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Molecular Dimension and Interaction Parameters of Polyacrylamide in Water-N,N-Dimethylformamide Mixtures

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The intrinsic viscosities $[\eta]$ of polyacrylamide (PAM) having different average molecular weights are measured in various mixtures of water (good solvent) and N, N dimethyl formamide (DMF, nonsolvent) at different temperatures. The observed results show a significant variation of cosolvency as a function of solvent composition (ϕ_{DMF}). The nature of curves in $[\eta]$ vs. ϕ_{DMF} plot at different temperatures indicates the existence of two antagonistic effects. The unperturbed dimensions (K_θ) of the polymer are determined by a number of methods, which agree well with each other. The temperature coefficient of unperturbed dimension (K'), molecular extension factors (α_n), characteristic ratio (C_α) and chain rigidity (σ) are evaluated and the effects of temperature, solvent composition are discussed. The volume related parameter V_E and shape factor ν were also computed, which shows the shape of polymer molecules to be more or less spherical in solution.

Keywords polyacrylamide (PAM), intrinsic viscosity $[\eta]$, unperturbed dimension (UD), cosolvent, volume related parameter (V_E), temperature coefficient of UD (K')

Introduction

The unperturbed dimension (UD) of a given polymer in a solvent does not depend on the nature of the solvent, as long as the solvent has no influence on the rotation of the chain segments (1, 2). This is true in many cases, especially for nonpolar polymer-solvent pairs, but in the cases of polar polymer-polar solvents systems, the unperturbed dimension vary considerably with the nature of the solvent. Most of the polymeric materials are soluble only in a limited number of primary solvents, but they could be made soluble in all proportions in mixtures consisting of two or more solvents, which may be individually poor solvent for the polymers (3). Several mixtures of nonsolvent are also known which produce good solvent systems or at least increase the solvency power of primary solvents (4). Although some studies on the solution viscosity properties of polyacrylamide in water are available in the literature, similar studies in other solvents or cosolvent systems are surprisingly little (5–11). In previous papers from this laboratory we have described the preparation (using montmorillonite microenvironment) and solution proper-

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ties (in water-DMSO mixtures) of very high molecular weight PAM (12–15). The present paper describes the results of our investigations on unperturbed dimensions, interaction parameters, volume related parameters and other aspects of unhydrolysed PAM in water-DMF mixtures. While DMF is a nonsolvent for PAM, water-DMF mixture acts as a cosolvent in some compositions.

Theoretical Considerations

The intrinsic viscosity (η) is related to unperturbed dimension K_θ , molecular weight M , and the hydrodynamic expansion factor α_n by the relation (16, 17):

$$[\eta] = \Phi(r_0^2/M)^{3/2}M^{1/2}\alpha_n^3 = K_\theta M^{1/2}\alpha_n^3 \quad (1)$$

where Φ is universal parameter ($\Phi = 2.5 \times 10^{23} \text{ mol}^{-1}$) and r_0^2 is the unperturbed mean square end-to-end distance. At theta temperature $\alpha = \alpha_n = 1$ and hence, evaluation of K_θ is possible using this equation. On the other hand, for evaluation of K_θ from intrinsic viscosity at temperature other than theta temperature, a number of equations have been proposed. Some of the equations are as follows:

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + K_\theta^{5/3}C_T(M/[\eta]) \quad (\text{Fox and Flory(FF)} \quad (16)) \quad (2)$$

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.363\Phi B(g(\alpha_n)M^{2/3}/[\eta]^{1/3}) \quad (\text{Kurata and Stockmayer(KS)} \quad (17)) \quad (3)$$

$$([\eta]/M)^{1/2} = K_\theta^{1/2} + 0.51\Phi BM^{1/2} \quad (\text{Stockmayer and Fixman(SF)} \quad (18)) \quad (4)$$

$$\{([\eta]/M)^{1/2}\}^{1/2} = K_\theta^{1/2} + 0.42K_\theta^{3/2}B(r_0^2/M)^{3/2}(M/[\eta]) \quad (\text{Berry}) \quad (18)) \quad (5)$$

