Paper: FS-201 (Forensic Analytial Chemistry) Topic: Solvent Extraction by Dr. Manoj Kumar Bharty Asstt. Professor Dept. of Chemistry, BHU

Solvent extraction technique is also called as Liquid-Liquid extraction which involves the selective transfer of solute from one liquid to another, two liquid should be completely immiscible to each other.

Example: If we take aqueous solution of NaCl and I_2 and shaken with CCl_4 solution (organic solution) then I_2 will be selectively transferred from the original aqueous solution to CCl_4 solution leaving behind NaCl in aqueous solution.



Fig.: Simple apparatus for solvent extraction.

As well using two liquid for the separation, hence the name o this technique is liquid-liquid extraction. Two terms distribution coefficient or partition coefficient (K_D) and distribution ratio (D) are used in solvent extraction method:

(1) Distribution coefficient or partition coefficient (K_D)

Nerst Distribution law
$$K_D = \frac{[A]_{org}}{[A]_{aq.}}$$

Where, $[A]_{org.}$ = concentration of solute A in organic phase

and $[A]_{aq.} =$ concentration of solute A in aqueous phase

Nerst distribution law or partition law says that there is a fixed relationship or fixed ratio in which the solute distributed itself at particular temperature and pressure. This distribution is independent of initial solute concentration.

At equilibrium condition, the chemical potential of the solute in two phases is equal which is usually achieved by shaking for few minutes. Solute should remain in same form for both phases.

(2) Distribution ratio (D)

Aqueous Phase: $HBz + H_20 \rightleftharpoons H_30^+ + Bz^-$

Benzoic acid Benzoate ion

Organic Phase: $2HBz \rightleftharpoons HBz_2$ (Dimerized)

Since,

$$\begin{split} K_{D} \text{ for } HBz &= \frac{[HBz]_{org.}}{[HBz]_{aq.}} \\ K_{D} \text{ for } Bz^{-} &= \frac{[Bz^{-}]_{org.}}{[Bz^{-}]_{aq.}} \\ K_{D} \text{ for } (HBz)_{2} &= \frac{[(HBz)_{2}]_{org.}}{[(HBz)^{2}]_{aq.}} \\ D &= \frac{[CA]_{org.}}{[CA]_{aq.}} \end{split}$$

$$(Conc^{n} of (HBz)_{2} \text{ in organic layer will be zero or negligible})$$

Therefore,

Where, [CA]_{org.} is sum of the concentrations of all species present in organic phase

[CA]_{aq.} is sum of the concentrations of all species present in aqueous phase.

$$D = \frac{[HBz]_{org.} + 2[(HBz)_2]_{org.}}{[HBz]_{aq.} + [Bz^-]_{aq.}}$$
(1)

$$HBz + H_2O \xrightarrow{Ka} H_3O^+ + Bz$$

Dissociation constant (K_a) = $\frac{[H^+][Bz^-]}{[HBz]}$

Or
$$[Bz^{-}] = K_a \frac{[HBz]}{[H^{+}]}$$
....(2)

$$2HBz \xrightarrow{K_d} (HBz)_2$$

Dimerization constant (K_d) = $\frac{[(HBz)_2]}{[HBz]^2}$

Or
$$[(HBz)_2] = K_d [HBz]^2$$
(3)

Substitute the values of $[Bz^{-}]$ and $[(HBz)_{2}]$ in equation (1), we get

$$D = \frac{[HBz]_{org.} + 2\{K_d[HBz]^2_{org.}\}}{[HBz]_{aq.} + K_a \frac{[HBz]_{aq.}}{[H^+]}}$$

Or
$$D = \frac{[HBz]_{org.}(1 + 2K_d[HBz]_{org.})}{[HBz]_{aq.}(1 + \frac{K_a}{[H^+]})}$$

Or
$$D = K_D \frac{(1+2K_d[HBz]_{org.})}{(1+\frac{K_a}{[H^+]})}$$

Since, $[HBz]_{org.} \ll 1$, therefore it has been neglected from the numerator.

Therefore,

$$\mathbf{D} = \frac{\mathbf{K}_{\mathbf{D}}}{\left(1 + \frac{\mathbf{K}_{\mathbf{a}}}{[\mathbf{H}^+]}\right)}$$

Quantitative expression for pH:

Case I: Concentration of $[H^+]$ is very high i.e. low pH (acidic condition), D value will be high and Benzoic acid will be present mostly as dimer in organic phase.

