

시간 분해 기법을 이용한 디메틸 술피록사이드와 디메틸 포름아미드-아닐린 용액에서 온도의존 유전이완에 관한 연구

Ajay Chaudhari*, C. S. Patil†, A. G. Shankarwar*, B. R. Arbad‡, and S. C. Mehrotra†

†Department of Chemistry, Dr.B.A.M. University, Aurangabad-431004(M.S.), India

*Department of Physics, Dr.B.A.M. University, Aurangabad-431004(M.S.), India

‡Department of Electronics and computer science, Dr.B.A.M. University, Aurangabad-431004(M.S.), India

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Temperature Dependent Dielectric Relaxation Study of Aniline in Dimethylsulphoxide and Dimethylformamide Using Time Domain Technique

Ajay Chaudhari*, C. S. Patil†, A. G. Shankarwar*, B. R. Arbad‡, and S. C. Mehrotra†

†Department of Chemistry, Dr.B.A.M. University, Aurangabad-431004(M.S.), India

*Department of Physics, Dr.B.A.M. University, Aurangabad-431004(M.S.), India

‡Department of Electronics and computer science, Dr.B.A.M. University, Aurangabad-431004(M.S.), India

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요 약. aniline-dimethylsulphoxide(DMSO)와 aniline-dimethylformamide(DMF) 계에서 dielectric relaxation에 관한 연구를 10 MHz-10 GHz 진동수 영역에서 여러 가지 다른 온도 그리고 농도에서 Time Domain Reflectometry(TDR) 방법을 이용하여 수행하였다. dielectric parameter 를 정적유전율, 이완시간, Kirkwood 상관계수, 잉여유전율, 잉여 역이완시간, 그리고 열역학적 parameter 들의 함수로 얻었다. 검정방법으로 최소자승법을 이용하였다. dielectric parameter 들이 온도와 농도에 대해 체계적으로 변하는 것을 볼 수 있었다.

ABSTRACT. The dielectric relaxation study for aniline-dimethylsulphoxide (DMSO) and aniline-dimethylformamide(DMF) has been carried out using the Time domain reflectometry (TDR) technique, at different temperature and concentrations, in the frequency range of 10 MHz to 10 GHz. The dielectric parameters viz. static permittivity, relaxation time, the Kirkwood correlation factor, excess permittivity, excess inverse relaxation time and thermodynamic parameters have been obtained. The calibration method based on least squares fit method has been used. The dielectric parameters show systematic change with temperature and concentrations.

INTRODUCTION

The dielectric relaxation study of solute solvent mixture at microwave frequency gives information about molecular interactions in the system, formation of monomers and multimers. In the study of dielectric relaxation parameters, the Kirkwood correlation factor of polar-polar mixtures has a considerable significance in providing valuable information about solute-solvent interaction.

The importance of measuring the dielectric constant of liquid lies in the fact that it provides valuable information about ordering of the molecules in the liquid state i.e. it quantifies the extent of polarization of the medium.

Barthel *et al.*¹ reported dielectric spectra of some amides in the frequency range 0.95-89 GHz at 25°C using the method of travelling waves. Bass *et al.*² reported dielectric properties of alkyl amides at 1-250 MHz using the Schering bridge technique at different

temperatures. Khirade *et al.*^{3,4} have reported the dielectric parameters of DMSO-alcohol, DMSO-2ethoxyethanol, DMF-alcohol and DMF-2ethoxyethanol mixtures, using the time domain technique. The relaxation time of aniline-benzene mixture are obtained by Suryavanshi and Mehrotra⁵ at 10 GHz in the temperature range 10-50 °C. Garbadu and Swain⁶ have studied aniline with alcohol with greater number of carbon atoms at 30 °C and at 450 KHz. Dielectric parameters for aniline-alcohol mixtures have been reported by Patil *et al.*⁷ using the time domain technique. Pattepur *et al.*⁸ have studied aniline-methanol mixtures with different concentrations and estimated a strong interaction between the two components in the aniline rich region only.

The objective of this paper is to report a detailed dielectric study of the aniline-DMSO and aniline-DMF mixtures using TDR^{9,10} in the temperature range 30-45 °C. In this study, aniline has been used as solvent and DMSO, DMF as solutes. Time domain reflectometry in reflection mode has been used to obtain the dielectric parameters viz. static permittivity, relaxation time. Using these parameters, the Kirkwood correlation factor, excess permittivity, excess inverse relaxation time and thermodynamic parameters have also been determined.

