Effect of Temperature and Thermodynamic Quality of Solvent over Unperturbed Chain Dimensions of Nylon 6

Musa Kaleem Baloch,[1] Mohsan Nawaz,[2] Arjamand Bano[3]

[1]*Department of Chemistry, Gomal University, Dera Ismail Khan, Pakistan*
[2]*Department of Chemistry, Hazara University, Mansehra, Pakistan*
[3]*Departmen of Mathematics, Gomal University, Dera Ismail Khan, Pakistan*

ABSTRACT: A nylon 6 sample having average molecular mass 4.825×10^5 g mol^{-1} was fractionated into five different fractions with respect to molecular mass, which ranged from 3691 to 999,000 g mol^{-1}. The light scattering and intrinsic viscosity measurements were made in *m*-cresol and its mixture with 1,4-dioxane. The second virial coefficient, radius of gyration and Mark Houwink's constant and unperturbed chain dimensions were determined by light scattering and viscosity measurement. It has been observed that all these parameters are composition of solvent and temperature dependent. The solvent having composition of 97% *m*-cresol and 3% dioxane, was best and it deteriorated with the increase/decrease in percentage of 1,4-dioxane in *m*-cresol. However, its thermodynamic quality was enhanced with the temperature. Such variation in quality of solvent was reflected in all the estimated parameters and showed maxima at this composition of solvent.

The unperturbed dimensions obtained by different methods though, differed in values but showed same trend and NA-MKB method gave close results to the one obtained through [η$_o$]. A new expression has also been proposed relating k_o to solvent quality and temperature and the data obtained by us for nylon-6 and the one obtained from the literature for dextran obeyed this expression up to large extent irrespective of the solvent composition and temperature. The proposed equations have also been applied to dextran/methoxy ethylene and dextran/ethylene glycol systems and worked well. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2351–2358, 2011

Key words: nylon 6; unperturbed chain dimensions; viscosity; light scattering; temperature and solvent dependence

INTRODUCTION

The conformational and thermodynamic properties of flexible and semi flexible macromolecules are related to unperturbed average dimensions and the excluded volume of a given polymer under specified environment.[1–3] The unperturbed dimension parameter (k_o), can be used to assess the unperturbed polymer chain dimensions as well as the chain stiffness of randomly coiled polymers and is a function of solvent and temperature.[4–6] The way it depends upon these parameters is still a mystery and the conclusion drawn by different investigators vary from one to an other author.[5–13] On the other hand, it is difficult and in some cases almost impossible to attain theta conditions, to obtain this parameter. Therefore, scientists are continuously trying to come up with new means and ways to acquire this information without attaining theta conditions.[12,13]

Though the number of equations proposed to estimate the unperturbed dimensions is quite high we discuss some of the well known and commonly used expressions and extend for the incorporation of the impact of temperature and quality of solvent over unperturbed dimensions. The most commonly used expression [eq. (1)] was given by Stockmayer and Fixman[14]

$$[\eta]/M^{0.5} - k_0 + 0.51\Phi BM^{0.5} \tag{1}$$

and Inagaki et al.[15] [eq. (2)]

$$[\eta']^{4/5}/M^{2/5} = 0:786k_0^{4/5} + 0:454k_0^{2/15}\Phi^{2/3}B^{2/3}M^{1/3} \tag{2}$$

Here, [η], M, k_o, Φ, and B stand for intrinsic viscosity, molecular mass of polymer, unperturbed parameter related to dimensions of the polymer molecules, Flory constant, and a constant related to second virial coefficient, respectively.

Recently an other equation has been proposed by Qian et al.[16] to determine [η]θ using low concentration (c), critical concentration (c^*), and density (ρ) of the polymer [eq. (3)]

Correspondence to: M. K. Baloch (musakaleem2001@yahoo.com).

$$[\eta]_\theta = \frac{[\eta][1 - \exp(-\frac{c}{c*})]}{\frac{0.77^3 \rho}{c*} - \exp(-\frac{c}{c*})} \quad (3)$$

In the mean time Ahmad and Baloch proposed another equation [eq. (4)] which also gave reasonably accurate results in an easy way.[17]

$$\frac{M^{1/2}}{[\eta]} = \frac{1}{2k_o} + \left(\frac{0.908}{\varphi_o^{1/3} r_o k_o^{2/3}}\right) M^{-1/2} \quad (4)$$

It was also pointed out that the unperturbed dimensions are function of temperature and quality of solvent; but due to nonavailability of the required data, could not proceed further.[17] Keeping in view the importance of these dimensions,[17–20] we have decided to modify the existing equation to incorporate the impact of quality of solvent and temperatures over the unperturbed dimensions; to get unperturbed dimensions of nylon 6 in mixed solvents at different temperatures.