Case II: Concentration of $[H^+]$ is low i.e. high pH (alkaline condition), D value will be less and Benzoic acid will be mostly present as Benzoate ion in aqueous phase.

Case III: Concentration of Benzoic acid which exist as dimer. Hence, on increasing concentration of Benzoic acid the extraction will be facilitate in organic phase.

Question: 1 gram of Benzoic acid dissolve in 100 mL of water is to be equilibrated with 100 mL of ether. The distribution coefficient, K_D is 100 and the dissociation constant, K_a is 6.5×10^{-5} . Calculate the distribution ratio, D, if the aqueous layer is at pH = 3, 5 & 7.

Solution: Given, $K_D = 100$

$$K_a = 6.5 \times 10^{-5}$$

(1) At pH = 3, i.e.
$$-\log[H^+] = 3 = > [H^+] = 10^{-3}$$

Since, $D = \frac{K_D}{\left(1 + \frac{K_a}{|H^+|}\right)}$

Or
$$D = \frac{100}{\left(1 + \frac{6.5 \times 10^{-5}}{10^{-3}}\right)}$$

Or $D = \frac{100}{(1.46.5 \times 10^{-2})}$
Or $D = \frac{100}{(1.065)}$
 \therefore $D = 93.9$
(2) At pH = 5, i.e. $-\log[H^+] = 5$ $=> [H^+] = 10^{-5}$
Since, $D = \frac{K_D}{\left(1 + \frac{K_B}{[H^+]}\right)}$
Or $D = \frac{100}{\left(1 + \frac{6.5 \times 10^{-5}}{10^{-5}}\right)}$
Or $D = \frac{100}{(1 + 6.5)}$
Or $D = \frac{100}{(1 + 6.5)}$
Or $D = \frac{100}{(1 + 6.5)}$
(3) At pH = 7, i.e. $-\log[H^+] = 7 => [H^+] = 10^{-7}$
Since, $D = \frac{K_D}{\left(1 + \frac{K_B}{[H^+]}\right)}$
Or $D = \frac{100}{\left(1 + \frac{6.5 \times 10^{-5}}{10^{-7}}\right)}$
Or $D = \frac{100}{\left(1 + 6.5 \times 10^{2}\right)}$
Or $D = \frac{100}{(1 + 6.5 \times 10^{2})}$
Or $D = \frac{100}{651}$
 \therefore $D = 0.15$

Multiple Extractions:

When the D value is high about 100 or more than 100 then a single extraction is able to transfer almost whole of the solute from one phase to another phase. But at low value of D, more than single extractions (multiple extractions) are required to complete transfer of solute from one phase to another phase.

Case (I): $V_{\text{org.}} = V_{\text{aq.}}$ (Volume of org. phase = volume of aq. phase)

Suppose, W gram of solute is present in aqueous phase and w gram of solute is present in organic phase. Then

$$K_{\rm D} = \frac{w}{W - w}$$

Or $K_{\rm D}W - K_{\rm D}w = w$

	$Or K_D W = w(1 + K_D)$					
	$\therefore \qquad w = \frac{K_D}{1+H}$	$\frac{W}{K_D}$ (Thi	is fraction con	nes in orga	nic phase)	
	÷	$f_{\text{org.}} = \frac{w}{W}$				
	or	$f_{\text{org.}} = \frac{\frac{K_D W}{1+K_D}}{W}$				
	[$f_{\text{org.}} = \frac{K_{\text{D}}}{1 + K_{\text{D}}}$				
	÷	$f_{aq.} = 1 - \frac{1}{1+1}$	K _D +K _D			
	or	$f_{aq.} = \frac{1+K_D}{1+K_P}$	-K _D D			
		$f_{aq.} = \frac{1}{1 + K_D}$	(Fractio	on left behi	nd in the org	anic phase)
	II nd Extraction:	$\left(\frac{1}{1+K_{\rm D}}\right)^2$ o	r multiple ext	raction: $\left(\frac{1}{1}\right)$	$\left(\frac{1}{1+K_{\rm D}}\right)^n$	
Case (II):		$V_{\text{org.}} \neq V$	V _{aq.} (Volu	me of org. p	ohase ≠volun	ne of aq. phase)
]	$K_{\rm D} = \frac{w/V_{\rm or}}{(W-w)/2}$	g. V _{aq.}		
Or		К	$_{\rm D} = \frac{{}_{\rm W} {}_{\rm V_{aq.}}}{{}_{\rm V_{org.}} ({}_{\rm W} - {}_{\rm V_{aq.}})}$	w)		
Or		К	$_{\rm D}V_{\rm org.}W-K_{\rm H}$	$_{\rm D}V_{\rm org.}w =$	wV _{aq.}	
Or		К	$_{\rm D} {\rm V}_{\rm org.} {\rm W} = {\rm w}$	$V_{aq.} + K_D V_{d}$	org.W	
Or		К	$_{\rm D}V_{\rm org.}W = W$	$V_{aq.} + K_D$	V _{org.})	
		·.	$\mathbf{w} = \frac{\mathbf{K}_{\mathbf{D}}\mathbf{V}_{\mathbf{o}}}{(\mathbf{V}_{\mathbf{aq.}} + \mathbf{K})}$	rg.W (DVorg.)		

