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Test of current viscosity theories for dilute polymer solutions in solvent-nonsolvent mixtures

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The linear expansion factor α_η for the fractions of a number of polymers in various solvent-nonsolvent mixtures has been determined using Stockmayer-Fixman's relationship. The validity of the Flory, Kurata and Ptitsyn theories has been tested in terms of the dependence of the function α_η on molecular weight using our data on poly m-methyl styrene and from available literature data. It has been found that Kurata theory (and in a few cases Ptitsyn theory) are in better agreement than that of Flory or Ptitsyn. Palit's viscosity-molecular weight relationship has been found to be satisfactory in almost all cases.

1. Introduction

Of the equations describing volume effects on the dimensions of macromolecules in a good solvent, the best known are Flory's (1948, 1949, 1951),

$$\alpha_\eta^5 - \alpha_\eta^3 = CM^{\frac{1}{2}} \qquad \cdots\ 1)$$

Kurata, Stockmayer and Roig's (1960),

$$\left(\alpha_\eta^3 - \alpha_\eta\right) \left(1 + \frac{1}{3\alpha_\eta^2}\right)^{\frac{3}{2}} = C'M^{\frac{1}{2}} \qquad \cdots\ (2)$$

and Ptitsyn' (1962)

$$[(4.68\,\alpha_\eta^2 - 3.68)^{3/2} - 1] = C'M^{\frac{1}{2}} \qquad \cdots\ (3)$$

Palit's (1955) equation which correlates intrinsic viscosity and molecular weight of polymers reads as follows

$$100\rho_o[\eta] = K_1 M^{\frac{1}{2}} - \ln M + K_2 \qquad \cdots\ (4)$$

where $K_1 = 1.09\ N^{\frac{1}{2}}\ \gamma\ v_{sp}{}^{2/3}/RT \simeq$ order of 10^{-2} and K_2 are constants.

The validity of equations (1), (2) (3) and (4) is tested in this paper in terms of α_η values obtained from new unpublished data and from available literature values calculated for solutions of several fractions of a number of polymers in different solvent-nonsolvent mixtures at different temperatures. The validity of these equations in case of single solvents has been tested in earlier communications (Sarkar & Palit 1967 ; Chaudhury, Sarkar & Palit 1968) where the method of computation of K and α_η (Stockmayer-Fixman) has been discussed.

2. Experimental Results and Discussion

1. Poly m-methyl styrene

Our method of treatment of the experimental data is illustrated in table I in some details. Our $\bar{M}_n$ and $[\eta]$ values at various temperatures are utilised to calculate K and α_η values. The $\bar{M}_n$ values are taken from a previous communication (Chaudhury, Sarkar & Palit 1968)

The values of α_η are found to increase with increase of molecular weight, indicating increased expansion of the molecule.

Graphical Test of the Four Equations

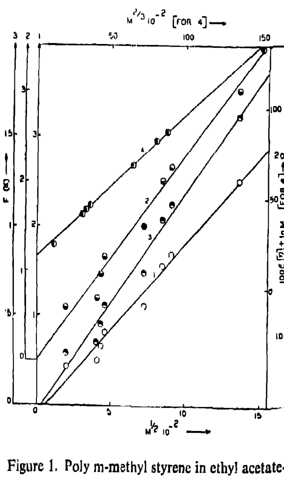

Figure 1. Poly m-methyl styrene in ethyl acetate-methanol mixture (9:1 V/V) at 30°C.

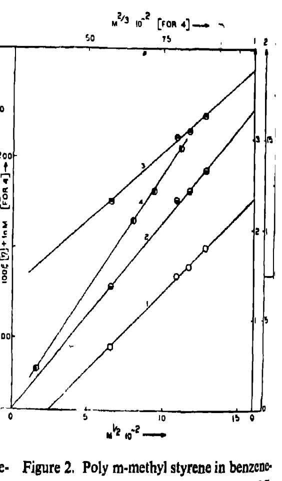

Figure 2. Poly m-methyl styrene in benzene-methanol mixture (9:1 V/V) at 30°C.