THEORETICAL BACKGROUND

Ahmad and Baloch related the unperturbed dimensions (k_o), intrinsic viscosity [η], and weight average molecular mass (M_w), average radius of gyration (R_g) and discussed the applicability of the derived expression for different materials.[17] The derivation of the expression is briefly revealed over here.

$$[\eta] = \frac{\varphi[6\langle R_g \rangle^2]^{3/2}}{M} \quad (5)$$

The Flory viscosity parameter (φ) is described as[13]

$$\varphi = \frac{\varphi_o}{\left[\varphi(q,L) + \frac{45}{32}\left[\frac{2\pi}{3}\right]^{1/2}\left[\frac{1}{3\sqrt{2}}\right]\frac{(Lq)^{1/2}}{R_H}\right]\langle R_g \rangle^{\frac{1}{2}}\left(\frac{L}{q}\right)} \quad (6)$$

q and L are persistence and contour length of the chain and R_H is the hydrodynamic radius. Furthermore,

$$S(L/q) = \left[1 - \frac{3q}{L} + 6\left(\frac{q}{L}\right)^2 - 6\left(\frac{q}{L}\right)^3\right]\left[1 - \exp\left(\frac{L}{q}\right)\right] \quad (7)$$

ϕ (q/L) was calculated by Kurata et al.[3] for different values of q/L and N (the degree of polymerization). On the other hand $R_g^{1/2}$ is related to q through L as follows,

$$\langle R_o^2 \rangle^{1/2} = \frac{\langle R_g^2 \rangle^{1/2}}{\alpha} \quad (8)$$

and

$$\langle R_o^2 \rangle = \frac{L_q S(L/q)}{3} \quad (9)$$

The value of $\varphi(q,L)$ and $S(L/q)$ for flexible polymers approach unity when N is large.

By combining eqs. (5)–(9) we get

$$\frac{M^{1/2}}{[\eta]} = \frac{1}{2k_o} + \left(\frac{0.908}{\varphi_o^{1/3} r_o k_o^{2/3}}\right) M^{-1/2} \quad (10)$$

Here r_o is equal to R_H/N. Introduction of heterogeneity correction factor $q_{w,z}$ in eq. (10) leads to the expression,

$$\frac{M^{1/2}}{[\eta]} = \frac{1}{2q_{w,z}k_o} + \left(\frac{0.908}{\varphi_o^{1/3} r_o q_{w,z} k_o^{2/3}}\right) M^{-1/2} \quad (11)$$

while

$$q_{w,z} = \frac{1}{h+1} \frac{\Gamma(h+3+\varepsilon)^{3/2}}{\Gamma(h+1)} + \frac{\Gamma(h+1)}{\Gamma(h+1.5+1.5\varepsilon)} \quad (12)$$

Here h is the well-known heterogeneity parameter and defined as

$$h = \left(\frac{M_w}{M_n} - 1\right)^{-1} \quad (12a)$$

Γ is the gamma function, and ε is related to Mark-Houwink constant "a" as

$$a = \frac{(1 + 3\varepsilon)}{2} \quad (12b)$$

If $\frac{M^{1/2}}{[\eta]}$ is plotted versus $M^{-1/2}$ intercept gives $\frac{1}{2k_o}$

$$k_o = \varphi_o A^3 \quad (13)$$

And a is related to $\langle R_o^2 \rangle$ as[13]

$$A = \left(\frac{\langle R_o^2 \rangle}{M}\right)^{1/2} \quad (14)$$

However, this expression does not take care of conformational behavior of the polymer. By the introduction of conformation factor, σ, we get[13]

$$A = \sigma\left(\frac{\langle R_o^2 \rangle}{M}\right)^{1/2} \quad (15)$$

Further the variation in conformation results different relationship among the radius of gyration and

the other dimensions. For example, due to such variations the relationship between $\langle R \rangle$, contour length, L, and chain stiffness parameter, λ, in the following way,

$$\lim_{\lambda L \to \infty} \langle R^2 \rangle = \frac{L}{\lambda} \quad \text{(For random flights)} \quad (16)$$

$$\lim_{\lambda L \to o} \langle R^2 \rangle = L^2 \quad \text{(For rods)} \quad (17)$$

Such types of variation will certainly alter the unperturbed dimensions by the variation in quality of solvent or temperature. The variation in quality of solvent due to addition of nonsolvent to a good solvent or change in temperature, results alteration in conformational behavior of the polymer chain[18] and hence a change in unperturbed dimensions over the variation in solvent as well as temperature is expected.

