(Molecular-weight Estimation from Experimental Data)
SHEET NO.2

At the end of this lecture, you should be able to:

- Estimate number-average molecular weight from the colligative properties (those properties of solutions that depend on the ratio of the number of solute particles to the number of solvent molecules in a solution).
- Estimate viscosity-average molecular weight from a viscometer measurements.
- Some different questions on molecular weight calcaultion.

Mustansiriyah University/ Materials Eng. Dept.
Dr Ahmed A. AYASH

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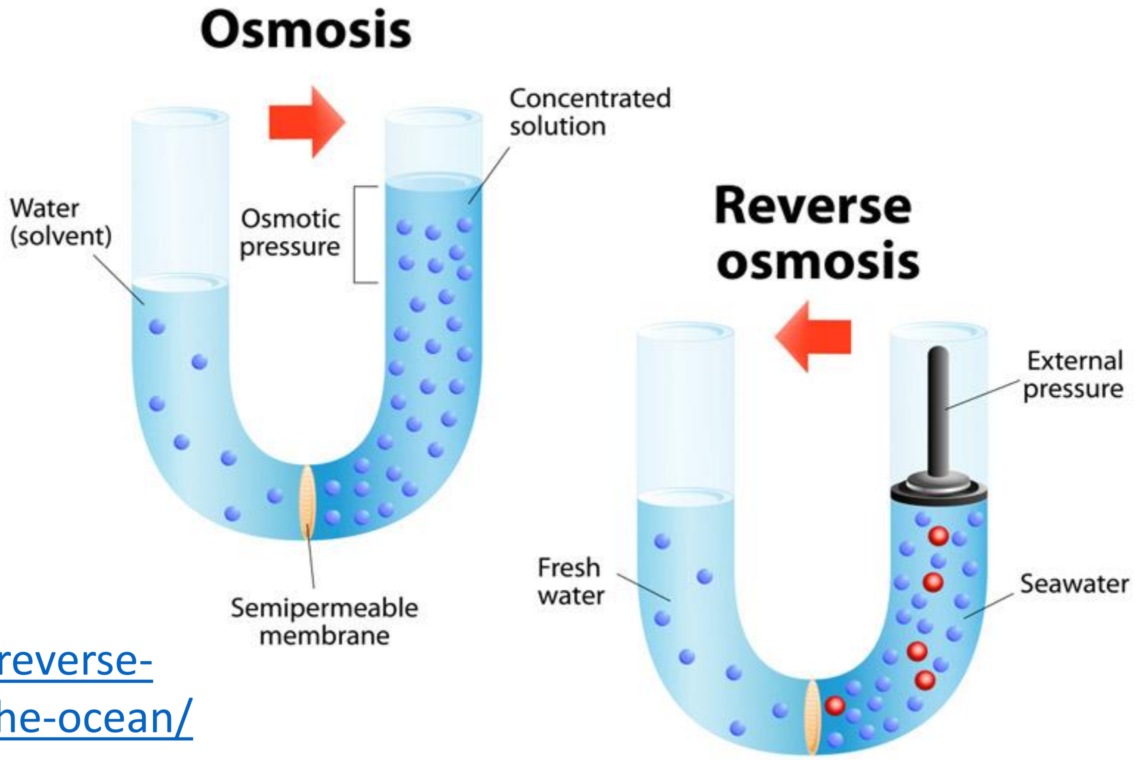
QUESTION 1:

Given the following data of osmotic pressure (π) of polycarbonate solution, what is the number-average molecular weight of this polymer? (T = 25°C; density = 1.0 g/cm3.)