Analysis of Flory Relation : According to equation (1) plots of $\alpha_\eta^5-\alpha_\eta^3$ against $M^{1/2}$ are expected to give a straight line passing through the origin. In mixture I the Flory plot shows a fairly good linear monotonic increase but it does not pass through the origin (figure 1 marked 1) ; abscissa intercept being at M≃4100. In mixture II (figure 2), good linearity is obtained but again an abscissa intercept at M≃26,800 is observed. In mixture III (figure 3), at 30°C linearity is poor and abscissa intercept is at M≃16,3000. At 40°C (figure 4), the linearity is again poor and abscissa intercept is at M≃7,100. At 50°C (figure 5), the linearity is very good with an abscissa intercept of M≃6600. So Flory theory is adequate with respect to linearity of the Flory plot but the latter does not conform to the theoretical necessity of passing through the origin.

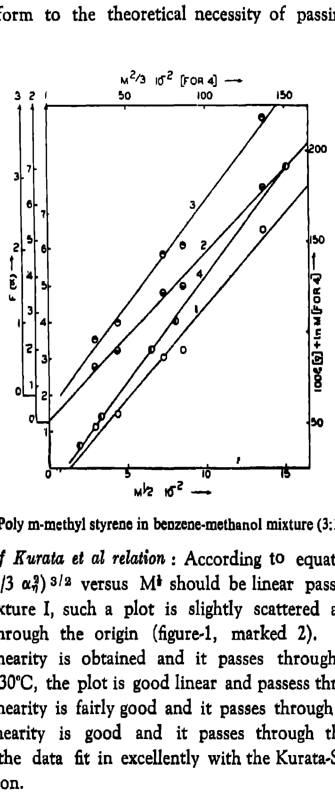

Figure 3. Poly m-methyl styrene in benzene-methanol mixture (3:1 V/V) at 30°C.

Analysis of Kurata et al relation : According to equation (2) plots of $(\alpha_\eta^3-\alpha_\eta)\,(1+1/3\,\alpha_\eta^2)^{3/2}$ versus $M^{1/2}$ should be linear passing through the origin. In mixture I, such a plot is slightly scattered about a straight line passing through the origin (figure-1, marked 2). In mixture II, fairly good linearity is obtained and it passes through the origin. In mixture III at 30°C, the plot is good linear and passess through the origin. At 40°C, the linearity is fairly good and it passes through the origin. At 50°C, the linearity is good and it passes through the origin. This suggests that the data fit in excellently with the Kurata-Stockmayer-Roig (K-S-R) equation.

Analysis of Ptitsyn Relation : According to equation (3) plots of $[(4.68\alpha_\eta^2-3.68)^{3/2}-1]$ against $M^{1/2}$ are expected to give a straight line passing through the origin. In mixture 1, such a plot is found to be scattered and does not pass through the origin but gives an abscissa inter-

TABLE 1. EXPERIMENTAL VALUES OF INTRINSIC VISCOSITIES [η] IN VARIOUS SOLVENTS AT DIFFERENT TEMPERATURES

Fr. No.	$\bar{M}_n \times 10^{-5}$	Mixture I $CH_3COOC_2H_5$(90): CH_3OH(10) K.10^4 = 6.73 30°C		Mixture II C_6H_6 (90) : CH_3OH (10) K.10^4 = 9.59 30°C		K.10^4 = 7.87 30°C		Mixture III C_6H_6 (75) : CH_3OH (25) K.10^4 = 7.11 40°C		K.10^4 = 8.37 50°C	
		[η]	a_η	[η]	a_η	[η]	a_η	[η]	a_η	[η]	a_η
T_1	18.5200	1.195	1.092	—	—	1.769	1.182	—	—	—	—
1	8.2480	.742	1.067	—	—	—	—	—	—	—	—
2	7.2350	.688	1.063	1.920	1.329	·920	1.112	—	—	—	—
8	6.1090	—	—	1.680	1.308	—	—	—	—	1.004	1.153
5	5.2550	.560	1.047	1.520	1.298	·773	1.107	0.810	1.163	0.900	1.141
7	2.6605	—	—	—	—	—	—	0.535	1.134	0.585	1.107
4_2	2.1430	.347	1.036	—	—	—	—	—	—	—	—
5A	1.9050	.321	1.030	.707	1.191	0.410	1.060	0.416	1.103	—	—
5B	1.6790	.295	1.023	—	—	—	—	—	—	—	—
5D	0.8356	—	—	—	—	0.262	1.048	0.252	1·070	0.289	1.061
5E	0.3964	.142	1.020	—	—	—	—	—	—	—	—