EXPERIMENTAL

Material

Poly ε-caprolactam, commercially known as nylon 6 having average molecular mass 4.825×10^5 g mol^{-1} and provided by BASF, Germany was used during this investigation. The solvent (*m*-cresol), nonsolvent (1,4-dioxane), and precipitant (methanol) used for the characterization and/or fractionation were supplied by Fluka, Germany; all were of analytical purity grade and used as such.

Fractionation of polymer

The polymer was fractionated by standard procedure of fractional precipitation using *m*-cresol/methanol system.[7] The temperature was kept constant at 25°C, through out the fractionation process. To have minimum polydispersity of the fractionated samples, the fractionation process was carried out by slow addition of precipitant and vigorous stirring of the system. The precipitated amount was properly separated from the solution/system and dried at low temperature under vacuum.

Sample preparation

The original solution was prepared gravimetrically for each set of sample/solvent system. Solutions of various concentrations were made by diluting the original solution with the given solvent (0.2–1.0 g dL^{-1}). Great care was taken during the preparation of these solutions to keep the system uniform and homogeneous. For observing the effect of nonsolvent over the behavior of polymer, the polymer solutions were prepared in different percent (0–20% v/v) composition of 1,4-dioxane in *m*-cresol.

Laser light scattering measurements

The static laser light scattering measurements were carried out with the help of MALS DAWN EOS. The instrument was supplied by Wyatt Technology, USA. The static laser light scattering measurements were carried out for all the samples at different angles; molecular mass, M_w, the second virial coefficient (A_2), and radius of gyration (R_g) were determined using the Zimm and Debye methods. For the measurements of light scattering, the solutions and the solvents were filtered through Whatman Anotop 25 membrane filters, having pore size 0.2 and 0.02 μm, respectively.

Viscosity measurements

Viscosity of the pure solvent and that of the solution was measured using Cannon-Ubbelohde type capillary viscometers. The dimensions of capillary of the viscometers used were selected in such a way that the shear effect be negligible. Viscometers were calibrated over the required temperature range and the kinetic energy corrections were made whenever applicable. Measurements were made in a thermostat, manufactured by F.G Bode and Co, laboratory equipment Hamburg, Germany, the temperature of which could be maintained to ±0.01°C of the required one. Viscosity was also measured at different (20–60°C) temperatures to measure the flow activation energy.

RESULTS AND DISCUSSION

The weight average molecular weight (M_w) of the fractionated samples of nylon 6 was obtained through static LLS using the following equation, known as Zimm plots method.[21]

$$\frac{Kc}{R(\theta)} = \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^2 \rangle q^2\right) + 2A_2 c + \dots \quad (18)$$

Here

$$K = 4\pi^2 n^2 (dn/dc)^2 / (N_A \lambda_o^4) \quad (19)$$

$$q = 4\pi n / \lambda_0 \, \text{Sin} \, (\theta/2). \quad (20)$$

M_w, N_A, n, and λ_0 are weight-average molecular mass, Avogadro's number, solvent refractive index, and the wavelength of light in vacuum, respectively. c, $R_{(\theta)}$ being the concentration of polymer and Rayleigh scattering ratio, respectively.
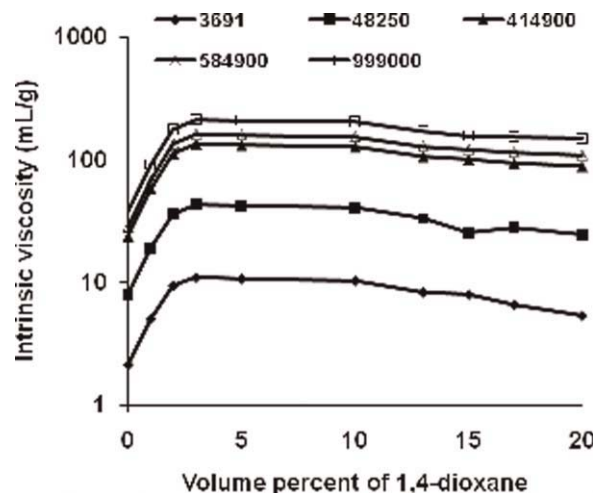
Figure 1 Intrinsic viscosity of nylon 6 as a function of molecular mass and volume percent of 1,4-dioxane in *m*-cresol.

