Experiment **7**

# Electrolytes

### *Ions and Molecules in Aqueous Solution*

## DISCUSSION

Expt 7 Electrolytes.wpd

### Electrical Conductivities of Pure Substances

The ability of any substance to conduct electricity often provides great insight into its chemical and physical character. Since electric current involves the flow of electrical charge, a conducting substance must provide a source of mobile, charged particles. The excellent conductivity of the metals, for example, involves the movement of the loosely held valence electrons of the metal atoms through the solid crystal lattice of the metal. In this case, there is no need for the atoms themselves to move.

Ionic compounds are usually recognized by inspection of their chemical formulas which are likely to contain both metals and nonmetals, *e.g.*, KCl and $Mg(NO_3)_2$. Ionic solids consist of a highly ordered crystal lattice of positively and negatively charged ions, but these charged particles are locked into their positions within the crystal and are unable to transport charge. Ionic compounds do become conductors, however, in the molten or liquid state since the ions are now free to migrate.

Molecular compounds generally have chemical formulas that contain only nonmetals, *e.g.*, $H_2S$ and $C_6H_{12}O_6$ . Molecular solids consist of discrete molecules which have no overall charge; that is, the molecules are neutral and cannot transfer charge even if they become mobile in the liquid state.

If one were to investigate a series of solids by measuring their relative conductivities in both the solid and molten states, it may be possible to classify each into one of three broad categories: metals, ionic compounds, and molecular solids.

**Electrical Conductivity**

| | Metals | Ionic cpds | Molecular cpds |
|---|---|---|---|
| Solid | Yes | No | No |
| Liquid | Yes | Yes | No |

### Solution Electrolytes

**Solution electrolytes** are compounds which dissolve or react in water to **produce mobile ions in solution**, and these solutions, therefore, **conduct electricity**. Many ionic compounds and some molecular compounds are capable of being solution electrolytes. The electrolytic behavior of five representative compounds ($CaBr_2$, HBr , $HCO_2H$ , $NH_3$, and $CH_3OH$) will be contrasted in the following discussion.

## Strong Solution Electrolytes

Calcium bromide ($CaBr_2$) is an ionic solid as indicated by the metal/nonmetal content of its chemical formula. As expected, $CaBr_2$ conducts electricity in the molten state but does not conduct as a solid. Furthermore, $CaBr_2$ dissolves in water to yield a solution that is an excellent conductor of electricity and, consequently, $CaBr_2$ is classified as a strong solution electrolyte. The ions present in the solid crystal lattice of $CaBr_2$ **dissociate** from one another and enter into the liquid solvent as individual ions. The ionic dissolution equation for $CaBr_2$ in water is:

$$CaBr_{2\,(s)} \rightarrow Ca^{2+}_{(aq)} + 2Br^{-}_{(aq)}$$

The symbol "aq", for aqueous, indicates solvation of the ions in solution by an indeterminate number of water molecules.[1] Since water itself is not chemically changed, note that $H_2O$ does not appear in the ionic dissolution equation.

Hydrogen bromide (HBr) is likely to be molecular since only nonmetals are present. In the pure state, HBr does not show electrical conductivity in any phase. The very fact that it is a gas under normal conditions is also a clue that the individual particles are neutral molecules, not charged ions. When HBr gas is bubbled through a volume of water, each HBr molecule participates in **a chemical reaction** by giving up a proton, $H^+$, to a water molecule to yield two ions, the hydronium ion, $H_3O^+$, and bromide ion, $Br^-$.

$$HBr_{(g)} + H_2O_{(\ell)} \rightarrow H_3O^{+}_{(aq)} + Br^{-}_{(aq)} \qquad \text{100\% ionization}$$

Since ions are being created from neutral molecules, this process may be described as an **ionization**. For HBr, effectively all the molecules reacted to produce ions. The solution is an excellent conductor of electricity, and, therefore, HBr is classified as a strong solution electrolyte.

