

Thermodynamic Parameters of Poly(ethylene glycol) from Dielectric Relaxation Studies

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ABSTRACT: Thermodynamic parameters, like change in free energy of activation (ΔG_{τ}^*), enthalpy of activation (ΔH_{τ}^*), and entropy of activation (ΔS_{τ}^*) of poly(ethylene glycol) with average molecular mass 400 Delton (PEG 400) in dilute solution of benzene were computed on the basis of theory of Eyring rate process. To estimate these, the dielectric relaxation time (τ), determined at various temperatures adopting Whiffen and Thompson model have been used. X-band microwave bench working at 9.59 GHz was employed to find temperature dependent real part

ϵ' of the complex dielectric permittivity ϵ^* and dielectric loss ϵ'' . The values of these ϵ' and ϵ'' are used to find τ values. Based on the results reported, the relaxation behavior of the stated polymer in nonpolar solvent is discussed. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: complex dielectric relaxation; thermodynamic parameters; poly(ethylene glycol); microwave absorption; enthalpy; entropy

INTRODUCTION

Microwave dielectric relaxations studies in general and specifically on polymers have gained importance in recent times, in view of the insight it can give in understanding molecular dynamics,^{1–6} which may influence the applications in different fields like Pharmaceutical excipients, cosmetic preparations, Industrial and biological solvents, Chemical intermediates, etc. The electric field vector component of the microwave influences the dipole moment of the individual unit of the polymer molecule and tends to orient them in the direction of the electric field vector.^{4–9} If appropriate frequency of the microwave is under use, then microwave frequencies are capable of influencing the orientation polarization of the polar polymer materials.^{10–14} The orientation polarization being temperature dependent^{2,15–20} helps to obtain meaningful information, like shape, size, and the rotating molecular entities. The molecular dynamics is characterized by the observed values of relaxation times^{4–9} in microwave frequency region. The dielectric relaxation measurements have been shown to be reliable for investigating the rotational

motion of a dipolar unit of a polar polymer in a dilute solution prepared with nonpolar solvent.

Further, such dielectric measurements and data on the relaxation behavior of the solute in the nonpolar solvent at different temperature may be exploited to estimate the thermodynamic parameters, such as, change in the activation energy (ΔG_{τ}^*), enthalpy of activation (ΔH_{τ}^*), and entropy of activation, (ΔS_{τ}^*).¹⁶ Most frequently used and simple method of determining τ was that of Whiffen and Thompson employed by Hosamani et al.¹⁶ and Sannaningannavar et al.²¹ Here, values of most probable relaxation timer, the real part ϵ' and the dielectric loss ϵ'' of the complex dielectric permittivity ϵ^* in the dilute solution of the single concentration of polar solute in nonpolar solvent at different temperatures and single frequency of the microwave are to be carried out.

Although, much work on the study of dielectric relaxation in relation to temperature of a variety of polymer substances is reported in the literature,^{2–6} such studies, using Whiffen and Thompson model, as adopted by Hosamani et al.¹⁶ still seems to be explored. This prompted us to carryout investigation on dielectric measurements in the range of temperatures (303–333 K) at single frequency 9.59 GHz, using the solution of poly(ethylene glycol) (PEG) of average molecular mass 400 Delton (PEG 400) in benzene. The low molecular mass PEG 400 is liquid at room temperature with a very low volatility. Because of its nontoxic, biodegradable, inexpensive, and widely available nature, it has been frequently used across the industrial sector for many

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applications.^{2,5,9} Having HO—(CH₂—CH₂—O)_n—H as the general formula, PEG 400 is soluble in organic solvent like benzene over good range of concentration. It has two end hydroxyl (—OH) and oxyethylene groups. These groups are responsible for its extraordinary hydrophilic nature. Having many hydrogen-bonding sites in their structure, they can enter into intra and inter molecular hydrogen bonding, giving rise to different conformations.^{2,9,22,23} Many investigations^{2,3,5} have proved beyond any reasonable doubt that the chains in the molecules are helically coiled and flexible. Molecules of this polymer exist in quasi-isolated state when dissolved in nonpolar solvents to form dilute solutions. Solvent environment can influence the molecular flexibility, coiling, and intramolecular interactions. This in turn may influence the dielectric relaxation mechanism. To ascertain all this, this investigation is under taken using PEG 400 in benzene. Earlier investigations^{2,3,5} have confirmed the possibility of reorientation and rotation of these chain end —OH groups around C—O bonds in dynamic equilibrium. The dielectric relaxation process involves reorientation and group rotations of polar units of the molecule. Hence, the dielectric relaxation process, like viscous flow is treated as a rate process to study the thermodynamic properties of PEG 400 in benzene.