The weight-average molar mass (M_w), the *z*-average radius of gyration (R_g), and the second virial coefficient (A_2) was obtained from these plots. The results obtained for M_w for different samples were 3.691×10^3, 4.825×10^4, 4.149×10^5, 5.849×10^5 and 9.99×10^5 g mol^{-1}.

The intrinsic viscosity of these samples was determined in pure *m*-cresol and its mixture with 1,4-dioxane using Huggins's eq. (21).[18]

$$\eta_{sp}/C = [\eta] + K_H[\eta]^2 c + \dots \qquad (21)$$

Here, $\eta_{sp} = \eta_r - 1$ with η_{sp}, η_r, and K_H being the specific viscosity, relative viscosity, and Huggins constant, respectively. The viscosity data plotted against concentration as per eq. (21) gave linear plots for each fraction of the polymer sample in the investigated range of polymer concentration and temperature. The intrinsic viscosity obtained at 20°C was plotted as a function of volume percent of 1,4-dioxane for various fractions of nylon 6 (Fig. 1). The

Figure 3 Flow activation energy of nylon 6 having molecular mass 9.99×10^5 g mol^{-1} as a function of volume percent of 1,4-dioxane in *m*-cresol.

data shows exactly the same trend as observed in case of polydispersed sample.[18] The intrinsic viscosity for the highest (9.99×10^5 g mol^{-1}) molecular mass fraction, measured at different temperatures was also plotted as a function of 1,4-dioxane contents (Fig. 2). The same trend for each sample of nylon 6 was observed as in case of nylon 12 in *m*-cresol[20] and it decreased with the increase in temperature. These observations indicate that the quality of the solvent deteriorates with the increase in temperature and hence polymer–solvent interactions decrease.[18–21] The flow activation energy for the sample having molecular mass equal to 9.99×10^5 g mol^{-1} was obtained using Arrhenius eq. (22).[9]

$$\log[\eta] = \log K - E_a/RT \qquad (22)$$

Here K is pre-exponential factor; E_a, R, and T are the flow activation energy, gas constant, and temperature in Kelvin, respectively. The results obtained for activation energy are displayed in Figure 3. The figure indicates that it increases with the increase in contents of 1,4-dioxin in *meta*-cresol. However, the rate of increase in energy is initially high and then

Figure 2 Intrinsic viscosity of nylon 6 having molecular mass 9.99×10^5 g mol^{-1} as a function of volume percent of 1,4-dioxane and temperature.

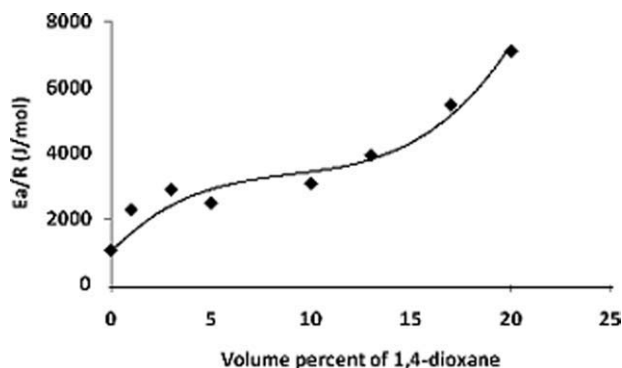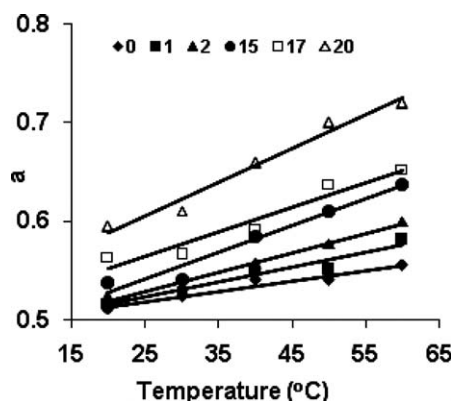**Figure 4** The value of "*a*" as a function of temperature and quality of solvent.
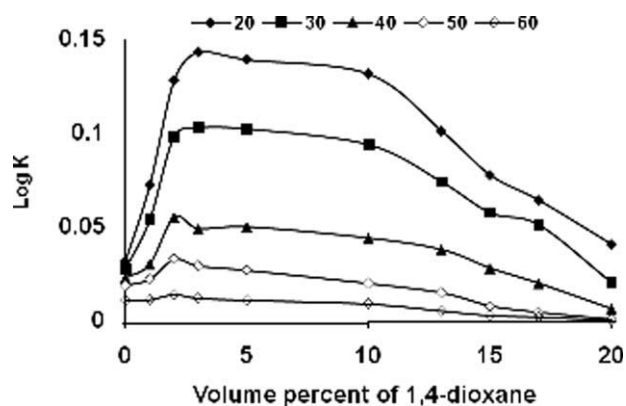
Figure 5 Log k as a function of thermodynamic quality of solvent and temperature.

