

Inter and Intra-molecular Forces of PMMA Polymer in Acetone

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Summary: The present investigation was carried out to study the solution properties of Poly(methylmethacrylate) PMMA in acetone by viscometric technique. Viscosity of six samples of PMMA in the molecular weight range, 3.35×10^4 to 2.132×10^6 , was studied at 10-30°C, with 5°C interval.

The reduced viscosity data were employed to determine the intrinsic viscosity $[\eta]$, Huggin's constant (K_H) and Kraemer's constant (K_K) at different temperatures. From the calculated values of the intrinsic viscosity and molecular weights the Mark-Houwink equation parameters 'K' and 'a' were estimated at different temperatures. The values of 'K' and 'a' support the idea that acetone is a good solvent for PMMA.

Inter (K_H) and intra-molecular (K_H') Huggin's coefficients were calculated for different PMMA samples. It was observed that the intra molecular attraction increases with rise in molecular weight of the polymer.

Introduction

Characteristics of a polymer may be defined and determined by various scientific techniques before its processing. Viscosity and light scattering are frequently used due to their incompleteness and optimum efficiency in measurements. Viscometry, in fact is highly advantageous for understanding flow behaviour of polymer solutions. Moreover, for a particular polymer solvent system, this method imparts knowledge more readily as to the shape, size, unperturbed chain dimensions and other inherent qualities of a polymer. The intrinsic viscosity is another outstanding parameter determined by solution viscosity and is a measure of the hydrodynamic volume of the polymer coil in a given solvent. Stating explicitly as per Mark-Houwink (MH) equation [1] the intrinsic viscosity of a given polymer solvent system at a known temperature is a unique function of molecular weight. The two empirical constants 'K' and 'a' are sensitive to interactions between solute and solvent molecules.

Since polymers behave differently in different solvents, therefore a solvent for a given polymer can be classified as good, theta and poor [2]. This has lead the polymer physicists to ponder about the size, shape and the forces of attraction between the polymer-polymer and polymer-solvent molecules in solution. They have tried to describe the properties of

polymers in solution with the help of models and theories.

Solution properties of polymers measured in term of intrinsic viscosity are related to the molecular weight through simple scaling relationship. The relation [3] in a generalized form can be written as:

$$[\eta] = KM^a \quad (1)$$

where $[\eta]$ is intrinsic viscosity, M is molecular weight of the polymer and 'K' and 'a' are constants, sensitive to the quality of the solvent and the molecular weight. For polymers dissolved in theta solvents it has been established that $a=0.5$ while in good solvents its values lie between 0.5-0.8.

Results and Discussion

Reduced viscosity was calculated from the measured flow times. The representative high and low molecular weights Huggin's and Kraemer's plots are shown in Figures 1, 2. In all samples, the data fit nicely to the Huggin's and Kraemer's equations as no curvature is observed and extrapolation to zero concentration for the estimation of intrinsic viscosity is quit feasible. Tables 1-3 give the values of the intrinsic viscosities $[\eta]$, Huggin's constant (K_H) and

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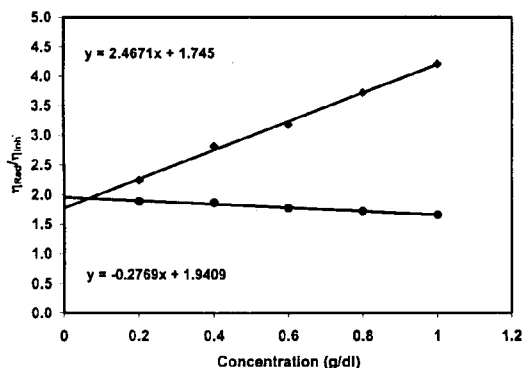


Fig. 1: Inherent/Reduced viscosity vs concentration for PMMA molecular weight 2.132E06 in acetone at 30 °C

