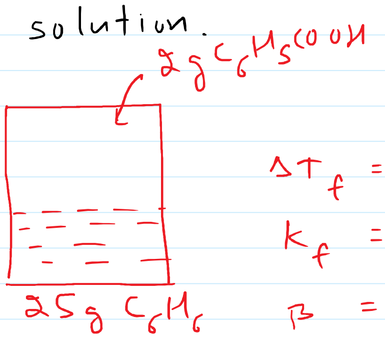
Question

2g of benzoic acid (C_6H_5COOH) dissolved in 25g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid. If it forms dimer in solution.

Answer



$\Delta T_f = 1.62\,K$

$k_f = 4.9\ K\,kg\,mol^{-1}$

$\beta = ?$

$C_6H_5COOH \rightarrow B$

$C_6H_6 \rightarrow A$

$$\Delta T_f = i\, m\, k_f$$

$$1.62 = i \frac{w_B \times 1000}{M_B \times w_A} \times k_f$$

$$1.62 = i \frac{2 \times 1000}{122 \times 25} \times 4.9$$

$$i = 0.504$$

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

$t = 0$ C

$t = \infty$ $C(1-\beta)$ $\frac{C\beta}{2}$ Total $C\left(1-\frac{\beta}{2}\right)$

$$i = \frac{C(1-\beta/2)}{C} = 1 - \beta/2$$

$$0.504 = 1 - \frac{\beta}{2}$$

$$\beta = 0.992$$

percentage association $= 100\beta = 99.2\%$

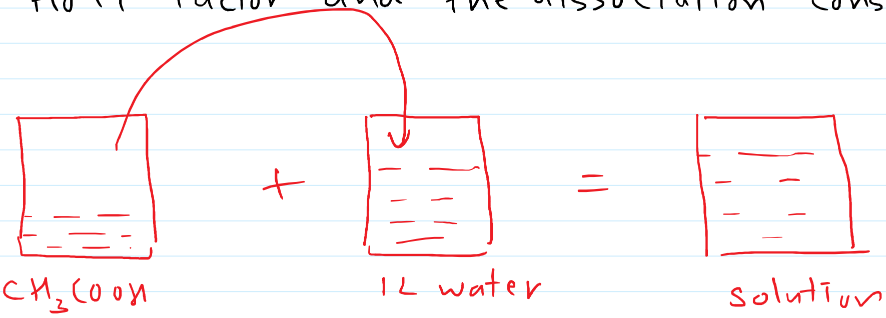
$$i = 1 + \left(\frac{1}{n} - 1\right)\beta$$

$$0.504 = 1 + \left(\frac{1}{2} - 1\right)\beta$$

Question

0.6mL of acetic acid (CH_3COOH) having density $1.06\ g\,mL^{-1}$ is dissolved in 1L of water. The depression in freezing point observed for this strength of acid was $0.0205^\circ C$. Calculate the van't Hoff factor and the dissociation constant of acid.

Answer



$\Delta T_f = 0.0205^\circ C$

$i = ?$

$K_a = ?$

0.6 mL

$d = 1.06\ g\,mL^{-1}$

$CH_3COOH \rightarrow B \qquad H_2O \rightarrow A$

$$n_B = \frac{w_B}{M_B} = \frac{d_B V_B}{M_B} = \frac{1.06 \times 0.6}{60} = 0.0106 \text{ moles}$$

$$w_A = d_A V_A = \frac{1\,kg}{L} \times 1\,L = 1\,kg$$

$$m = \frac{n_B}{w_A(\text{in kg})} = \frac{0.0106}{1} = 0.0106\ \frac{\text{moles}}{kg}$$

$$\Delta T_f = i\, m\, k_f$$

$$0.0205 = i \times 0.0106 \times 1.86$$

i) $i = 1.04$

ii) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

	CH_3COOH	CH_3COO^-	H^+	
$t=0$	c			
$t=\infty$	$c(1-\alpha)$	$c\alpha$	$c\alpha$	Total $= c(1+\alpha)$

$$i = \frac{c(1+\alpha)}{c} = 1+\alpha$$

$$1.04 = 1+\alpha$$

$$\alpha = 0.04$$

$i = 1 + (n-1)\alpha$

$1.04 = 1 + (2-1)\alpha$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

For dilute solution molarity ≃ molality

$C \simeq 0.0106\ M$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.0106 \times (0.04)^2}{1-0.04} = 1.8 \times 10^{-5}$$

Question

The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluroacetic acid increases in the order given above. Explain briefly.