cept, as obtained by the least square method, corresponding to M≃1300 (figure 1, marked 3). In benzene containin 10% methanol, good linearity is obtained but it gives an abscissa intercept corresponding to M≃5700. In benzene containing 25% methanol at 30°C, the plot is poorly linear and gives an abscissa intercept corresponding to M≃5000. At 40°C, the linearity is poor and the abscissa intercept corresponds to M≃2000. At 50°C, the linearity is good but it gives an abscissa intercept corresponding to M≃2000. This indicates that like Flory equation, Ptitsyn equation has got limited applicability in this case but in a sense it is better as its range of applicability is greater.

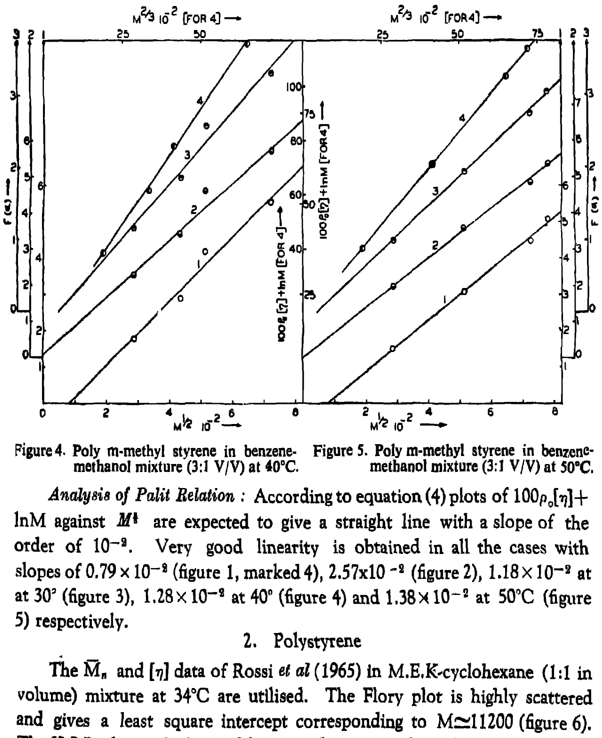

Figure 4. Poly m-methyl styrene in benzene-methanol mixture (3:1 V/V) at 40°C.

Figure 5. Poly m-methyl styrene in benzene-methanol mixture (3:1 V/V) at 50°C.

Analysis of Palit Relation : According to equation (4) plots of $100\rho_0[\eta]+$ lnM against $M^{\frac{1}{2}}$ are expected to give a straight line with a slope of the order of 10^{-2}. Very good linearity is obtained in all the cases with slopes of 0.79×10^{-2} (figure 1, marked 4), 2.57×10^{-2} (figure 2), 1.18×10^{-2} at at 30° (figure 3), 1.28×10^{-2} at 40° (figure 4) and 1.38×10^{-2} at 50°C (figure 5) respectively.

2. Polystyrene

The $\bar{M}_n$ and $[\eta]$ data of Rossi *et al* (1965) in M.E.K-cyclohexane (1:1 in volume) mixture at 34°C are utilised. The Flory plot is highly scattered and gives a least square intercept corresponding to M≃11200 (figure 6). The K-S-R plot is fairly good linear and it passes through the origin. The Ptitsyn plot is fairly good linear but gives an abscissa intercept at M≃2100.

Very good linear plot according to Palit equation is obtained with a slope of 1.93×10^{-2}.

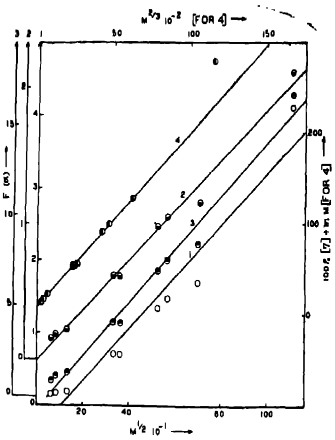

Figure 6. Polystyrene in MEK-cyclohexane (1:1 V/V) mixture at 34°C.

