

further improvements should be possible. The other advantages of the heterogeneous cells are: (i) the dark compartment need only be formally dark; it need not be protected from light since there is no photoactive material therein; (ii) whereas the homogeneous cell does not permit use of higher $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ ratios than the one chosen in the above experiments (Table 1), as at higher Fe^{2+} concentration the open circuit cell voltage itself decreases², there is no limitation on the composition of the dark compartment; and (iii) with the heterogeneous cell it should also be possible to store the light energy in the form of chemical free energy and then release it by discharging through an external load.

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Effect of Temperature & Concentration on Dissolution Potentials of Sodium Chloride, Bromide & Iodide

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Dissolution potential and diffusion potential of NaCl, NaBr and NaI have been measured at different temperatures and at different concentrations at 25°. True dissolution potential decreases and diffusion potential increases linearly with increasing temperature. The concentration dependence of diffusion potential has been discussed on the basis of Planck equation and an empirical relation for the variation of true dissolution potential with concentration is given.

DESPITE a good amount of experimental data on the dissolution potential of electrolytes¹⁻⁴, there is still no generalized mechanism for the

phenomenon. Recently^{5,6} the sign and magnitude of dissolution potential have been explained on the basis of the formation of electrical double layer at the solid/liquid interface. The dissolution potential has also been found^{3,7} to be influenced by the temperature of solvent and the concentration of the dissolved electrolyte. The purpose of the present study is to explain quantitatively the temperature and concentration dependence of true dissolution potential and diffusion potential of sodium halides.

Analytical reagent grade chemicals were used. All the measurements were made in deionized water prepared by using Elgastat B105 deionizer. As reported earlier⁸, the main contributions towards the observed dissolution potential are (i) true dissolution potential and (ii) diffusion potential that develops due to the formation of concentration gradient when electrode loaded with wet crystals is dipped into the cell. In order to find out the contribution of the diffusion potential to the overall observed dissolution potential it was also measured separately. The details of the experimental technique for measuring the observed dissolution potential and the diffusion potential have already been described⁸. The potentials were measured within an accuracy of ± 2 mV with respect to the clean platinum electrode dipping in the cell. The desired temperature was controlled with an accuracy of $\pm 0.1^\circ$. The concentration dependence was studied at $25^\circ \pm 0.1^\circ$ by measuring the potential in electrolytic solutions of different concentrations.

The potentials measured at different concentrations are given in Table 1 and their variation with temperature is shown in Figs. 1 and 2.

For the same electrolyte solutions at two different concentrations (C_1 and C_2) the diffusion potential is given by Planck equation⁹.

$$\text{Diff. pot.} = \frac{RT}{F} \left(\frac{u_+ - u_-}{u_+ + u_-} \right) \ln \frac{C_1}{C_2} \quad \dots(1)$$

where u_+ and u_- are the ionic mobilities. At a particular temperature, the concentration C_1 of the saturated diffusing solution is constant which is the condition of our experimental measurement of diffusion potential, Eq. (1) reduces to

$$\text{Diff. pot.} = A - B \ln C_2 \quad \dots(2)$$

TABLE 1 — EFFECT OF CONCENTRATION ON DISSOLUTION POTENTIAL AT 25°C

Concentration (g eq/lit)	Sodium chloride			Sodium bromide			Sodium iodide		
	Obs. dissoln pot. (mV)	Diff. pot. (mV)	True dissoln pot. (mV)	Obs. dissoln pot. (mV)	Diff. pot. (mV)	True dissoln pot. (mV)	Obs. dissoln pot. (mV)	Diff. pot. (mV)	True dissoln pot. (mV)
0.0000	-120	-40	-80	-238	-70	-168	-380	-112	-268
0.0001	-110	-38	-72	-230	-68	-162	-268	-100	-168
0.001	-92	-36	-56	-214	-66	-148	-250	-90	-160
0.005	-82	-34	-48	-202	-64	-138	-236	-86	-150
0.01	-74	-30	-44	-194	-60	-134	-232	-72	-160
0.05	-64	-22	-42	-192	-52	-140	-226	-60	-166
0.1	-60	-20	-40	-180	-40	-140	-220	-54	-166
0.2	-50	-14	-36	-170	-36	-134	-210	-44	-166

