

Dielectric relaxation studies of four different varieties of rapeseed-mustard oil at different temperatures

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Abstract Dielectric properties of four rapeseed-mustard oil samples of crop year 1998 having different percentage composition of different fatty acids have been studied at 100 KHz, 8.93 GHz and optical frequency of the *D*-lines of sodium. Temperature variation of dielectric properties has also been investigated in the temperature range from 303 to 333 K. ϵ_0 and ϵ_∞ both are decreasing with increase in temperature, for each sample under investigation. However, variation of ϵ' with temperature exhibits the presence of either a peak or a valley at some temperature in all the four samples, though less prominent in the sample PCC-2. This may be attributed to the modification in the packing of dipoles at this temperature either due to increase in the overall dipolar correlation or due to reduction in the overall dipolar correlation. The macroscopic relaxation time and various thermodynamic parameters have also been calculated for the dielectric relaxation process. Negative values of molar entropy of activation indicate the existence of cooperative orientation of molecules arising out of steric forces. No specific dependence of dielectric parameters on constituent fatty acids is observed.

Keywords Dielectric properties, temperature variation, rapeseed-mustard oil

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1. Introduction

Among the studies on the interaction between electromagnetic fields and living matters, microwave spectroscopy of agriculture and biological substances is one of the increasing importance. The extensive use of domestic and industrial devices for food preparation, such as microwave ovens and defrosting apparatus *etc.*, justifies the need for an even better knowledge of the effects of EM radiation on the food stuff. Microwave spectroscopy can be a useful technique for investigating some properties of tissues or proteins, and seems potentially able to give diagnostic information [1].

Recently, dielectric behaviour of albumin and yolk of avian egg was studied by Lokhande *et al* [2], soya bean oil and mustard oil by Khanna and Upadhyay [3], biologically and pharmaceutically important low molecular weight ethylene glycols by Sengwa and Kaur [4], Human Sera and Erythrocytes by Bianco *et al* [5].

However, little information is available for many agri-food materials. Rapeseed-mustard oil is one of the most important edible oils being consumed largely in India and elsewhere. Rapeseed-mustard group of oils are comprised of different varieties having different fatty acid composition. Except for minor amount of impurities, dietary fats and oils consist of triglycerides or esters of glycerol and high molecular or long chain aliphatic acids, both saturated or unsaturated [6], known as fatty acids. The value and suitability of mustard oil for nutritional or industrial uses are determined by its fatty acid composition. Low erucic acid rapeseed oil is more suitable for edible purposes. The HEAR [High Erucic Acid Rapeseed] oil was for a long time under use for domestic lighting. Other industrial uses came into being at a later stage. It can be used as a Lubricant or as a diesel fuel substitute. It is under limited use for the latter purpose, in view of cheapness of the diesel oil. Absence of essential fatty acids like linoleic acid in the diet results in hair fall,

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eczema like skin eruptions, slow healing of wounds and dry scaly skin. Because of their importance the WHO has recommended that at least 3% of the diet should contain linoleic acid [6].

In the present study, we have determined dielectric properties of different varieties of rapeseed-mustard oil having different percentage composition of fatty acids, along with relaxation times and thermodynamical parameters.

The macroscopic relaxation time (τ_m), molar free energy of activation (ΔF_c), molar entropy of activation (ΔS_c) and molar enthalpy of activation (ΔH_c) have also been worked out for these samples, which may provide valuable information for future research in this field.

2. Material and experimental details

For the present investigations, different samples of rapeseed-mustard of crop year 1998 namely Hyola-401, M-21, PCC-2, PYS-842, have been procured from National Research Centre on rapeseed-mustard located at Sear, Bharatpur (India). Fresh oil from these seeds was obtained by using a baby expeller. This oil was then filtered by fine filters. To get the fatty acid profile one drop of oil was taken in capped glass test tube. To it 1 ml of petroleum ether (60–80°C) was added and mixed with very slowly. After keeping for one hour at room temperature, 1.5 ml of 0.05 M sodium methoxide was added to it and kept at room temperature for one hour. Then 1.5 ml of 8% sodium chloride solution was added to it. Layers were separated. 1 μ l from upper layer was injected on G.L.C. (NUCON 5765 model). Fatty acid profiles were obtained using SP-2300 (2%) + SP-2310 (3%) stainless steel column using flame ionization detector (FID). The oven temperature was maintained at 240°C and the injector and the detector were both maintained at 290°C.