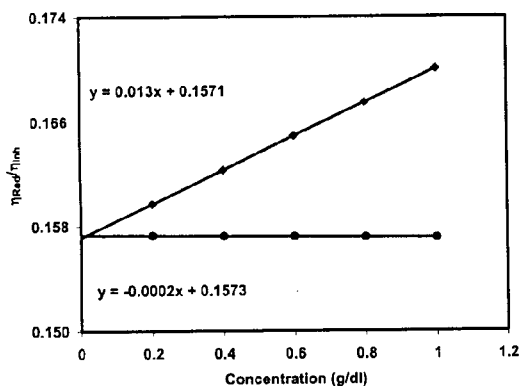


Fig. 2: Inherent/Reduced viscosity vs concentration for PMMA molecular weight 3.35E04 in acetone at 30 °C

Table-1. Intrinsic viscosities $[\eta]$ for different PMMA samples in acetone at different temperatures.

Temp (°C)	Molecular weights					
	2.13E+06	1.15E+06	1.14E+06	5.96E+05	3.30E+05	3.35E+04
10	1.619	1.125	1.115	0.758	0.527	0.134
15	1.673	1.125	1.127	0.773	0.537	0.138
20	1.704	1.139	1.137	0.800	0.540	0.146
25	1.723	1.148	1.147	0.813	0.549	0.147
30	1.745	1.171	1.160	0.840	0.565	0.157

Table-2: Huggin's coefficient (K_H) for PMMA samples in acetone at different temperatures.

Temp (°C)	Molecular weights					
	2.13E+06	1.15E+06	1.14E+06	5.96E+05	3.30E+05	3.35E+04
10	0.931	0.572	0.579	0.546	0.537	0.509
15	0.867	0.593	0.579	0.565	0.532	0.488
20	0.843	0.592	0.590	0.552	0.559	0.524
25	0.819	0.570	0.561	0.554	0.515	0.526
30	0.810	0.558	0.569	0.551	0.516	0.527

Kraemer's constant (K_K) in acetone at different temperatures. The K_H and K_K are established from slopes and $[\eta]$ is obtained from the intercepts of the graphs of reduced/inherent viscosities vs. concentration.

The intrinsic viscosities in acetone given in Table 1 show increase with temperature and molecular weights. The reason for increase of intrinsic viscosity $[\eta]$ with molecular weight is obvious i.e. with increase in molecular weight, the size of the polymer molecule increases, which is reflected in higher values of the intrinsic viscosity. With increase in temperature, the thermodynamic quality of the solvent (acetone) improves, resulting better solvation solution of the polymer molecules. Due to this fact the intrinsic viscosity increases with temperature. Acetone, being a known good solvent, wherein the polymer swells more and as such occupies more space and thus its flow time increases. As intrinsic viscosity represents the volume of polymer molecule in the solution per unit weight of polymer, therefore, in good solvent this volume would be larger as compared to poor solvents under similar conditions.

Figure 3 shows a double logarithmic plot of the intrinsic viscosity vs molecular weight. From the intercept and slope of the graph the Mark-Houwink constants ' K ' and ' a ' were obtained respectively. The values of these constants thus obtained are given in Table 4 along with literature values. Where as the value of ' a ' indicates the nature of the solvent [2]. ' a ' < 0.5 indicates poor nature of the solvent, ' a ' > 0.5 indicates good solvent while ' a ' = 0.5 indicates theta condition. From the value of ' a ' it may be concluded that acetone is a good solvent for PMMA because at all the temperatures ' a ' > 0.5. In Table 4 the ' K ' and ' a ' values of PMMA in acetone are listed, which are in good agreement with literature [4,5] values. Putting these values in the Mark-Houwink equation the following relationships were obtained, at different temperatures for PMMA in acetone.

