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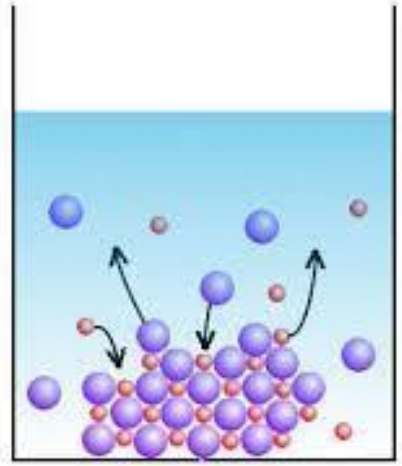
Physical Pharmacy

Electrolytes 2

Electrolytes

Activity and Activity Coefficients

- Any solution may have an “effective concentration” or, as it is called, an activity.



- The activity, in general, is less than the actual concentration of the solute, not because the strong electrolyte is only partly ionized, but rather because some of the ions are effectively “taken out of play” by the electrostatic forces of interaction.

- At infinite dilution, in which the ions are so widely separated that they do not interact with one another, the activity (a) of an ion is equal to its concentration, expressed as molality or molarity or mole fraction

Electrolytes

Activity and Activity Coefficients

- It is written on a molal basis at infinite dilution as:

  a =m or a / m = 1

- As the concentration of the solution is increased, the ratio becomes less than unity because the effective concentration or activity of the ions becomes less than the molal concentration.

- This ratio is known as the practical activity coefficient, γm, on the molal scale, and the formula is written, for a particular ionic species, as

$$\frac{a}{m} = \gamma_m \qquad \textbf{Or} \qquad a = \gamma_m\, m$$

Electrolytes

Activity and Activity Coefficients

- On the molarity scale, another practical activity coefficient, γc, is defined as

$$\frac{a}{c} = \gamma_c \qquad \textbf{Or} \qquad a = \gamma_c\, c$$

- And on the mole fraction scale, a rational activity coefficient is defined as

$$\frac{a}{x2} = \gamma_{x2} \qquad \textbf{Or} \qquad a = \gamma_{x2}\, x_2$$

- One sees from above equations that these coefficients are proportionality constants relating activity to molality, molarity, and mole fraction, respectively, for an ion.

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Electrolytes

Activity and Activity Coefficients

- The activity coefficients take on a value of unity (=1) in infinitely dilute solutions, when the activity equal to concentration.
- The three coefficients usually decrease and assume different values as the concentration is increased
- Sometimes the activity coefficient increase by increasing the concentration of the electrolytes.
- For example ,the mean values of for NaCl, $CaCl_2$, and $ZnSO_4$ are plotted in Figure below against the square root of the molality.
- The activity coefficient approaches unity with increasing dilution.

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As the concentrations of some of the electrolytes are increased:

- The curves pass through minima and rise again to values greater than unity,**Why**?

- The initial decrease in the activity coefficient with increasing concentration is due to the interionic attraction, which causes the activity to be less than the stoichiometric concentration.

$$\frac{a}{m} = \gamma_m$$ **(a decrease , m increase so γm decrease)**

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As the concentrations of some of the electrolytes are increased:

- The rise in the activity coefficient following the minimum in the curve of an electrolyte, such as HCl and CaCl2, can be attributed to the attraction of the water molecules for the ions in concentrated aqueous solution.

- This solvation reduces the interionic attractions and increases the activity coefficient of the solute

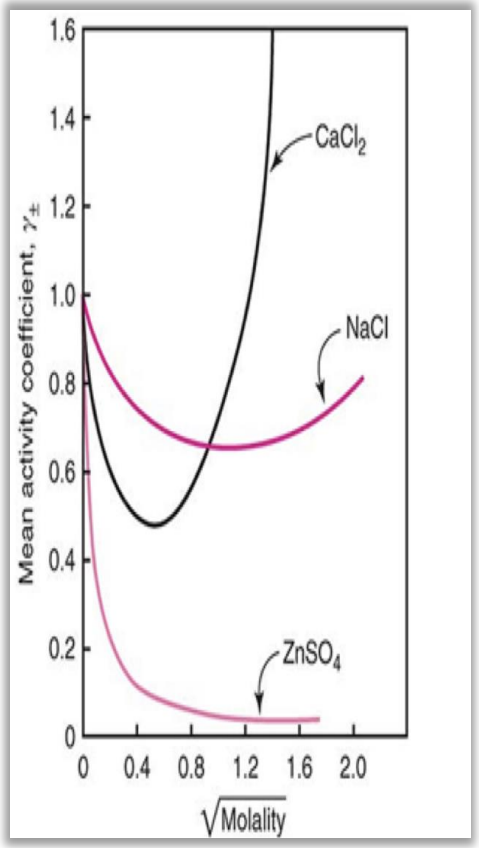

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Table 6-1 Mean Ionic Activity Coefficients of Some Strong Electrolytes at 25 °C On the Molal Scale