Besides these, several other equations have also been reported (19–22). According to equations given above, the value of K_θ is obtained from the intercepts on the ordinates of the plots of the quantity on the left-hand side vs. the function of M and $[\eta]$ on the right hand side. Viscosity data are also used to calculate the volume related parameter V_E of the polymer. Recently, it has been used to determine the shape of protein and some other acrylate copolymer molecules in solution (23). V_E is calculated by plotting Y against concentration C , where:

$$Y = (\eta_r^{1/2} - 1)/C(1.35\eta_r^{1/2} - 0.1). \quad (6)$$

From the plot V_E is obtained as an intercept since:

$$\text{Lt}_{C \rightarrow 0} Y = V_E. \quad (7)$$

The shape factor ν (24) is calculated from the relation:

$$[\eta] = \nu V_E. \quad (8)$$

The value of ν has been shown to be 2.5 for spherical particles of any polymer (25).

Experimental

The crude monomer (acrylamide, Fluka, Switzerland, AR) was purified by recrystallization from methanol and dried in vacuum at 45°C overnight. Low molecular weight polymers (viscosity average molecular weight 2.3×10^5 , C-type) were prepared via

redox polymerization of acrylamide monomer initiated by 1.5×10^{-3} M FeCl_3 and 0.04 M thiourea (TU) redox system at 50°C . To obtain medium molecular weight polymers (viscosity average molecular weight 1.6×10^6 , B-type) 0.4 M monomer and 0.06 M TU in aqueous suspension of ferric vermiculite (FeV) were used at 60°C temperature and at $\text{pH} = 1.98$ (12–15). High molecular weight polymers (viscosity average molecular weight 8.9×10^6 , A-type) were purchased from Across Organics (Belgium). Solvent N,N-dimethyl formamide (Merck, India) used for the present study was stored over P_2O_5 for nearly 10 h and distilled before use.

The viscosity behaviors of these three types (A, B and C) of polymer solutions were studied at three different temperatures (30° , 40° and 50°C) using a suspended level Ubbelohde viscometer. The temperature of the thermostat was controlled within range of $\pm 0.1^\circ\text{C}$ and, the flow times were measured by a digital stopwatch with accuracy ± 0.1 sec.

The intrinsic viscosities were evaluated as average values of the intercepts of the plots of η_{sp}/C vs. C , where:

$$\eta_{\text{sp}}/C = (\eta) + K_{\text{H}}[\eta]^2C \quad (9)$$

where C is the concentration of the polymer in solution and K_{H} is the Huggins constant. Molecular weight of the polymer was calculated from the intrinsic viscosity data as described elsewhere (13).

Results and Discussion

Intrinsic Viscosity

The nature of interaction between liquids governs the solubility of a polymer in binary liquid mixtures. The changes in molecular dimension of the polymer in these systems are manifested in the varied molecular extension parameters and the unperturbed dimension due to the interaction with two component liquid mixtures (1). Viscosities of pure water-DMF system show positive deviation from ideality, which suggests that there is association of the liquids through hydrogen bonding. The viscosity vs. composition plot of water-DMF system in absence of polymer exhibits a maximum at $\varphi_{\text{DMF}} = 0.27$ (26). Excess Gibbs free energy ΔG^{E} values are large and positive for this system indicating specific interactions between molecules (27, 28). In general, for a flexible polymer in poor solvent, the intrinsic viscosity increases with rise in temperature, whereas in good solvent it decreases with temperature. In athermal solvents, however, it is independent of temperature (29). The polymer chains are expanded most at the temperature at which $[\eta]$ is maximum. The variation of $[\eta]$ of all three types of polymer at different temperatures and solution compositions are shown in Figures 1–3.

The result shows that with increasing the amount of nonsolvent (DMF) up to a certain limit, intrinsic viscosity also increases for all types of PAM. This variation is, however, distinguishable from the variation observed in case of a pure solvent system. Intrinsic viscosity reaches its maximum value near $\varphi_{\text{DMF}} = 0.2$ for the polymer type-A, near $\varphi_{\text{DMF}} = 0.3$ for the polymer type-B and near $\varphi_{\text{DMF}} = 0.4$ for the polymer type-C. This indicates that energetically the most favorable solvent composition is different for different types of PAM. The higher the molecular weight of the polymer, smaller is the concentration of DMF required for showing the cosolvency effect. The decrease in $[\eta]$ after the maximum is explained by decrease in unperturbed mean square end-to-end distance. At a higher co-solvency condition, the energetic weighting factor favors the extended configuration of the polymer molecules. The extended long chains are sur-

