Evaluation Of Huggins' Constant, Kraemer's Constant And Viscosity Concentration Co-Efficient Of Polymer PVA(Mw = 1,25,000) In Distilled Water, 1N NaOH And 1N KOH

S. Panda¹, G.C. Mohanty², R.N. Smal³, A.P. Mohapatra⁴, M.K.Nayak⁵, A.Acharya⁶, G.S. Roy⁷

- 1. Dept. of Physics, S.B. Women's College, Cuttack 753001, Orissa, India.
- 2. P.G. Dept. of Physics, G.M. (Auto) College, Sambalpur 768004, Orissa, India
 - 3. Dept. of Physics, Ravenshaw Univestiy, Cuttack 753 003, Orissa, India.
 - 4. Dept. of Physics, DRIEMS, Cuttack, Orissa, India
- 5. Dept. of Physics, Krupajal Engineering College, Bhubaneswar, Orissa, India
 - 6. Tata Consultancy Services, Kalingapark, Bhubaneswar, Orissa, India
 - 7. Plot No. 6, Budheswari Colony, Bhubaneswar 751006, Orissa, India.

gsroy2004@gmail.com

Abstract: Reduced viscosity η_{sp}/c and inherent viscosity $\ln \eta_{rel}/c$ of dilute solution of PVA (Mw = 1,25,000) have been calculated by measuring the flow time of the polymer solution in solvents like distilled water, 1N NaOH and 1N KOH at six different temperatures ranging from 250C to 500C. From extrapolation of curve (η_{sp}/c) versus C and ($\ln \eta_{rel}/c$) versus C, thermoviscosity parameters like Huggins¹ constant (K_H'), Kraemer's constant (K_H'') and viscosity concentration co-efficient (a_2) have been estimated, which enable us to know the interaction of the polymer molecules in these solvents.

[S.Panda, G.C. Mohanty, R.N. Samal3, A.P. Mohapatra, G.S. Roy, M.K. Nayak. Evaluation Of Huggins' Constant,Kraemer's Constant And Viscosity Concentration Co-Efficient Of Polymer PVA (Mw = 1,25,000) in distilled Water, 1N NaOH And 1N KOH. Researcher. 2010;2(12):5-9]. (ISSN: 1553-9865). http://www.sciencepub.net.

Key Words: Huggins' Constant; Kraemer's Constant; Intrinsic Viscosity.

1. Introduction

Solvation dynamics^{1,2} and its experimental as well as theoretical studies have given rise to renewed interest in the field of research activities^{3,4} in liquids. Viscosity^{5,6} measurements of polymer solution shows the existence of molecular interactions between the polymer and the solvents. From the measurements, the extent of interaction can also be predicted.⁷⁻¹⁰

Here we have made an investigation on molecular interaction of polymer PVA ($M_w = 1,25,000$) in solvents like distilled water 1N NaOH, 1N KOH at six different temperatures 25°C, 30°C, 35°C, 40°C, 45°C, 50°C and evaluated various thermoviscosity parameters, which are able to throw light on the property of polymer PVA.

2. Theory:

The specific viscosity¹¹⁻¹³ of the polymer solution may be generally expressed as:

Considering the dilute solutions, terms higher than the second order are neglected, giving,

$$\eta_{sp}/c = a_1 + a_2C$$
 (2) According to Huggins¹⁴,

$$a_2 = K_H [n]^2$$

So that

$$\eta_{sp}/c = [\eta] + K_{H'} [\eta]^2 C$$
(3)

Huggins' Constant

 $K_{\rm H}$ ' = Slope of the curve $(\eta_{\rm sp} / c \sim c) / [\eta]^2$ (4)

The intrinsic viscosity can be calculated with the help of Kraemer's equation¹⁵.

$$\ln \eta_{rel} / c = [\eta] + K_{\rm H} "[\eta]^2 \dots (5)$$

Kraemer's Constant

$$K_{\rm H}$$
" = Slope of the curve (ln $\eta_{\rm rel}/c \sim c$) / [η]²

Finally, viscosity concentration coefficient¹⁶ can be calculated by the equation.

$$a_2 = .201 [\eta]^{2.28}$$
(7)

3. Experiment:

Requisites:

(i) Polymer: The polymer PVA (Mw = 1,25,000) is used as such without any further purification.

(ii) Solvents : - The solvents such as aqueous solutions of NaOH and KOH are BDH (AR) grade and used as such throughout the experiment. A freshly prepared solution (1wt%) of samples were prepared in solvents like distilled water, 1N NaOH, 1N KOH.

(iii) Viscometer – The solution viscosities of polymer solution as well as solvent were determined by Ubbelohde Suspended Level Viscometer (USLV) for our study. It is designed in such a manner that, the measurement is unaffected by the volume of the solution taken.