 \because

$$f_{\text{org.}} = \frac{w}{w}$$
$$f_{\text{org.}} = \frac{\frac{\kappa_D v_{\text{org.}} w}{(v_{\text{aq.}} + \kappa_D v_{\text{org.}})}}{w}$$

Or

 $f_{\text{org.}} = \frac{\overline{(V_{\text{aq.}} + K_{\text{D}} V_{\text{org.}})}}{W}$ $f_{\text{org.}} = \frac{K_{\text{D}} V_{\text{org.}}}{(V_{\text{aq.}} + K_{\text{D}} V_{\text{org.}})} \quad (\text{Fraction left behind in the aqueous phase})$

$$:: f_{aq.} = 1 - \frac{K_D V_{org.}}{(V_{aq.} + K_D V_{org.})}$$

Or
$$f_{aq.} = \frac{V_{aq.} + K_D V_{org.} - K_D V_{org.}}{V_{aq.} + K_D V_{org.}}$$
$$\therefore \quad f_{aq.} = \frac{V_{aq.}}{V_{aq.} + K_D V_{org.}}$$
$$\mathbf{II^{nd} Extraction:} \quad \left(\frac{V_{aq.}}{V_{aq.} + K_D V_{org.}}\right)^2 \quad \text{ or multiple extraction: } \left(\frac{V_{aq.}}{V_{aq.} + K_D V_{org.}}\right)^n$$

Question: (i) If 4 grams of butyric acid is to be extracted from 500 mL of water with 500 mL of ether, then what will be weight of butyric acid extracted, if distribution coefficient (K_D) for system is 3.

Solution: $V_{\text{org.}} = V_{\text{aq.}}$

$$w = \frac{K_{\rm D}W}{1+K_{\rm D}}$$

or $w = \frac{3\times4}{1+3} = \frac{12}{4}$
 $w = 3$ gram

(ii) However, if ether is used in two successive 250 mL portion then what will be the amount of butyric acid extracted in ether?

$$V_{\text{org.}} \neq V_{\text{aq.}}$$
$$\therefore w = \frac{K_{\text{D}}V_{\text{org.}}W}{(V_{\text{aq.}} + K_{\text{D}}V_{\text{org.}})}$$
$$or \quad w = \frac{3 \times 250 \times 4}{500 + 3 \times 250}$$
$$or \quad w = \frac{3000}{1250}$$
$$\therefore w = 2.4 \text{ gram}$$

Amount of butyric acid left = (4 - 2.4) gram

= 1.6 gram

IInd Extraction:

$$w = \frac{K_{\rm D} V_{\rm aq.} W}{V_{\rm aq.} + K_{\rm D} V_{\rm org.}}$$

or $w = \frac{3 \times 250 \times 1.6}{500 + 3 \times 250}$

$$or w = \frac{1200}{1250}$$

 $\therefore w = 0.96 \text{ gram}$

Total amount of butyric acid extracted = (2.4 + 0.96) gram

= 3.34 gram

$$\begin{array}{l} \because \ f_{aq.} = \left(\frac{V_{aq.}}{V_{aq.} + K_D V_{org.}}\right)^2 \\ \text{or} \ \ f_{aq.} = \left(\frac{500}{500 + 3 \times 250}\right)^2 \\ \text{or} \ \ f_{aq.} = \left(\frac{500}{1250}\right)^2 \\ \text{or} \ \ f_{aq.} = \left(\frac{2}{5}\right)^2 = \frac{4}{25} \\ \therefore \ \ f_{aq.} = 0.16 \\ \because \ \ f_{org.} = 1 - f_{aq.} \\ \text{or} \ \ \ f_{org.} = 1 - 0.16 \\ \therefore \ \ \ f_{org.} = 0.84 \end{array}$$

