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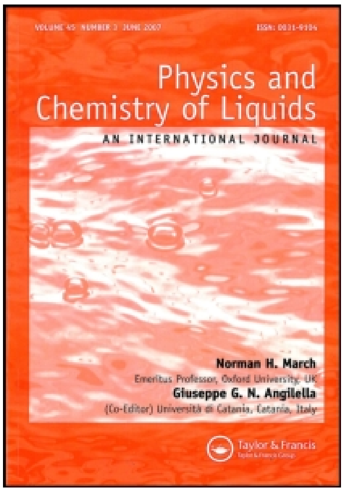

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Evaluation of Viscosity-Molecular Weight Constant (*K*), Short Range Parameter (*A*) and Long Range Parameter (*B*) of Dextran in Polar Solvents

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To cite this Article Mahapatra, A. P. , Samal, R. K. , Samal, R. N. and Roy, G. S.(2001) 'Evaluation of Viscosity-Molecular Weight Constant (*K*), Short Range Parameter (*A*) and Long Range Parameter (*B*) of Dextran in Polar Solvents', Physics and Chemistry of Liquids, 39: 3, 343 — 356

To link to this Article: DOI: 10.1080/00319100108031667

URL: http://dx.doi.org/10.1080/00319100108031667

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Phys. Chem. Liq., 2001, Vol. 39, pp. 343–356
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EVALUATION OF VISCOSITY–MOLECULAR WEIGHT CONSTANT (*K*), SHORT RANGE PARAMETER (*A*) AND LONG RANGE PARAMETER (*B*) OF DEXTRAN IN POLAR SOLVENTS

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(Received 3 March 2000)

The viscosity–molecular weight constant (*K*), the short range parameter (*A*) and long range parameter (*B*) have been evaluated in binary mixture of Dextran of three different molecular weights in three different solvents *i.e.*, distilled water, 1(N) NaOH and 1(N) KOH, at temperatures ranging from 25°C to 50°C. The study reveals that the viscosity–molecular weight constant (*K*) decreases with increase in temperature for polar solvents. The short range parameter (*A*) shows the same trend as shown by *K* and the long range parameter (*B*) exhibits no definite trend with the variation of temperature.

Keywords: Viscosity–molecular weight constant (*K*); Short range parameter (*A*); Long range parameter (*B*)

1. INTRODUCTION

Earlier various researchers [1–4] studied about the structures of different polymers by following different techniques which had given

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valuable informations regarding their utility in various fields. We used the viscometric measurement technique [5, 6] to evaluate some of the thermo-viscosity parameters of polysaccharide polymer Dextran. Extending our earlier study we have calculated some other parameters like viscosity molecular weight constant (K), Short range parameter (A) and long range parameter (B) of Dextran of three different molecular weight *i.e.*, $\bar{M}_w = 19500$, 75000 and 250000 in three different solvents at various temperatures ranging from 25°C to 50°C. To evaluate 'K', 'A' and 'B' various researchers proposed different graphical procedures. Stockmayer–Fixman, Fox–Flory and Kurata–Stockmayer had given various equations involving variation of intrinsic viscosity with molecular weight and plotting the graph the ordinate intercept provides the value of K and the slope provides the value of 'B'.

2. THEORY

Earlier to study the unperturbed dimension of a polymer molecule, the viscosity measurements were carried out in an ideal solvent as well as at ideal temperature. Since it is not experimentally convenient, attempts have been made to compute the unperturbed dimension from viscosity measurements using a solvent at any temperature. One such relationship is that given by Stockmayer and Fixman [7] which is represented as,

$$[\eta] = K(\bar{M}_w)^{1/2} + 0.51\phi_o B\bar{M}_w \tag{1}$$

where B is the long range parameter and ϕ_o is the universal constant.

In order to determine the viscosity–molecular weight constant (K) and long range parameter (B) of a polymer molecule in any solvent at any temperature, another relationship is given by Fox–Flory [8] which is represented as,

$$[\eta]^{2/3}/(\bar{M}_w)^{1/3} = K^{2/3} + 0.857K^{2/3}\phi_o B\frac{\bar{M}_w}{[\eta]} \tag{2}$$

Kurata and Stockmayer [9] had also given the following relation for determination of 'K' and 'B' which is represented as,

$$[\eta]^{2/3}/(\bar{M}_w)^{1/3} = K^{2/3} + 0.363\phi_o Bg(\alpha_n)[(\bar{M}_w)^{2/3}[\eta]^{-1/3}] \tag{3}$$

where α_n is the volume expansion factor and $g(\alpha_n)$ is the coefficient dependent on α_n.