The dielectric constant (ϵ_0) at 100 KHz was measured by using a dipole meter by directly measuring the capacitance and calibrating it for standard liquids. The dielectric constant at optical frequency was obtained by squaring the refractive index measured at the frequency of the D-lines of sodium, measured with the help of an Abbe's refractometer. The measurements of wavelength in the dielectric and that of voltage standing wave ratio were made at frequency 8.93 GHz using a slotted wave-guide and a short circuited plunger. The calculation of dielectric permittivity (ϵ') and dielectric loss (ϵ'') were made following the method of Heston *et al* [7] adopted for short-circuited terminations. The values of ϵ' and ϵ'' so obtained are accurate within $\pm 1\%$ and $\pm 5\%$ respectively. All these measurements were made at four temperatures, *viz.* 303, 313, 323 and 333 K using a temperature regulating system and a constant temperature water bath.

The macroscopic relaxation time is determined by using the equation

$$\epsilon^* = \epsilon_0 \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau_m}$$

where ϵ^* is the complex permittivity at angular frequency ω .

On using $\epsilon^* = (\epsilon' - j\epsilon'')$, and separating real and imaginary parts, we get

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau_m^2} \quad (1)$$

$$\text{and } \epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)}{1 + \omega^2\tau_m^2} \omega\tau_m \quad (2)$$

Substituting the values of ϵ_0 , ϵ' , ϵ'' , ϵ_∞ and ω in eq. (1), we may obtain the value of τ_m (macroscopic relaxation time). Molar free energy of activation is determined by Eyring's equation [8] for the dielectric relaxation

$$\tau_m = (A/T) \exp(\Delta F_c / RT); \Delta F_c = \Delta H_c - T\Delta S_c, \quad (3)$$

where $A = h/k$, R = gas constant and T = temperature (K), and ΔF_c is the molar free energy of activation, ΔH_c is the molar enthalpy of activation and ΔS_c is the molar entropy of activation

The slopes of the straight lines obtained by plotting $\log(\tau_m T)$ versus $(1/T)$, when multiplied with gas constant R gives the value of ΔH_c . Knowing the value of ΔF_c and ΔH_c , we can get the values of ΔS_c using eq. (3).

3. Results and discussion

Table 1 shows the compositions of fatty acids in different samples under study. The fatty acid-composition is obtained by taking chromatograms of the different samples under investigation. Chromatogram of one such sample *viz.* PCC-2 is given for example (Figure 1). Peaks corresponding to different retention times are of different fatty acids

Table 1. Fatty acid composition (%) in different samples of rapeseed-mustard oil (crop year 1998)

Variety	Palmitic	Stearic	Oleic	Linoleic	Linolenic + Eicosenoic	Eruic
	16.0*	18.0*	18.1*	18.2*	18.3* + 20.1*	22.1*
Hyola-401	3.87	Tr**	63.19	21.00	11.10	0.81
M-21	3.88	1.17	33.03	35.56	15.39	11.44
PCC-2	2.94	Tr.**	14.25	17.90	20.34	44.54
PYS-842	2.27	Tr**	11.75	14.76	13.62	57.59

*These denote number of carbon atoms to number of double bonds in the corresponding fatty acids

**Trace only.

present in these samples. Table 2 shows different fatty acids corresponding to different retention time (in minute). Table 3 shows the values of dielectric constants at 100 KHz, 8.93 GHz and at optical frequency of sodium D-lines along with loss factor ϵ'' at 8.93 GHz for different varieties of rapeseed-mustard oil at 303, 313, 323 and 333 K. At any

temperature from 303 to 333 K experimental values of ϵ_0 , ϵ' , ϵ'' and ϵ_∞ are not giving any indication regarding the systematic variation of dielectric data with percentage composition of any fatty acid present in the samples under investigation. This may be attributed to the complexity of triglyceride structure, as the characteristics and particularly the physical properties of a fat are considerably dependent upon how the fatty acids are distributed within the glyceride molecules and what are their chain lengths [9].

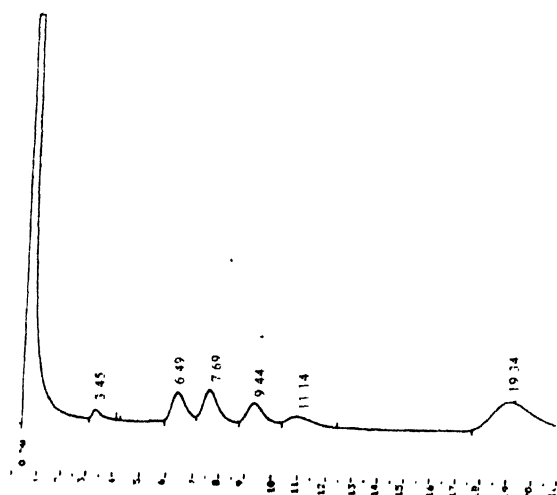


Figure 1. Chromatogram of PCC-2.

Table 2. Retention time (min) of different fatty acids

Fatty acids	Retention time (min)
Palmitic	3.45
Stearic	5.81
Oleic	6.49
Linoleic	7.69
Linolenic	9.44
Ficosenoic	11.14
Erucic	19.34

Table 3. Experimental values of ϵ_0 , ϵ' , ϵ'' , ϵ_∞ , τ_m , ΔF_ϵ , ΔH_ϵ and ΔS_ϵ for different samples at 303, 313, 323 and 333 K.