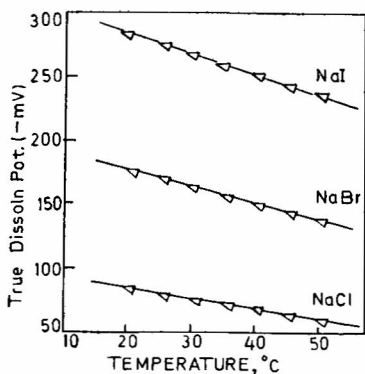


Fig. 1 — Dependence of true dissolution potential on temperature

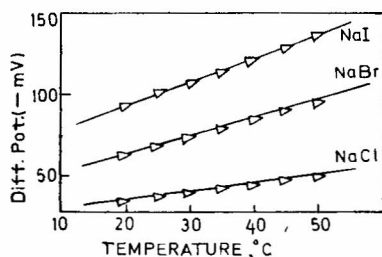


Fig. 2 — Dependence of diffusion potential on temperature

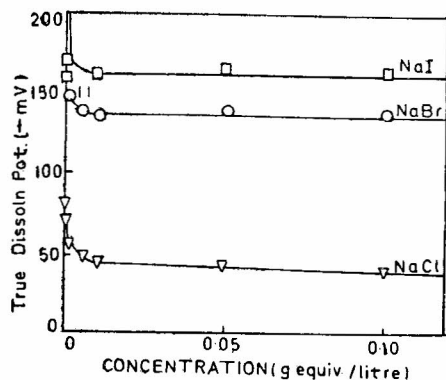


Fig. 3 — Plots of true dissolution potential versus concentration of electrolyte

where constants A and B are given by

$$\frac{RT}{F} \left(\frac{u_+ - u_-}{u_+ + u_-} \right) \ln C_1 \text{ and } \frac{RT}{F} \left(\frac{u_+ - u_-}{u_+ + u_-} \right)$$

respectively and C_2 is the concentration of the electrolytic solution in the cell. This leads to a linear relationship of diffusion potential with $\log C_2$. Further, it is noteworthy that the intrapolation of the curve to zero diffusion potential meets the saturation point. This is obvious because the process of diffusion ceases when both the diffusing solutions of the same electrolyte are saturated, i.e. the same concentration.

The observed dissolution potential has been found to decrease exponentially with concentration. This is in agreement with the observation of Rastogi *et al.*³. However, the true dissolution potential does

not decrease exponentially with concentration (Fig. 3) but the data fit the following empirical relations:

$$(\text{True dissoln pot.})_{\text{NaCl}} = 3e^{-461C} - 40C + 44$$

$$(\text{True dissoln pot.})_{\text{NaBr}} = 22e^{-1277C} - 40C + 142$$

$$(\text{True dissoln pot.})_{\text{NaI}} = 104e^{-3329C} - 18C + 164$$

It can be seen from Figs. 1 and 2 that true dissolution potential decreases and the diffusion potential increases linearly with increasing temperature. The linearity of diffusion potential is in accordance with Eq. (1)

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pH Effect on Acridine Orange Dye

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The basic and the acid forms of acridine orange dye interchange in the pH range 10.0–11.5 yielding an equilibrium constant $(3.19 \pm 0.21) \times 10^4$ litre mole⁻¹ at 25°. The dye base is very unstable, and unlike methylene blue, it undergoes no demethylation in basic environment.

DETAILED physico-chemical properties of acridine orange dye have been presented recently^{1,2}. It has been reported that in a close pH range (10.0–11.5) the basic and acid forms of the dye undergo a remarkable visible spectral interchange through a sharp isosbestic point at 445 nm. Although physico-chemical properties of dyes in acidic and basic environments reveal interesting features^{3,4}, such a conspicuous acid-base conversion phenomenon (Fig. 1) has not been reported on dye systems. In this note the quantitative aspect of this conversion phenomenon together with some other effects of pH are reported. No systematic study of acridine orange dye (AO) at higher pH was made in the past.

The equilibrium constant of the acid-base conversion (represented by Eq. 1) process has been

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