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Effect of Strong Electrolytes on Edible Oils Part III: Viscosity of canola oil in 1,4-dioxane in the presence of HCl, NaOH and NaCl at different Temperatures

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ABSTRACT: Effect of strong electrolytes on the viscosity of canola oil in 1,4 dioxane was undertaken. The viscosity of oil in 1,4 dioxane was found to increase with the concentration of oil and decrease with rise in temperature. Strong electrolytes reduce the rate of flow of oil in 1,4 dioxane. It was noted that amongst these electrolytes, NaOH is more efficient reducing electrolyte than HCl and NaCl. The study was also extended in terms of ion-ion and ion-solvent interactions. The values of Jones-Dole coefficients (A and B) were evaluated graphically. The increase in negative values of A-cefficient with temperature is due to agitation of the molecules at higher temperature, dissociation and partial association of electrolytes in 1,4 dioxane. The positive values of B-cefficient show that these electrolytes behave as structure breaker in 1,4 dioxane. Distortion of the solvent structure is not appreciable (small), which resulted in the positive values of B-coefficient. Fluidity parameters were also evaluated and the change in these values with temperature and concentration of oil shows that the electrolytes behave as structure breaker. The energy of activation, latent heat of vaporization and molar volume of oil were also evaluated and discussed. @JASEM

Omega-3 and Omega-6 are important fats associated with a nutrient diet. The primary sources of Omega-6 are maize, soya, canola, safflower and sunflower oils. These oils are overbundent in the typical diet, which explains our excess Omega-6 levels. These oils also contain considerable quantity of Omega-3 but best sources of Omega-3 are fish, flaxseed and walnut oils. Omega-3 in fish is high in two fatty acids essential to human health DHALEPA. These two fatty acids are pivotal in preventing heart disease, cancer and many other diseases. For people who cannot contemplate eating fish, the Omega-3 must come from alpha-linolenic acid. This can be achieved by increasing intake of Omega-3 rich food such as flaxseed (linseed oil), rapeseed (canola) oil, China seed, Walnut oil and dark green leafy vegetables. The ideal ratio of Omega-3 and Omega-6 fats is 1:1. Usually majority of people do not maintain this ratio. Probably it is completely economical problem. Our earlier papers (Khan et al, 2005) report the effect of strong electrolytes (HCl, NaOH and NaCl) on the rates of flow of sunflower oil and maize oil using 1,4-dioxane as solvent. Viscosities of these oils in 1,4-dioxane get increased with increasing concentration of the oils and decreased with increase in temperatures. Unsaturated ingredients of these oils play an important role in this connection. Thermal effect activation radically, the acids which causes the polymerization result in increasing the viscosity. The saturated ingredients behave as chain transfer agent and terminate the growing polymer chain of these monoglycerides and diglycerides present in the oils. Beside, the shape of the molecules also influences the viscosity. Liquids with large irregular shaped molecules are generally known to be more viscous than those with small symmetrical molecules. This paper deals with the effect of strong electrolytes on viscosity of canola oil in 1,4-dioxane at different temperatures.

EXPERIMENTAL

Material: The electrolytes like (HCl, NaOH and NaCl), oxalic acid of E.merck and 1,4-dioxane (BDH) are used without further purification. Canola oil was extracted from dried, dehulled seeds. The density of oil was measured at different temperatures with a difference of 5 K. These are 0.978 (298 K), 0.975 (303 K), 0.972 (308 K), 0.967 (313 K), 0.962 (318 K) and 0.955 (323 K) g/cm^3.

Procedure: Viscosities were measured according to the procedure given elsewhere (Khan et al, 2005). The viscosity of canola oil solutions in 1,4-dioxane was measured at different temperatures ranging 298-323K with the Ostwald viscometer type Techniconominal constant 0.1(Cs/S) capillary ASTMD 445. Three observations were taken to ensure the reproducibility of the measurements.

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Table 1: Viscosities of Canola oil in 1,4 –dioxane at different temperatures (K).