Figure 7 R_g as a function of solvent composition and molecular mass.

slows down up to some extent and it increases once again when the amount of 1,4-dioxane is about 12%. These observations conclude that the polymer molecules interactions increase as compared to polymer solvent with the deterioration of the solvent quality and hence more energy is needed to flow.

The values of Mark-Houwink (k and a) constants are also obtained by plotting the data according to Mark-Houwink ($[\eta] = k\,M^a$) equation.[13] Figure 4 displays the values of "a" as a function of temperature, obtained for various percentage of 1,4-dioxane in m-cresol. The value of "a" increases linearly with the increase in temperature, indicating the deterioration in quality of the solvent with the temperature.[4,22]

Figure 5 illustrates the value of "k" as a function of increasing contents of 1,4-dioxane for different temperatures. The trend in the values of "k" is like that of intrinsic viscosity. It first increases and then decreases after attaining maximum value at 3% 1,4-dioxan. This figure also indicates that the value of "k" decreases with the increase in temperature. It is due to the fact that the chain dimension of polymer molecules in solution are influenced by both long-range (excluded volume) and short-range (rotational isomeric) effects.[4,18,22] Further, the energy of interac-
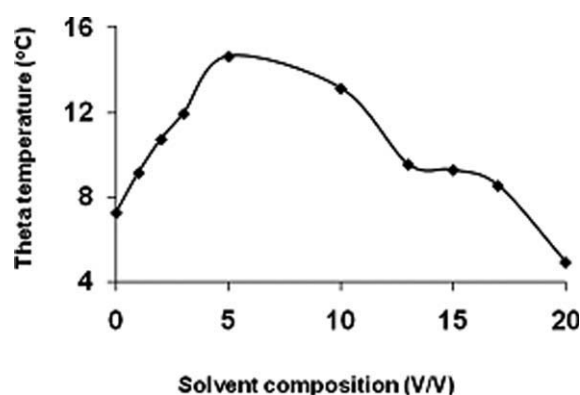
tion between polymer and solvent is high in good solvent and hence the polymer molecules tend to expand to increase the number of polymer–solvent contacts. As a result, the volume which one polymer segment excludes from another is large. Whereas, in poor solvents the energy of interaction is unfavorable, the polymer will contract to increase the amount of polymer–polymer contacts, resulting in low excluded volume.[20]

Theta temperature was obtained by plotting the value of "a" as a function of solvent composition and extrapolating to a = 0.5. The results obtained are displayed in Figure 6. The data show similar trend as observed in case of intrinsic viscosity and k values, indicating the variation of solvent quality with the composition of the mixture.

R_g (radius of gyration) obtained from Zimm plots, is displayed as a function of solvent composition in Figure 7 and shows maxima at about 3% 1,4-dioxan. Further to it, solvent impact was higher in case of high molecular mass as compared to low molecular mass material. The second virial coefficient displayed for 5.85×10^5 g mol^{-1} also shows similar trend (Fig. 8), concluding that the solute–solvent interactions are higher at 3% 1,4-dioxan in m-cresol

Figure 6 Theta temperature as determined through extrapolation technique as a function of solvent composition.