Question: Suppose that partition coefficient value for water-chloroform system is 10. Calculate the percentage of solute extracted from 50 mL of water by 100 mL of chloroform.

- (i) Chloroform (CHCl₃) is used all at once. $(V_{org.} \neq V_{aq.})$
- (ii) 100mL CHCl₃ is divided into 5, 20 mL of partition which are implied one after other.

Solution:
$$ag{f}_{aq.} = \frac{V_{aq.}}{V_{aq.} + K_D V_{org.}} = \frac{50}{50 + 10 \times 100} = \frac{50}{1050} = \frac{1}{21}$$

:.
$$f_{\text{org.}} = 1 - f_{\text{aq.}} = 1 - \frac{1}{21} = \frac{20}{21}$$

 \Rightarrow Percentage of solute extracted = $f_{org.} \times 100 = \frac{20}{21} \times 100 = 95.2 \%$

$$:: f_{aq.} = \left(\frac{V_{aq.}}{V_{aq.} + K_D V_{org.}}\right)^n = \left(\frac{50}{50 + 10 \times 20}\right)^5 = \left(\frac{50}{250}\right)^5 = \left(\frac{1}{5}\right)^5 = \frac{1}{3125}$$

:.
$$f_{\text{org.}} = 1 - f_{\text{aq.}} = 1 - \frac{1}{3125} = \frac{3124}{3125}$$

 \Rightarrow Percentage of solute extracted = $f_{\text{org.}} \times 100 = \frac{3124}{3125} \times 100 = 99.96 \%$

Counter current distribution principle (Craig counter current extraction):

Counter current distribution is a particular type of system where both the phases are changed each time; lower phase is fresh in each vessel. Now, adding fresh upper phase which is transferred from 1 to 2, 2 to 3 and so on and equal amount is again added to 1. This process is continuous process in which solute is distributed between two phases, according to distribution coefficient.

Number of vessels



Fig.: Successive distribution of solute in the Craig process. Fraction of total solute in each layer of each vessel, for D = 1 and $V_S = V_M$.

No of vessel is one more than the no of transfer. Hence first vessel is leveled as zero (transfer is zero).

Number of transfers

Number of Vessels

0	1
1 st	1 1
2 nd	1 2 1
3 rd	1 3 3 1
4 th	1 4 6 4 1
5 th	1 5 10 10 5 1

The number of each line of table is the successive terms in the expansion of the binomial $(p+q)^{n}$, i.e.,

$$(p+q)^{n} = p^{n} + np^{n-1}q + \frac{n(n-1)}{2!}p^{n-2}q^{2} + \frac{n(n-1)(n-2)}{3!}p^{n-3}q^{3} + \dots + q^{n}$$

Where, p is the fraction of total solute in lower phase (stationary phase). q is the fraction of total solute in upper phase (mobile phase). n is number of extraction (transfer).

We define the distribution coefficient,

Where, C_s is concentration of solute in stationary phase.

C_M is concentration of solute in mobile phase.

Then,

And,

$$p = \frac{C_{S}V_{S}}{C_{S}V_{S}+C_{M}V_{M}} \dots (2)$$

or
$$p = \frac{\frac{C_{S}V_{S}}{C_{M}}}{\frac{C_{S}V_{S}}{C_{M}}+\frac{C_{M}V_{M}}{C_{M}}}$$

$$\therefore \quad p = \frac{K_{D}V_{S}}{K_{D}V_{S}+V_{M}}$$

And,
$$q = \frac{C_{M}V_{M}}{C_{S}V_{S}+C_{M}V_{M}}$$

$$or \quad q = \frac{\frac{C_{M}V_{M}}{C_{M}}}{\frac{C_{S}V_{S}+C_{M}V_{M}}{C_{M}}}$$

$$\therefore \quad q = \frac{V_{M}}{K_{D}V_{S}+V_{M}}$$

$$\therefore \quad (p+q)^{n} = \left(\frac{K_{D}V_{S}}{K_{D}V_{S}+V_{M}} + \frac{V_{M}}{K_{D}V_{S}+V_{M}}\right)^{n}$$

Question: Calculate the percentage distribution of substance after three transfers in a Craig apparatus for which $V_S = 2 \text{ mL}$ and $V_M = 4 \text{ mL}$. The distribution coefficient, K_D is 3.