Molality (m)	HCl	NaCl	KCl	NaOH	$CaCl_2$	H_2SO_2	Na_2SO_2	$CuSO_2$	$ZnSO_2$
0.000	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.005	0.93	0.93	0.93	–	0.79	0.64	0.78	0.53	0.48
0.01	0.91	0.90	0.90	0.90	0.72	0.55	0.72	0.40	0.39
0.05	0.83	0.82	0.82	0.81	0.58	0.34	0.51	0.21	0.20
0.10	0.80	0.79	0.77	0.76	0.52	0.27	0.44	0.15	0.15
0.50	0.77	0.68	0.65	0.68	0.51	0.16	0.27	0.067	0.063
1.00	0.81	0.66	0.61	0.67	0.73	0.13	0.21	0.042	0.044
2.00	1.01	0.67	0.58	0.69	1.55	0.13	0.15	–	0.035
4.00	1.74	0.79	0.58	0.90	2.93	0.17	0.14	–	–

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Electrolytes

Activity of the Solvent

- The activity of the solvent is defined on the mole fraction scale.
- When a solution is made infinitely dilute, it can be considered to consist essentially of pure solvent.
- Therefore, X1 = 1, and the solvent behaves ideally in conformity with Raoult's law.
- Under this condition, the mole fraction can be set equal to the activity of the solvent, or

$$a = X_1 = 1$$

Electrolytes

Activity of the Solvent

- As the solution becomes more concentrated in solute, the activity of the solvent ordinarily becomes less than the mole fraction concentration, and the ratio can be given, as for the solute, by the rational activity coefficient,

$$\frac{a}{x1} = \gamma x_1 \qquad \textbf{Or} \qquad a = \gamma x_1 \, x_1$$

- The activity of a volatile solvent can be determined rather simply.

- The ratio of the vapor pressure, P_1, of the solvent in a solution to the vapor pressure of pure solvent, $P°_1$ is approximately equal to the activity of the solvent at ordinary pressures:

$$\mathbf{a_1 = P_1 / P°_1}$$

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Electrolytes

Activity of the Solvent : Example 6-10 , Calculating Escaping Tendency

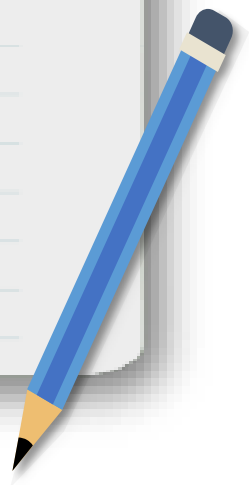
The vapor pressure of water in a solution containing 0.5 mole of sucrose in 1000 g of water is 17.38 mm and the vapor pressure of pure water at 20°C is 17.54 mm , What is the activity (or escaping tendency) of water in the solution?

Answer

$a_1 = P_1 / P°_1$

$a_1 = 17.38 / 17.54$

$=0.991$



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Activity of the Solvent : Q11:

a/ The vapor pressure of water over an aqueous solution of a drug is 721 mmHg at 100°C. What is the activity of water in this solution?

Answer

100°C is the boiling point of water; that is mean it is a point at which the vapor pressure of water = atm presuure which is 760 mmHg

$a_1 = P_1 / P°_1$

$a_1 = 721 / 760$

$=0.949$

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Activity of the Solvent : Q11:

b/ Methanol has a boiling point of 64.7°C. The vapor pressure of methanol in a methanolic solution of sulfonamide is 703 mmHg , What is the activity of methanolin this solution at 64.7°C?

Answer

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Activity of the Solvent : Q11:

c/ Chlorine has a vapor pressure of 10 atm.at 35.6°C. In a mixture of chlorine and carbon tetrachloride, the vapor pressure of chlorine is 9.3 atm at 35.6° C. What is the activity of chlorine in the mixture?

Answer

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Activity of the Solvent : Q11:

d/ Formic acid has a vapor pressure 40 mmHg at 24°C .In a mixture of formic acid and acetic acid, formic acid has a vapor pressure of 32.2 mmHg at 24°C. What is the activity of formic acid in the mixture?