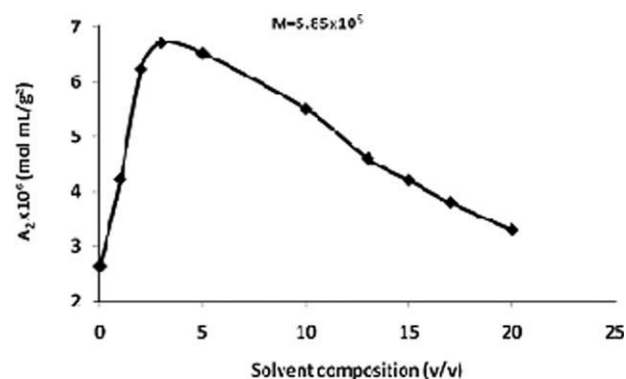**Figure 8** Second virial coefficient as a function of solvent composition.
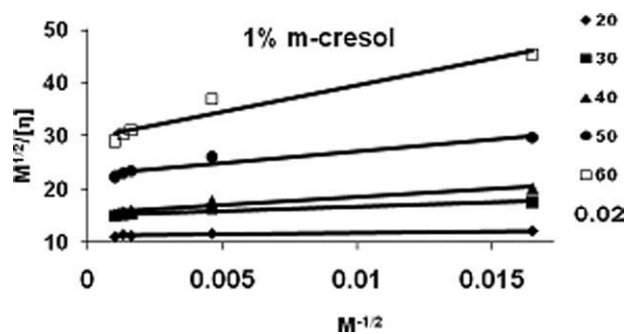
Figure 9 Plots of N. A-M. K. B eq. (10) for the estimation of unperturbed dimensions (k_o).

Figure 11 k_o values obtained by using N, eq. (10), ISK, eq. (2), SF, eq. (1), Q, eq. (3) and calculated from $[\eta]_o$ obtained by extrapolation (when $a = 0.5$) and at two different (20 and 60°C) temperatures as a function of solvent composition.

as stated earlier and the mixture behaves as a best solvent at the reported composition.

The intrinsic viscosity data has also been plotted against molecular mass as per eq. (10) and displayed in Figure 9. It can be noted that the equation works well at all the investigated temperatures and the samples having different molecular mass as reported before.[22] The k_o obtained from these plots is displayed in Figure 10. The figure shows that k_o first increases with the addition of 1,4-dioxan and then decreases, showing maxima at the ratio of 97/3 v/v of m-cresol to 1,4-dioxan. Further, such impact is high for low temperature and vice versa. This behavior is due to variation in thermodynamic quality of solvent as the quality of m-cresol as a solvent for nylon first increases and then decreases with the addition of 1,4-dioxane.[18]

The values of k_o were also obtained using SF, ISK, Q methods and displayed in Figure 11 along with the values obtained using N.A.M. K. B equation [eq. (10)] and calculated from $[\eta]_o$, obtained for theta temperature (corresponding to $a = 0.5$). It can be noted that all the curves are almost of the same shape indicating that the results obtained by our proposed equation are correct, accurate, and closer to the calculated one. These plots further indicate that the values obtained at 20°C through different
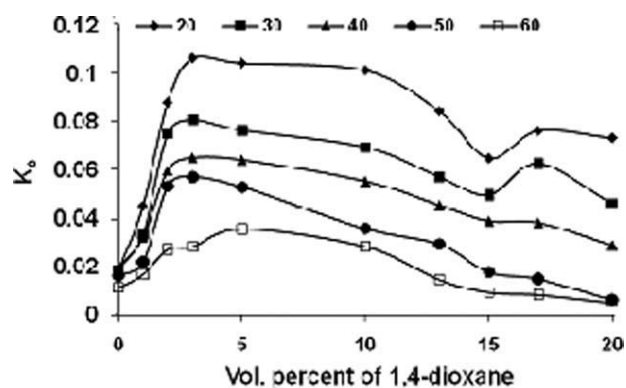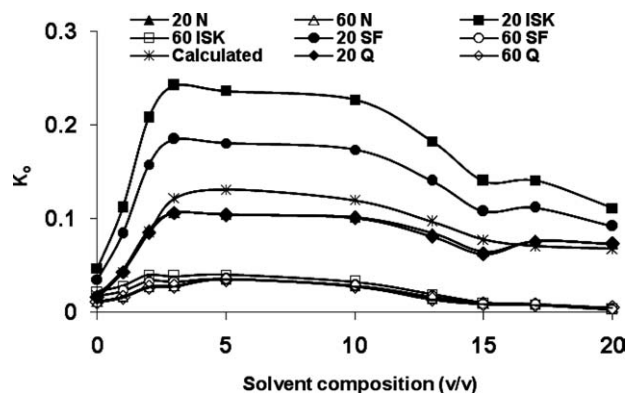
equations are in the order of ISK > SF > calculated > Q = NB. However, the values obtained at 60°C are almost the same. The reason for such variation is the change in conformation with the thermodynamic quality of the solvent as pointed out in theory section. The results obtained for k_o using NB equation is noted to decrease with the increase in temperature irrespective of solvent mixture ratio; and the slope of the plots increases with the increase in ratio of 1,4-dioxan (Fig. 12). It is can be concluded that the unperturbed dimensions are thermodynamic quality of solvent dependent. To see a combined effect of temperature and solvent, k_o is plotted against the second virial coefficient multiplied by $20/t'$ (Fig. 13). Here 20°C has been taken as a reference temperature. As can be seen from the figure, all the data points (irrespective of solvent ratios and the temperature) fit to a straight line equation and the r^2 came out as 0.8, showing a nice fit. Therefore we can propose an empirical equation relating k_o, second virial coefficient, A_2 and t', temperature of the system at which the measurements are made as follows
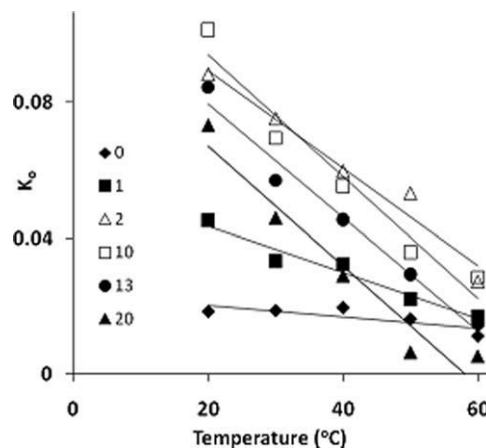