The $\bar{M}_n$ and $[\eta]$ data of Bawn *et el* (1950) in toluene-heptane mixtures and in toluene-methyl alcohol mixtures at 25°C are utilised.

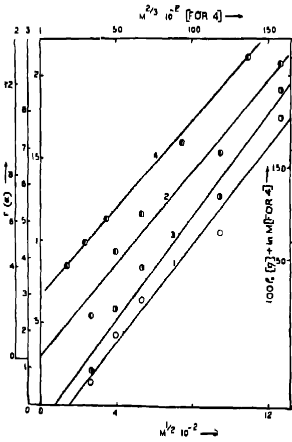

Figure 7. Polystyrene in toluene containing 10% heptane at 25°C.

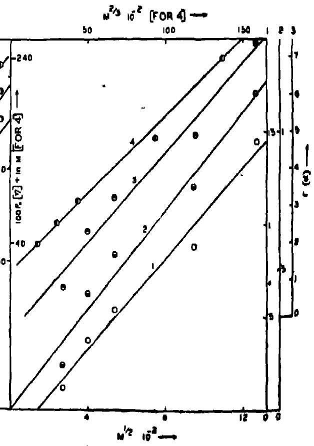

Figure 8. Polystyrene in toluene containing 20% heptane at 25°C.

In 10% heptane (figure 7), all the first three plots are scattered but while the K-S-R plot passes through the origin, the Flory and Ptitsyn plots give abscissa intercepts corresponding to M $\simeq$21600 and 5100. Very good linear Palit plot is obtained with a slope of 1.91×10^{-2}. In 20% heptane (Fig. 8) exactly similar results are obtained — the abscissa intercepts in case of Flory and Ptitsyn plots are at M $\simeq$19400 and 4900 respectivly and the value of K_1 in the case of Palit equation is 1.67×10^{-2}.

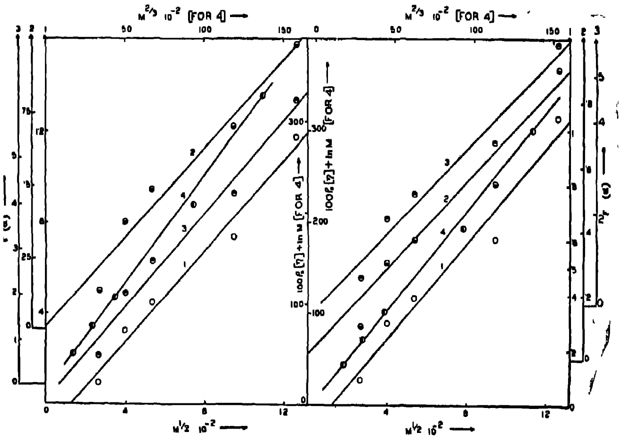

Figure 9. Polystyrene in toluene containing 30% heptane at 25°C.

Figure 10. Polystyrene in toluene containing 40% heptane at 25°C.

In 30% heptane (figure 9), the observation is the same — the Flory and Ptitsyn equations are valid above M$\simeq$16400 and 4500 and the value of slope in case of Palit equation is 2.38×10^{-2}. In 40% heptane (figure 10), the Flory plot is scattered and gives an abscissa intercept at M $\simeq$ 14800. Very poor linearity is observed in case of K-S-R equation but it passess through the origin. The Ptitsyn plot is scattered and gives an abscissa intercept at M $\simeq$4100. Very good linearity is obtained in case of Palit plot with a slope of 2.16×10^{-2}.