π/C **(pa L/g)**	**0.255**	**0.26**	**0.27**	**0.27**	**0.29**	**0.295**
C (g/L)	**0.001**	**0.009**	**0.015**	**0.019**	**0.023**	**0.029**

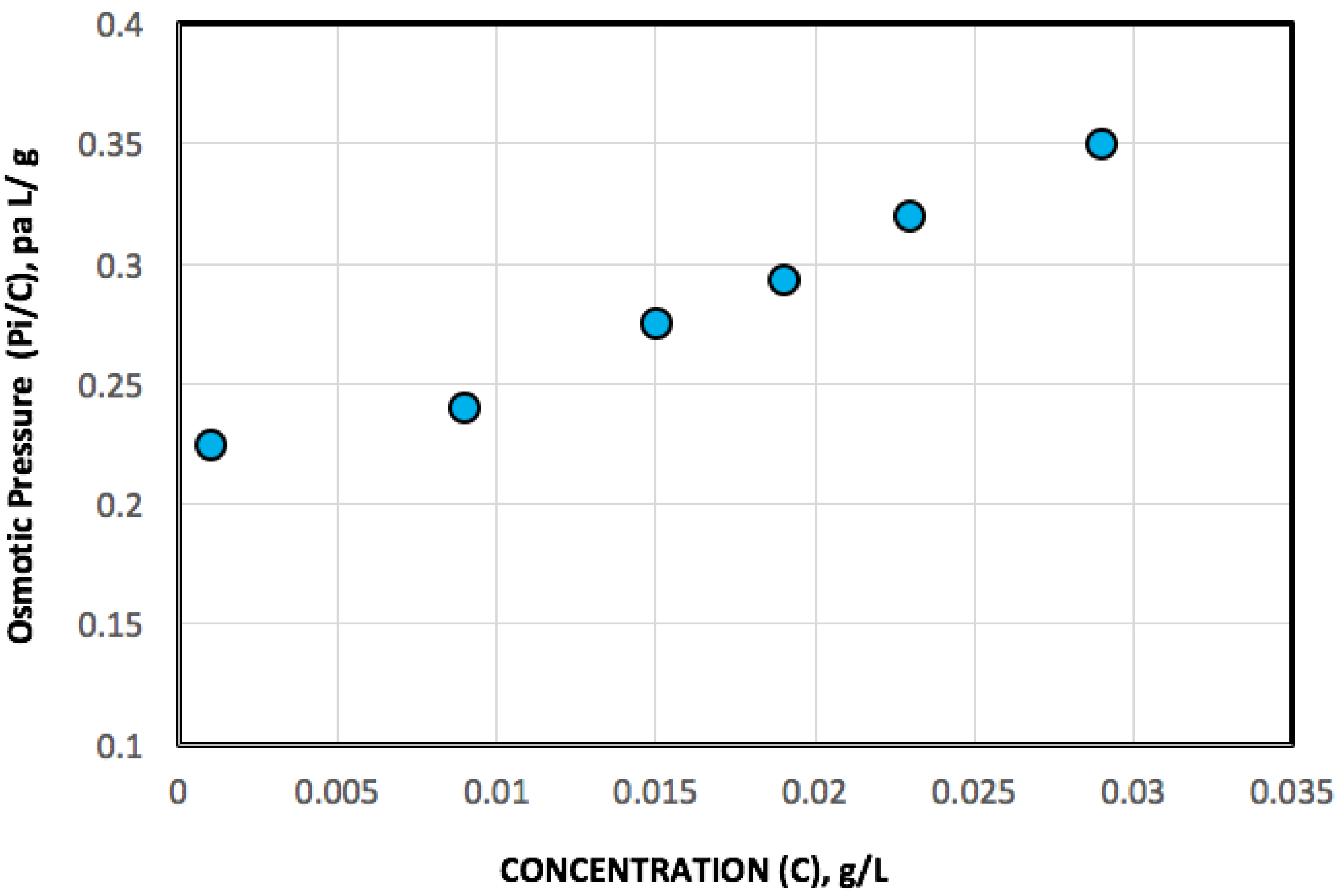


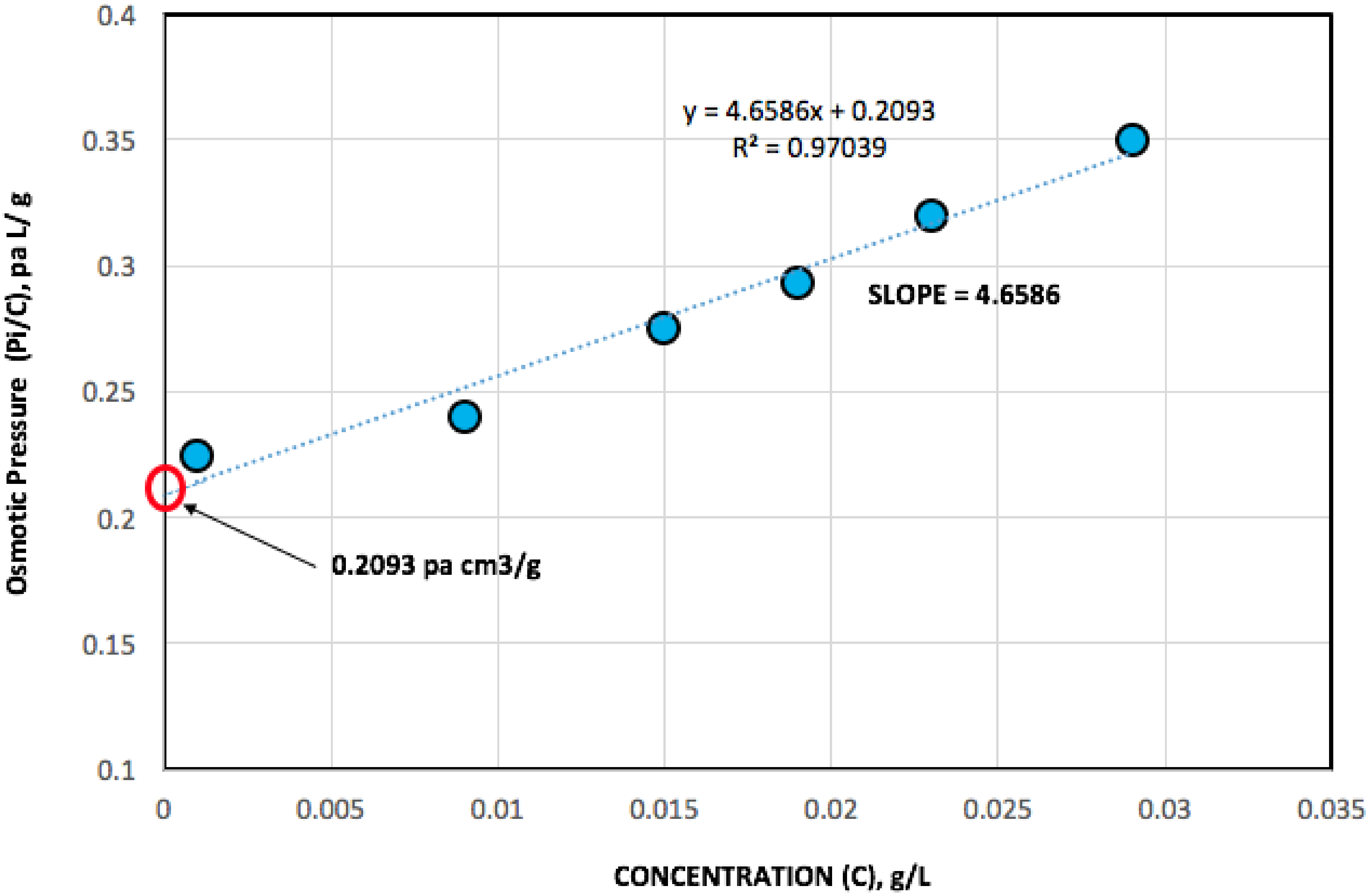
https://www.protec-arisawa.com/reverse-osmosis-the-power-to-dominate-the-ocean/