Concentration of oil (%)	Viscosity (cp) at different temperature (K)					
	298	303	308	313	318	323
5	1.358	1.222	1.154	1.056	1.017	0.938
10	1.581	1.436	1.330	1.227	1.156	1.044
15	1.845	1.672	1.555	1.431	1.195	1.121
20	2.122	1.890	1.780	1.620	1.524	1.424
25	2.552	2.293	2.138	1.940	1.809	1.714
$[HCl]10^3$ ($mol.dm^{-3}$)	Viscosity of 5% Canola oil solution in presence of electrolyte.					
1.0	1.378	1.246	1.137	1.004	0.928	0.900
2.0	1.414	1.279	1.155	1.020	0.957	0.928
3.0	1.432	1.296	1.171	1.034	0.972	0.943
4.0	1.451	1.313	1.188	1.050	0.987	0.958
5.0	1.487	1.331	1.205	1.066	0.958	0.973
$[NaOH]10^3$ ($mol.dm^{-3}$)						
1.0	1.381	1.261	1.249	1.048	1.016	0.937
2.0	1.416	1.278	1.235	1.079	1.032	0.952
3.0	1.451	1.295	1.205	1.094	1.063	0.981
4.0	1.469	1.312	1.222	1.110	1.079	0.997
5.0	1.488	1.329	1.239	1.126	1.094	1.012
$[NaCl]10^3$ ($mol.dm^{-3}$)						
1.0	1.361	1.243	1.137	1.002	0.913	0.858
2.0	1.396	1.261	1.154	1.018	1.928	0.873
3.0	1.415	1.278	1.170	1.033	1.943	0.887
4.0	1.433	1.295	1.187	1.049	1.958	0.903
5.0	1.451	1.312	1.204	1.065	1.973	0.918

RESULTS AND DISCUSSION

Density of extracted oil was measured at different temperatures with a difference of 5 K. It decreases slightly with change in temperature. The densities of maize oil, soyabeen oil, sunflower oil at 298 K are respectively as 0.960, 0.986, and 0.978 gm/cm^3 where as that of canola is 0.981 gm $/cm^3$. It shows that this oil is thick and spread slowly due to the bonding of ingredients present in the oil. Viscosity of canola oil and its solutions in 1,4-dioxane were measured at different temperatures ranging 298-323 K (Table 1). The viscosity of oil solutions gets increased with the increment of concentration of oil and decrease with the increase in temperature. The relative molecular mass of canola oil was also calculated graphically by plotting $1/V_o \ln \eta / \eta_o$ versus V_o at different temperatures over the range of 298-323 K. The representative linear plot is shown in Fig 1 with the correlation coefficient of 0.09.

$$V_{c \to o}\ [1/V_o \ln \eta / \eta_o] \qquad (1)$$

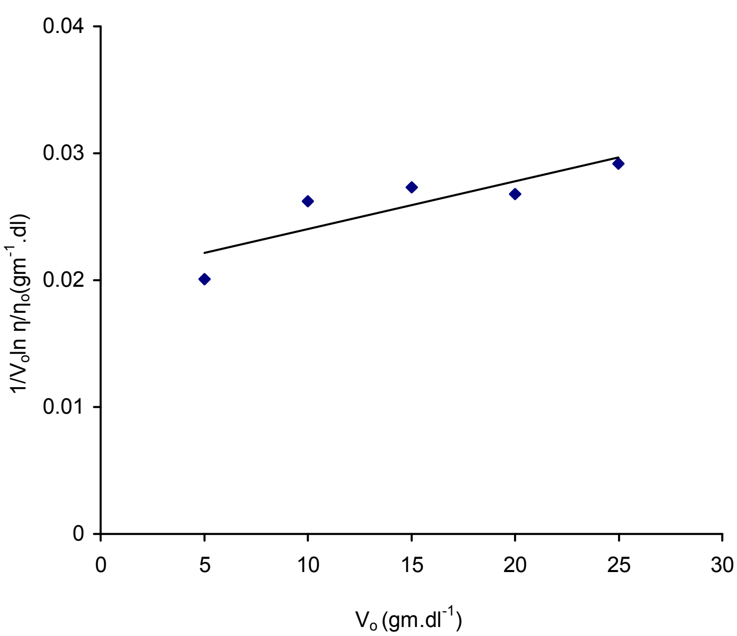

Fig 1: Plot of $1 / V_o \ln \eta / \eta_o$ versus V_o of canola oil in 1,4-dioxane at 303 K.

Here V_o is the percent volume of oil, η and η_o are respectively the viscosity of solutions and solvent. The relative molecular mass "M" of the oil was calculated from the following relation (Das et al 1983, Shama 2004).

$$[\,\eta\,] = 2.0 \times 10^{-4} M^{0.76} \qquad (2)$$

The relative molecular mass of the canola oil calculated as 287.79. Following the same procedure, the molecular masses of some other oils view to compare with canola oil are also measured. The molecular masses of coconut, maize, sunflower and soyabean oils are so determined respectively as 723.69, 643.43, 171.82, 192.44 and 705.17 g/mol. It shows that the molecular masses of oils depend upon the ingredients present in the oils with different ratio. Unsaturation of these oils is also other factors, which change the physiochemical parameters.