In 5% methanol (figure 11), poor linearity is observed in case of Flory and Ptitsyn equations with abscissa intercepts at M$\simeq$19700 and 4600 respectively. The K-S-R plot, though scattered, passes through the origin. Very good linear Palit plot is obtained with a slope of 2.35×10^{-2}. In 10% methanol (figure 12), all the three plots are scattered but while the K-S-R

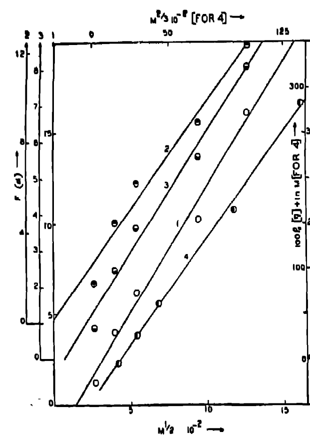

Figure 11. Polystyrene in toluene containing 5% heptane at 25°C.

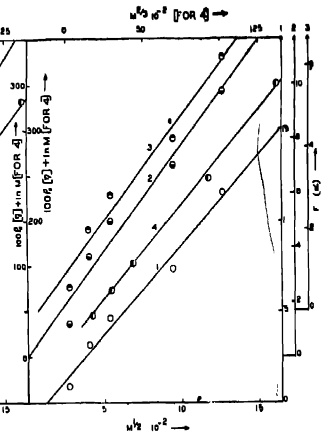

Figure 12. Polystyrene in toluene containing 10% heptane at 25°C.

plot passes through the origin, the Flory and Ptitsyn plots give abscissa intercepts at M≃14900 and 3600 respectively. Very good linear plot according to Palit equation is obtained with a slope of 2.08×10^{-2}.

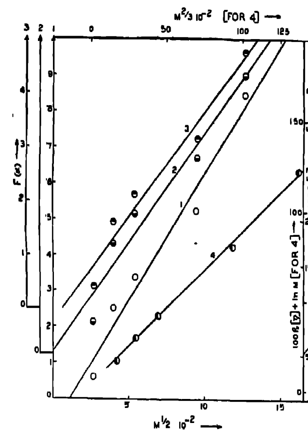

Figure 13. Polystyrene in toluene containing 15% heptane at 25°C.

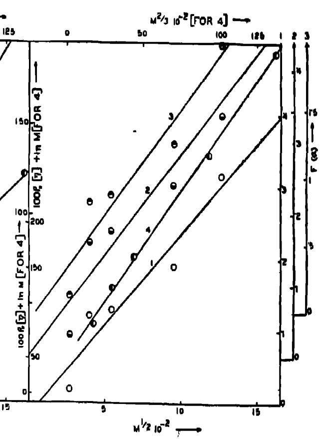

Figure 14. Polystyrene in toluene containing 20% heptane at 25°C

In 15% methanol (figure 13), more or less similar results are obtained—the Flory and K-S-R Plots are valid above M $\simeq$ 13100 and 4100 respectively. Good linear plot according to Palit equation is obtained with a slope of 1.71×10^{-2}. In 20% methanol (figure 14), the Flory and Ptitsyn plots are scattered and give abscissa intercepts at M $\simeq$ 4600 and 1700 respectively. The K-S-R plot, though highly scattered, passes through the origin. Very good linearity is obtained in case of Palit equation and it has a slope of 1.23×10^{-2}.

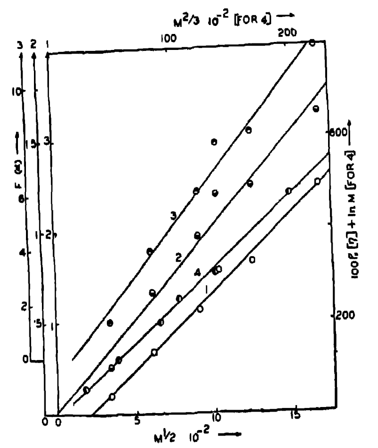

Figure 15. Polystyrene in chloroform containing 10% methanol at 25°C.

The $\bar{M}_w$ and $[\eta]$ data of Oth & Desreux (1954) are utilised. In chloroform containing 10% methanol (figure 15), good linearity is obtained in case of Flory equation, but it gives an abscissa intercept at M $\simeq$ 44000. Very poor linearity is obtained in case of K-S-R equation but it passes through the origin. Ptitsyn plot is poorly linear and it gives an abscissa intercept at M $\simeq$ 9000. Very good linear plot according to Palit equation is obtained with a stope of 2.40 × 10 ^{2}.