The short range parameter 'A' which is a function of the unperturbed dimension of the polymer depends upon the solvent used as well as on the temperature of the polymer solution. Yamakawa [10] had given the following relation for determination of short range parameter 'A' which is represented as,

$$A = \left(\frac{K}{\phi_o}\right)^{1/3} \tag{4}$$

where 'K' is the thermo-viscosity parameter which depends upon the nature of the solvent and temperature of the polymer solution and ϕ_o is the universal constant independent of polymer type, solvent as well as temperature and its value is 2.84×10^{21}.

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3. EXPERIMENT

The materials and the method followed to findout various thermo viscosity parameters are same as reported earlier [5, 6].

4. RESULTS AND DISCUSSIONS

4.1. Determination of Viscosity–Molecular Weight Constant (K) by

(*a*) *Stockmayer–Fixman Plot* Stockmayer Fixman [7] equation relating intrinsic viscosity $[\eta]$ with molecular weight $(\bar{M}_w)$ is represented as,

$$[\eta] = K(\bar{M}_w)^{1/2} + 0.51\phi_o B\bar{M}_w$$

Which can be written in a more convenient form as,

$$[\eta]/(\bar{M}_w)^{1/2} = K + 0.51\phi_o B(\bar{M}_w)^{1/2} \tag{5}$$

We plot a graph by taking $([\eta]/(\bar{M}_w)^{1/2})$ along Y-axis and $(\bar{M}_w)^{1/2}$ along X-axis. The ordinate intercept provides the value of K. This curve is repeated for all the six temperatures as well as for the three solvents we have chosen which are shown in Figures 1 to 3 and the values of 'K' are represented in Tables I to III.

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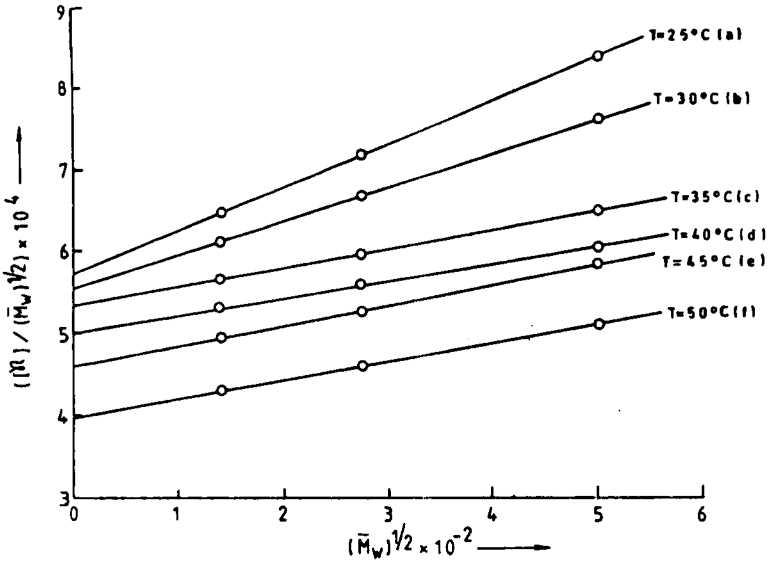

FIGURE 1 Stockmayer–Fixman's plot for Dextran of different molecular weight in distilled water at different temperatures.