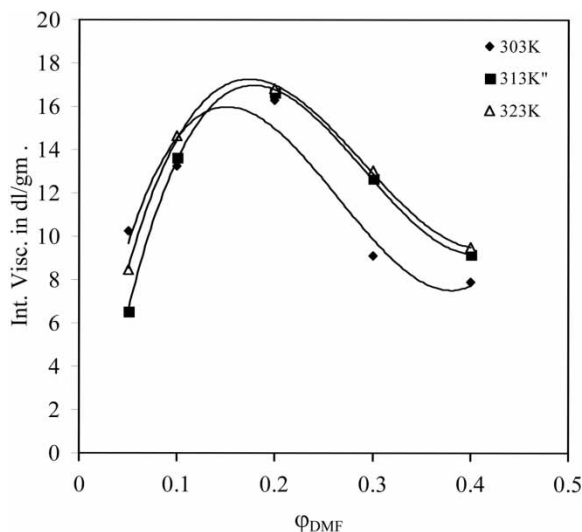


Figure 1. Plot of intrinsic viscosity vs. fraction of DMF for type-A PAM.

rounded by solvated hull and longer the chain less is the amount of DMF required for attaining the cosolvency condition. At low value of ϕ_{DMF} of pure solvent systems, the viscosity should decrease with temperature but in the present ternary system (water + DMF + PAM) $[\eta]$ is found almost invariant with temperature of the system. Increase in temperature of a polymer solution generates two antagonistic effects (30, 31). Firstly, an increase in temperature generally leads to an increase in the solubility. This results in uncoiling of the polymer chain leading to an increase in intrinsic viscosity with temperature. Secondly, increase in temperature may lower the rotational barrier, thereby enhancing the degree of rotation about a skeletal bond, forcing the molecular chains to assume more compact coiled configuration. This leads to decrease in intrinsic viscosity with increase in temperature.

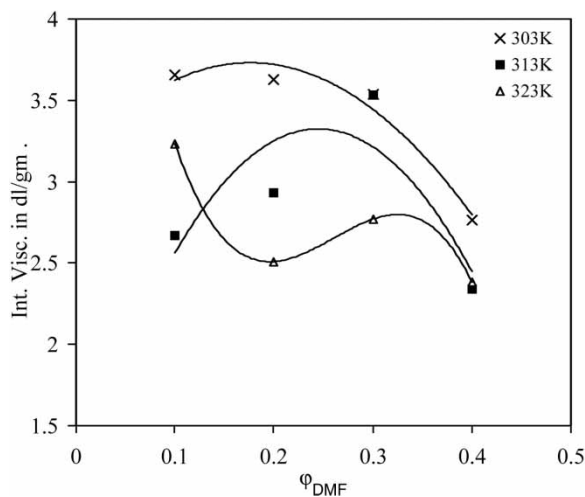


Figure 2. Plot of intrinsic viscosity vs. fraction of DMF for type-B PAM.

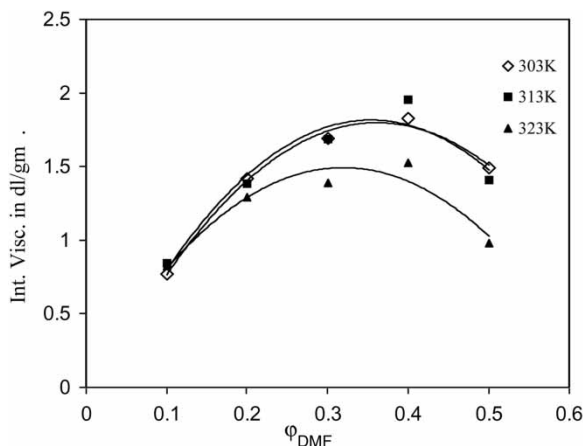


Figure 3. Plot of intrinsic viscosity vs. fraction of DMF for type-C PAM.