In 20% methanol (figure 16), good linearity is obtained both in case of Flory equation and Ptitsyn equation, but they give abscissa intercepts at M $\simeq$ 30400 and 7400 respectively. The K-S-R plot, although poor, passes through the origin. Very good linearity is obtained in case of Palit plot with a slope of 1.47×10^{-2}.

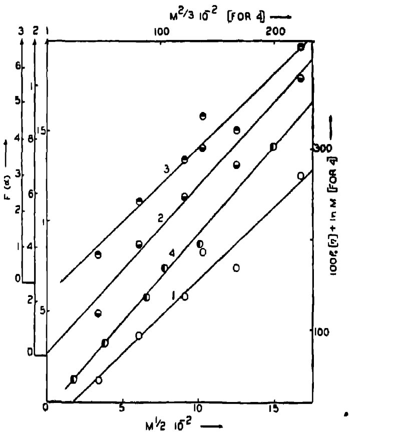

Figure 16. Polystyrene in chloroform containing 20% methanol at 25°C.

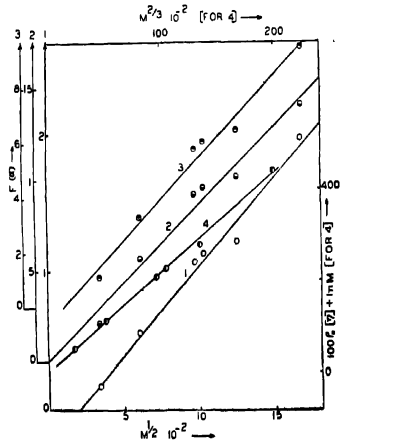

Figure 17. Polystyrene in toluene containing 10% methanol at 25°C.

In toluene-methanol mixture containing 10% methanol (figure 17), both the Flory and Ptitsyn plots are very poor and give abscissa intercepts at M ≃ 38700 and 7900 respectively. The K-S-R plot, although scattered, passes through the origin. Very good linear plot according to Palit equation is obtained with a slope of 2.17×10^{-2}.

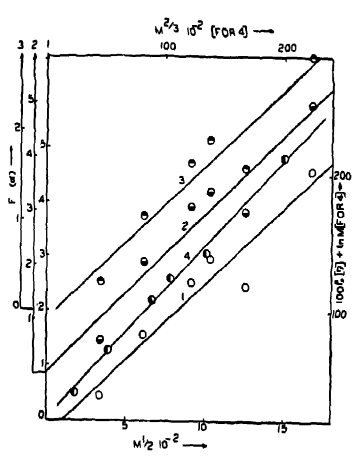

Figure 18. Polystyrene in MEK containing 5% methanol at 25°C.

In MEK-methanol mixture containing 5 % methanol (figure 18), all the first three plots are highly scattered and while the K-S-R plot passes through the origin, the Flory and Ptitsyn plots give abscissa intercepts at M≃11600 and 3400 respectively. Good linear plot according to Palit equation is obtained with a slope of 0.95×10^{-2}.

3. Amylose acetate

The $\bar{M}_w$ and $[\eta]$ data of Patel et al (1965) are utilised. In case of 65/35% choroform-cyclohexane mixture at 15°C (figure 19), good linear Flory plot is obtained with an abscissa intercept at M≃53700. Very good linearity is obtained in case of K-S-R plot and it passes through the origin. Ptitsyn plot is very good linear with abscissa intercept at M≃7800. Plot according to Palit equation is good linear with a slope of 6.54×10^{-2}.

In 50/50% chloroform-cyclohexane mixture at 15°C (figure 20), the Flory plot is scattered and gives an abscissa intercept at M≃51700. Fairly good

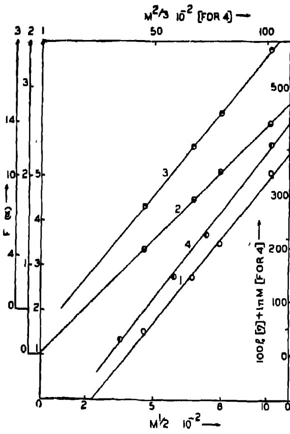

Figure 19. Amylose acetate in 65/35% chloroform-cyclohexane mixture at 15°C.