EXPERIMENTAL

Aniline (Merck grade), DMSO (spectrochem grade) and DMF (HPLC grade) were used without further purification. The solutions were prepared by mixing aniline and DMSO, Aniline and DMF with different concentrations at room temperature, assuming ideal mixing behaviour. The mole fractions were calculated from the volume fraction and density data.

The complex permittivity spectra were studied using the TDR. A Tektronix 7854 sampling oscilloscope with 7S12 TDR unit has been used. A fast rising step voltage pulse of 25 psec rise time generated by a tunnel diode was propagated through a coaxial line system. The sample was placed at the end of the coaxial line in a standard military application (SMA) coaxial cell of 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were done under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this

experiment, a time window of 5 ns was used. The reflected pulses without sample $R_r(t)$ and with sample $R_s(t)$ were digitized in 1024 points and transferred to the computer through a general purpose interface bus (GPIB) card.

The temperature controller system with a water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of ± 1 °C. The sample cell was surrounded by an heat insulating container through which the water of constant temperature using a temperature controller system was circulated. The temperature at the cell was checked using the electronic thermometer.

DATA ANALYSIS

The time dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$, over the frequency range from 10 MHz to 10 GHz using the Fourier transformation.^{11,12}

$$\rho^*(\omega) = (c/j\omega d)[p(\omega)/q(\omega)] \quad (1)$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_r(t)-R_s(t)]$ and $[R_r(t)+R_s(t)]$, respectively. c is the velocity of light, ω is the angular frequency, d is the effective pin length, and $j = \sqrt{-1}$. The Complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying the bilinear calibration method.⁹ The calibrating liquids used here are the aniline and the respective solvent mixed with the aniline. Experimental values of ϵ^* were fitted with the Debye equation.¹³⁻¹⁵

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau} \quad (2)$$

with ϵ_0 (static permittivity) and τ (relaxation time) as fitting parameters. The value of ϵ_∞ (permittivity at high frequency) was taken to be 2 for all the systems studied since, for the frequency range considered here, ϵ^* is not sensitive with respect to ϵ_∞ . A nonlinear least-squares fitting method¹⁶ was used to determine the dielectric parameters.

RESULTS AND DISCUSSION

The ϵ_0 and density values of pure liquids used are

Table 1. Data for the pure liquids at 30 °C

	ϵ_0		ρ (g-cm ⁻³)	
	This work	Lit.	This work	Lit.
Aniline	6.05	6.0 ⁷	1.01314	1.01317 ^a
DMSO	46.90	46.95 ³	1.090507	1.09042 ^b
DMF	37.62	38.27 ¹	0.939791	0.93967 ^b

^aRiddie J.A., Bunger W.B., Sakano T.K., Org. Solvent, 4th edition, John Wiley & Sons, New York, 1986.

^bP. Rajasekhar and K.S.Reddy, Thermochem-Acta. 117. 379 (1987).

given in Table 1 along with literature values. The static permittivity and relaxation time obtained by fitting experimental data in the Debye equation are listed in Table 2-3. The values of static permittivity decrease as the percentage of aniline in the respective solute increases. for all the temperatures. The values of relaxation time increase upto 60% and 85% of aniline in aniline-DMSO and aniline-DMF mixtures, respectively, after which those decrease. for all temperatures.

The information related to solute-solvent interaction may be obtained by excess properties¹⁷ related to the permittivity and relaxation time in the mixture. The excess permittivity, ϵ^E , which provides qualitative information about formation of multimers in the mixture, can be computed as

$$\epsilon^E = (\epsilon_m - \epsilon_0) - [(\epsilon_A - \epsilon_0)X_A + (\epsilon_B - \epsilon_0)X_B] \quad (3)$$

where 'x' is the mole fraction and suffix m, A, B represents mixture, solvent and solute respectively.

Similarly, the excess inverse relaxation time (τ^E)¹⁸ which gives information regarding the dynamics of solute-solvent interaction and represents the average broadening of dielectric spectra, can be defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A + (1/\tau)_B X_B] \quad (4)$$

The variation of excess properties with mole fraction of aniline, at temperatures 30, 35, 40 and 45 °C, for both the systems are shown in Figs 2 and 3. In both the systems studied, ϵ^E values are positive indicating the parallel alignment of the dipole and formation of monomeric or polymeric structures, which increase the total number of dipoles. The excess inverse relaxation time values are negative for both the systems except for the aniline DMF at 30, 40 and 45 °C for which those are slightly positive

Table 2. Temperature dependent dielectric relaxation parameters for Aniline+DMSO binary system.