$$[\eta]_{10^\circ\text{C}} = 2.526\text{E-}04 \text{ M}^{0.602} \quad (2)$$

$$[\eta]_{15^\circ\text{C}} = 2.699\text{E-}04 \text{ M}^{0.598} \quad (3)$$

$$[\eta]_{20^\circ\text{C}} = 3.114\text{E-}04 \text{ M}^{0.589} \quad (4)$$

$$[\eta]_{25^\circ\text{C}} = 3.170\text{E-}04 \text{ M}^{0.590} \quad (5)$$

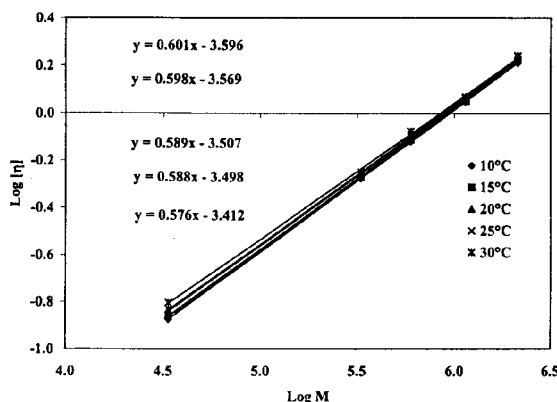
$$[\eta]_{30^\circ\text{C}} = 3.865\text{E-}04 \text{ M}^{0.575} \quad (6)$$

Table-3: Kraemer's coefficient (K_K) for PMMA samples in acetone at different temperatures.

Temp (°C)	Molecular weights					
	2.13E+06	1.15E+06	1.14E+06	5.96E+05	3.30E+05	3.35E+04
10	-0.053	-0.080	-0.080	-0.039	-0.049	-0.017
15	-0.064	-0.075	-0.080	-0.062	-0.053	-0.031
20	-0.067	-0.073	-0.075	-0.068	-0.041	-0.005
25	-0.071	-0.075	-0.080	-0.069	-0.065	-0.005
30	-0.074	-0.078	-0.078	-0.072	-0.063	-0.008

Table-4: Mark-Houwink constants 'K' and 'a' for PMMA at different temperatures in acetone.

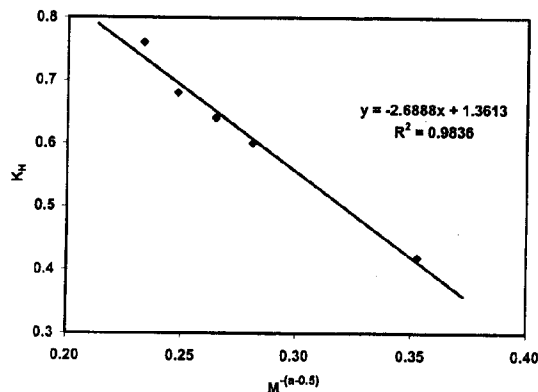
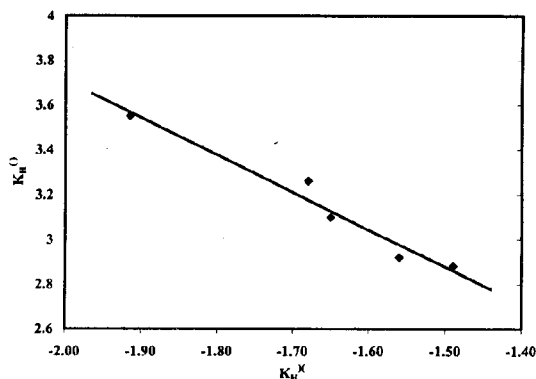
Temp (°C)	Present work		Literature values [10]	
	'K'	'a'	'K'	'a'
10	2.526E-04	0.602	-	-
15	2.699E-04	0.598	-	-
20	3.114E-04	0.589	3.90E-04	0.76
25	3.170E-04	0.590	5.30E-04	0.70
30	3.865E-04	0.575	2.30E-04	0.63

Fig. 3: Double logarithmic plot of $[\eta]$ vs molecular weight for PMMA in acetone at different temperatures.