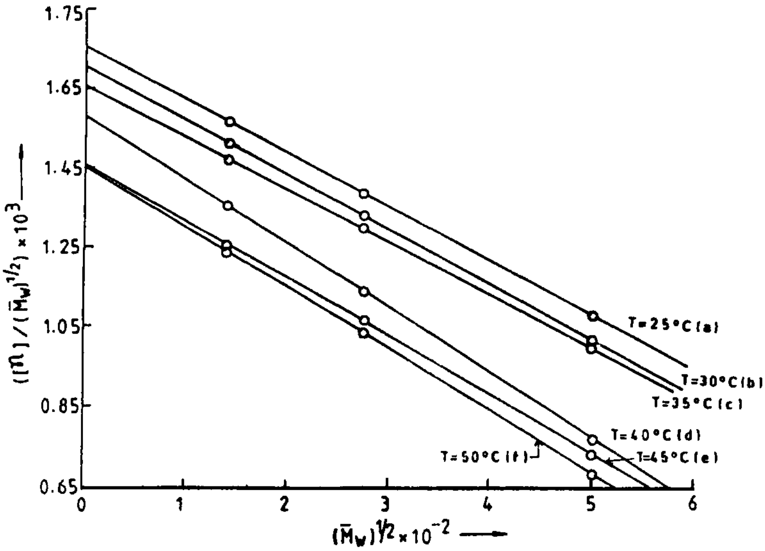

FIGURE 2 Stockmayer–Fixman's plot for Dextran of different molecular weight in 1(N) NaOH at different temperatures.

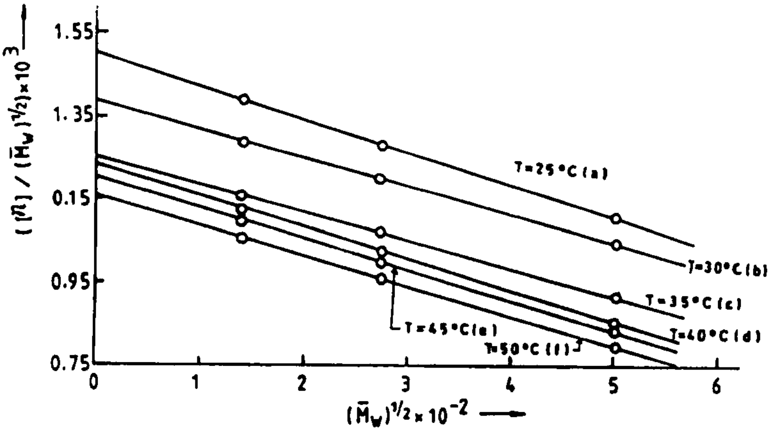

FIGURE 3 Stockmayer – Fixman's plot for Dextran of different molecular weight in 1(N) KOH at different temperatures.

TABLE I Values of K of Dextran in different solvents at different temperature from various plots, Solvent – Distilled water

	$K \times 10^3$ *from*			
Temperature in °C	*Stockmayer – Fixman's plot*	*Fox – Flory's plot*	*Kurata – Stockmayer's plot*	*Mean-Value*
25	57.512	54.842	57.004	56.453
30	55.504	54.229	56.384	55.372
35	53.518	53.011	53.314	53.280
40	50.006	50.005	50.452	50.154
45	46.121	46.186	46.186	46.164
50	39.533	39.682	39.687	39.634

TABLE II Values of K of Dextran in different solvents at different temperature from various plots, Solvent – 1(N) NaOH

	$K \times 10^3$ *from*			
Temperature in °C	*Stockmayer – Fixman*	*Fox – Flory*	*Kurata – Stockmayer*	*Mean-Value*
25	176.508	170.107	174.603	173.739
30	172.013	165.650	166.538	168.067
35	165.524	159.039	163.879	162.814
40	159.001	152.519	162.995	158.172
45	146.540	148.223	158.602	151.122
50	146.032	143.968	156.856	148.952

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TABLE III Values of K of Dextran in different solvents at different temperature from various plots, Solvent – 1(N) KOH

	$K \times 10^3$ *from*			
Temperature in °C	*Stockmayer – Fixman*	*Fox – Flory*	*Kurata – Stockmayer*	*Mean-Value*
25	150.504	144.815	141.435	145.585
30	139.036	134.753	131.864	135.218
35	125.313	123.002	118.133	122.149
40	123.524	118.530	116.551	119.535
45	120.807	114.269	112.627	115.901
50	116.000	110.682	108.362	111.681

From these plots we found that 'K' decreases with the increase in temperature in these polar solvents *i.e.*, distilled water, 1(N) NaOH, 1(N) KOH. The variation shows the similar trend as that of variation of intrinsic viscosity $[\eta]$ with temperature [5].