Vol. % of Aniline	ϵ_0		τ (ps)	
	30 °C		35 °C	
0	46.90	20.15	45.12	17.32
02	45.28 (1) [†]	20.84 (3)	44.57 (2)	19.24 (5)
04	43.93 (1)	21.08 (3)	43.66 (1)	20.00 (4)
05	43.30 (1)	21.93 (3)	42.72 (9)	20.91 (2)
06	43.01 (9)	22.07 (2)	42.34 (4)	21.35 (1)
08	42.07 (1)	22.40 (4)	41.50 (9)	22.75 (2)
10	41.22 (1)	24.74 (4)	39.25 (1)	22.99 (3)
15	39.56 (1)	25.90 (4)	37.65 (6)	23.91 (1)
20	37.98 (1)	31.35 (5)	37.52 (5)	25.88 (1)
40	28.50 (8)	38.29 (4)	27.71 (5)	34.10 (2)
50	25.75 (6)	39.91 (3)	24.15 (8)	36.14 (5)
60	21.99 (7)	40.92 (5)	21.20 (4)	38.24 (2)
80	17.41 (5)	38.31 (4)	16.48 (2)	36.87 (2)
85	11.57 (3)	37.47 (4)	11.19 (5)	34.44 (7)
90	9.85 (2)	31.83 (4)	9.49 (1)	28.98 (3)
95	8.04 (10)	25.95 (3)	7.32 (1)	26.54 (3)
100	6.05	16.08	5.82	14.96

	40 °C		45 °C	
	0	44.99	15.43	44.02
02	44.23 (1)	16.83 (3)	43.71 (1)	16.01 (3)
04	43.30 (8)	17.19 (2)	43.06 (1)	16.62 (3)
05	42.48 (1)	17.43 (3)	41.94 (1)	17.19 (3)
06	42.00 (8)	17.79 (2)	41.77 (1)	17.54 (3)
08	40.78 (7)	18.60 (2)	40.39 (9)	18.35 (3)
10	39.07 (1)	20.60 (3)	38.44 (1)	20.32 (3)
15	37.75 (7)	20.78 (2)	37.17 (1)	20.55 (3)
20	36.44 (5)	22.84 (1)	35.54 (8)	22.49 (2)
40	26.76 (5)	31.01 (2)	26.42 (3)	30.71 (1)
50	23.70 (5)	35.78 (2)	23.38 (2)	32.59 (1)
60	20.32 (2)	37.24 (2)	19.64 (8)	36.97 (6)
80	15.99 (2)	34.62 (2)	15.61 (2)	36.19 (2)
85	10.43 (2)	30.22 (3)	9.61 (1)	29.80 (2)
90	9.14 (2)	27.58 (3)	8.46 (1)	26.48 (2)
95	7.03 (1)	21.53 (3)	6.63 (1)	20.93 (3)
100	5.73	13.85	5.44	12.53

[†]Numbers in brackets indicate uncertainty, 45.28 (1), means 45.28 + 0.01.

in the DMF region and for 35 °C these values are clearly positive in the middle region or the region where solute and solvent concentration is appreciably more.

The positive values of the excess inverse relaxation time indicate the faster rotation of the dipoles of the system whereas negative values indicate slower rotation of

Table 3. Temperature dependent dielectric relaxation parameters for Aniline+DMF binary system

Vol. % of Aniline	ϵ_0		τ (ps)	
	30°C		35°C	
00	37.62	10.40	34.44	9.87
02	35.05 (7)	10.76 (2)	32.44 (1)	10.21 (3)
04	34.26 (1)	11.04 (3)	32.31 (8)	10.40 (2)
05	34.24 (9)	11.47 (3)	31.74 (1)	10.99 (4)
06	33.86 (8)	12.08 (2)	31.36 (1)	11.24 (3)
08	32.17 (1)	12.80 (5)	31.20 (7)	11.81 (2)
10	31.78 (6)	13.83 (2)	30.34 (1)	11.99 (4)
15	31.04 (7)	14.55 (2)	29.73 (7)	12.50 (2)
20	29.71 (1)	17.35 (4)	28.27 (7)	14.77 (3)
40	29.06 (3)	20.40 (1)	26.73 (4)	17.20 (1)
50	23.36 (4)	29.33 (2)	22.13 (3)	26.38 (1)
60	20.43 (3)	32.64 (2)	19.24 (3)	28.95 (2)
80	13.65 (3)	36.66 (3)	12.95 (2)	29.64 (3)
85	11.42 (2)	37.29 (4)	11.36 (3)	32.98 (4)
90	10.10 (3)	33.51 (5)	9.49 (3)	32.06 (5)
95	7.92 (2)	26.63 (5)	7.59 (2)	26.12 (5)
100	6.05	16.08	5.82	14.96