Table 2: Ion- ion and Ion- solvent interactions of 5% Canola oil with 1,4-dioxane in presence of strong electrolytes at different temperatures (K).

Temp (K)	Ion-Ion and Ion-Solvent Interactions as A and B Coefficient of Jones-Dole equation		
	HCl	NaOH	NaCl
	A-Coefficient $(dm^3mol^{-1})^{1/2}$		
298	-2.804	-1.671	-1.686
303	-3.307	-2.752	-2.433
308	-4.570	-3.727	-2.603
313	-5.738	-5.013	-3.014
318	-5.904	-5.194	-3.303
323	-5.566	-5.459	-4.163
B-Coefficient (dm^3mol)			
298	44.833	11.975	27.914
303	51.144	44.748	35.494
308	59.870	50.395	41.419
313	71.661	68.653	44.458
318	77.590	71.521	48.917
323	83.038	73.268	59.026

Table 1 includes the observations obtained by the effect of different concentration of HCl (1.0-5.0 x 10^{-3} $mol.dm^{-3}$) on the viscosities of 5% (v/v) canola oil in 1,4-dioxane at different temperatures ranging 298-323 K with a difference of 5 K. These results reveal that the viscosity of oil solutions increases with increase in concentration of electrolytes and decreases with rise in temperature. On comparison with the viscosity obtained in the presence and absence of electrolytes, it is observed that electrolytes reduce the viscosity of canola oil solutions. The viscosity of 5% canola oil solutions at 298 K is 1.358 cp whereas it in the presence of 1.0 x 10^{-3} $mol.dm^{-3}$ HCl, the viscosity drops to 1.378 cp. Similarly Table-1 contains the observations due to NaOH and NaCl which behave in the same way as HCl does. But it is noted that NaOH is more efficient reducing electrolyte than HCl and NaCl for canola oil. On the other hand for sunflower and maize oil, HCl is more efficient reducing agent. Now it is very necessary to study the results in the light of the ingredients compositions of the systems. Usually oils are composed of saturated and unsaturated ingredients. Palmitic acid ($C_{16}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$) are saturated fatty acids whereas Oleic acid ($C_{17}H_{33}COOH$), linoleic acid ($C_{17}H_{31}COOH$) and linolenic acid ($C_{17}H_{29}COOH$) are unsaturated ingredients. These are essential fatty acids, which our body does not synthesize. The increase in viscosity at various temperatures in the presence and absence of the electrolytes is due to the unsaturation of ingredients present in the oil. Linolenic acid contains two double bonds, which also cause the increase in the rate of flow. Due to thermal effect probably radical are formed which activate the ingredients of oil resulting increase in viscosity. It may be observed in the kitchen, the continuous heating of oil makes it viscous and sticky which is certainly due to thermal polymerization of unsaturated essential fatty acids and saturated fatty acids probably behave as a chain transfer agent. In canola oil, linolenic acid is in enough quantity, which is main source of Omega-3 fat.

$CH{-}CH_2{-}CH{=}CH{-}C_2H_5$

$\|$

$CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7{-}COOH$

Since strong electrolytes reduce the viscosity of oils as shown in Table 1, results show that the viscosity of oil in 1,4-dioxane solvent are higher as compared to the viscosities in the presence of strong electrolytes like HCl, NaOH and NaCl. The results are also analyzed by the variation in pH values. The values of pH in 1,4-dioxane is observed as 2.15-2.0 and for the concentration of 5% (v/v) oil solutions in 1,4-dioxane, the pH reduced to 2.9 this reveals that the hydrogen ion concentration increases by dissolving the oil in the solvent. Same results are also obtained by titrating the oil solutions against standard sodium hydroxide. As more volume of NaOH consumed to titrate the oil solutions as compared to 1,4-dioxane. It shows that electrolysis reduces the rate of flow and when a strong electrolyte of acidic nature as strong HCl is added to solutions, further a decrement in rate of flow is observed. It is probably due to the increase in the coiling and increases in concentration of monomers and decrease in intermolecular interactions. By adding strong electrolytes of alkaline nature such as NaOH it is observed that with the increase in pH the rate of flow is reduced as compared to acidic medium as in alkaline medium oil molecules form the sodium salt of stearic acid [CH_3─$(CH_2)_{16}$─COONa]. As a result the long chain association is decreasing due to the decrease in intermolecular interactions (Das et al 1983).