Another point of interest to record is that the value of K is the least in case of water which act as a poor solvent for the polymer Dextran and is maximum in case of NaOH among the three polar solvents we had chosen as NaOH is the best among the solvents we had selected for the polymer Dextran.

(*b*) The Fox – Flory [8] equation used for determination of viscosity – molecular weight constant 'K' is represented as,

$$[\eta]^{2/3}/(\bar{M}_w)^{1/3} = K^{2/3} + 0.857K^{2/3}\phi_o B\bar{M}_w/[\eta]$$

We plot a graph by taking $([\eta]^{2/3}/(\bar{M}_w)^{1/3})$ along Y-axis and $(\bar{M}_w/[\eta])$ along X-axis, then the ordinate intercept provides the value of $K^{2/3}$ from which K can be calculated. The above curve is drawn for six different temperatures for a particular solvent and repeated for the three solvents we had selected. These curves are shown in Figures 4 to 6 and the values of K are represented in Tables I to III.

From these above curves we found that the values of 'K' in different solvents at different temperatures show the same trend as the values of 'K' obtained by Stockmayer – Fixman's Plot.

(*c*) *Kurata – Stockmayer Plot* In order to determine the viscosity – molecular weight constant 'K' in any solvent at any temperature, Kurata – Stockmayer [9] had given the following relation,

$$[\eta]^{2/3}/(\bar{M}_w)^{1/3} = K^{2/3} + 0.363\phi_o Bg(\alpha_n)[(\bar{M}_w)^{2/3}[\eta]^{-1/3}]$$

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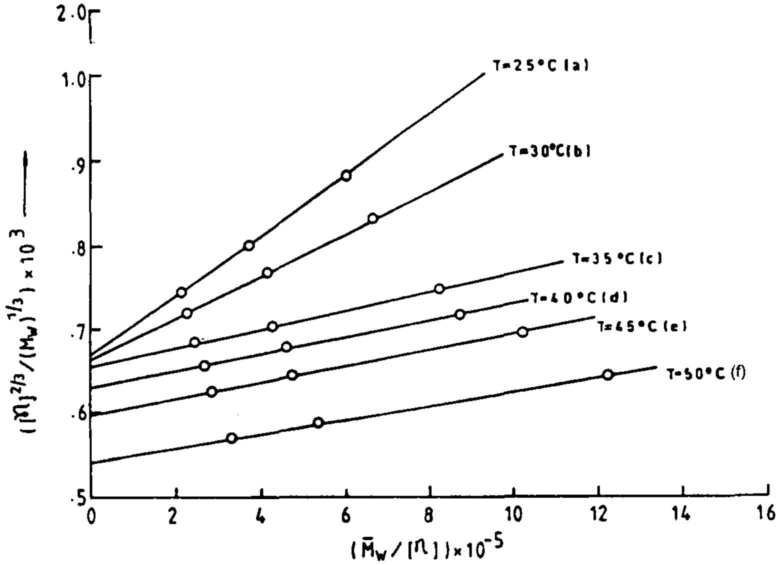

FIGURE 4 Fox–Flory's plot for Dextran of different molecular weight in distilled water at different temperatures.

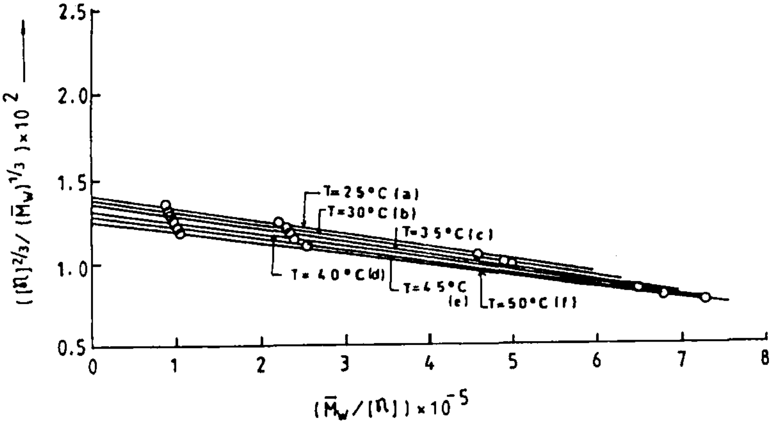

FIGURE 5 Fox–Flory's plot for Dextran of different molecular weight in 1(N) NaOH at different temperatures.