SOLUTION:

The relation between the osmotic pressure , concentration and the number-average molecular weight is as follows (please this equation is given in the M.wt lecture):

$$\left(\frac{\pi}{c}\right)_{C=0} = \frac{RT}{M_n} + A_2C \qquad (1)$$




y = 4.6586x + 0.2093
R² = 0.97039
SLOPE = 4.6586
0.2093 pa cm3/g
Osmotic Pressure (Pi/C), pa L/ g
CONCENTRATION (C), g/L
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035

Now, return to Eq. 1:

$$\left(\frac{\pi}{c}\right)_{C=0} = \frac{RT}{M_n} + A_2C \qquad (1)$$

Comparing this equation with the general form of a line equation , it is easy to note that the term $\frac{RT}{M_n}$ represents the intercept value (the red circled area in the graph).

Therefore, one can conclude that the value of the term $\frac{RT}{M_n}$ is 0.2093 pa cm^3/g and hence Mn = 8314*298/0.2093 (or Mn = 11,837,419 g/mole).

NOTE: the gas constant (R) is 8314 $L \cdot Pa \cdot K^{-1} \cdot mol^{-1}$

QUESTION 2:

Given the following data of the falling time of polystyrene-cyclohexane solution in a viscometer, what is the viscosity-average molecular weight of this polymer? (T = 35°C)

Falling time (sec)	t_0 = 3	8	14	22	32	44	56
C (g/L)	0	0.1	0.2	0.3	0.4	0.5	0.6

SOLUTION:

The viscosity average molecular weight is correlated with the intrinsic viscosity through Mark-Howink equation as follows:

$$[\eta] = K\overline{M}^a$$

$[\eta]$: intrinsic viscosity

K , a : constant for specific polymer and solvent

$\overline{M}$: average molecular weight

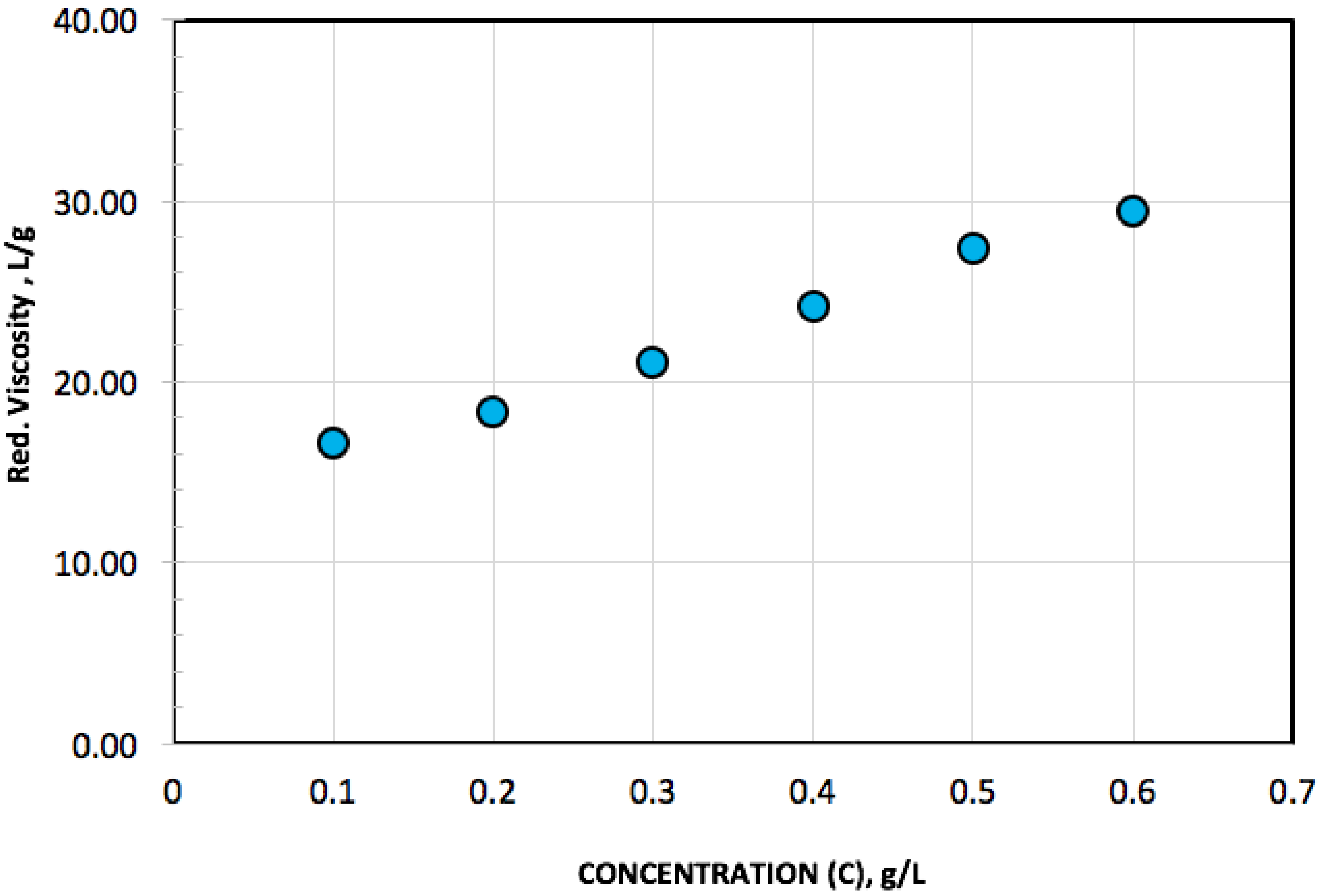
The intrinsic viscosity in the above equation can be found from the reduced viscosity When the polymer solution concentration approaching zero (i.e. very dilute solution) :