THEORY

Dielectric relaxation process is treated as rate process, involving the rotation of the dipolar molecules from one position to another leading to different states. This type of motion is possible only when they acquire enough activation energy to overcome the potential barrier. According to the Eyring expression for τ in terms of molar free activation energy ΔG_{τ}^* used by Hosamani et al.¹⁶ is

$$\tau = (h/kT)\exp(\Delta G_{\tau}^*/RT) \quad (1)$$

with

$$\Delta G_{\tau}^* = (\Delta H_{\tau}^*) - T(\Delta S_{\tau}^*) \quad (2)$$

where ΔG_{τ}^* = molar free energy of activation, ΔH_{τ}^* = molar enthalpy of activation, and ΔS_{τ}^* = molar entropy of activation.

For the calculation of the relaxation time τ at any temperature T , the expression for loss tangent $\tan \delta$ computed by measured values of ϵ' and ϵ'' , employing Whiffen and Thompson model, as was done by Sannaningannavar et al.¹⁹ and Ayachit and coworkers²⁰ was adopted. According to them

$$(\epsilon''/\epsilon') = \tan \delta = [(\epsilon' + 2)^2/\epsilon'] \times [(4\pi n\mu^2)/27kT][\omega\tau/(1 + \omega^2\tau^2)] \quad (3)$$

This is the valid expression that can be used under the fair approximation $\epsilon''^2 \ll (\epsilon' + 2)^2$

$$\therefore \tan \delta = P[\omega\tau/(1 + \omega^2\tau^2)] \quad (4)$$

With

$$P = [(\epsilon' + 2)^2/\epsilon'][(4\pi n\mu^2)/27kT] \quad (5)$$

and

$$n = d_{12}WN/M$$

Here, N , W , M , k , d_{12} , T , h , ω , and μ are Avogadro's number, mass fraction, molecular weight, Boltzman constant, density of solution, absolute temperature, Planck's constant, angular frequency ($\omega = 2\pi f$, with f as microwave frequency), and dipole moment, respectively.

Whiffen and Thompson have taken eq. (4) as the basis for determination of τ at different temperatures.

As $\tan \delta \rightarrow$ maximum, $\omega\tau \rightarrow 1$, therefore,

$$(\tan \delta)_{\max} = (P/2) \quad (6)$$

From eqs. (5) and (6), we get $[\tan \delta/(\tan \delta)_{\max}] = [2\omega\tau/(1 + \omega^2\tau^2)]$, this equation is quadratic in nature having two roots. Appropriate root is selected depending on the value of temperature T_m corresponding to $(\tan \delta)_{\max}$. The values of the relaxation time τ so obtained are used to evaluate thermodynamic parameters. Equation (1) can be rewritten as

$$\Delta G_{\tau}^* = 2.303RT \log(kT\tau/h) \quad (7)$$

Combining eqs. (2) and (7), the following expression can be obtained

$$2.303R \log(kT\tau/h) = [(\Delta H_{\tau}^*)/T] - \Delta S_{\tau}^* \quad (8)$$

The graph of $2.303R \log(kT\tau/h)$ versus $(1/T)$ is expected to be straight line, with a slope yielding the value of ΔH_{τ}^* . Knowing the ΔH_{τ}^* ; ΔS_{τ}^* values are calculated using eq. (2).

EXPERIMENTAL

Analytical reagent (AR) grade PEG of average molecular mass 400 Delton, supplied by Himedia Laboratories. Mumbai was used to prepare a solution using AR grade solvent benzene. The density of pure PEG 400 was calculated and was found to be 1.128 g cm^{-3} , which is in agreement with the literature value. Solute and solvent are used without any