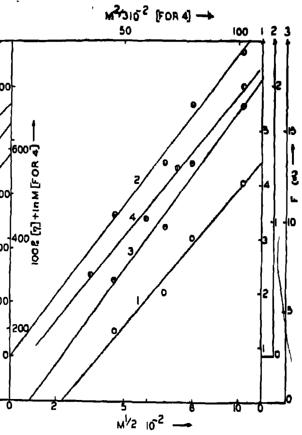

Figure 20. Amylose acetate in 50/50% chloroform-cyclohexane mixture at 15°C.

linearity is obtained in case of K-S-R equation and it passes through the origin. Ptitsyn plot is fairly good linear with an abscissa intercept at M—8300. Good linear plot according to Palit equation is obtained with a slope of 5.24×10^{-2}.

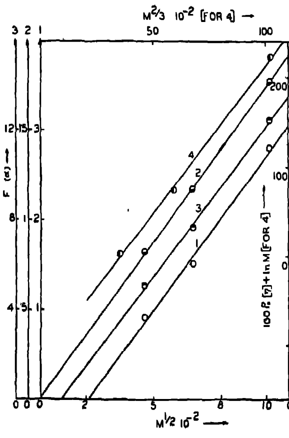

Figure 21. Amylose acetate in 50/50% nitromothane-methanol mixture at 40°C.

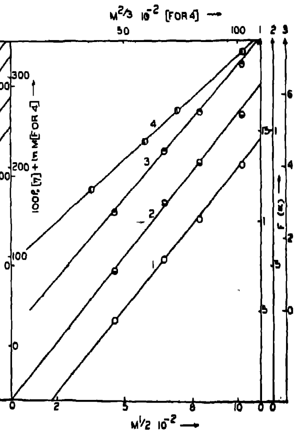

Figure. 22. Amylose acetate in 35/65% nitromethane-methanol mixture at 40°C.

In 50/50% nitromethane-methanol mixture at 40°C (figure 21), fairly good linear Flory plot is obtained with an abscissa intercept at $M \simeq 45200$. Very good linearity is obtained in case of K-S-R equation and it passes through the origin. Ptitsyn plot is good linear with an abscissa intercept at $M \simeq 8400$. Good linear plot according to Palit equation is obtained with a slope of 3.31×10^{-2}.

In 35/65% nitromethane-methanol mixture at 40°C (figure 22), Flory plot is good linear but it has an abscissa intercept at $M \simeq 30100$. K-S-R plot is fairly good linear and it passes through the origin. Good linear plot is obtained in case of Ptitsyn equation but it has an abscissa intercept corresponding to $M \simeq 7100$. Very good linear plot according to Palit equation is obtained with a slope of 2.32×10^{-2}.

Discussion

In the 22 different polymer-solvent-nonsolvent systems studied, it is observed (table 2) that as regards linearity of the $F(\alpha_\eta)$ vs. $M^{\frac{1}{2}}$ plot, Flory plot is found to be best in 12 cases while K-S-R equation is best in 6 cases and Ptitsyn equation is best in 4 cases only. It is evident that from the stand-point of linearity Flory equation is the best. However, as redards the criteria of passing through the origin, the K-S-R equation is satisfactory in almost all cases while the Flory and the Ptitsyn equations are not satisfactory even in a single case ; they always give abscissa intercepts, Ptitsyn shows a lower intercept than Flory. Palit plot is very good linear in 20 cases and good in the remaining 2 cases ; the theoretical slope of the order of 10^{-2} is obtained in all cases.

It is therefore concluded that considering the two criteria together viz., the linearity and the passing through origin, the K-S-R plot is somewhat better than the Ptitsyn or Flory plot. Hence the K-S-R equation, based on an equivalent ellipsoid model, it best suited to interpret the molecular expansion of the polymers discussed. Palit's equation excellently correlates intrinsic viscosity and molecular weight of polymers.

Thanks are due to C. S. I. R. (India) for the award of a Junior Research Fellowship to D. K. S.