$$[\eta] = \lim_{c \to 0} (\eta_{red})$$

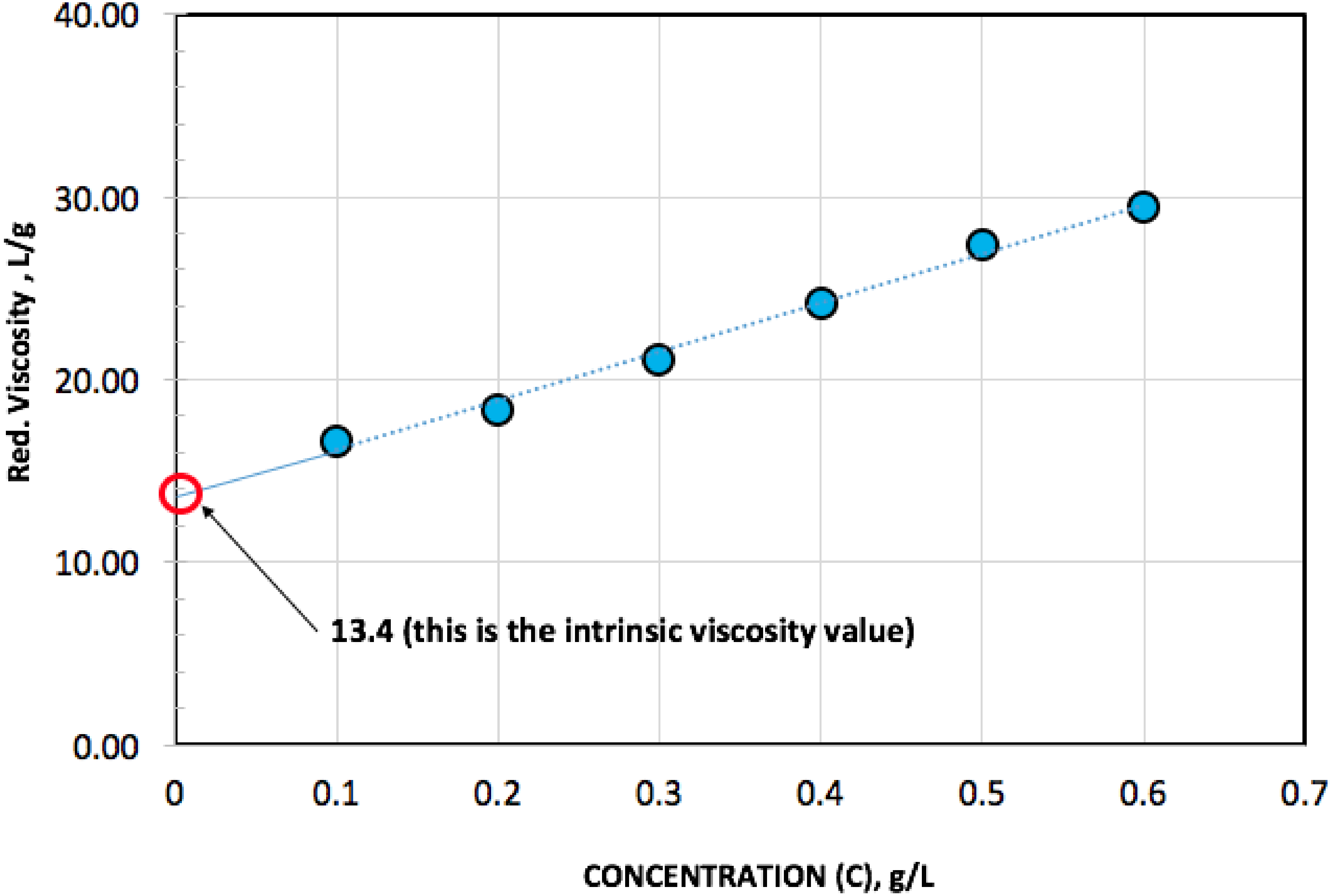
This can be found graphically by plotting the reduced viscosity against the concentration using the given data :

Falling time (sec)	**t_0 = 3**	**8**	**14**	**22**	**32**	**44**	**56**
C (g/L)	**0**	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**0.6**
η_{red}	**0**	**16.67**	**18.33**	**21.11**	**24.17**	**27.33**	**29.44**

NOTE: $\eta_{red} = \dfrac{t - t_0}{t_0 * c} = \dfrac{\eta_{sp}}{c}$ **this equation is given in the M.wt Lecture.**



40.00
30.00
20.00
10.00
0.00
Red. Viscosity , L/g
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
CONCENTRATION (C), g/L



40.00
30.00
20.00
10.00
0.00
Red. Viscosity , L/g
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
13.4 (this is the intrinsic viscosity value)
CONCENTRATION (C), g/L

Mark-Howink equation Constants