Temperature Coefficient of Unperturbed Dimension

The effect of temperature on UD can be attributed to the change in flexibility of a macromolecular chain as well as to polymer solvent interactions. Some solvents at certain temperatures hinder internal rotations in macromolecules due to favorable interactions, which lead to extended uncoiled conformation of the polymer. Previous workers attributed this variation in UD to the specific solvent effect resulting from hydrogen bonding or other polar interactions. In case of mixed solvents, preferential adsorption leads to similar observations and the effects are correlated to cohesive energy density of the polymer and the solvent. Unperturbed dimension (K_θ) is related to statistical parameter (r_0^2) and unperturbed mean square end-to-end distance by Flory equation as follows:

$$K_\theta = \Phi_0(r_0^2/M_w) \quad (10)$$

On differentiating Equation (10) with respect to T, the temperature coefficient of unperturbed dimension may be obtained.

$$d \ln K_\theta / dT = 3/2 \{d \ln(r_0^2)\} / dT = K' \quad (11)$$

Here, K' , the temperature coefficient of unperturbed dimension provides information about configuration of chain molecules and also predict the configuration-dependent prop-

Table 1

Temperature co-efficients of unperturbed dimension at different DMF compositions

Φ_{DMF}	$k' \text{ deg}^{-1}$
0.1	0.0161
0.2	0.0212
0.3	0.0330
0.4	0.0168

erties of polymer chain and energies of bond conformations in the molecules. From Table 1, it is seen that the value of K' changes with solvent composition.

The value of K' increases up to $\varphi_{\text{DMF}} = 0.3$ and then decreases. That is PAM molecules expand more up to $\varphi_{\text{DMF}} = 0.3$. It also reveals the presence of low energy configuration in this solvent composition at high temperature. However, at $\varphi_{\text{DMF}} = 0.4$, K' again assumes lower value indicating more compact structure and the existence of high-energy configuration of the polymer.

Unperturbed Dimension

The UD of the polymer chain is the dimension where volume exclusion due to long-range segmental interaction is nullified by its interaction with a definite solvent (theta solvent) (19). UD is the end-to-end dimension of the polymer chain under theta condition and can be determined from intrinsic viscosity measurement at this condition. In the present study, Kurata-Stockmayer equation under non-theta condition (17) has been used to derive K_θ of PAM in different water-DMF mixtures. The results are summarized in Table 2.

The value of K_θ obtained from various methods of measurements viz. S-F, K-S-F, and K-S agree well with each other except in a few composition of solvents. It is apparent that at $\varphi_{\text{DMF}} = 0.4$ the polymer has the highest unperturbed dimension and this result is in general true for all the adopted methods for K_θ calculation. Above the φ_{DMF} value of 0.4 the cosolvency of the system is lost and the polymer is precipitated out (for PAM of type-C precipitation starts at $\varphi_{\text{DMF}} = 0.5$) from the solution. At $\varphi_{\text{DMF}} = 0.1$ the polymer shows lowest K_θ for all the methods of calculation. The effect of temperature is interesting. With an increase in temperature, r_0^2 and hence K_θ , decrease due to greater freedom of rotation around the skeletal bonds (19). However,

Table 2
Unperturbed dimension of PAM in water + DMF mixtures
at different temperatures and methods

Temperature in °C	φ_{DMF}	$K_\theta \times 10 \text{ (cm}^3\text{g}^{-3/2} \text{ mol}^{1/2}\text{)}$		
		K-S	S-F	K-S-F
30	0.1	0.484	0.679	1.843
	0.2	1.377	1.399	2.522
	0.3	3.189	3.181	3.261
	0.4	3.391	3.338	3.191
40	0.1	0.328	0.332	1.483
	0.2	1.125	0.958	2.141
	0.3	2.532	2.509	3.041
	0.4	3.367	3.167	3.092
50	0.1	0.260	0.343	1.641
	0.2	0.900	0.578	1.828
	0.3	1.650	1.562	2.301
	0.4	2.423	2.302	2.527

such a temperature dependence of K_θ can be attributed not only to the change in flexibility of macromolecular chains but also to the specific polymer solvent interaction (32). The effect may also be correlated to the cohesive energy density of the polymer and the solvent (33).

Molecular Extension Factor

The molecular extension factor (α_n), which represents the effect of long-range interaction, can be described as an osmotic swelling of the chain by the solvent-polymer interaction. It has been calculated from the relation:

$$\alpha_n^3 = (\eta)/K_\theta M_v^{1/2} \tag{12}$$

where K_θ has been taken from the K-S plot. The actual end-to-end distance, $\alpha_n K_\theta$, of the polymer molecule is also computed, which is shown in Table 3.