Figure 10 k_o calculated from N. A-M. K. B eq. (10) as a function of temperature and solvent composition.

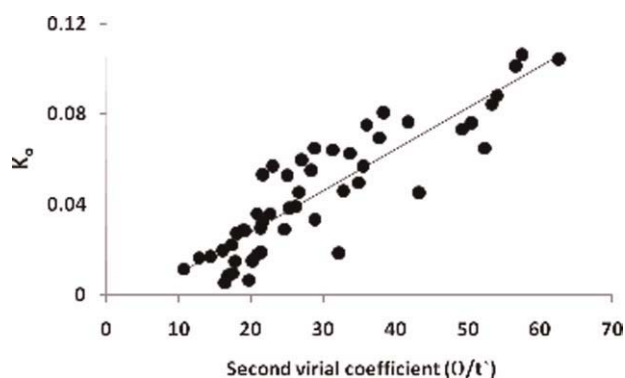**Figure 12** k_o obtained through eq. (10) as a function of temperature for various solvent composition.

Figure 13 k_o obtained using eq. (10) as a function of second virial coefficient (obtained for 5.85×10^5 g mol^{-1} molecular mass fraction) multiplied by dimensionless temperature.

Figure 15 Plots of N.A-M. K. B eq. (10) for the estimation of unperturbed dimensions (k_o) for dextran/ethylene glycol system at different temperatures. The data has been taken from Catiker and Guner.[10]

$$k_o = k'_o + bA_2 \frac{\theta}{t'} \qquad (23)$$

Further to it the proposed equation is analogous to the one given in Ref. [13].

Here k'_o is k_o measured at a particular thermodynamic quality of solvent (at theta temperature) in our case at 20°C. The t' is the temperature at which the measurements were made and equal to $\theta + t$ and b is a constant depending upon the solute solvent system.

To make the expression simpler, the equation can be modified to

$$k_0 = k'_0 + b\chi \qquad (24)$$

Here χ is the solvent–solute interaction parameter which is a function of thermodynamic quality of solvent and temperature.

Application to other systems

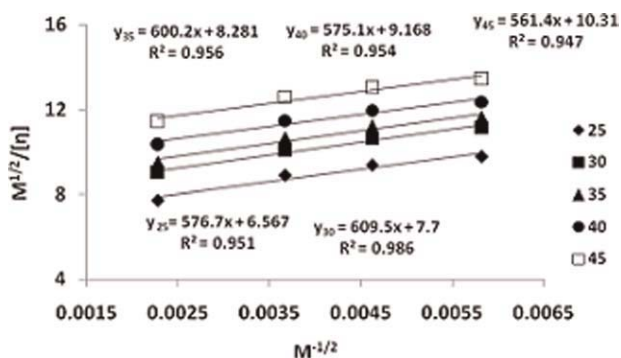We have applied eq. (10) to dextran/methoxy ethylene glycol and dextran/ethylene glycol system for

the determination of k_o, using the data available in the literature.[10,23] It can be seen that the equation fit very well giving r^2 value more than 0.95 for all the temperatures and both the solvents (Figs. 14 and 15). The results obtained for k_o are plotted versus temperature and noted to decrease with the temperature for both the solvents, however, the slopes are little bit different (Fig. 16). The k_o values are also plotted according to eq. (23) in Figure 17. It can be noted that the data for both the solvents fit well to a single straight line equation with r^2 value equal to 0.948. Keeping in view these facts, it is concluded that the unperturbed dimensions are function of thermodynamic quality of solvent and temperature, and eq. (23) or its simplified form eq. (24) work well for every type of system. It can be noted that Equations (10) and (23) give even better fit for dextran as compared to nylon 6 samples; it is most probably due to narrow molecular mass range of dextran as compared to nylon 6 sample and the variation in interactions is less as compared to nylon 6 samples; as in case of dextran, only two solvents system has been considered whereas for nylon it was ten.