The most common examples of molecular substances that produce electrolytic solutions are acids and bases. Brønsted-Lowry acid/base theory defines an **acid** as a proton donor and a **base** as a proton acceptor. An acid/base reaction in which water is both the solvent and a reactant can be referred to as **hydrolysis**. In the reaction of HBr with $H_2O$, HBr is the acid (gives up a proton to water), and water is the base (accepts the proton). Adding a proton to water forms the hydronium ion, $H_3O^+$, and the presence of this ion in solution is evidence for acidic hydrolysis:

$$H_2O + HA \rightarrow \mathbf{H_3O^+} + :A^- \qquad \text{Acidic hydrolysis}^{2}$$

A base added to water may cause water to act as an acid, giving up one of its protons to the base. This generates the hydroxide ion, $OH^-$, which is evidence for basic hydrolysis:

$$H_2O + :B^- \rightarrow \mathbf{OH^-} + HB \qquad \text{Basic hydrolysis}^{3}$$

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1 Essentially, the collective ion-dipole solvation by the polar water molecules that are clustered around the individual ions overcomes the strong, collective ion-ion forces of the solid crystal lattice.

2 Note that the general acid here, HA , is written as having no overall charge. This is arbitrary, as acids may also have positive or negative charge(s).

3 Note that common bases may have no charge as well as negative charge(s).

**Weak Solution Electrolytes**

Formic acid, $HCO_2H$, is a molecular liquid and, as expected, does not demonstrate electrical conductivity in any pure state. Aqueous formic acid solutions are found to be slightly acidic and only poor conductors of electricity, so formic acid is classified as a weak solution electrolyte. Only a relatively low concentration of ions has been generated, one of which must be hydronium ion. The ionization (acidic hydrolysis) of the $HCO_2H$ molecules apparently occurs to a very limited extent.

$$HCO_2H_{(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + HCO_2^-{}_{(aq)} \qquad \sim 3\% \text{ ionization}$$

In reality, the reverse reaction competes with the forward ionization reaction. A condition is quickly reached in which the forward rate and the reverse rate become equal. At this point there is no change in the relative quantities of reactants to products. For $HCO_2H$, the proportions distinctly favor the molecular reactants over the ionic products, hence the limited conductivity. The state just described is called **dynamic chemical equilibrium** and is indicated by the opposing arrows ($\rightleftharpoons$) in the chemical equation.

Ammonia, $NH_3$ , is molecular and a weak solution electrolyte that yields a slightly basic solution. A limited ionization has occurred, but here the solute ammonia acts as a base and removes a proton from water generating the hydroxide ion (basic hydrolysis).

$$NH_{3\,(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \qquad \sim 1\% \text{ ionization}$$

**Nonelectrolytes in Solution**

Methanol, $CH_3OH$, is molecular and miscible in water. On dissolving methanol in water there is no detectable increase in the conductivity of water; therefore no ions are produced and it may be fairly assumed that $CH_3OH$ remains 100% molecular in solution. Methanol is classified as a **nonelectrolyte**.

$$CH_3OH_{(\ell)} \rightarrow CH_3OH_{(aq)} \qquad \text{Molecular dissolution}$$

**Ionic Hydrolysis.**

Previous discussion has demonstrated the potential for molecules to undergo acidic or basic hydrolysis and yield $H_3O^+$ or $OH^-$ ions in solution. Many ions also hydrolyze in aqueous solution. If a solution prepared by the dissolution of an ionic compound is found to be either acidic or basic, it is likely that the ions in solution have caused a subsequent hydrolysis[4]. For example, a solution of NaCN is found to be alkaline, *i.e.*, excess $OH^-$ has been generated. It turns out that $CN^-$ ion is somewhat basic and causes water to act as an acid:

$$NaCN_{(s)} \rightarrow Na^+_{(aq)} + CN^-_{(aq)} \qquad \text{Ionic dissolution}$$

$$CN^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)} \qquad \text{Ionic hydrolysis (basic)}$$

A number of ions are acidic enough to force water into the role of base, thereby generating excess $H_3O^+$ ion. Ammonium bromide solution is acidic:

$$NH_4Br_{(s)} \rightarrow NH_4^+{}_{(aq)} + Br^-_{(aq)} \qquad \text{Ionic dissolution}$$

$$NH_4^+{}_{(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_{3\,(aq)} + H_3O^+_{(aq)} \qquad \text{Ionic hydrolysis (acidic)}$$

[4] This assumes is that the $OH^-$ ion was not part of the ionic solid. Note that $H_3O^+$ is too unstable to be part of the ionic solid.

## EXPERIMENTAL

The following procedure is designed to characterize the aqueous solutions of a series of molecular and ionic compounds. The steps are outlined as follows.

