ESTIMATION OF THE UNPERTURBED CHAIN DIMENSIONS OF POLY(VINYL CHLORIDE) POLYMER BY VARIOUS METHODS

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ABSTRACT: *Flory Fox, Kurata-Stockmayer, Berry, Inagaki-Suzuki-Kurata, Stockmayer-Fixman and Ahmad-Baloch methods based on the excluded volume theory have been applied to poly(vinyl chloride)-cyclohexanone system to obtain K_θ and the radius of gyration. A discussion on the reliability of these methods is given. The Stockmayer-Fixman and Ahmad-Baloch methods are found to be equally applicable.*

KEY WORDS: *Unperturbed chain dimensions, PVC, K_θ , Radius of gyration, Intrinsic viscosity.*

The conformational and thermodynamic properties of flexible macromolecules can be described by short range and long range interaction parameters [1-3]. The short range interaction parameters are related to the unperturbed chain dimensions of a given polymer under theta conditions. However, it is sometimes difficult to study these parameters in a theta solvent, usually due to the non existance of a suitable theta solvent in which study can be made at ordinary temperatures. To overcome this problem, various extrapolation procedures have been proposed [3-8]. These procedures involves measurement of the parameters of interest in a good solvent and then extrapolation to the unperturbed state. The use of all of these has been frequently challanged and every method has some drawback [9-14]. In the present study we use these methods to estimate the unperturbed chain dimensions of poly(vinyl chloride) in cyclohexanone. Only few studies have been reported for this system [15,16].

Poly(vinyl chloride) i.e., PVC was fractionated by using THF/H_2O as solvent nonsolvent respectively. Molecular weights of all the fractions were measured by Brice Phoenix light scattering photometer. Viscosity measurement were carried out by an Ostwald viscometer at 30 °C. Intrinsic viscosities of each fraction were calculated by Huggins and Kraemer's equations. Values of the molecular weights and intrinsic viscosities thus obtained are listed in Table 1.

The intrinsic viscosity data treated according to various methods discussed above is given in Figs. 1-3. The Flory-Fox(FF) plot in Fig. 1 shows a large

scattering. This is quite natural because FF equation is found to be inadequate for determining the unperturbed dimensions for most of the polymers, particularly from the data in good solvents [17]. The data also do not fit the Berry(B) equation. This method shows deviations for the low molecular weight samples. It was suggested by *Flory* [18] that for low molecular weight samples the chain stiffness contributes to the intrinsic viscosity and thus extrapolation from viscosity data may be erroneous. Better fits to the experimental data are observed for the Kurata-Stockmayer(KS) and Inagaki-Suzuki-Kurata(ISK) method as shown in Fig. 2. A plot of the data to recently proposed method by Ahmed-Baloch (AB) equation is also shown in Fig. 3. the data fits quite well to the molecular weight range studied. These plots show that only SF and AB equations can be used reliably for the estimation of the unperturbed chain dimensions of PVC- cyclo-hexanone system. The K_θ values obtained from all the above mentioned methods are listed in Table 2. The AB method gives somewhat higher values of K_θ , but they are in good agreement to the derived values of the K_θ from literature [19,20]. The radius of gyration calculated from these K_θ values is shown in Table 3. As discussed earlier that the K_θ determined through FF, B, ISK and KS methods are not reliable, so we choose to compare the radius of gyration values obtained by SF and AB methods with the existing data. Molecular weight dependence of the radius of gyration calculated by SF and AB method give the following linear fits respectively:

$$< R^2_{g,\theta} > = 0.1416 \, M^{0.5}_w \qquad \text{Å (SF Method)}$$

$$< R^2_{g,\theta} > = 0.2316 \, M^{0.5}_w \qquad \text{Å (AB Method)}$$

Here the exponents are those for a theta solvent. Similar equations are obtained from *Wolf* et al. [16] data which are:

$$< R^2_{g,\theta} > = 0.2909 \, M^{0.5}_w \qquad \text{Å (AB Method)}$$

$$< R^2_{g,\theta} > = 0.3159 \, M^{0.5}_w \qquad \text{Å (SF Method)}$$

Here R_g values obtained from AB method are slightly lower than the SF method. This comparison shows that both SF and AB methods give better
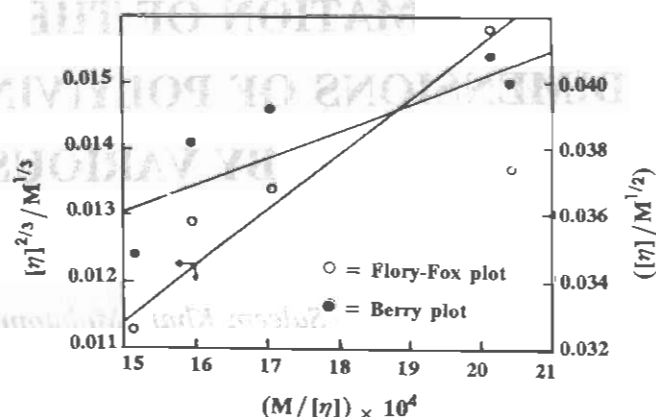
estimates of the radius of gyration.

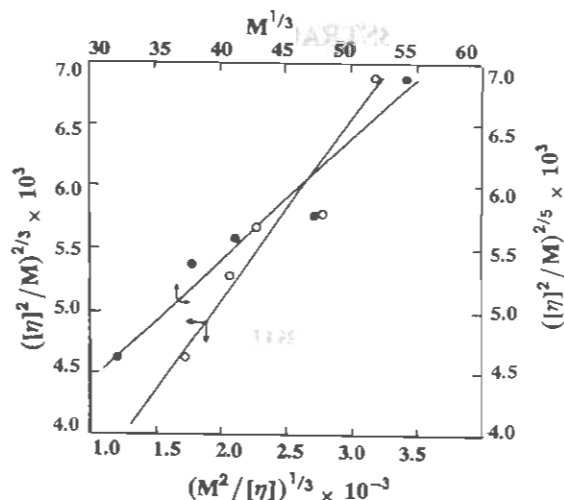Fig. 1: *Flory-Fox and Berry plots*

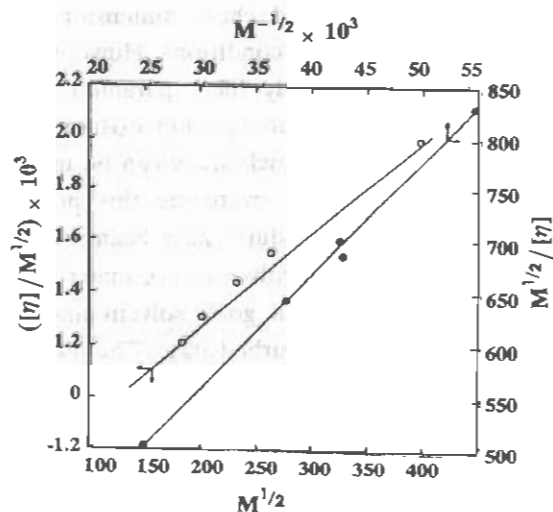Fig. 2: *Kurata-Stockmayer(○) and Inagaki-Suzuki-Kurata(●)* plots

Fig. 3: *Stockmayer-Fixman(○) and Ahmad-Baloch(●) plots*

Table 1: [η] and M_w values for different fractions of PVC

Sample	M_w(g/mole^{-1})	[η], g/dl
FR.I	159889.82	0.790
UNFR.	106179.78	0.520
FR.II	69775.38	0.410
FR.III	54324.12	0.340
FR.IV	33293.92	0.220

Table 2: $K_θ$ values for PVC-cyclohexanone system

Method	$K_θ$
FF	2.4233×10^{-3}
KS	1.6693×10^{-3}
B	1.3533×10^{-3}
ISK	1.1320×10^{-3}
SF	8.4233×10^{-3}
AB	3.2800×10^{-3}

Table 3: Radius of gyration values($A°$)for PVC-cyclohexanone

Method/Sample	UNF	FR.I	FR.II	FR.III	FR.IV
FF	63.51	77.93	51.49	45.43	35.56
KS	56.09	68.83	45.69	40.20	31.41
B	52.23	64.18	42.40	37.41	29.29
ISK	49.28	60.47	39.95	35.25	27.59
SF	44.66	54.80	36.20	31.94	25.00
AB	69.59	85.39	56.64	49.77	38.97

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