<u>Ans:</u>

Order of acidic strength:

$CH_3COOH < Cl_3CCOOH < F_3CCOOH$ $F > Cl > H$

Stronger is acid, more is its dissociation, hence higher is van't Hoff factor (i)

$$\Delta T_f \propto i$$

Higher is i, more is ΔT_f

thus order of ΔT_f is

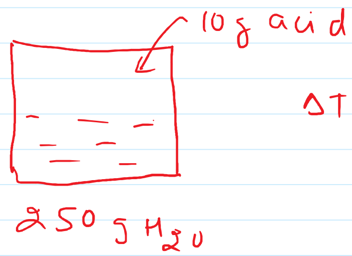
$CH_3COOH < Cl_3CCOOH < F_3CCOOH$.

Question

Calculate the depression in freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water.

$K_a = 1.4 \times 10^{-3}$, $K_f = 1.86\ K\ kg\ mol^{-1}$.

<u>Answer</u>



$\Delta T_f = ?$

$CH_3CH_2CHClCOOH \rightarrow B$, $H_2O \rightarrow A$.

$M_B = 122.5$

$$m = \frac{w_B \times 1000}{M_B \times W_A} = \frac{10 \times 1000}{122.5 \times 250} = 0.3264\ \frac{mol}{kg}$$

$$m = \frac{W_B \times 1000}{M_B \times W_A} = \frac{10 \times 1000}{122.5 \times 250} = 0.3264 \ \frac{mol}{kg}$$

For dilute solution molarity (C) $\simeq$ molality

$$C \simeq 0.3264 \ \frac{mol}{kg}$$

$$k_a = \frac{C\alpha^2}{1-\alpha}$$ ✓

Take $1-\alpha \simeq 1$, as $\alpha << 1$

$$k_a = C\alpha^2$$

$$\alpha = \sqrt{\frac{k_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$

$$CH_3CH_2CHClCOOH \rightleftharpoons CH_3CH_2CHClCOO^- + H^+$$

$t=0$	x			
$t=\infty$	$x(1-\alpha)$	$x\alpha$	$x\alpha$	Total $= x(1+\alpha)$

$$i = \frac{x(1+\alpha)}{x} = 1+\alpha$$

$$= 1 + 0.065 = 1.065$$

$$i = 1 + (n-1)\alpha$$
$$= 1 + (2-1)\alpha$$

$$\Delta T_f = i m k_f$$

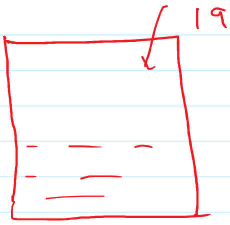
$$= 1.065 \times 0.3264 \times 1.86 = 0.65 \ k$$

Question

19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

Answer

19.5 g CH_2FCOOH (B)



500 g H_2O (A)

$\Delta T_f = 1°C$

$i = ?$

$k_a = ?$

$$m = \frac{W_B \times 1000}{M_B \times W_A} = \frac{19.5 \times 1000}{78 \times 500} = 0.5 \ m$$

$$\Delta T_f = i m k_f$$

$$1 = \bar{i} \times 0.5 \times 1.86$$

$$\bar{i} = 1.075$$

$$\bar{i} = 1 + (n-1)\alpha$$

$$1.075 = 1 + (2-1)\alpha$$

$$\alpha = 0.075$$

$$k_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.5(0.075)^2}{1-0.075} = 3.07 \times 10^{-3}$$