Table3: Fluidity parameters a, k, α_1, β_1, α_2, and β_2 of 5%(v/v) Canola oil solution in 1,4-dioxane at various temperatures.

Temp (K)	Fluidity Parameters					
	k	a	α_1	β_1	α_2	β_2
298	0.704	0.3760	0.3853	-0.1233	0.4491	-0.1588
303	0.639	0.3736	0.3534	-0.1273	0.4110	-0.1627
308	0.605	0.3680	0.3308	-0.1274	0.3845	-0.1628
313	0.562	0.3622	0.3119	-0.1338	0.3613	-0.1694
318	0.557	0.3330	0.2698	-0.1189	0.3192	-0.1584
323	0.495	0.3514	0.2390	-0.1107	0.2813	-0.1462

Actually the intermolecular attractive forces do not allow free flow of molecules in a liquid and strength of intermolecular forces will be measured of the viscosity of liquid. The greater value of attractive intermolecular forces form aggregated and bulky structures in solutions that rate of flow of liquid enhances the viscosity. While on the other hand repulsive forces break the aggregated molecules in their simplest units and it decreases the viscosity of liquid. The shape and structure of molecules of a liquid play specific role on affecting the rate of flow. Liquid with large irregular shaped molecules are generally known to be more viscous then those with small and symmetrical molecules. Similarly hard symmetrical molecules have less elastic collision amongst themselves. Thus the collisions of large molecules involve the loss of kinetic energy and as a consequence the intermolecular forces determining the molecules tend to stick together. This increases the viscosity of liquids. In this connection Jones-Dole enunciated an equation for the reducing effect of electrolytes on the viscosity of large molecules. This equation represents ion-ion and ion-solvent interactions (Jones et al 1929).

$$\eta / \eta_o = 1 + A\sqrt{C} + B.C \qquad (3)$$

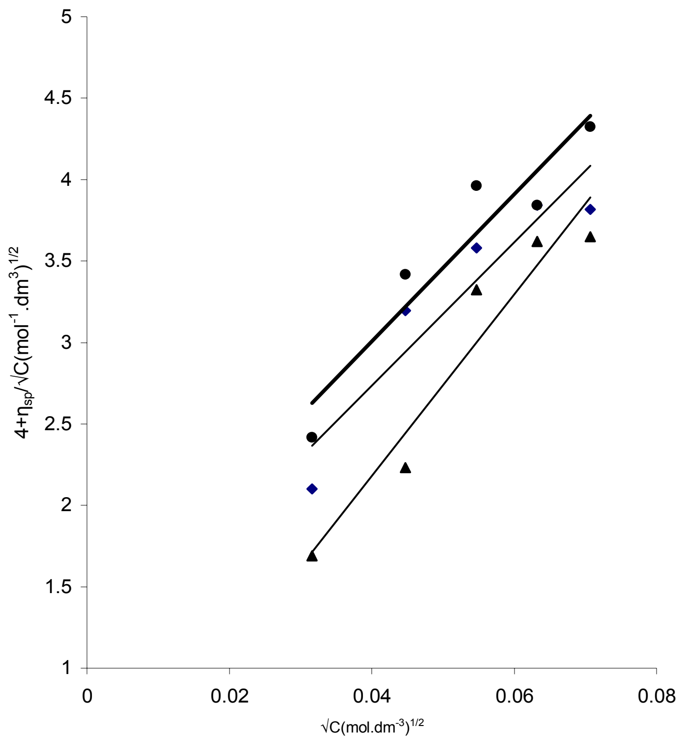

Fig.2: Plot of $\eta_{sp}/\sqrt{C}$ versus $\sqrt{C}$ of Canola oil in electrolytes at 298 K.

Here η / η_o is the relative viscosity, C is the concentration, A and B are the Jones-Dole coefficients representing ion-ion and ion-solvent interactions showing the behavior of electrolytes. The negative values of A-coefficient do not have any significance (Das et al 1997, Saeed et al 2002). The decrease in A-coefficient with the rise in the temperature is due to the thermal agitation at higher temperature and also due to reduction of attractive forces (Saeed et al 2002). However the A-coefficient may be increased with the increase in temperature due to this interpenetration effect (cat ions-cat ions) and (cat ions-an ions) (Falken et al 1932).