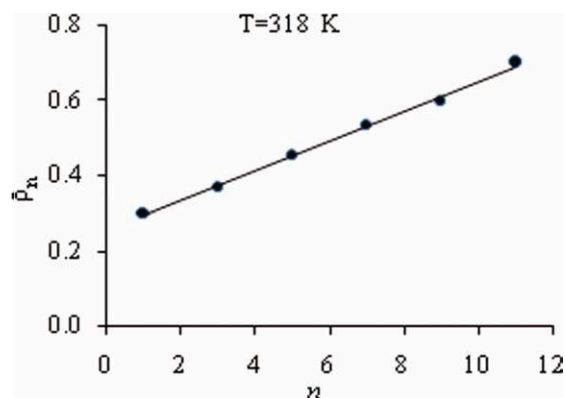


Figure 1 Variation of ρ_n with n . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

further distillation. Guide wave length λ_g , dielectric filled guide wave length λ_d and voltage standing wave ratio ($1/\rho_n$) was measured using X-band microwave bench working at 9.59 GHz frequency. The technique adopted to determine ϵ' and ϵ'' was due to Robert and Van-Hippel²⁴ and modified by Dakin and Works.^{25,26} The relations used to compute ϵ' and ϵ'' were

$$\epsilon' = (\lambda_0/\lambda_c)^2 + (\lambda_0/\lambda_d)^2 \quad (9)$$

$$\epsilon'' = (2/\pi)(\lambda_0^2/\lambda_g\lambda_d)(\text{slope of graph } \rho_n \rightarrow n) \quad (10)$$

With λ_0 , λ_c and ρ_n representing free space wave length, cut off wave length, and inverse standing wave ratio corresponding to n th resonating length with n taking only odd values 1, 3, 5, ...

The wave lengths λ_d and inverse standing wave ratios ρ_n were measured in the dielectric medium, in the form of dilute solution of PEG 400 in benzene having mass fraction 0.01540 at fixed frequency 9.59 GHz and different temperatures in the range (303–333 K), employing a slotted wave guide, short circuit plunger, using procedure described in literature.²¹ Seven different sets of ρ_n against n , one for each temperature selected to do investigations were obtained. Equations (9) and (10) were chosen to compute the values of permittivity ϵ' and dielectric loss ϵ'' . The values of ϵ' and ϵ'' , obtained here are

TABLE II
Coefficients A_0 and A_1 Values of Linear Equation $\rho_n = A_0 + A_1n$, Correlation Coefficient R^2 , and Standard Deviation SD

Temperature (K)	A_0	A_1	R^2	SD
303	0.0195	0.0416	0.9944	0.013
308	0.2977	0.0612	0.9854	0.024
313	0.3171	0.0430	0.9750	0.025
318	0.2539	0.0396	0.9963	0.010
323	0.2722	0.0317	0.9616	0.027
328	0.2803	0.0332	0.9879	0.015
333	0.3313	0.0260	0.9825	0.013

accurate within ± 1 and $\pm 3\%$, respectively. All these measurements were carried out at temperatures 303, 308, 313, 318, 323, 328, and 333 K, using constant temperature water bath having accuracy ± 0.1 K.

RESULTS AND DISCUSSION

The experimental values of ρ_n and their variation with n at each temperature indicate a good linear correlation between ρ_n and n . Out of seven tables and seven plots one corresponding to each temperature, representing variation of ρ_n as function of n , a sample graph (Fig. 1) corresponding to temperature 318 K and a sample table (Table I) for temperature 328 K are reported here. The coefficients of linear equation $\rho_n = A_0 + A_1n$ representing the variation of ρ_n with n are reported along with the correlation coefficient R^2 values and standard deviation (SD) values in Table II. The R^2 values, being quite close to unity, lie between 0.9616 and 0.9963 with SD values between 0.010 and 0.027. This establishes the linearity, thereby making experimentally determined dielectric loss ϵ'' quantities more reliable and accurate enough to use them in this investigation.

The dielectric constant ϵ' and dielectric loss ϵ'' appropriate to each temperature are reported in Table III, along with the values of dielectric relaxation time, τ , computed using Whiffen and Thompson model, following recently adopted methodology of Hosamani et al.¹⁶ It is observed that the ϵ' values decrease with increase in temperature. Due to increase in the molar volume of the polar molecules

TABLE I
Inverse Standing Wave Ratio ρ_n , ($d\rho_n/dn$), Correlation Coefficient R^2 , and Standard Deviation (SD) at 328 K

Compound	n values	ρ_n	$d\rho_n/dn$	R^2	SD
PEG 400 in benzene having mass fraction 0.01540	1	0.32317	0.0332	0.9879	0.015
	3	0.38879			
	5	0.42350			
	7	0.50087			
	9	0.58510			
	11	0.65429			

TABLE III
 ϵ' , ϵ'' , and τ at Different Temperatures and Thermodynamic Parameters ΔG_{τ}^* , ΔH_{τ}^* and ΔS_{τ}^* for PEG 400 in Benzene