Polymer	Solvent	Temperature, °C	Molecular Weight Range × 10^{-4}	$K^b \times 10^3$	a^b
Polystyrene (atactic)[c]	Cyclohexane	35 [d]	8-42[e]	80	0.50
	Cyclihexane	50	4-137[e]	26.9	0.599
	Benzene	25	3-61[f]	9.52	0.74
Polyethylene (low pressure)	Decalin	135	3-100[e]	67.7	0.67
Poly(vinyl chloride)	Benzyl alcohol	155.4[d]	4-35[e]	156	0.50
	Cyclohexanone	20	7-13[f]	13.7	1.0
Polybutadiene					
98% cis-1,4, 2% 1,2	Toluene	30	5-50[f]	30.5	0.725
97% trans-1,4, 3% 1,2	Toluene	30	5-16[f]	29.4	0.753
Polyacrylonitrile	DMF[g]	25	5-27[e]	16.6	0.81
	DMF	25	3-100[f]	39.2	0.75
Poly(methyl methacrylate-co-styrene)					
30-70 mol%	1-Chlorobutane	30	5-55[e]	17.6	0.67
71-29 mol%	1-Chlorobutane	30	4.18-81[e]	24.9	0.63
Poly(ethylene terephthalate)	M-Cresol	25	0.04-1.2[f]	0.77	0.95
Nylon 66	M-Cresol	25	1.4-5[f]	240	0.61

The intrinsic viscosity from the plot is 13.4 and Mark-Howink constants are 0.08 and 0.5 for *K* and *a* , respectively.