We plot a graph by taking $([\eta]^{2/3}/(\bar{M}_w)^{1/3})$ along Y-axis and $((\bar{M}_w)^{2/3}/[\eta]^{1/3})$ along X-axis, then the ordinate intercept provides the value of $K^{2/3}$ from which the value of K can be calculated.

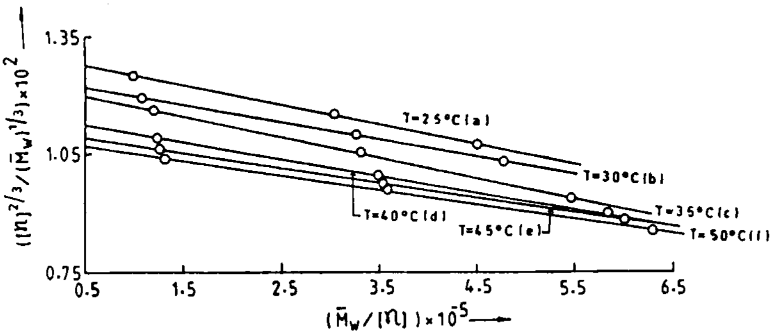

FIGURE 6 Fox – Flory's plot for Dextran of different molecular weight in 1(N) KOH at different temperatures.

The above curve is plotted for a particular solvent at six different temperatures and the same curve is repeated for the three different solvents we had selected. The curves are shown in Figures 7 to 9 and the values of *K* are represented in Tables I to III.

The values of '*K*' in different solvents at different temperatures show the same trend as the values of '*K*' obtained by Stockmayer – Fixman and Fox – Flory. The mean value of three different values of *K* obtained from three different plots namely Stockmayer – Fixman,

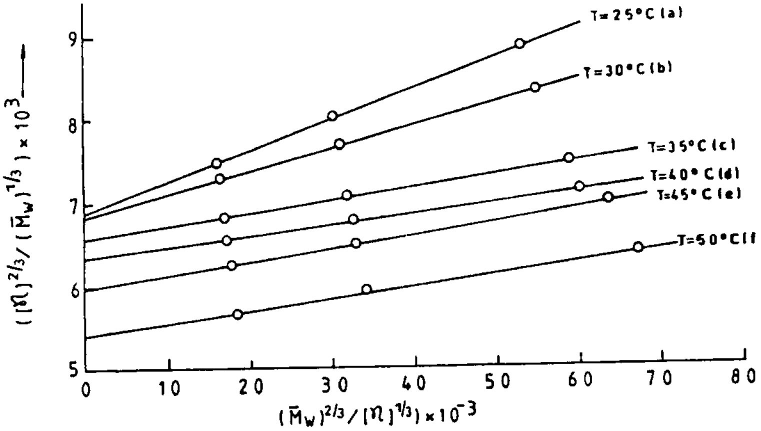

FIGURE 7 Kurata – Stockmayer's plot for Dextran of different molecular weight in distilled water at different temperatures.

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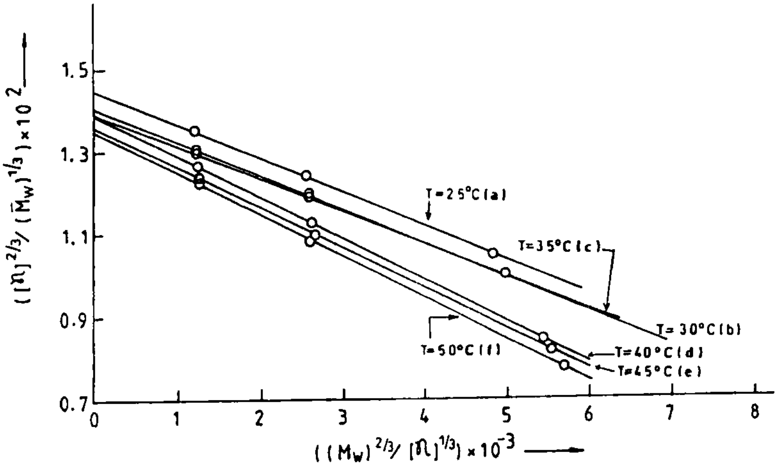

FIGURE 8 Kurata–Stockmayer's plot for Dextran of different molecular weight in 1(N) NaOH at different temperatures.