It is observed that $\alpha_n K_\theta$ attains its highest value at $\phi_{DMF} = 0.4$ for all fractions of the polymer. As the number of segmental interaction of the polymer molecules increases with molecular weight, the value of α_n also increases. This trend is observed at all temperatures under the study.

Chain Rigidity

The characteristic ratio (C_α), which serves as a measure of short-range interactions such as bond angle restrictions and steric hindrances, are also influenced by the torques exerted on the chain by solvent molecules. This effect is, however, small in many cases. The characteristic ratio C_α is a parameter that compares the unperturbed mean square end-to-end distance to the dimension of the chain if each segment was freely jointed. Steric

Table 3
Molecular extension factor and coil dimensions of PAM at different temperatures in water + DMF mixtures

Temperature in °C	Φ_{DMF}	Type-A		Type-B		Type-C	
		α_n	$\alpha_n \times K_\theta \times 10$	α_n	$\alpha_n \times K_\theta \times 10$	α_n	$\alpha_n \times K_\theta \times 10$
30	0.1	2.260	1.096	1.883	0.912	1.487	0.720
	0.2	1.723	2.373	1.327	1.827	1.287	1.772
	0.3	1.065	3.396	0.995	3.173	1.031	3.288
	0.4	0.996	3.377	0.897	3.042	1.037	3.517
40	0.1	2.602	0.855	1.932	0.635	1.743	0.6727
	0.2	1.845	2.075	1.322	1.516	1.360	1.530
	0.3	1.286	3.257	1.073	2.717	1.111	2.814
	0.4	1.049	3.532	0.851	2.866	1.062	3.576
50	0.1	2.880	0.750	2.224	0.580	1.867	0.486
	0.2	1.994	1.795	1.352	1.217	1.436	1.293
	0.3	1.496	2.468	1.489	2.456	1.203	1.984
	0.4	1.185	3.600	0.955	2.315	1.093	2.648

factor σ , the characteristic ratio C_α , and $(r_0^2/M)^{1/2}$ are calculated in the usual manner from the following equations (34).

$$\sigma = (\langle r^2 \rangle_0/M)^{1/2} / (\langle r^2 \rangle_{of}/M)^{1/2} \quad (13)$$

$$(\langle r^2 \rangle_{of}/M)^{1/2} = (\langle r^2 \rangle_{of}/N)^{1/2} (1/M_0)^{1/2} \quad (14)$$

$$C_\alpha = (K_\theta/\phi_0)^{2/3} (M_0/2L^2) \quad (15)$$

Where $\langle r^2 \rangle_{of}$ is the unperturbed mean square end-to-end distance for a freely rotating chain, N is the degree of polymerization, M_0 is the molecular weight of the monomer and L is the backbone bond length ($L = 0.154$ nm). For vinyl polymers the value of $(\langle r^2 \rangle_{of}/N)^{1/2} = 3.08 \times 10^{-8}$ cm (35). The computed values of σ , C_α , and $(r_0^2/M)^{1/2}$ for PAM at different solvent compositions and temperatures are given in the Table 4.

Cowie observed that the range of values of σ normally encountered is about 1.5–2.5 (46). In our previous study with water- DMSO mixtures the values of σ were within 1.07–2.36. In the present study, it ranged between 1.29 and 3.03. Like UD, other parameters viz., σ , C_α and $\alpha_n K_\theta$ also give their highest values at the maximum values of ϕ_{DMF} .

Volume Related Parameter

The representative plot of Y vs. C (Equation (6)) is shown in Figure 4. V_E is obtained from the intercept of the straight line on y axis. The volume related parameter is a function of temperature and a measure of volume of the solvated polymer molecules. Computed data of V_E and ν are shown in Table 5.