Solution: Given, n = 3, $V_S = 2$ mL, $V_M = 4$ mL and $K_D = 3$.

$$p = \frac{K_D V_S}{K_D V_S + V_M} = \frac{3 \times 2}{3 \times 2 + 4} = \frac{6}{10} = 0.6$$

$$q = \frac{V_M}{K_D V_S + V_M} = \frac{4}{3 \times 2 + 4} = \frac{4}{10} = 0.4$$

$$\because (p+q)^n = p^n + np^{n-1}q + \frac{n(n-1)}{2!}p^{n-2}q^2 + \frac{n(n-1)(n-2)}{3!}p^{n-3}q^3 + \dots + q^n$$

$$\therefore (p+q)^3 = p^3 + 3p^2q + 3pq^2 + q^3$$

or $(p+q)^3 = (0.6)^3 + 3(0.6)^2(0.4) + 3(0.6)(0.4)^2 + (0.4)^3$
or $(p+q)^3 = 0.216 + 0.432 + 0.288 + 0.064$
or $(p+q)^3 = 21.6\% + 43.2\% + 28.8\% + 6.4\%$

Thus, the first four vessels contain 21.6 %, 43.2 %, 28.8 % and 6.4 %, respectively.

Possible schematic representation of overlapping and non-overlapping of peaks depends upon the D value and no of extractants:



Applications of Craig counter current extraction:

- 1) It is very powerful and practical tool in biochemistry for extremely difficult separation of substances that are chemically similar.
- 2) Antibiotics and hormones can be separated.
- 3) Proteins like insulin, ribonuclease, lysozyme and serum albumins have been separated.
- 4) It is used for pharmaceutical separations.

Extraction System:

Several extraction systems are used to enhance the extraction. Some of them are given below:

- 1) Chelate extraction
- 2) Extraction by salvation
- 3) Ion pair formation
- 4) Synergic extraction

(1) Chelate extraction

Extraction of the metal ion proceeds by the formation of chelate of close ring structure. Chelate ligands form cyclic compound with metals. Metal ions combines with poly-functional bases capable of occupying two or more position in co-ordination sphere of metal ion. Depending upon number of donor sites in the ligands, they are classified as bidentate, tridentate, hexadentate etc.



The nature of these complexes is hydrophobic. So, they are easily extracted in the organic phase.

(2) Extraction by salvation

Extracted species get solvated in the organic phase, e.g. extraction of cobalt. Cobalt can be extracted in octanol in the presence of perchlorate ion.

 $[Co(R - OH)_{6}^{2+}.2ClO_{4}^{-}]$

Extraction of uranium with methyltriphosphate with HNO₃.

(3) Ion pair formation

(i) Extraction proceeds with the formation of uncharged species which in turn get extracted into the organic phase. e.g., extraction of Fe^{3+} from HCl with diethyl ether.

$$Fe(H_2O)_6^{3+} + HCl \rightleftharpoons FeCl(H_2O)_5^{2+} + H^+$$

$$FeCl(H_2O)_5^{2+} + HCl \rightleftharpoons FeCl_2(H_2O)_4^+ + H^+$$

$$FeCl_2(H_2O)_4^+ + HCl \rightleftharpoons FeCl_3(H_2O)_3 + H^+$$

$$FeCl_3(H_2O)_3 + HCl \rightleftharpoons FeCl_4(H_2O)_2^- + H^+$$

$$FeCl_4(H_2O)_2^- [H]^+ \rightleftharpoons FeCl_4(H_2O)^- H^+] \equiv FeCl_4^-H^+ + H_2O$$

Ultimately $FeCl_4^-$ species generated in the aqueous phase with excess of HCl. $FeCl_4^-$ forming ion pair with H⁺. This ion is easily separated into the organic phase.