Temp (K)	ϵ_0	ϵ'	ϵ''	ϵ_∞	$\tau_m (\times 10^{12})$ Sec	ΔF_ϵ (K Cal/mole)	ΔH_ϵ (K. Cal/mole)	ΔS_ϵ (Cal/mole deg.)
Hyola-401								
303	3.6625	2.4556	0.2400	2.1963	38.4	3.3060	0.866	-8.05
313	3.6120	2.5025	0.2440	2.1874	33.4	3.3480		-7.92
323	3.5812	2.5380	0.2998	2.1785	30.3	3.4130		-7.88
333	3.5437	2.5124	0.3235	2.1720	31.0	3.5540		-8.07
M-21								
303	3.2175	2.4798	0.2756	2.2052	29.2	3.1410	0.150	-9.87
313	3.1875	2.4927	0.1934	2.1992	27.4	3.2250		-9.82
323	3.1562	2.4992	0.2146	2.1933	26.1	3.3170		-9.80
333	3.1275	2.4830	0.1613	2.1844	26.1	3.4400		-9.87
PCC-2								
303	3.2312	2.4575	0.2270	2.2022	31.0	3.1770	1.808	-4.51
313	3.2125	2.4798	0.2022	2.1963	28.6	3.2520		-4.61
323	3.1687	2.5290	0.1727	2.1904	24.5	3.2760		-4.54
333	3.1562	2.5731	0.2229	2.1815	21.7	3.3180		-4.53
PYS-842								
303	3.0618	2.4368	0.2278	2.1933	28.7	3.1300	0.674	-8.10
313	3.0250	2.3861	0.3193	2.1892	32.1	3.3230		-8.46
323	2.9812	2.4200	0.2682	2.1844	27.5	3.3510		-8.28
333	2.9625	2.4512	0.3029	2.1756	24.2	3.3900		-8.15

Figures 2 and 5 show the behaviour of ϵ_0 and ϵ_∞ for all the four samples, at temperatures ranging from 303 to 333 K. Both ϵ_0 and ϵ_∞ are decreasing with increase in

shape either to become spherical or to become elongated at some temperature. Elongated shape may be containing dipoles in a parallel alignment that enhances the value of ϵ'

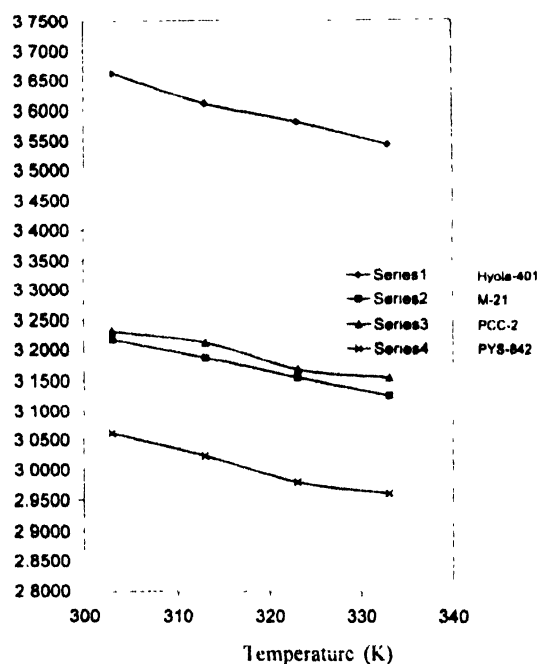


Figure 2. Dielectric constant (ϵ_0) of the four samples at frequency 100 KHz as a function of temperature.

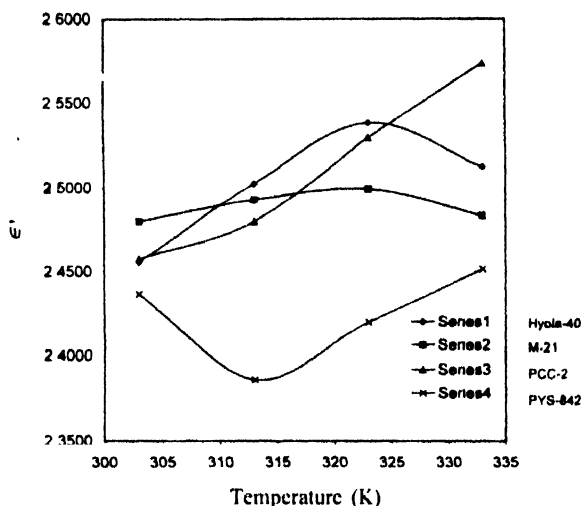


Figure 3. Dielectric constant (ϵ') of the four samples at frequency 8.93 GHz as a function of temperature

temperature for each sample under investigation. The increase in temperature may cause decrease in overall dipolar correlation and so both ϵ_0 and ϵ_∞ decrease progressively at higher temperatures. However, in these samples, ϵ' does not show regular variation with change in temperature from 303 to 333 K as shown in Figure 3. In this figure, we find the presence of either a peak or a valley at some temperature in the samples under investigation. This strongly indicates about modification in the packing of dipoles which alter its

