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NOTE

Studies on The Dissolution and Precipitation Potentials of The Sodium Salts of Organic Acids

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The dissolution and precipitation potentials of sodium salts of aliphatic organic acids have been calculated on the basis of mechanism of generation of electric potential of electrolytes. The comparison with the experimental data shows that true dissolution potential does not depend on the concentration of the medium, true precipitation potential also does not depend on undercooling.

Key Words: Dissolution potential, Precipitation potential, Organic sodium salts.

Potential difference of considerable magnitude is developed when (i) solvent freezes from a very dilute solution[1-4], (ii) precipitation of molten electrolyte takes place[5,6], (iii) dissolution or precipitation of electrolytes takes place[7-15]. Rastogi *et al.*[7] had reported their interesting preliminary studies on the freezing and melting potential of organic acids. As a matter of fact organic electrolytes present an interesting aspect of interfacial electrochemistry. Keeping in this view, studies on the dissolution and precipitation potential of sodium salt of organic acids was undertaken.

The experimental techniques for the measurement of these potentials were same as already reported by Rastogi and Khan[11,12]. Bright platinum electrodes were used both as reference electrode and the electrode on which the process of precipitation and dissolution occurred. One of the electrode was kept in a glass vessel filled with conductivity water and maintained at a constant temperature with the help of a thermostate. The other electrode was dipped in the precipitation or dissolution cell. The electrodes were connected to a high impedance ($R > 1014$) electrometer (Annadigi, Hyderabad). The other relevant potentials (diffusion, phase) were also measured by the similar technique.

The dissolution, precipitation, diffusion and phase potentials of the sodium salts of formic acid, acetic acid, propanoic acid, butanoic acid were determined. The magnitude of the true dissolution and true precipitation potentials were calculated from equation given as[5]:

$$(\Delta\phi)_{\text{True diss.}} = (\Delta\phi)_{\text{obs diss.}} - [(\Delta\phi)_{\text{phase.}} + (\Delta\phi)_{t}] \qquad (1)$$

$$(\Delta\phi)_{\text{True pption.}} = (\Delta\phi)_{\text{obs pption.}} - [(\Delta\phi)_{\text{phase.}} + (\Delta\phi)_{\text{diff}}] \qquad (2)$$

where $(\Delta\phi)_{\text{phase.}}$, $(\Delta\phi)_{t}$ and $(\Delta\phi)_{\text{diff}}$ are the phase potential, the potential of the cell with transference which is set up during the course of the dissolution[16] and diffusion potential, respectively. Rastogi *et al.* [11,12] and Khan *et al.*[16] have already given sufficient theoretical justification for the use of above equations in order to evaluate the magnitude of true dissolution and true precipitation potentials. The data obtained on the measurement of these potentials have been presented in Table-1. The data were examined in the light of available theories of dissolution and precipitation potentials. Most of these observation are in accordance with the reported theory[9]. It may be noted that the sign of true dissolution potential is opposite to that of true precipitation potential in almost every case. These observations are in accordance with the predictions made by Khan *et al.*[16].

TABLE-1
DISSOLUTION, PRECIPITATION, PHASE AND DIFFUSION POTENTIALS OF THE SODIUM SALTS OF ORGANIC ACIDS

Salt	$(\Delta\phi)_{\text{obsdiss}}$ (mV)	$(\Delta\phi)_{\text{obs pption}}$ (mV)	$(\Delta\phi)_{\text{phase}}$ (mV)	$(\Delta\phi)_{t}$ (mV)	$(\Delta\phi)_{\text{diff}}$ (mV)	$(\Delta\phi)_{\text{diss.}}$ [equation-1] (mV)	$(\Delta\phi)_{\text{pption}}$ [equation-2] (mV)
Sodium formate	-590	+275	-105	-95	-45	-390	+425
Sodium acetate	-295	+65	-29	-121	-35	-145	+129
Sodium propanoate	-287	+52	-37	-124	-31	-126	+120
Sodium butanoate	-149	+15	-54	-40	-15	-55	+84

Dissolution and precipitation potentials of the order of several hundred millivolts (more than 500 mV) could be observed almost invariably. These observations have been presented in Table-2. Potential difference of several volts could easily be produced by putting a number of sodium formate dissolution cells in a series. The dissolution current of sodium formate was also determined (Table-3) and its magnitude was found to be quite appreciable. The dissolution current density was evaluated by determining the area of the electrode on which dissolution occurred.

TABLE-2
DISSOLUTION AND PRECIPITATION POTENTIALS OF Na-FORMATE AT VARIOUS TEMPERATURES

Temperature (ºC)	Observed dissolution potential (-volts)	Observed precipitation potential (+ volts)
25	-0.590	+0.275
30	-0.605	+0.285
35	-0.630	+0.340
40	-0.645	+0.375
45	-0.665	+0.380

TABLE-3
DISSOLUTION POTENTIAL AND DISSOLUTION CURRENT OF SODIUM FORMATE AT 25 ºC BY MAKING USE OF A NUMBER OF DISSOLUTION CELLS CONNECTED IN A SERIES

Number of cells	Dissolution potential (volts)	Dissolution current (mA/cm^2)
1	-0.590	0.015
2	-1.125	0.036
3	-1.690	0.050
4	-2.100	0.065
10	-5.550	0.160

Conclusion

However, sodium formate was found to be an interesting exception in comparison to all other cases of dissolution and precipitation potential reported so far. Present priminary studies shows that sodium formate and such other electrolytes have a great potentiality for the practical use of these very interesting galvanic effect. Further studies on these lines are in progress and quite useful and interesting results are expected to follow.

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