Vol. % of Aniline	ϵ_0		τ (ps)	
	40°C		45°C	
0	33.70	9.20	32.67	8.60
02	31.76 (9)	9.29 (3)	31.09 (1)	8.69 (4)
04	31.55 (8)	10.18 (3)	29.88 (1)	9.77 (4)
05	31.35 (8)	10.47 (3)	29.49 (1)	10.15 (4)
06	30.69 (1)	10.78 (7)	28.04 (1)	10.46 (5)
08	29.85 (8)	11.35 (3)	26.91 (1)	10.96 (7)
10	29.68 (7)	11.50 (2)	28.45 (1)	11.23 (4)
15	29.50 (3)	12.29 (1)	26.66 (6)	11.99 (4)
20	28.18 (4)	14.20 (1)	25.66 (6)	14.07 (3)
40	26.25 (2)	15.31 (1)	24.30 (7)	14.98 (3)
50	21.10 (4)	24.39 (2)	19.19 (4)	23.55 (2)
60	18.39 (4)	27.66 (3)	15.91 (4)	24.61 (3)
80	12.32 (3)	28.63 (4)	11.23 (3)	25.44 (5)
85	10.80 (5)	29.88 (7)	9.97 (2)	28.07 (3)
90	8.98 (3)	28.45 (5)	8.25 (2)	27.05 (5)
95	7.11 (2)	24.25 (7)	6.27 (2)	22.25 (7)
100	5.73	13.85	5.44	12.53

the dipoles of the system. As expected, the solute-solvent interaction gets weaker with increasing temperature. Due to this fact, the corresponding excess properties get reduced at higher temperature.

The Kirkwood correlation factor¹⁸ 'g' is also a parameter that affords information regarding orientation of electric dipoles in polar liquids. The 'g' for a pure liquid may be obtained with the expression

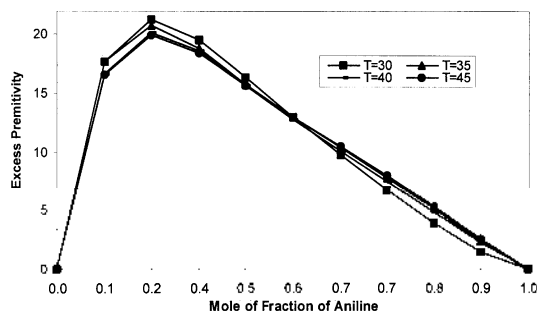


Fig. 1. Excess permittivity Vs mole fraction of Aniline in DMSO.

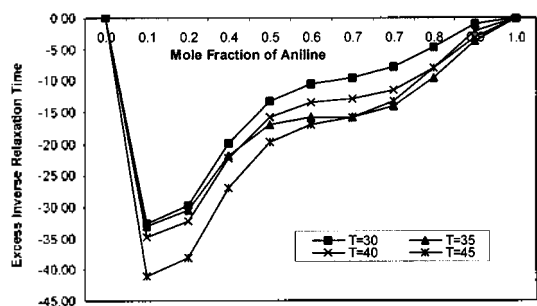


Fig. 2. Excess inverse relaxation time Vs mole fraction of Aniline in DMSO.

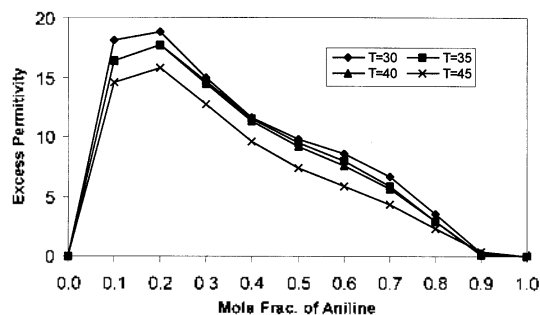


Fig. 3. Excess permittivity Vs mole fraction of Aniline in DMF.

$$\frac{4\pi N\mu^2 p}{9k^2 M^2} \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty - 2)^2} \quad (5)$$

where μ is the dipole moment in the gas phase, p is the density at temperature T , M is the molecular weight, k is the Boltzmann constant, and N is Avogadro's number.