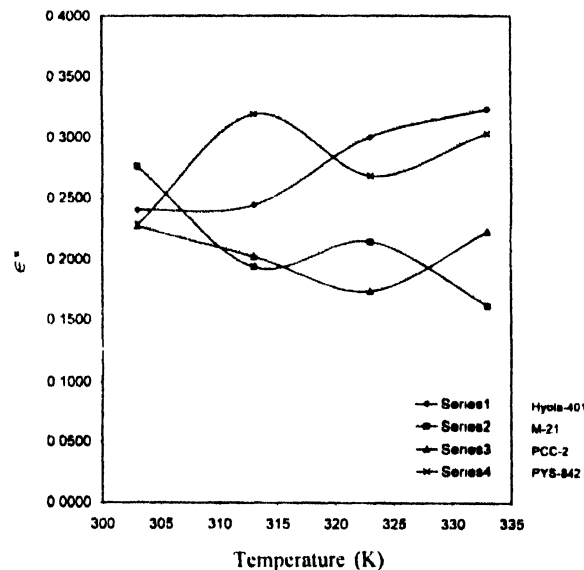


Figure 4. Loss factor (ϵ'') of the four samples at frequency 8.93 GHz as a function of temperature

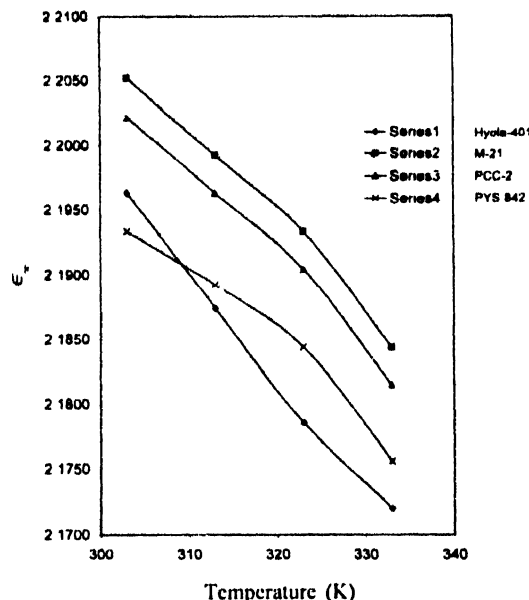


Figure 5. Dielectric constant (ϵ_∞) of the four samples at optical frequency of sodium light as a function of temperature.

while spherical shape contains reduced overall dipolar correlation. This behaviour is exhibited by all the samples, though less prominent in one sample *i.e.* PCC-2. Figure 4 shows the behaviour of ϵ'' for all the four samples with increase in temperature from 303 to 333 K. Behaviour of ϵ'' also does not show a systematic variation with change in temperature from 303 to 333 K. Similar results for ϵ' and ϵ'' were reported by Venkatesh *et al* [10]. These workers determined ϵ' and ϵ'' for tylose (complex food material)

ethanol and ethanol/hexane mixture and reported similar behaviour of ϵ' and ϵ'' with change in temperature where for some temperature range ϵ' and ϵ'' are decreasing with increase in temperature while for other temperature ranges these are either constant or increasing with increase in temperature. Sengwa and Kaur [4] have also reported similar results in oligomers of ethylene glycol showing no regular variation in ϵ' and ϵ'' with temperature in this frequency range. It is also seen from the same table that macroscopic relaxation time (τ_m) for each sample is decreasing, in general, with increase in temperature from 303 to 333 K. This shows more compact clustering of molecules at low temperature due to which more time is taken in reorientation process. It is also seen from the same table that there is no systematic trend in the variation of macroscopic relaxation time with increase in temperature which can be attributed to long chain intramolecular interactions in the triglyceride molecules of the samples under investigation.

Table 3 also shows the calculated values of molar free energy of activation (ΔF_c) for each sample under investigation. ΔF_c values for each sample are increasing with increase in temperature from 303 to 333 K. This can be explained on the basis that as the temperature increases, thermal agitation increases and the molecules require more energy to come to the activated state. From the same table, it is also evident that for all the samples under investigation, the ΔH_c values are less than the corresponding ΔF_c values, resulting in negative molar entropy of activation, ΔS_c values. This indicates the existence of cooperative orientation of the molecules arising out of steric forces [11] to yield more ordered state.

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