4. Method:

We used the viscometric technique to measure the flow time of the pure solvent solution as well as polymer solvent solution with the help of an Ubbelohde type suspended level dilution viscometer. Flow time of distilled water was measured at six different temperatures from 25^{0} C to 50^{0} C. Aqueous solutions of 1N NaOH, 1N KOH were prepared and their efflux time were measured at six different temperatures ranging from 25^{0} C to 50^{0} C. One percent PVA solutions were prepared in the above mentioned solvents and their efflux times were measured in the above temperature range. The concentration (C) of the polymer solution was gradually reduced by adding solvent solution and the flow time was measured in each of the concentration (C ranges from 1 to 0.33333) at the above temperatures range.

5. Result and discussion:

The flow times (t_o) of above mentioned pure solvents were measured at six different temps ranging from 25^{0} C to 50^{0} C. The flow times (t) of polymer PVA (Mw = 1,25,000) in the above mentioned solvents were measured in different temperatures. The relative viscosity ($\eta_{rel} = t/t0$) and specific viscosity ($\eta_{sp} = (t-t_0) / t$)

t₀) were calculated. For different concentrations, reduced viscosity (η_{sp} /c) and inherent viscosity ($\ln \eta_{rel}$ /c) were also calculated. Graphs were plotted between reduced viscosity (η_{sp} /c) versus concentration(C) for all three solvents at six different temperatures. Another set of graphs were plotted between inherent viscosity ($\ln \eta_{rel}$ /c) versus concentration (C). Extrapolating the graphs for concentration C = 0, the intrinsic viscosity, viscosity concentration co-efficient (a_2), Huggins' const (K_H ') were calculated for all three solvents. In aqueous solutions of the polymer PVA ($M_{uv} = 1,25,000$), the plot

of (η_{sp} / c) versus (C) gives straight line as illustrated in figures 1 to 3. These curves were extrapolated for infinite dilution i.e, C = 0, then the Y-intercept gives the value of intrinsic viscosity $[\eta]$ and the slope of the curve gives viscosity concentration co-efficient (a₂). Using equation

(3) Huggins' constant (K_{H}) can be calculated for six different temperatures and for three different solvents as shown in Table 1–III.

From the above plots, we have drawn the following conclusions:

(i) We have taken the polymer PVA of high molecular weight (Mw = 1,25,000) we get high value of intrinsic viscosity [η]. This is in agreement with the theory, because of strong molecular force of attraction.

(ii) The viscosity concentration co-efficient (a_2) calculated by equation (7) is in good agreement with the experimental result obtained from the slope of the curve (η_{sp} / c) versus (C). But the deviation of experimental value of (a_2) from the theoretical value of (a_2) is more at

temperature 25 °C (for the three solvents). This is probably due to the fact that the effect of temperature on intrinsic viscosity $[\eta]$ has not been taken into consideration while deriving equation (7) (for low temperature).

(iii) It is to be noted that the intrinsic viscosity of the given polymer solution decreases with rise in temperature in polar solvents like distilled water, 1N NaOH and 1N KOH. It may be due to the fact that with increase in temperatue, the intermolecular distance increases. As a result the attractive molecular force between molecules decreases and hence $[\eta]$ decreases.

(iv) Comparing the curves with Huggins' equation, we found that $K_{H'}$ is positive for PVA solution in distilled water, 1N NaOH and KOH. The high value between solute (PVA) and solvents distilled water, 1N NaOH and 1N KOH. Increase in dilution, the force of attraction reduces and hence viscosity (η_{rel} , η_{sp} , η_{red} , η_{inh}) decreases. The plot of (ln η_{rel} /c) versus (C) gives straight line as shown in the figures 1 to 3. These curves are extrapolated for infinite dilution i.e. C = 0, then the Y-intercept gives the value of intrinsic viscosity [η]

(according to equation (5). The slope of the curve divided by $[\eta]^2$ gives Kraemer's constant $(k_{\rm H}^{"})$. Comparing the curves with equation (6), we see that $K_{\rm H}^{"}$ is positive for the above mentioned solvents. It is not worthy that $(K_{\rm H}^{'} - K_{\rm H}^{"})$ is in the same range for all the three solvents. Its value is nearly 0.7 (.015). Earlier¹⁷ we have found that $(K_{H}' - K_{H}'')$ for solvent Urea (PVA in 4M urea) is nearly 0.5. It may be due to the fact that PVA is readily soluble in 4M Urea, whereas polymer PVA takes 8 – 10 hours to dissolve in above mentioned three solvents, heated to temperatuo









TABLE 1 : Intrisic viscosity[η], Viscosity concentration co-efficient (a₂), Huggins' constant (K_H'), Kraemer's constant (K_H'') of PVA (M_w = 1,25,000) in distilled water at six different temperatures ranging from 25[°]C to 50[°]C.