For a mixture of two polar liquids, say A and B Eq. (5) was modified^{19,20} as

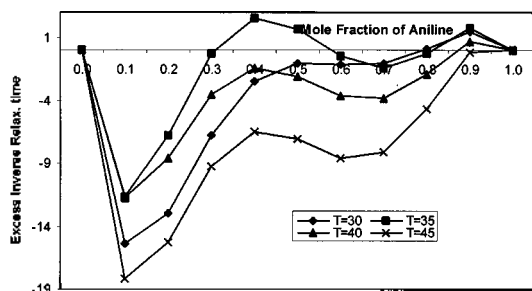


Fig. 4. Excess inverse relaxation time Vs mole fraction of Aniline in DMF.

$$\frac{4\Pi N}{9kT} \left(\frac{\mu_A^2 \rho_A}{M_A} \phi_A + \frac{\mu_B^2 \rho_B}{M_B} \phi_B \right) g^{eff} = \frac{(\epsilon_{00} - \epsilon_{\infty})(2\epsilon_{00} + \epsilon_{\infty})}{\epsilon_{00}(\epsilon_{\infty} + 2)^2} \quad (6)$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture with ϕ_A and ϕ_B the volume fractions of the components. In Eq. 6, the value of g^{eff} changes from ϕ_A to ϕ_B as the concentration of component B increases from 0 to 100%.

The calculated values of g^{eff} for both the systems are tabulated in Table 4. The values of g^{eff} are less than unity for pure aniline and aniline-rich region indicating anti-

Table 4. Values of the kirkwood correlation factor g^{eff} for Aniline-DMSO and aniline-DMF binary systems

Vol. fraction of solutes	Temperature (°C)				Temperature (°C)			
	30	35	40	45	30	35	40	45
	Aniline DMSO				Aniline DMF			
0.00	0.81	0.78	0.77	0.75	0.81	0.78	0.77	0.75
0.10	0.77	0.77	0.78	0.78	0.73	0.68	0.68	0.68
0.20	0.75	0.76	0.76	0.77	0.69	0.66	0.65	0.62
0.40	0.75	0.75	0.76	0.76	0.67	0.63	0.63	0.60
0.50	0.77	0.77	0.77	0.78	0.66	0.62	0.62	0.57
0.60	0.79	0.79	0.79	0.80	0.64	0.63	0.61	0.55
0.80	0.85	0.81	0.82	0.82	0.67	0.64	0.64	0.62
0.85	0.92	0.88	0.90	0.90	0.71	0.69	0.69	0.62
0.90	1.05	1.05	1.04	1.02	0.77	0.74	0.75	0.68
0.95	1.01	0.99	0.97	0.97	0.94	0.86	0.86	0.80
1.00	1.46	1.37	1.36	1.36	1.04	0.99	0.95	0.85

Table 5. Values of molar enthalpy and molar entropy for aniline-DMSO and aniline-DMF mixtures^a

% of Aniline	Dimethyl sulphoxide		Dimethyl. formamide	
	$\Delta H^*(kJ mol^{-1})$	$\Delta S^*(J mol^{-1} K^{-1})$	$\Delta H(kJ mol^{-1})$	$\Delta S(J mol^{-1} K^{-1})$
00	13.10 (23)	3.26 (01)	7.67 (22)	0.53 (00)
02	12.87 (23)	3.09 (01)	9.19 (22)	0.91 (00)
04	11.27 (22)	2.47 (00)	3.64 (20)	0.78 (00)
05	12.05 (22)	3.50 (01)	4.54 (22)	0.97 (0.1)
06	11.39 (22)	3.61 (01)	5.03 (21)	1.02 (00)
08	10.21 (22)	4.66 (01)	5.53 (21)	1.15 (00)
10	8.66 (21)	2.06 (00)	8.15 (21)	3.06 (00)
15	10.82 (22)	2.69 (00)	7.05 (21)	3.52 (01)
20	15.47 (23)	4.32 (01)	8.19 (21)	3.88 (01)
40	9.59 (21)	2.68 (00)	14.20 (23)	3.64 (01)
50	7.32 (20)	1.95 (00)	9.26 (21)	1.69 (01)
60	2.57 (19)	1.51 (00)	11.72 (22)	1.64 (01)
80	1.20 (18)	2.55 (00)	15.58 (23)	3.69 (01)
85	2.98 (19)	3.02 (00)	12.68 (22)	1.39 (01)
90	4.95 (20)	3.46 (01)	9.62 (21)	1.65 (00)
95	11.07 (22)	4.88 (01)	7.21 (21)	1.84 (00)
100	10.62 (22)	0.85 (00)	10.62 (22)	0.85 (00)

parallel alignment of electric dipoles in this region.