TABLE 2. TABULAR SUMMARY OF RESULTS

Polymer	Solvent-Nonsolvent (Volume ratio)	Temp °C	Linearity and Abscissa Intercepts in terms of M				General Remarks	
			Flory plot Eq. 1	K-S-R plot Eq. 2	Ptitsyn plot Eq. 3	Palit plot Eq. 4, $K_1 . 10^8$	Best linear Eq.	Eq. that passes through the origin among 1, 2 & 3
Poly m-methyl styrene	Ethyl Acetate-Methanol (9 : 1)	30	fairly good 4050	very poor 0	scattered 1340	very good .79	4,1	2
	Benzene-Methanol (9 : 1)	30	good 26,800	good 0	good 5690	very good 2.57	4,1	2
	(3 : 1)	30	poor 16,300	good 0	poor 5,000	very good 1.18	4,2	2
		40	poor 7100	fairly good 0	poor 203	very good 1.28	4,2	2
		50	very good 6600	good 0	good 2000	very good 1.38	4,1	2
Polystyrene	MEK-Cyclohexane (1 : 1)	34	highly scattered 11200	fairly good 0	fairly good 2100	very good 1.93	4,2	2
	Toluene-Heptane (9 : 1)	25	scattered ,21600	scattered 0	scattered 5070	very good 1.91	4,1	2
	(8 : 2)	25	scattered 19400	scattered 0	scattered 4920	very good 1.67	4,1	2
	(7 : 3)	25	scattered 16400	scattered 0	scattered 4510	very good 2.38	4,1	2
	(6 : 4)	25	scattered 14800	very poor 0	scattered 408	very good 2.16	4,1	2

TABLE 2.—(*Contd.*)

Polymer	Solvent-Nonsolvent (Volume ratio)	Temp °C	Linearity and Abscissa Intercepts in terms of M				General Remarks	
			Flory plot Eq. 1	K-S-R plot Eq. 2	Ptitsyn plot Eq. 3	Palit plot Eq 4, $K_1.10^3$	Best linear Eq.	Eq. that passes through the origin among 1, 2 & 3
Polystyrene	Toluene-Methanol (9.5 : 0.5)	25	poor 19700	scattered 0	poor 4580	very good 2.35	4,1	2
	(9 : 1)	25	scattered 14900	scattered 0	scattered 3630	very good 2 08	4,1	2
	(8 5 : 1.5)	25	scattered 13100	scattered 0	scattered 4070	good 1.71	4,3	2
	(8 : 2)	25	scattered 4650	highly scattered 0	scattered 1720	very good 1.23	4, None	2
	Chloroform-Methanol (9 : 1)	25	good 44000	very poor 0	poor 8960	very good 2.40	4,1	2
	(8 : 2)	25	good 30400	poor 0	good 7380	very good 1.47	4,1	2
	Toluene-Methanol (9 : 1)	25	very poor 38700	scattered 0	very poor 7940	very good 2.17	4,1	2
	MEK-Methanol (9 5 : 0.5)	25	highly scattered 11600	highly scattered 0	highly scattered 3430	good 0.95	4,2	2
Amylose Acetate	Chloroform-Cyclohexane (6 5 : 3 5)	15	good 53700	very good 0	very good 7770	good 6.54	2 & 3	2
	(1 : 1)	15	scattered 51700	fairly good 0	fairly good 8330	good 5.24	4,3	2

TABLE 2.—(*Contd.*)

Polymer	Solvent-Nonsolvent (Volume ratio)	Temp °C	Linearity and Abscissa Intercepts in terms of M				General Remarks	
			Flory plot Eq. 1	K-S-R plot Eq. 2	Ptitsyn plot Eq. 3	Palit plot Eq. 4, $K_1 \cdot 10^2$	Best linear Eq.	Eq. that passes through the origin among 1, 2 & 3
Amylose Acetate	Nitromethane : Methanol (1 : 1)	40	fairly good 45200	very good 0	good 8420	good 3,31	2	2
	(3.5 : 6.5)	40	good 30100	fairly good 0	good 7050	very good 2,32	4,1	2

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