Answer

$a_1 = P_1 / P°_1$

$a_1 = 32.2 / 40$

$=0.805$

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Activity of the Solvent : Q12:

The vapor pressure of pure water at 25°C is 23.8 mmHg

a/ Compute the lowering of vapor pressure of water when 25 g. of CaCl2(Mwt= 110.99g/mole) is added to 100g. of water. (no association of ions)

b/ Compute the activity and activity coefficient of water in the solution

Answer : a

$\Delta P / P^\circ_1 = i\ 0.018\ m$

$\Delta P = i\ 0.018 m P^\circ 1$

$CaCl2 \longrightarrow Ca^{+2} + 2Cl^{-1}$

m =Wt/Mwt x 1000/wt of solvent

m =25/110.99 x 1000/100 =2.25

$\Delta P = 3 \times 0.018 \times 2.25 \times 23.8$

= 2.89 mmHg

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Electrolytes

Activity of the Solvent : Q12:

The vapor pressure of pure water at 25°C is 23.8 mmHga/ Compute the lowering of vapor pressure of water when 25 g. of CaCl2(Mwt= 110.99g/mole) is added to 100g. of water. (no association of ions) b/ Compute the activity and activity coefficient of water in the solution

Answer : b

$a_1 = P_1 / P°_1$

$\Delta P = P_{solvent} - P_{solution}$

$2.89 = 23.8 - P_{solution}$

$P_{solution} = 20.91 mmHg$

$a_1 = 20.91 / 23.8 = 0.879$

$\gamma_{X1} = a / X_1$

$X1 = n1/n1+n2$

$n1 = Wt1 / Mwt1 = 100/ 18 = 5.55$

$n2 = Wt2 / Mwt2 = 25/ 110.99 = 0.225$

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Electrolytes

Activity of the Solvent : Q12:

The vapor pressure of pure water at 25°C is 23.8 mmHga/ Compute the lowering of vapor pressure of water when 25 g. of CaCl2(Mwt= 110.99g/mole) is added to 100g. of water. (no association of ions) b/ Compute the activity and activity coefficient of water in the solution

Answer : b

$X1 = 5.55 / 5.55+0.225 = 0.96$

$\gamma_{X1} = 0.879 / 0.96 = 0.915$

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Electrolytes

Activity of the Solvent : Q14:

The vapor pressure of pure water at 25°C is 23.8 mmHg is lowered when100 g. of nonelectrolyte, glucose (Mwt= 180.16g/mole) is added to 1000g. of water

a/ Compute the activity and activity coefficient of water in the solution

b/ Compute the activity and activity coefficient of glucose

Answer : a

$\Delta P / P^\circ_1 = i\ 0.018\ m$

$\Delta P = i 0.018 m P^\circ 1$

$m = Wt/Mwt \times 1000/wt\ of\ solvent$

$m = 100/180.16 \times 1000/1000 = 0.56$

$\Delta P = 0.018 \times 0.56 \times 23.8$

$\approx 0.24 mmHg$

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Electrolytes

Activity of the Solvent : Q14:

The vapor pressure of pure water at 25°C is 23.8 mmHg is lowered when100 g. of nonelectrolyte, glucose (Mwt= 180.16g/mole) is added to 1000g. of water

a/ Compute the activity and activity coefficient of water in the solution

b/ Compute the activity and activity coefficient of glucose

Answer : a : For water in solution

$a_1 = P_1 / P°_1$

$\Delta P = P_{solvent} - P_{solution}$

$0.24 = 23.8 - P_{solution}$

$P_{solution} = 23.56$ mmHg

$a_1 = 23.56 / 23.8 = 0.99$

$\gamma_{X1} = a / X_1$

$X1 = n1/n1+n2$

$n1 = Wt1 / Mwt1 = 1000/ 18 = 55.5$

$n2 = Wt2 / Mwt2 = 100/ 180.16 = 0.55$

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Electrolytes

Activity of the Solvent : Q14:

The vapor pressure of pure water at 25°C is 23.8 mmHg is lowered when100 g. of nonelectrolyte, glucose (Mwt= 180.16g/mole) is added to 1000g. of water

a/ Compute the activity and activity coefficient of water in the solution

b/ Compute the activity and activity coefficient of glucose

Answer : a : For water in solution

$X1 = 55.5/ 55.5+0.55 = 0.99$

$\gamma_{X1} = 0.99 / 0.99 = 1$ (Dilute solution)

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Electrolytes

Activity of the Solvent : Q14:

The vapor pressure of pure water at 25°C is 23.8 mmHg is lowered when100 g. of nonelectrolyte, glucose (Mwt= 180.16g/mole) is added to 1000g. of water

a/ Compute the activity and activity coefficient of water in the solution

b/ Compute the activity and activity coefficient of glucose

Answer : b/For Glucose

- Glucose is non- electrolyte
- No association of ions

Therefore a=conc.

So $\gamma_m = 1$

Electrolytes

Activity of the Solvent : Q14:

The vapor pressure of pure water at 25°C is 23.8 mmHg is lowered when 15 g. of a strong electrolyte NaOH(Mwt=40g/mole)is added to 100g, of water at 25°CCompute the activity and activity coefficient of water in the solution

Answer :

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Thank You !

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