Temp. in [°] C	Intrinsic viscosity	$a_2 = K_H^{+} * (ex pt. Value)$	a ₂ =.201 * (theo value)	Huggins' constant (K _H ')	Kraemer's Constant (K _H ")	(K _H '-K _H ")
25	0.760	0.539	0.744	0.933	0.189	0.744
30	0.635	0.486	0.494	1.205	0.367	0.838
35	0.580	0.405	0.402	1.204	0.431	0.773
40	0.537	0.421	0.337	1.460	0.565	0.895
45	0.467	0.313	0.245	1.435	0.564	0.871
50	0.433	0.345	0.206	1.804	0.907	0.897

TABLE – II Intrinsic Viscosity [η], Viscosity concentration co-efficient (a_2), Huggin's constant (K_H '), Kraemer's constant (K_H '') of PVA (Mw = 1,25,000) in 1N NaOH at six different temperatures ranging from 25° C to 50° C.

Temp. in [°] C	Intrinsic viscosity	a =K ² H *(expt. Value)	a_=.201 * (theo value)	Huggins' constant (K _H ')	Kraemer's Constant (K _H ")	(K _H '-K _H ")
25	0.583	0.274	0.406	0.806	0.109	0.697
30	0.540	0.246	0.341	0.843	0.144	0.699
35	0.514	0.223	0.305	0.844	0.167	0.677
40	0.473	0.203	0.252	0.907	0.259	0.648
45	0.420	0.207	0.192	1.173	0.465	0.708
50	0.348	0.209	0.125	1.726	0.925	0.801

TABLE – III Intrinsic Viscosity [η], Viscosity concentration co-efficient (a_2), Huggin's constant (K_H '), Kraemer's constant (K_H '') of PVA (Mw = 1,25,000) in 1N KOH at six different temperatures ranging from 25 C to 50 C

Temp. in ⁰ C	Intrinsic viscosity	a ₂ =K _H *(expt. Value)	a =.201 * (theo value)	Huggins' constant (K _H ')	Kraemer's Constant (K _H '')	(K _H '-K _H ")
25	0.655	0.285	0.530	0.644	0.040	0.604
30	0.607	0.271	0.446	0.736	0.106	0.630
35	0.567	0.240	0.381	0.747	0.096	0.651
40	0.514	0.260	0.305	0.984	0.273	0.711
45	0.455	0.262	0.231	1.266	0.512	0.754
50	0.361	0.285	0.136	2.187	1.212	0.975

Acknowledgement :

One of the Authors, S. Panda , has expessed her whole hearted thanks to Dr. (Mrs.) R. Paikray, H.O.D., Physics, Ravenshaw University, Cuttack, Orissa for providing Laboratory facilities during this investigation.

References:

[1] Roy S, Komath S and Bagchi B, Proc Indian Acad Sci Chem Sci, 79 (1993) 105.

- [2] Bagchi B, J Chem Phys, 95 (1991) 93, 467.
- [3] Chandra A and Bagchi B, J Phys Chem, 93 (1989) 6996.
- [4] Huggins M L, J Am Chem SOC, 64 (1994) 2716.
- [5] Dash U.N., Roy G.S., Talukdar M, Moharatha D, Ind. Jour., of Pure and Applied Physics Vol. 48, (2010) 651
- [6] Dash U.N., Roy G.S., Moharatha D, Talukdar M., Physics and Chemistry of liquids(In press)
- [7] Ramamoorthy, K. (1973). Ind. J. Pure Appl. Phys, 11, 556.
- [8] Mishra, R.L. and Pandey, J.D. (1977), Ind. J. Pure Appl. Phys. 15, 870.
- [9] Mahapatra A.P., Samal R.K., Samal R.N. and Roy, G.S. (1999) Ultra Scientist of Phys. Sci. 11 (1).
- [10] Mahapatra, A.P., Samal, R.K.; Samal R.N. and Roy, G.S. Phy and Chem. Liq. 2001, Vol. 39, pp 161 -181.
- [11] Dieu, H.A. (1954); J. Poly. Sci., 12, 417.
- [12] Ukita, J., Naito, R. and Kominami, T. (1955). J.
- Chem. SOC. Japan, Ind. Chem. Sect, 58, 128.
- [13] Kuroiwa, T. (1952), ibid; 7, 253.
- [14] Huggins, M.L. (1942). J. Am Chem. Soc, 64, 2716.
- [15] Kraemer, E.O. (1938). Ind. Eng. Chem. Soc, 30
- [16] Matsumoto, M. and Imai, K. (1957). J. Poly. Sci, 24, 125.
- [17]Panda S, mohanty G.C, Samal R.N, Roy G.S ()

10/28/2010