1) Inspect the chemical formula of the solute and classify it as **ionic or molecular** by generalizing that a formula containing both a metal and nonmetals is likely to be ionic, while a compound with only nonmetals is likely to be molecular (be alert for polyatomic ions).

2) Then each solution will be tested for electrolytic strength using the procedure outlined below. It is the option of the instructor to perform all of these conductivity tests as a demonstration.

   **Your instructor will demonstrate the safe use of the conductivity apparatus. Pay strict attention. There is a small, but real, possibility of injury by electric shock.** Note that conductivity measurements are affected by experimental conditions which must be controlled. It is important that the surface area of the electrodes exposed to each solution be the same in order to fairly compare your results. To accomplish this, use the same volume (30-mL) of each solution in a 50-mL beaker. Each set of electrodes needs to be rinsed between measurements. Record the data for each compound as to which light or neither light came on. This data will allow you to conclude either a strong, weak, or non-solution electrolyte.

3) For each compound, place about 2 mL of the aqueous solution into a small, **clean, dry** test tube and add 3 or 4 drops of bromthymol blue (HBtB) indicator solution. Record the color. If the color becomes a distinct blue, the solution is basic (or alkaline). Yellow indicates an acidic solution, while green indicates neutrality. The laboratory will provide examples for comparison.

4) Identify the ions and/or molecules present in the solution in significant concentration and **write their formulas in the box provided before any equations are written**.

   - If the compound is a strong solution electrolyte, a large concentration of ions is present in the solution. These may be the constituent ions of an ionic compound, or they may be the ions produced by the reaction of a very strong molecular acid with water. If the compound is a weak solution electrolyte, a low concentration of ions has been produced in solution, which usually indicates the partial ionization (equilibrium) of a weak molecular acid or base.

   - If the solution is found to be acidic, $H_3O^+$ has been generated. Since $H_3O^+$ is not stable in a solid ionic crystal lattice, it must have been produced by the acidic hydrolysis of either a strong molecular acid, a weak molecular acid, or an ion that is present from the dissolution of an ionic compound.

   - If the solution is basic, excess $OH^-$ ion has been generated. Hydroxide ion is stable in some ionic solids and may have been delivered to solution via an ionic dissolution. It may also have been produced by the basic hydrolysis of a molecule or ion.

   - Since water is the solvent, $H_2O$ is always present in abundance. If water is a chemical reactant and participates in acidic or basic hydrolysis, it becomes part of the chemical equation(s) describing the system. Water is not included in a simple ionic or molecular dissolution equation, except for the symbol "aq" which is used to indicate the solvation by water of individual ions or molecules, because the water does not change chemically. If an ion participates in hydrolysis following dissolution, $H_2O$ is included as a reactant in the hydrolysis equation because the water does change chemically.

## List of Solutions to be Tested

0.10M of the following solutes

1) d.i. water
2) NaCl
3) HCl
4) $C_2H_5OH$
5) NaOH
6) $NH_3$
7) $HNO_3$
8) $KNO_3$
9) $KNO_2$
10) $HC_2H_3O_2$
11) $NaC_2H_3O_2$
12) $C_{12}H_{22}O_{11}$
13) $Na_2CO_3$
14) $NaHCO_3$
15) $NaHSO_4$
16) $H_2SO_4$
17) $CH_2(OH)CH_2(OH)$
18) $Na_3PO_4$
19) $NH_4Cl$
20 $Al_2(SO_4)_3$

**PreLaboratory Assignment:**
1) Determine if each solute is Ionic or Covalent/Molecular.

**During Laboratory:**
1) Record the data for each solution.
2) Determine if each solute in water is either strong, weak, or non-electrolyte.
3) Determine if each solute in water is either acidic, basic, or neither A/B (neutral).
4) Determine if each solute in water undergoes either ionic dissolution, molecular dissolution, or molecular ionization.
5) Write all the molecular dissolution equations, in increasing numerical order.
6) Write all the ionic dissolution equations, in increasing numerical order.
7) Determine if any ionic dissolution equations fail to explain the acidity or basicity of solution.
8) Write all the molecular ionization equations, in increasing numerical order.
   8a) If strong electrolyte use "$\rightarrow$" type of arrow.
   8b) If weak electrolyte use "$\rightleftharpoons$" type of arrow.
9) Write hydrolysis reactions for any ionic dissolution equations which did not explain acidity/basicity.
   9a) Use "$\rightleftharpoons$" type of arrow.