Electrochemistry course
ACME Faculty, EHVE course
B.Sc. Studies, II year, IV semester
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Fundamentals of ionics

Electrolyte - reminder

Liquid or solid that conducts electricity by means of its ions. Ions can move when they have freedom of movement. That freedom can be provided by molten salt (ionic liquid), specific structure of solid enabling ionic mobility or (most commonly) solvation of ions in the solution by solvent molecules (and as a result - shielding them from counter-ions and causing dissociation).
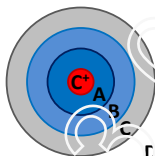
Solvation once more

Disturbance of solvent structure by an ion:

A – I solvation layer (directly coordinated by a cation)

B – II and further solvation layers (attracted electrostatically by a cation and can interact with other solvent molecules – *e.g.* through the hydrogen bonds)

C – solvent structure disturbed by the cation presence in the vicinity

D – original solvent structure

Dynamic equilibrium

- It is a phenomenon observed when on a large scale (*e.g.* billions of billions of molecules) a statistical equilibrium is observed, *i.e.* mean value of a given parameter is steady, but individual molecules often change their state.
- In practice dynamic equilibrium is defined as an equilibrium of two opposite processes, which occur at the same rate (in a given conditions). In case of solvation solvent molecules are all the time joining and leaving solvation layer (*e.g.* are knocked out of it). However, mean solvent molecules in solvation layer of a given ion stays the same.

Dynamic equilibrium

- In dissociation or solvation case dynamic equilibrium forms because solvent molecules and ions are bumping on each other (and at the vessel walls) all the time (due to chaotic moves, vibrations, etc.). Thus, constant exchange of molecules in solvation layers is taking place. Due to that, "puncture" of solvation layer by the counter-ion can happen, if it will be not full or/and counter-ion would bump with proper angle and momentum.

Solvent

- Solvent in the electrolyte formation process is required to solvate ions (shields them against association or crystal formation) and dissociate compound into ions (strength of interaction with part of the compound tears it from the other part of the compound at the ionic bond).
- The measure of how solvent is eager to interact with ions and how good its molecules are shielding ions against interaction with other ions (counter-ions) is dielectric constant (relative permittivity).

Dielectric constant (ε)

ε is dimensionless, because it is ratio of material permittivity to ε_0 – <u>permittivity of free space</u>. It means, that if certain ions attract each other in vacuum with a certain force, then in a medium (solvent/solution) with a <u>relative</u> permittivity (dielectric constant) ε, they would attract each other ε times more weakly.

Salt as a material with low ε value is decreasing overall dielectric constant of a solution (when considered for next ions/salts addition to that solution).

Dielectric constant

Dielectric constant of a material (in that case solvent/solution) can be measured with two methods:
*   Capacitance method – requires measurement of a capacitance of a capacitor with vacuum between its plates. Next, material to be measured is placed between those plates and the capacitance measurement is repeated. Dielectric constant is calculated from the capacitance formula:

$$C = \varepsilon \, \varepsilon_0 \, A/d \qquad \text{, where:}$$

ε – dielectric constant of a material between plates;
ε_0 – permittivity of free space;
A – capacitor plates surface (surface of the cross-section of a capacitor);
d – distance between plates.

Dielectric constant

*   Dielectric spectroscopy (principle of operation is similar to that of impedance spectroscopy, but works at much higher frequencies) – enable dielectric constant measurements with an a.c. signal.
    At the THz frequency order of magnitude relaxation effects of material allows to determine dielectric constant of a material (as a value of extrapolation at 0).
    In practice it is possible to conduct that measurement at the lower frequencies as well.

Dielectric constant is temperature-dependent (for some materials differences are of magnitude order for 50°C temperature change).

Dielectric constant

material	ε (at 20°C)	material	ε (at 20°C)
vacuum	1	glyme	~7
toluene	2	diglyme	~7
ethanol	25	PEO	5
DMF	36		
AN	37	SiO_2	3.9
PC	63	PE	2.3
water	80	PP	2.2
H_2SO_4	~90	glass	~5
EC	100	paper	~4
salts (including ionic liquids)			5-15

Solvent-ion interactions

Dielectric constant is not the only way to measure interactions of solution components, as there are secondary parameters such as <u>donor number</u> and <u>acceptor number</u>. Also the temperature dependence of dielectric constant is important – in case of some materials it is not changing much, others show enormous change over only few centigrades.

Ionic activity

Increase of ionic concentration above infinitesimal concentration (any non-zero concentration) cause ions to meet and interact with each other as well as change their activity (theoretical) into non-ideal one. It means, that parameters deviate from those calculated by theoretical formulae upon ionic concentration increase. Theoretical equations describe ideal system exclusively (even those taking the concentration into account are taking concentration value as it was group of individual ions not interacting with each other and as the solvent would interact with ions to a maximum extent).