As the temperature increases, the solvation decreases and hence, V_E decreases. This is true in most of the cases except for the polymer of type-A. It is to be noted that as the molecular weight decreases the solvated volume also becomes smaller. A poor solvent

Table 4
Steric factor, characteristic ratio and unperturbed dimension of PAM as a function of DMF fraction and temperature

Temperature in °C	Φ_{DMF}	$r_0^2/M^{1/2} \times 10^9$ in $\text{cm.g}^{1/2}\text{mol}^{1/2}$	C_α	σ
30	0.1	5.787	0.772	1.585
	0.2	8.198	1.549	2.246
	0.3	10.845	2.711	2.971
	0.4	11.070	2.824	3.030
40	0.1	5.084	0.595	1.392
	0.2	7.662	1.353	2.099
	0.3	10.043	2.325	2.751
	0.4	11.043	2.811	3.025
50	0.1	4.706	0.510	1.289
	0.2	7.115	1.167	1.949
	0.3	8.706	1.747	2.385
	0.4	9.897	2.257	2.711

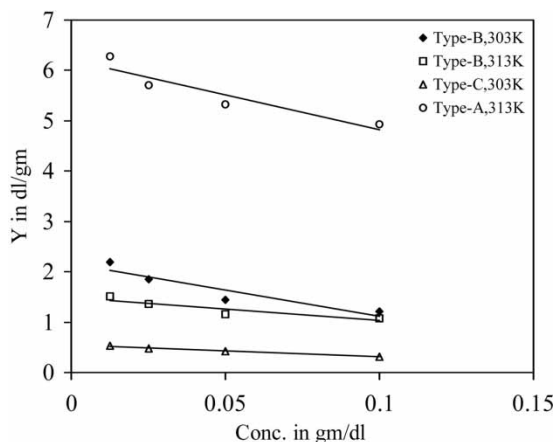


Figure 4. Plot of Y vs. concentration (gm/dl).

system results in the less solvation of the polymer molecules, and hence the nature of variation of V_E is almost similar to the nature of variation of $[\eta]$ with ϕ_{DMF} .

The shape factor ν gives an idea about the shape of the polymer molecules in solution (24). Ideally it is 2.5 for spherical particles. Rakshit et al. (36) suggested the conformation of hydrolyzed PAM other than spherical ($\nu = 2.5-8.7$). It is interesting to note that ν values of unhydrolyzed PAM in the present study are very close to 2.5 and are not affected by solvent, molecular weight and the temperature of the study.

Table 5

Volume related parameter V_E and shape factor values of PAM at different solvent compositions and temperature

Temperature in °C	Type-A		Type-B		Type-C		
	Φ_{DMF}	V_E	ν	V_E	ν	V_E	ν
30	0.1	5.27	2.51	1.47	2.50	0.40	—
	0.2	6.31	2.58	2.37	—	0.56	2.54
	0.3	3.42	2.65	1.40	2.52	0.60	2.84
	0.4	3.82	2.07	1.11	2.50	0.60	3.05
40	0.1	5.66	2.41	1.16	2.30	0.40	2.12
	0.2	6.45	2.58	1.56	—	0.53	2.58
	0.3	4.64	2.74	1.40	2.51	0.60	2.88
	0.4	3.77	2.43	1.04	2.34	0.64	3.06
50	0.1	5.75	2.55	1.36	2.37	0.32	2.53
	0.2	6.54	2.57	1.15	2.20	0.45	2.81
	0.3	5.04	2.58	1.17	2.37	0.48	2.88
	0.4	4.04	2.16	1.03	2.32	0.56	2.73

Conclusions

The changes in molecular dimension of unhydrolyzed PAM in the water-DMF system are manifested in the varied molecular extension parameters as a result of interaction with two-component liquid. $[\eta]$ and V_E data show that higher the molecular weight of the polymer smaller is the concentration of DMF required for developing cosolvency effect. Solutions of all three polymers of different molecular weights generated two antagonistic effects with the increase in temperature-uncoiling for increased solvation and coiling for higher degree of rotation around the skeleton bonds. As a result, there have been no visible effect of temperature on $[\eta]$ is apparent. Temperature coefficient (K') values of unperturbed dimension indicate polymer molecules to passes low energy configuration up to $\varphi_{\text{DMF}} = 0.3$ and a high energy more compact configuration thereafter. Unperturbed dimension (K_θ), actual end to end distance ($\alpha_n K_\theta$), characteristic ratio (C_α) and the steric factor, σ , assume their highest values at $\varphi_{\text{DMF}} = 0.4$ and are decreased with temperature. But α_n , which represents the long-range interaction, assumes its lowest value at this solvent composition and increases with temperature. Shape factor values of unhydrolyzed PAM molecules are very close to 2.5 and are not affected by solvent composition, molecular weight and temperature of the study.

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