The values of Huggin's constant for all samples at different temperatures are listed in Table 2. It can be seen that at a given temperature, the values of K_H increase with increase in molecular weight. According to Gundert and wolf [6] the molecular weight dependence of K_H is a composite function of inter $K_H^{(i)}$ (and intra-molecular $K_H^{(i)}$) Huggin's coefficients. This idea is based on the concept that when solvent is added at a polymer both inter and intra- molecular contacts are opened up. Furthermore, the extent to which inter-molecular contacts are opened up is normally different than the intra-molecular contacts. The K_H dependence of molecular weight can be expressed by the equation (7) proposed by Gundert and wolf [6]

$$K_H = \frac{K_H^{(i)} + K_H^{(i)}}{2} + \frac{K_H^{(i)} - K_H^{(i)}}{2} \frac{K_H^{(i)}}{K_H^{(i)}} M^{-(a-0.5)} \quad (7)$$

In figure 4 K_H is plotted as function of $M^{-(a-0.5)}$ at different temperatures. The values of $K_H^{(i)}$ and $K_H^{(i)}$ (obtained from the graph are plotted in Figure 5 which show a linear relationship between $K_H^{(i)}$ and $K_H^{(i)}$, showing that $K_H^{(i)}$ decreases with increase in $K_H^{(i)}$. It should be noted that each point in this graph represents a different temperature.

Fig. 4: Plot of K_H vs $M^{-(a-0.5)}$ for PMMA in acetone at 30°C.Fig. 5: Dependence of the intra-molecular Huggin's coefficient $K_H^{(i)}$ on the inter-molecular Huggin's coefficient $K_H^{(i)}$ for PMMA in acetone.

The data in Figures 6 and 7 show the plots of K_H vs. temperature and molecular weight respectively. As is obvious from this figure, the temperature is non-effective on the lower molecular weight sample i.e. 3.35×10^4 to 1.145×10^6 . For higher molecular weight samples i.e. 2.132×10^6 a decrease in K_H with increase in temperature is observed. This decrease in K_H values of high molecular weight polymer samples with temperature may be due to that

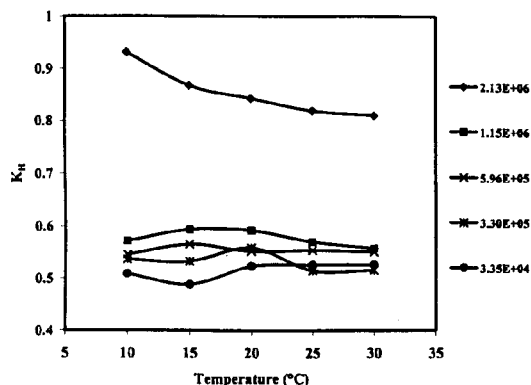


Fig. 6: Dependence of Huggin's coefficient (K_H) on temperature of different molecular weights of PMMA.

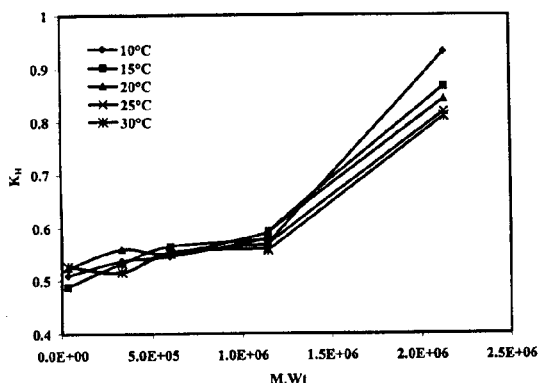


Fig. 7: Dependence of Huggin's coefficient (K_H) on molecular weights of PMMA at different temperatures.

at low temperature the polymer coil is not fully dissolved because of greater intra-molecular attraction of the coil. Therefore, the K_H values at low temperature are high. As we increase the temperature, the solvent quality improves and the intra-molecular attraction decreases causing the K_H values to drop while in case of lower molecular weight, temperature has no effect on intra-molecular attraction [6]. The dependence of K_H on the molecular weight of the polymer is also apparent from figure 7 in which we plot K_H vs molecular weight at different temperatures.