Ionic activity

In reality ionic activity depends on concentration, but it is not the same as concentration. Concentration instead of the ionic activity can be used for extremely diluted solutions only, where deviations from theory are negligible. In practice (for useful solutions) ionic activity is used:

$$a_i = c_i\, \gamma_i$$

where a – ionic activity; c – concentration; γ – activity coefficient;

Ionic activity

Activity coefficient γ can be calculated from the empirical formula, where the simplest and basic formula (enriched with additional elements and parameters when complexity increases for use with higher and higher concentrations) is:

$$\log \gamma_i = -A\, z_i^2\, I^{1/2}/(1+I^{1/2})$$

where: $A = 0.5091$ (water at 25°C); I – ionic strength; z – ionic charge (its electrovalence);
Ionic strength can be calculated from the formula:

$$I = \tfrac{1}{2}\, \Sigma\, (z_i^2 c_i)$$

where: c – concentration. It is the sum of all ions present in the solution. For solutions of one binary salt
$I = c$.

Ionic activity

Example for NaCl ($z_{Na}=1$, $z_{Cl}=1$, so $I=c$).

$\log \gamma_{Na} = -A \cdot z_{Na} \cdot I^{1/2}/(1+I^{1/2})$
$\log \gamma_{Na} = -0.5091 \cdot 1 \cdot c^{1/2}/(1+c^{1/2})$

For **0.0001 mol/kg** concentration:

$\log \gamma_{Na} = -0.5091 \cdot 0.01/(1+0.01) = -0.005091/1.01$
$\gamma_{Na} = 10^{(-0.00504)} = \textbf{0.988}$

Thus, result is quite close to 1 (1.2% deviation).

Ionic activity

For **0.01 mol/kg** concentration:

$\log \gamma_{Na} = -0.5091 \cdot 0.1/(1+0.1) = -0.05091/1.1$
$\gamma_{Na} = 10^{(-0.04628)} = \textbf{0.899}$

Thus, deviation is higher than 10%.

For **1 mol/kg** concentration (much more complex formulae should be used for such concentration for better results):

$\log \gamma_{Na} = -0.5091 \cdot 1/(1+1) = -0.5091/2$
$\gamma_{Na} = 10^{(-0.2546)} = \textbf{0.556}$

Thus, deviation is higher than 44%.

Ionic activity

In practice ionic activity is used everywhere when theory considers ionic concentration – pH calculation, determining half-cell potential from the Nernst formula and other similar equations, *e.g.*:

$pH = -\log(a_{H_3O^+})$

$E = E^0 + R \cdot T/(z \cdot F) \cdot \ln(a_{ox}/a_{red})$

Phenomena in the solution

- Salt/acid/base dissolution
- Dissociation (partial for weak electrolytes)
- Associations formation
- **Acid-base equilibria**
- **Complex formation**

Solubility of hardly soluble compounds

- Any equilibrium process constant is described by the following formula:

K = Π[product] / Π[substrate]

([] means molar concentration;
Π – product of all reagents of a given type)

- In practice, for the higher concentrations (where it has any notable effect), [x] is x's activity.
- In case of solubility of hardly soluble salts:

$$M_nX_{m(s)} = nM^+ + mX^-$$

the equilibrium constant formula is:

$K_{sp} = [M^+]^n[X^-]^m/[M_nX_{m(s)}]$

Where activity of a substance in a standard state (in case of salt – solid state) is equal to 1.

Solubility product

- For small concentrations $K_{sp} = [M^+][X^-] = c^2$. In order to simplify the formula while taking into account potential interactions with other salts with the common ions, maximum solubility of hardly soluble salts is given by this equilibrium constant K_{sp} (solubility of soluble salts is given in g/100g).

Due to the form of the formula for K_{sp} this quantity has been named the **solubility product (K_{sp})**.

Solubility product

K_{sp} AgI = $1.5 \cdot 10^{-16}$ (water, at 25°C)

$[Ag^+][I^-] = 1.5 \cdot 10^{-16}$ $c^2 = 1.5 \cdot 10^{-16}$ $c = 1.22 \cdot 10^{-8}$

Maximum concentration of AgI solution in water at 25°C is $1.22 \cdot 10^{-8}$M.

K_{sp} Ag$_2$CrO$_4$ = $4.1 \cdot 10^{-12}$ $[Ag^+]^2[CrO_4^-] = 4.1 \cdot 10^{-12}$

$(2c)^2 \cdot c = 4c^3 = 4.1 \cdot 10^{-12}$ $c = (4.1 \cdot 10^{-12}/4)^{1/3}$

$c = 1.008 \cdot 10^{-4}$M – maximum concentration of Ag$_2$CrO$_4$ solution in water at 25°C

Solubility product

K_{sp} AgI = $1.5 \cdot 10^{-16}$ (water, at 25°C)

$[Ag^+][I^-] = 1.5 \cdot 10^{-16}$

If a solution in which we try to dissolve AgI already contains any Ag^+ ions (*e.g.* already dissolved AgNO$_3$ in a given solute), than the solubility of AgI will be lower, *e.g.* for a 0.01M AgNO$_3$ solution:

$[Ag^+] \cdot [I^-] = (0.01+c) \cdot c = c^2 + 0.01c = 1.5 \cdot 10^{-16}$

We can calculate that c = $1.5 \cdot 10^{-14}$M,

which means solubility of AgI in water that already contains 0.01M AgNO$_3$ is $1.5 \cdot 10^{-14}$M (while solubility without any previous Ag^+ or I^- content was $1.22 \cdot 10^{-8}$M).