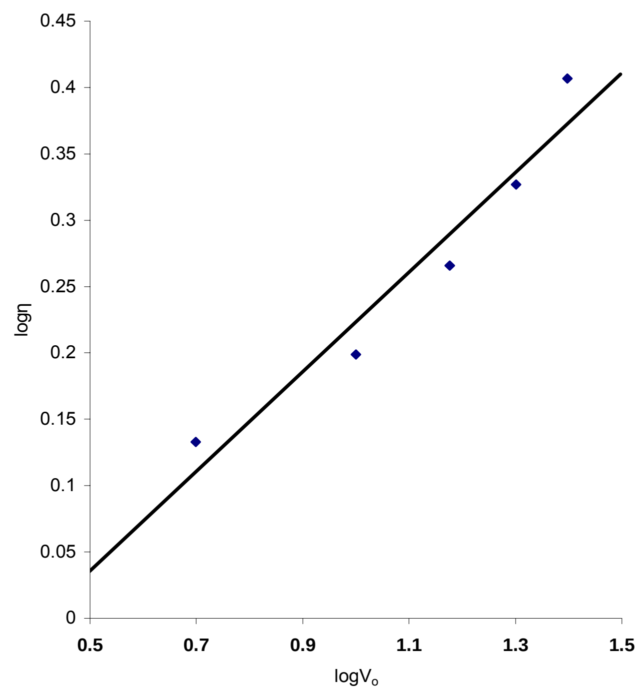

Fig 3: Plot of log η versus log V_o of Canola oil in 1,4-dioxane at 298 K.

Table 2 includes ion-ion and ion-solvent interactions of canola oil with 1,4-dioxane in presence of electrolytes at different temperatures and the results are shown in the form of A and B coefficients. The value of A and B-coefficients were determined graphically (Fig 2) by plotting $\eta_{sp}/\sqrt{C}$ versus $\sqrt{C}$. The intercept and the slope of this plot explain the complete and incomplete dissociation and ion association of electrolytes (A-values) with canola oil and also provides information about atoms related to the salvations of ions (B-values) and their effects on the structure of 1,4-dioxane in the vicinity of oil particles. The results shown in Table 2 indicate the increase in negative values of A-coefficient with temperature (-2.84 to –5.58 for HCl, -1.671 to –5.459 for NaOH and –1.686 to –4.163 for NaCl) ranging at 298-323 K. The increase in negative values of A-coefficient may be due to the agitation at the higher temperature and also shows the dissociation and (partially) ion association of electrolytes in the solvent. But in the case of sunflower (Khan et al, 2005) and maize oil (Khan et al, 2006) the values obtained are irregular showing an incomplete dissociation and ion association of electrolytes in 1,4-dioxane. On the other hand B-values obtained are all positive for HCl, NaOH and NaCl and get increased with rise in temperature. It reveals that electrolytes behave as structure breaker in 1,4-dioxane. The increase of B-coefficient with the rise of temperature further shows that decrease in rate of flow may be due structure of 1,4-dioxane. Distortion of solvent structure is not appreciable (small) which results positive values of B-coefficient. Similar observations were also obtained for the systems of sunflower and maize oil in 1,4-dioxane with strong electrolytes and for the system of sodium citrate solutions in acidic aqueous methanol (Berry et al 1980, Donald et al 1995, Khan et al, 2005).

Fluidity parameters were also determined graphically by using following relations, (Aderson et al 1999):

$$\log \eta = \log k + a \log V_o \qquad (4)$$

$$\eta / V_o = \alpha_1 + \beta \eta \qquad (5)$$

$$1 / V_o = \alpha_2 / \eta + \beta^* \qquad (6)$$

where a, k, α_1, β, α_2 and β^* are empirical constants and these are structural parameters.

Table 4: Energy of activation (ΔE_v), Latent heat of vaporization (ΔL_v) and Molar volume (V_m) of Canola oil (5% v/v) in 1,4-dioxane.