Now,, applying Mark-Howink equation gives:

$$13.4 = 0.08\ (M_v)^{0.5} \Rightarrow M_v = 28000\ g/mol.$$

H.W: Repeat QUESTION 2 using the value of the inherent viscosity where:

$$[\eta]_K = \lim_{c \to 0}\ (\eta_{inh})$$

QUESTION 3

Assume that the molecular weight distribution shown in the figure below are for polyvinyl chloride. For this data compute: (1) the number average molecular weight , (2) the number degree of polymerization , and 3) the weight average molecular weight.

Molecular weight range (g/mole)	**Mole fraction (x_i)**
5000 - 10000	0.05
10000 - 15000	0.16
15000 - 20000	0.22
20000 - 25000	0.27
25000 - 30000	0.2
30000- 35000	0.08
35000 - 40000	0.02

SOLUTION:

1) $\overline{M_n} = \frac{\sum_i^n N_i M_i}{\sum_i^n N_i} = \sum_i^n x_i M_i$; where x_i is the mole fraction. (1)

Molecular weight range (g/mole)	Mole fraction (x_i)	Mean M_i	$X_i\ M_i$
5000 - 10000	0.05	7500	375
10000 - 15000	0.16	12500	2000
15000 - 20000	0.22	17500	3850
20000 - 25000	0.27	22500	6075
25000 - 30000	0.2	27500	5500
30000- 35000	0.08	32500	2600
35000 - 40000	0.02	37500	750
			$Mn = \sum_i^n x_i M_i$ = 21150 g/mole

2) $\overline{Dp} = \frac{Mn}{Mo} = \frac{21150}{Mo}$; where M_o for vinyl chloride (CH_3CH_2Cl)

M_o for vinyl chloride (CH_3CH_2Cl) = 3(12)+3(1)+35.5 =62.5 g/mole

$$\overline{Dp} = \frac{M_n}{Mo} = \frac{21150\text{ g/mole}}{62.5\text{ g/mole}} = 338$$

3) $$\overline{M_w} = \frac{\sum_i^n w_i M_i}{\sum_i^n w_i} = \sum_i^n y_i M_i \qquad (2)$$

where y_i is the mass fraction

Since mole fraction is given in the data, one may need to convert each mole fraction to mass fraction using the following relation:

$$y_i = \frac{\text{xi } M_i}{M_n} \qquad (3)$$

Now use eqs. 2 and 3 to build the following table:

Molecular weight range (g/mole)	Mole fraction (x_i)	Mean M_i	Y_i *(from Eq. 3)*	$y_i M_i$
5000 - 10000	0.05	7500	0.0177	132.98
10000 - 15000	0.16	12500	0.0945	1182.03
15000 - 20000	0.22	17500	0.1820	3185.58
20000 - 25000	0.27	22500	0.2872	6462.77
25000 - 30000	0.2	27500	0.2600	7151.30
30000- 35000	0.08	32500	0.1224	3995.27
35000 - 40000	0.02	37500	0.0354	1329.79
				$Mw = \sum_i^n y_i M_i$ = 23439.72 g/mole

HOMEWORK (using both inhernet and reduced viscosity vakues) :