(ii) Crown Ether:

Example: Work as Host and Guest: i.e. Host-Guest formation:









Hydrophobic in nature and highly soluble in organic solvents, so, easily extracted in organic phase. Metal ion fitted in the cavity. So, crown ethers act as hosts and metal ions are guests. It increases the reactivity of the complexes.

(iii) Extraction by metal ion with tertiary amine:

$$(R_3N)_{\text{org.}} + (H^+)_{\text{aq.}} + (A^-)_{\text{aq.}} \rightleftharpoons (R_3NH^+A^-)_{\text{org.}}$$
$$(R_3NH^+A^-)_{\text{org.}} + (B^-)_{\text{aq.}} \rightleftharpoons (R_3NH^+B^-) + (A^-)_{\text{org.}}$$

Anions can be extracted with anion in the presence of metal ions, tertiary amines mineralizes. Primary and secondary anions extractions perform with organic carboxilic acid.

(4) Synergic Extraction

Two extractants are used to enhance extraction. Extraction may be chelating ligand or solvating solvents or may be comprise two chelating reagents or two solvating solvents. Optimum conditions for the extraction are chelating agents should neutralize the metal ion by chelating and the solvent should coordinate less strongly than the chelating ligands.

Example: Extraction of uranium with 6-tributyl phosphate and 2-thenoyl trifluoro acetate.

Percent Extracted:

The distribution ratio D is a constant independent of the volume ratio. However, the fraction of the solute extracted will depend on the volume ratio of the two solvents. If a larger volume of organic solvent is used more solute must dissolve in this layer to keep the concentration ratio constant and to satisfy the distribution ratio.

The fraction of solute extracted is equal to the millimoles of solute in the organic layer divided by the total number of millimoles of solute. The millimoles are given by the molarity times the milliliters.

Thus, the percent extracted is given by,

% E =
$$\frac{[S]_0 V_0}{[S]_0 V_0 + [S]_a V_a} \times 100 \%$$

Where, V_0 is volume of organic phase and V_a is volume of aqueous phase. [S]₀ is concentration of solute in organic phase and [S]_a is concentration of solute in aqueous phase, respectively.

It can be shown from this equation that the percentage extracted is related to the distribution ratio by,

$$\% E = \frac{100 \text{ D}}{\text{D} + \frac{\text{Va}}{\text{Vo}}}$$

If, $V_a = V_0$

Then, % $E = \frac{100 \text{ D}}{\text{D}+1}$

Extraction will be quantitative (99.9%) for D values of 1000. In this case, equal volumes, the solute can be considered quantitatively retained if D is less than 0.001. It is essentially quantitatively extracted if D is greater than 1000. The percent extracted changes only from 99.5 to 99.9 % when D is increased from 200 to 1000.

Question: 20 mL of an aqueous solution of 0.10 M butyric acid is shaken with 10 mL ether. After, the layers are separated; it is determined by titration that 0.5 mole butyric acid remains in the aqueous layer. What is the distribution ratio and what is the percent extracted?

Solution: We started with 2.0 mmol butyric acid and so 1.5 mmol was extracted. The concentration in the ether layer is 1.5 mmol/10mL = 0.15 M

The concentration in the aquous layer is 0.5 mmol/20mL = 0.025 M

Therefore, D =
$$\frac{[CA]_{org.}}{[CA]_{aq.}}$$

D = $\frac{0.15}{0.025}$

Distribution ratio, D = 6.0

Since, 1.5 mmol was extracted, the percent extracted is

$$\frac{1.5}{2.0} \times 100\% = 75\%$$

% E =
$$\frac{100 \text{ D}}{\text{D} + \frac{\text{Va}}{\text{Vo}}}$$

% E = $\frac{100 \times 6}{6 + \frac{20}{10}}$
Or % E = $\frac{600}{8}$
Or % E = 75 % (Percent extracted in organic phase).

Note: Molarity = mole/litre

Or Molarity = mmol/mL

 $0r \quad 0.10 = mmol/20 => mmol = 2.0$

Assignment:

Question: Calculate the concentrations and amounts in each phase after extraction of 100 mL of 10^{-2} M acetanilide in water with 100 mL of ether if distribution coefficient is 3.0 at 25°C. What will be the effect of using 1000 mL of ether?

OR