Figure 14 Plots of N.A-M. K. B eq. (10) for the estimation of unperturbed dimensions (k_o) for dextran/methoxy ethylene glycol system at different temperatures. The data has been taken from Guner and Catiker.[23]
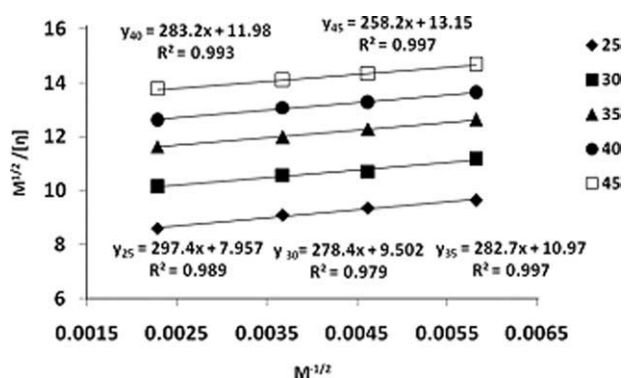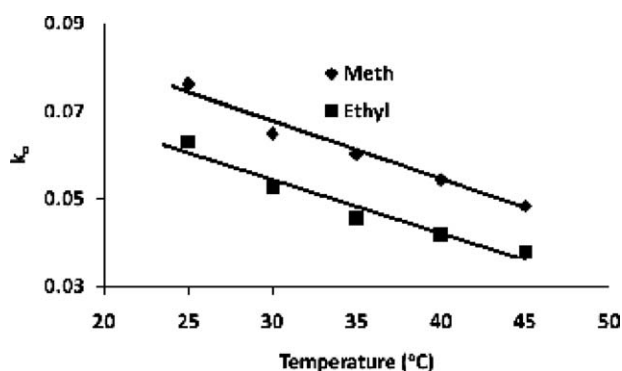

Figure 16 k_o obtained through eq. (10) as a function of temperature for (Meth) dextran in methoxy ethylene glycol and (Ethyl) dextran in ethylene glycol.
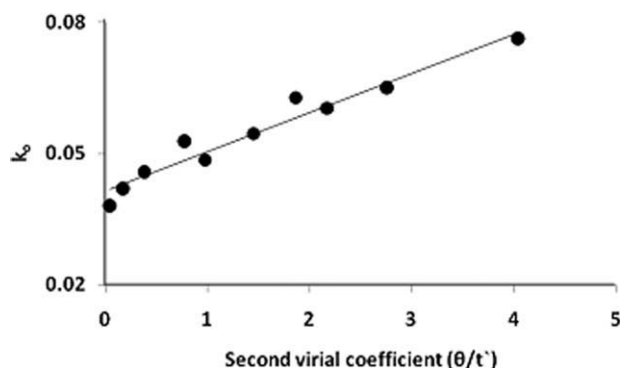
Figure 17 k_o obtained using eq. (10) as a function of second virial coefficient (obtained for molecular mass of 7.4×10^4 g mol^{-1}) multiplied by dimensionless temperature.

CONCLUSIONS

The unperturbed dimensions of the fractionated nylon 6 have been determined using different available equations which utilize the viscosity results of the system. The results conclude that most of the equations provide not only a similar trend but the same values within the limit of certain variation. The NA-MKB expression has also been extended to incorporate the effect of solvent–solute interactions and temperature over the dimensions. The results obtained as a function of ratio of solvent to nonsolvent and temperature indicates that unperturbed dimensions are dependent over the solvent–solute interactions and temperature. An expression has also been proposed to correlate the unperturbed dimensions with the second virial coefficient and/or temperature. The NA-MKB expression has also been applied to dextran/methoxy ethylene and dextran/ethylene glycol systems for determination of k_o and it worked well. The k_o values obtained in this way were fitted to new proposed equation and it has been concluded that the expression fits well, irrespective of solute–solvent system and/or temperature.

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