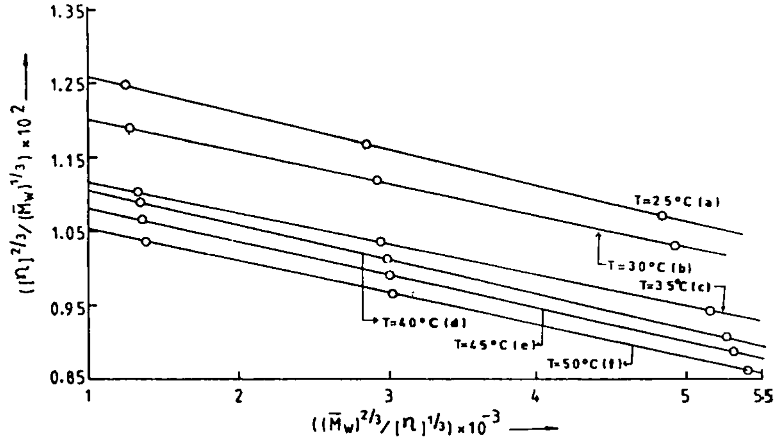

FIGURE 9 Kurata-Stockmayer's plot for Dextran of different molecular weight in 1(N) KOH at different temperatures.

Fox–Flory and Kurata–Stockmayer for a particular solvent at a particular temperature are then calculated which are shown in Tables I to III.

4.2. Evaluation of Short Range Parameter 'A'

The short range parameter 'A' can be calculated using the relation given by Yamakawa [10] which is represented as,

$$A = (K/\phi_o)^{1/3}$$

The values of viscosity–molecular weight constant 'K' obtained from three different plots for a particular solvent at a particular temperature is used in the above equation to evaluate the short range parameter 'A', which are shown in Tables IV to VI.

From these calculations we found that the short range parameter 'A' is the least in case of solvent water and is maximum for NaOH among the three solvents we have chosen. The short range parameter 'A' decreases with the increase in temperature for a particular solvent.

Finally the mean values of 'A' for a particular solvent at a particular temperature are calculated which are represented in Tables IV to VI.

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4.3. Evaluation of Long Range Parameter 'B'

The long range parameter 'B' can be calculated by using various relations given by different researchers.

(*a*) *Stockmayer–Fixman Plot* Using equation (5) we plot a graph by taking $(\bar{M}_w)^{1/2}$ along X-axis and $([\eta]/(\bar{M}_w)^{1/2})$ along Y-axis. Then dividing the slope of the curve by $0.51\phi_o$, provides us the value of B. The curve is repeated for the three solvents as well as for six different temperatures which are shown in Figures 1 to 3, and the values of B obtained from Stockmayer–Fixman plot is represented in Tables IV to VI.

From these plots we found that 'B' is the least in case of water and maximum for NaOH. No particular trend is observed in the variation of 'B' with temperature for a particular solvent. This is due to the fact that the relative variation of intrinsic viscosity $[\eta]$ with temperature is not uniform for a particular solvent.

(*b*) *Fox–Flory Plot* Using equation (2) we plot a graph by taking $([\eta]^{2/3}/(\bar{M}_w)^{1/3})$ along Y-axis and $(\bar{M}_w/[\eta])$ along X-axis, then dividing

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TABLE IV Values of short range parameter (*A*) and long range parameter (*B*) of Dextran in different solvents at different temperatures, Solvent–Distilled water