Solubility product

If one adds soluble salt to the concentrated solution of a hardly soluble salt with a common ion, then the worse soluble salt precipitates:

K_{sp} CuCl = 10^{-6} K_{sp} AgCl = $1.6 \cdot 10^{-10}$

Concentrated solution of AgCl has a concentration of $1.26 \cdot 10^{-5}$M.

Upon addition of CuCl to obtain 10^{-4}M concentration (of CuCl) AgCl precipitates:

$[Ag^+][Cl^-] = 1.6 \cdot 10^{-10}$ $x \cdot (10^{-4}+1.26 \cdot 10^{-5}) = 1.6 \cdot 10^{-10}$

$x \cdot 0.0001126 = 1.6 \cdot 10^{-10}$ $x = 1.421 \cdot 10^{-6}$.

Precipitate weight will be approximately
$1.26 \cdot 10^{-5}$M - $1.421 \cdot 10^{-6}$M = $1.118 \cdot 10^{-5}$M AgCl.

(multiplied by amount of a solution)

Solubility product

Salt effect is an increase in solubility of a hardly soluble salt upon addition of a soluble salt without common ions with the first one.
The effect takes place because addition of large amount of ions increases ionic strength of a solution, thus decreasing ionic activity coefficients in a solution. Thanks to that, solubility product is lower (as solubility product is a product of activities, not concentrations!) and more of a hardly soluble salt can be dissolved.

Acids and bases dissociation in water

- Acids dissociate into the proton (in H_3O^+ form, as proton immediately combines with water molecule) and the acid radical (anion). If acid has more than one hydrogen atoms that can dissociate as protons, then it happens in stages (protons dissociate one at a stage, with each stage having its own equilibrium).
- Bases dissociate into the hydroxide anion (OH^-) and the cation (usually metal cation). (similarly to acids, if base has more than one OH- group, then they dissociate in stages - one group at a time)

Solubility product cont'd

- Apart from the salt effect, also addition of acid (H_3O^+ ions) effects in higher solubility of hardly soluble bases (dissociating into OH- ions). It is due to the neutralization reaction, thanks to which OH- ions amount decreases and more of the base can dissolve (however, it works only with the dissociated ions, so it works as much as high dissociation degree of a compound is).
- Hydrolysis of a compound also increases solubility, although the resulting solution have different compound dissolved in it (as hydrolysis is a reaction with water).

Hydrolysis

- If ion is strongly interacting with water molecules of solvating layer and that attraction is stronger than strength of O-H bond in water, then the **hydrolysis** takes place.
- Cations draw OH^- part to them (cation draws the negative charge stronger than proton can do it in this situation).
- Anions draws H^+ to them (pulling it from the rest of the water molecule – OH^-).

Weak electrolytes dissociation

Dissociation degree: $\alpha = c_{ion}/c_{substance}$
Equilibrium constant of $CA = C^+ + A^-$ dissociation is described by a formula: $K = [C^+][A^-]/[KA]$
As amount of ions from the dissociation degree is by definition $\alpha \cdot c$, then amount of undissociated substance is $(1-\alpha) \cdot c$. Thus:
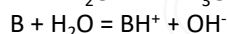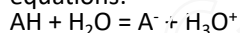
$$K = \alpha \cdot c \cdot \alpha \cdot c/((1-\alpha) \cdot c) = \alpha^2 \cdot c/(1-\alpha)$$

In case of weak electrolytes – they do not dissociate fully and dissociation degree is very low, even much below 1%. Thus for very low dissociation degrees dissociation constant is: $K \approx \alpha^2 \cdot c$.

Weak electrolytes dissociation

Dissociation of acids and bases goes similarly to that of salts, although in case of weak acids and weak bases it runs according to the following equations:
$AH + H_2O = A^- + H_3O^+$
$B + H_2O = BH^+ + OH^-$
It means that theoretically, when calculating **acidity constant** (K_a) and **basicity constant** (K_b), one should take into account water concentration as well.
Despite that, as weak acids and weak bases are dissociating to a small degree, ionic concentrations are so small in comparison to water concentration, that there is no need to take water into account (its percent change is negligible when compared to that of ions).

Weak electrolytes dissociation

- $K_a = [H_3O^+][A^-]/[HA]$
- $K_b = [BH^+][OH^-]/[B]$

In practice K_a and K_b are used to describe and compare acids and bases strength (respectively).

In order to simplify the notation of such a low values (often high negative powers of 10), it is transformed with p operator (-log(x)) and noted as:

pK_a and pK_b.

E.g. $K_a = 1.73 \cdot 10^{-5}$ is $pK_a = 4.76$