
10. Bockris, J. O., Modern aspects of electrochemistry, No. 2 (Butterworths, London), 1959, 123.

seen from Fig. 1 that decay curve of each electrolyte consists of two straight lines meeting at a point where the effect due to dissolution process completely vanishes. Thus the observed potential corresponding to this point of interesection is the actual value of diffusion potential. The average values of diffusion potential obtained from a number of decay curves of each electrolyte are given in Table 1. An examination of Table 1 shows very good agreement between the experimental and graphical values of the diffusion potential for all the three electrolytes. It is of interest to note from Fig. 1 that all the three decay curves have the trend to approach zero potential value with the passage of time. This is as expected, since the diffusion process also ceases and the solution in experimental cell achieves equilibrium state. These results further confirm our previous results that the observed dissolution potential is a sum of the true dissolution potential and the diffusion potential.

The diffusion potential of an electrolyte in solution arises as a result of concentration gradient and when the ionic mobilities are not equal. As far as concentration gradient is concerned, the

161