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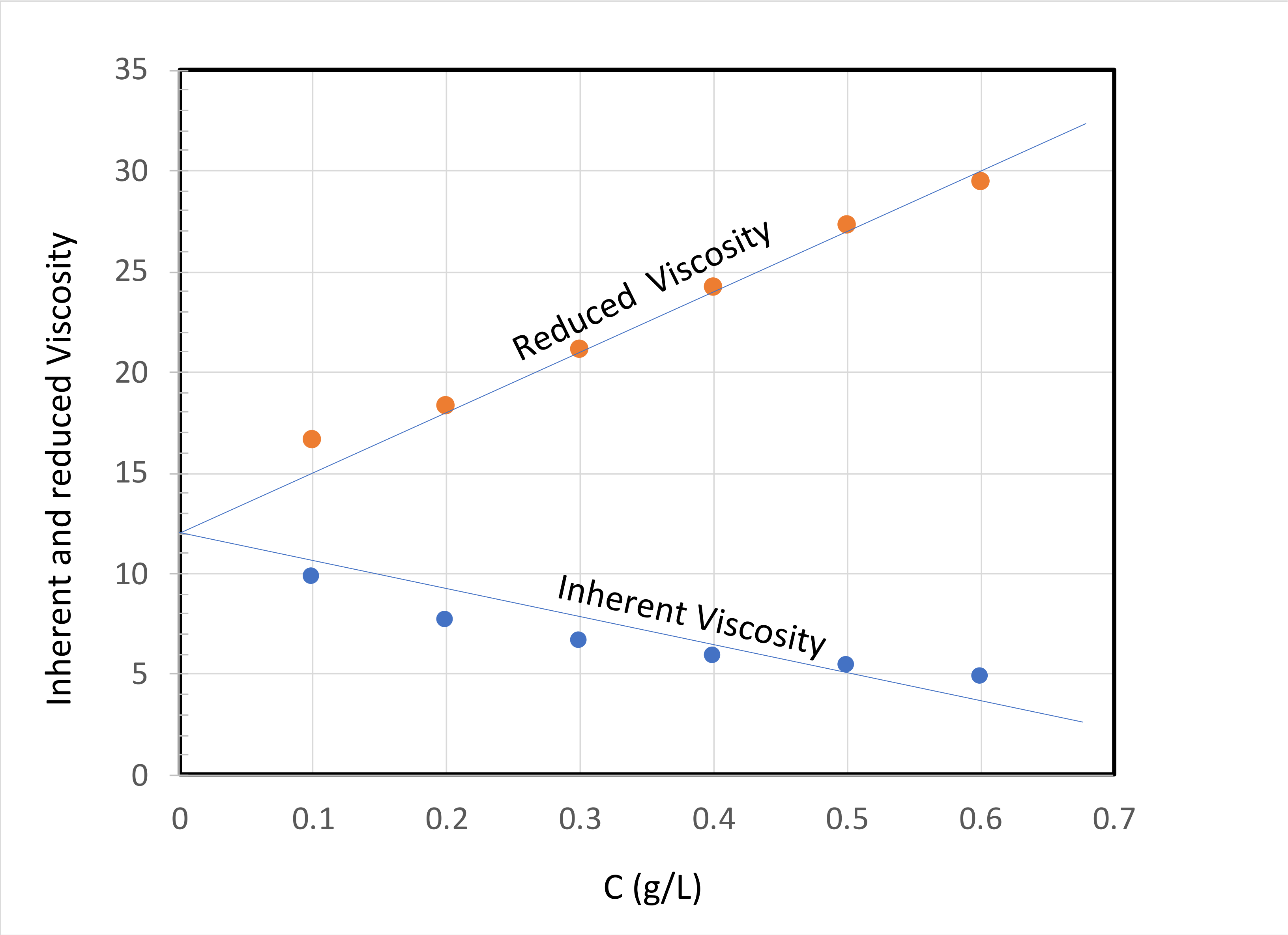
K , a : constant for specific polymer and solvent
$\overline{M}$: average molecular weight


35
30
25
20
15
10
5
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Inherent and reduced Viscosity
C (g/L)
Reduced Viscosity
Inherent Viscosity

THANK YOU
FOR
YOUR ATTENTION