The thermodynamic parameters such as molar energy of activation ΔH^* and molar entropy of activation ΔS^* were obtained using the Arrhenius rate equation²²

$$\tau = (h/kT) \exp [(\Delta H^* - T\Delta S^*)/RT] \quad (7)$$

and are listed in Table 5.

CONCLUSION

Dielectric relaxation parameters, thermodynamic parameters and Kirkwood correlation factor are reported for aniline + DMF, and aniline – DMSO mixtures for various temperature and concentrations. In these systems the various dielectric parameters afford evidence of significant intermolecular interactions in the solute rich region only. All the parameters studied change with the temperature in accord with increasing structure breaking effects.

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REFERNECES

1. Barthel, J.; Bachhuber, K.; Buchner, R.; Gill, J. B.; Klebauer, M. *Chem. Phys. Lett.* **1990**, *62*, 167.
2. Bass, S. J.; Nathan, W. I.; Meighan, R. M.; Cole, R. H. *J. Phys. Chem.* **1964**, *68*, 509.
3. Khirade, P. W.; Chaudhari, A.; Shinde, J. B.; Helambe, S. N.; Mehrotra, S. C. *J. Chem. Engn. Data* **1999**, *44*, 879.
4. Khirade, P. W.; Chaudhari, A.; Shinde, B.; Helambe, S. N.; Mehrotra, S. C. *J. Sol. Chem.* **1999**, *28*(8), 1031.
5. Suryavanshi, B. M.; Mehrotra, S. C. *Ind. J. Pure & Appl. Phys.* **1991**, 482.
6. Garbadu, K.; Swain, B. B. *Ind. J. Phys.* **1994**, *68B*(3), 271.
7. Patil, S. P.; Chaudhari, A. S.; Lokhande, M. P.; Shankarwar, A. G.; Helambe, S. N.; Arbad, B. R.; Mehrotra, S. C. *J. Chem. Engn. Data* **1999**, *44*, 875.
8. Fatepur, R. H.; Hosamani, M. T.; Deshpande, D. K.; Mehrotra, S. C. *J. Chem. Phys.* **1994**, *101*, 9956.
9. Cole, R. H.; Berberian, J. G.; Mashimo, S.; Chryssikos, G.; Bums, A.; Tombari, E. *J. Appl. Phys.* **1989**, *66*, 793.
10. Puranik, S. M.; Kumbharkhane, A. C.; Mehrotra, S. C. *J. Microwave Power Electromag. Theory* **1991**, *26*, 196.
11. Shanon, C. E. *Proc. IRE* **1949**, *37*, 10.
12. Samulon, H. A. *Proc. IRE* **1951**, *39*, 175.
13. Ilavriak, S.; Negami, S. *J. Polymer Sci. Polymer Symp.* **1966**, 99.
14. Cole, K. S.; Colege, R. H. *J. Chem. Phys.* **1941**, *9*, 341.
15. Davidson, D. W.; Cole, R. H. *J. Chem. Phys.* **1950**, *18*, 1484.
16. Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw Hill: New York, **1969**, 104.
17. Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973.
18. Frohlich, H. *Theory of dielectrics*; Oxford university press: London, 1949.
19. Kumbharkhane, A. C.; Puranik, S. M.; Mehrotra, S. C. *J. Mol. Liquids* **1992**, *51*, 261.
20. Kumbharkhane, A. C.; Puranik, S. M.; Mehrotra, S. C. *J. Solution Chem.* **1993**, *22*, 219.
21. Moumouzlas, G.; Panopoulos, D. K.; Ritzoulis, G. *J. Chem. Eng. Data* **1991**, *36*, 20.
22. Glasstone, S.; Laidler, K. J.; Eyring, H. *The theory of rate processes*; Mc Graw Hill: New York, 1941.