Figure. 7 further shows an increase in K_H values with rise in molecular weight of the polymer sample. As envisaged from the past discussion that PMMA sample has higher intra-molecular attraction

and thus intra-molecular attraction increases with the rise in molecular weight of the polymer. Therefore, with increase in intra-molecular attraction the polymer coil will not dissolve well due to which higher values of K_H will be observed. These results show that at higher temperature the contribution of $K_H^{(1)}$ to K_H is higher than that of $K_H^{(2)}$.

Experimental

Materials

Six samples of PMMA were utilized. Four of the samples obtained from Pressure Chemicals having molecular weights 2.132×10^6 , 1.145×10^6 , 1.141×10^6 , 5.96×10^5 with Mw / Mn 1.08, 1.06, 1.06 and 1.08 respectively and the other two samples of molecular weights 3.3×10^5 and 3.35×10^4 with Mw / Mn 1.11 and 1.10 respectively were procured from Polysciences Inc. The solvent acetone was obtained from BDH Pool England.

Solution Preparation

Dilute solutions of PMMA in the concentration range of 0.2 to 1.0 g/dL were prepared in acetone. A specific calculated amount of sample for stock solutions was weighed and enough solvent added to it. Complete dissolution of the material achieved after 48 hours with occasional shaking. The solution was made to the mark with solvent. Preparation of solution of required concentration was accomplished by dilution method.

Measurements and Calculations

Ubbelohde viscometer [7] was utilized for viscosity measurement. The flow times of various solvents and solutions were measured with in the range of 10 to 30°C to an accuracy of 0.01 seconds for acetone with 5°C increment by using a stopwatch. Polystat constant temperature circulator of Cole Parmer USA controlled the temperature.

Reduced viscosity (η_{Red}) values were calculated from the flow time of polymer solution (t) and respective solvent (t_0). Various empirical equations [8,9] from which we can determine the intrinsic viscosity $[\eta]$ are.

Huggin's equation

$$\eta_{Red} = [\eta] + K_H[\eta]^2 C \quad (8)$$

Kraemer's equation

$$\ln(\eta_{rel})/C = [\eta] + K_K[\eta]^2 C \quad (9)$$

The unit of intrinsic viscosity $[\eta]$ is mL/g in cgs system and L/Kg in SI system, which shows that $[\eta]$ is a measure of volume occupied by unit mass of polymer[10]. Mark-Houwink equation relates the molecular weight of the polymer with its intrinsic viscosity $[\eta]$ by equation (1).

Conclusions

From the above discussion it is inferred that with increase in temperature the solvent (acetone) quality and intrinsic viscosity increase. At given temperature, K_H increase with the increases in molecular weight. This Molecular weight dependence of K_H is a composite function of inter ($K_H^{(i)}$) and intra-molecular ($K_H^{(i)}$) Huggin's coefficient. Temperature has no effect on K_H values of lower molecular weight i.e. upto 1.145×10^6 , but for higher molecular weight K_H decreases with increase in

temperature. The intra-molecular attraction increases with the rise in molecular weight of the polymer.

References

1. J.F. Rabek "Instrumental Methods in Polymer Chemistry", John Wiley and Sons, New York, (1980).
2. Atager, "Physical Chemistry of Polymers", Mir Publishers Moscow. (1972).
3. H. Fujita, *Macromolecules*, **21**, 179 (1988).
4. H. Fujita, "Polymer Solutions", Elsevier Science Publisher, New York, (1990).
5. K. Mahmood, A. Saeed and A. Khan, *J. Chem. Soc. Pak.* **25**, 16 (2003).
6. F. Gundert and B.A. Wolf, *Makromol. Chem.*, **187**, 2969 (1986).
7. F. Abve, K. Horita, Y. Einaga and H. Yamakawa., *Macromolecules*, **27**, 725(1994).
8. M.L. Huggin, *J. Am. Chem. Soc.*, **64**, 2716 (1942).
9. E.O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938)
10. S. Krause and E. E. Cohn, *J. Phys. Chem.*, **67**, 1479 (1963).