Temperature (K)	ϵ'	ϵ''	τ (ps)	ΔG_{τ}^* (cal mol ⁻¹)	ΔH_{τ}^* (cal mol ⁻¹)	ΔS_{τ}^* (cal mol ⁻¹ K ⁻¹)
303	2.39266	0.02665	42.57	3367.2	5256.9	6.2
308	2.36485	0.03892	16.59	2856.3		7.8
313	2.36154	0.02732	6.82	2359.4		9.3
318	2.35298	0.02510	6.11	2337.6		9.2
323	2.35167	0.02009	4.64	2208.8		9.4
328	2.33765	0.02096	4.92	2290.2		9.1
333	2.32234	0.01634	3.73	2151.6		9.3

in solution, there may be decrease in the molecular interactions leading to decrease in the value of ϵ' with temperature increase. Table III indicates that, the value of ϵ'' first increases with T , reaches maximum value at 308 K and then decreases with increase in the value of T . The rate at which electrical energy is converted into heat energy in the medium depends on the value of ϵ'' , because ϵ'' values depend on nature of the solute molecules as well as on solvent environment.

The loss tangent $\tan \delta = \epsilon''/\epsilon'$ varies with temperature as in Figure 2. This expected kind of variation of $\tan \delta$ with T has maximum value at temperature $T_m = 308$ K and approves the applicability of the theory of Whiffen and Thompson in the case of sample under investigation. The dielectric relaxation time τ values evaluated by this method are also reported in Table III. The τ values are temperature dependent because, solvent environment and its temperature are found to affect the relaxation process. Moreover, in dilute solutions with nonpolar liquid as solvent, rotation, and reorientation of the polar entities are not hindered much compared with those in pure solute in the liquid form. The dipole-dipole interactions in dilute solutions are relatively too small because in such solutions, polar solute molecules are in quasi-isolated state. This is the reason for small values of τ in the dilute solutions.

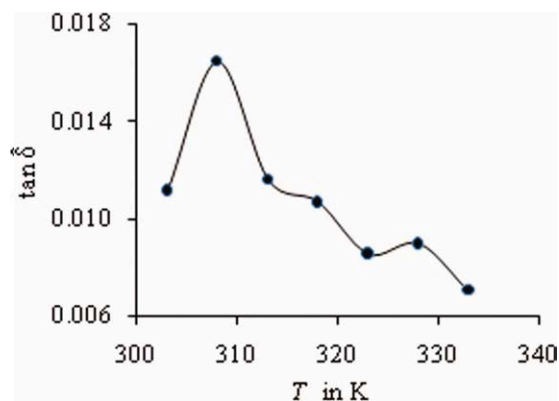


Figure 2 Variation of loss tangent ν/s T . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As the temperature increases, kinetic energy of the quasi-isolated solute molecules in solution increases. This result in the decrease in steric hindrance experienced by the polar molecules in the solution, as a result there may be decrease in the τ values with temperature. These macromolecules in the solution are more or less coiled. The intra molecular interactions are main sources of constraints for local motions. The opposition to local motions becomes weaker and weaker owing to weakening of the intramolecular interactions with raise in the temperature. Due to this, there may be decrease in τ values with increase in T . The backbones of PEG 400 polymer molecules are not stiffened in dilute solutions, instead, they get loosened more and more as T increases. This is also the reason for decrease τ values with raise in temperature. The coiling of molecular chain, flexibility, and mobility of polymer PEG 400 segments in solution are dependent on T . Therefore, these too will have their own contribution in decreasing the value of τ with increase in T .

The relaxation rate depends strongly on the temperature. The theory of thermal activation over potential barrier described by Blythe and Bloor,⁶ employed by earlier workers^{16,19-21} can successfully be adopted to estimate the thermodynamic parameters such as change in molar free energy of activation ΔG_{τ}^* , change in molar enthalpy of activation ΔH_{τ}^* , and change in molar entropy of activation ΔS_{τ}^* . Here, transition of polymer molecule from one state to another, overcoming the potential barrier of certain height takes place. The two states involved are taken to represent two different orientations of the polar groups in the molecule. Hence, the reaction coordinate is the angle of rotation about the bond. The entire methodology is in line with the Eyring rate process theory. The polar molecule derives certain amount of energy in excess of thermal energy to overcome the potential barrier by thermal fluctuations occurring in the dilute solution. This accounts for the strong dependence of the relaxation rate on temperature.