	$A \times 10^8$ *in cm from*			*Mean*	$B \times 10^{28}$ *in* cm^3 *from*			*Mean*
Temperature in °*C*	*Stockmayer–Fixman plot*	*Fox–Flory plot*	*Kurata–Stockmayer plot*	$A \times 10^8$ *in cm*	*Stockmayer–Fixman plot*	*Fox–Flory plot*	*Kurata–Stockmayer plot*	$B \times 10^{28}$ *in* cm^3
25	2.771	2.683	2.718	2.724	3.587	2.091	4.881	3.520
30	2.694	2.673	2.708	2.692	2.736	1.581	3.409	2.575
35	2.661	2.652	2.658	2.657	1.558	0.734	1.567	1.286
40	2.602	2.602	2.609	2.604	1.381	0.665	1.151	1.066
45	2.532	2.534	2.534	2.533	1.686	0.660	1.205	1.184
50	2.406	2.409	2.409	2.408	1.560	0.632	0.757	0.983

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TABLE V Values of short range parameter (A) and long range parameter (B) of Dextran in different solvents at different temperatures, Solvent – 1(N) NaOH

	$A \times 10^8$ *in cm from*			*Mean*	$B \times 10^{28}$ *in* cm^3 *from*			*Mean*
Temperature in °C	*Stockmayer – Fixman plot*	*Fox – Flory plot*	*Kurata – Stockmayer plot*	$A \times 10^8$ *in cm*	*Stockmayer – Fixman plot*	*Fox – Flory plot*	*Kurata – Stockmayer plot*	$B \times 10^{28}$ *in* cm^3
25	3.961	3.913	3.947	3.940	9.084	2.509	12.210	7.934
30	3.927	3.878	3.885	3.897	9.589	2.583	11.603	7.925
35	3.877	3.826	3.864	3.856	8.901	2.400	10.490	7.264
40	3.826	3.773	3.857	3.819	11.035	2.564	12.311	8.637
45	3.723	3.737	3.822	3.761	9.863	2.054	11.976	7.964
50	3.719	3.701	3.808	3.743	10.713	2.417	12.018	8.383

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TABLE VI Values of short range parameter (*A*) and long range parameter (*B*) of Dextran in different solvents at different temperatures, Solvent – 1(N) KOH

	$A \times 10^8$ *in cm from*			*Mean*	$B \times 10^{28}$ *in cm*^{3} *from*			*Mean*
Temperature in °C	*Stockmayer – Fixman plot*	*Fox – Flory plot*	*Kurata – Stockmayer plot*	$A \times 10^8$ *in cm*	*Stockmayer – Fixman plot*	*Fox – Flory plot*	*Kurata – Stockmayer plot*	$B \times 10^{28}$ *in cm*^{3}
25	3.756	3.708	3.679	3.714	5.517	1.637	5.215	4.123
30	3.658	3.620	3.594	3.624	4.732	1.516	4.034	3.427
35	3.534	3.512	3.465	3.504	4.770	1.749	3.156	3.225
40	3.517	3.469	3.449	3.478	5.222	1.541	3.476	3.413
45	3.491	3.427	3.410	3.443	5.197	1.426	3.179	3.267
50	3.444	3.390	3.367	3.400	5.077	1.382	2.735	3.065

the slope of the curve by 0.857 $K^{2/3}\phi_o$ we get the value of long range parameter *B*.

The above curve is repeated for a particular solvent at six different temperatures as well as for the three different solvents we had chosen. These curves are shown in Figures 4 to 6 and the values of '*B*' are represented in Tables IV to VI.

The variation in the values of '*B*' shows the same trend as the values of '*B*' obtained by Stockmayer – Fixman.

(*c*) *Kurata – Stockmayer Plot* Using Kurata – Stockmayer equation (*i.e.*, Eq. (3)) we plot a graph by taking $([\eta]^{2/3}/(\bar{M}_w)^{1/3})$ along *Y*-axis and $((\bar{M}_w)^{2/3}/[\eta]^{1/3})$ along *X*-axis, then dividing the slope of the curve by $0.363\phi_o g(\alpha_n)$, provided us the value of '*B*'. This curve is repeated for all the three solvents at six different temperatures. These are shown in Figures 7 to 9 and the values of '*B*' are represented in Tables IV to VI.

The values of '*B*' obtained from Kurata – Stockmayer plot show the same trend as the values of '*B*' obtained from Stockmayer – Fixman and Fox – Flory's plot.

Finally the mean values of long range parameter '*B*' for a particular solvent at a particular temperature are calculated.

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