PEGs are tightly coiled in benzene and hence exhibit multiple relaxation behavior due to multiplicity of polar units in the chain. This is expected to

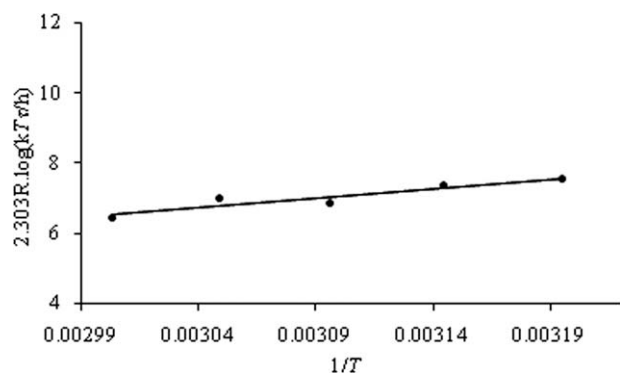


Figure 3 Plot to determine enthalpy of activation.

contribute toward the observed average value of relaxation time τ . Further, the method adopted determines the average value of relaxation time τ appropriate to all weight fractions, in the whole concentration range, and assumes the absence of any solute-solute interaction, which is nearly true in the case of dilute solutions. In view of this, the values of ΔG^* and ΔS^* determined may be given an importance to the extent that they are of right order and the trend in change in these quantities. However, it would be difficult to draw any conclusion on their exact values and the discussions hereafter are in line with this.

The linearity (Fig. 3) observed in the variation of $2.303R \log(kT\tau/h)$ against $(1/T)$ indicates that the dielectric relaxation process can be treated as rate process like viscous flow, over the range of temperature selected. The parameters ΔG_τ^* , ΔH_τ^* , and ΔS_τ^* calculated using Eyring rate equations are presented in Table III. The ΔG_τ^* for PEG 400 in benzene is found to lie in the range 2151.6–3367.2 cal mol⁻¹. This order is in agreement with reported values¹¹ of activation energy needed for rotation and reorientation of dipoles from one state to another. Due to thermal fluctuations, the conditions in the neighborhood of the quasi-isolated polar molecules, at given moment may not be perfectly identical. Therefore, the free energy of activation required for overcoming the barrier varies at least by small amount. Hence, the ΔG_τ^* values obtained at each temperature are mean values, having decreasing trend with raise in temperature. In the case of dielectric relaxation process only rotation and reorientations are involved whereas, rotational as well as translational motions are involved in the case viscous flow. Hence, the ΔG_τ^* for relaxation process is smaller than that for viscous flow ΔH_η^* .

The enthalpy of activation ΔH_τ^* depends on nature of the local environment of the molecule. The ΔH_τ^* value is larger than the values of ΔG_τ^* at all temperatures. Due to this, the ΔS_τ^* values at all temperatures are positive. The entropy of the system is the mea-

sure of orderly nature of the system. The quasi-isolated polar PEG 400 molecules in dilute solutions have large degree of molecular freedom to rotate and reorient about the single bonds. The chain end hydroxyl groups (—OH) are known to have appreciable mobility. They are able to rotate about the C—O bond, which joins it to the skeleton. As result of all this polar molecule can assume number of conformations. For the same reason the activated state is less ordered than normal state making ΔS_τ^* values positive. The environment plays noncooperative role leading to improper alignment of dipolar entities, in the activated state. Therefore activated state is less stable and disordered than normal state. The interactions between quasi-isolated polar molecules in dilute solutions, though cannot be perfectly zero, and may be small enough to be noticed. However, there is a possibility of change in the bond angles leading to increase in the dipole moment, hence the instability. The decrease in the value of ΔG_τ^* with increase in T may indicate a gradual change in the relaxation mechanism.

CONCLUSIONS

The dielectric relaxation study is of great significant use in understanding the dynamical behavior of macromolecules in dilute solution with nonpolar solvent. The real part ϵ' of complex dielectric permittivity decreases with increase in temperature; whereas dielectric loss ϵ'' increases first and then decreases after reaching maximum as temperature of dilute solution of PEG 400 in benzene increases. The intramolecular interactions play dominant role in dilute solutions. The polar polymer molecules are in quasi-isolated state in dilute solution, hence intermolecular interactions are weak. The backbones of PEG 400 polymer molecules are not stiffened in dilute solutions, instead, they get loosened more and more as temperature increases. The relaxation mechanism is also governed by rotations and reorientations of chain end hydroxyl groups. Such orientation polarization dielectric relaxation is observed in microwave region. In the dilute solution of PEG 400 in benzene, environment around each quasi-isolated polar molecule is noncooperative, thereby making activated state more disordered and less stable with respect to normal state.

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