Electrolyte	Energy of Activation	Latent heat of vaporization	Molar volume of oil
$[HCl]10^3$ (mol.dm^{-3})	ΔE_v (kJ.mol^{-1})	ΔL_v (kJ.mol^{-1})	V_m (10 e^8) (dl)
1.0	13.82	34.55	8.90
2.0	13.96	34.90	8.21
3.0	14.03	35.07	7.84
4.0	14.04	35.11	7.31
5.0	14.18	35.47	7.20
$[NaOH]10^3$			
1.0	11.82	29.55	4.35
2.0	11.90	29.76	4.35
3.0	12.11	30.27	3.45
4.0	12.45	31.14	3.36
5.0	12.49	31.24	3.20
$[NaCl]10^3$			
1.0	14.84	37.11	1.33
2.0	14.90	37.27	1.38
3.0	15.18	37.97	1.28
4.0	15.33	38.34	1.10
5.0	15.19	37.99	1.12
Oil Conc. % (v/v)	Without Electrolyte		
5	11.49	28.73	2.80
10	12.39	30.97	2.82
15	12.72	31.80	4.26
20	12.73	31.83	2.68
25	16.25	40.64	14.90

The intercept and slope of the plot log η versus log V_o (Fig 3) gives the values of ‘k’ and ‘a’ respectively whereas the values of α_1, β are obtained from the plots of η / V_o versus η (Fig 4). The plot of $1/V_o$ versus $1/\eta$ (Fig 5) gives the values of α_2 and β^*. These values are given in Table 3. The values of a, k decrease with the increase in temperature, whereas the values of β are negative and irregular decrease or increase in β values are observed. The plot of $1/V_o$ versus $1/\eta$ introduces the values of α_2 and β^*. Here α_2 values get decrease with the rise in temperature whereas β^* values are negative and irregular. All these values are temperature dependent and are structure parameters. Similar results were also obtained for maize and sunflower oil in 1,4-dioxane (Khan et al, 2005).

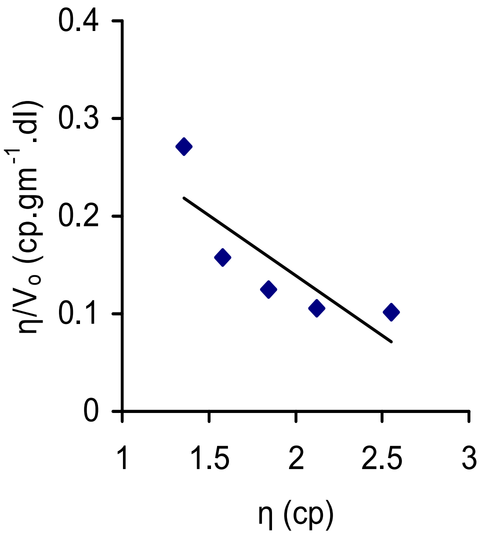

Fig 4: Plot of η / V_o versus η of Canola oil in 1,4-dioxane at 298 K.

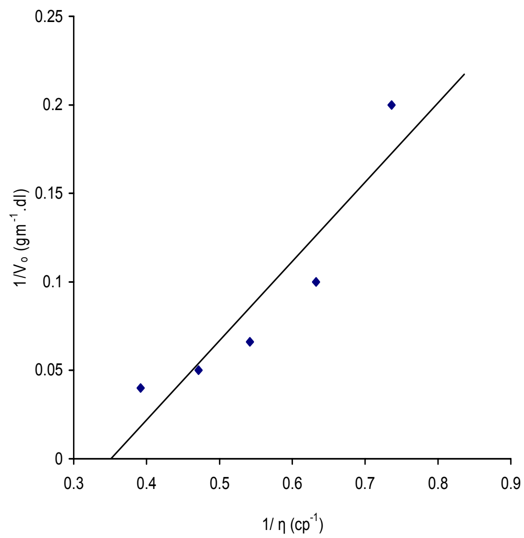

Fig 5: Plot of 1 / V_o versus 1 / η of Canola oil in 1,4-dioxane at 298 K.

Table 4 summarizes the values of energy of activation (ΔE_v), latent heat of vaporization (ΔL_v) and molar volume of oil (V_m) were obtained for canola oil 1,4-dioxane without using any electrolyte. The values of energy of activation (ΔE_v) and molar volume of oil (V_m) were determined from the slope and intercept of the linear plot log η versus 1/T (Fig 6) respectively. The values of slope obtained was used in calculating determining the energy of activation (ΔE_v) using the following relations (Atkins 1990, Berry et al 1980):

$$\Delta E_v = \text{Slope} \times R \times 2.303 \qquad (7)$$

Whereas the latent heat of vaporization (ΔL_v) was determined from the relation:

$$\Delta E_v = 0.4\, \Delta L_v \qquad (8)$$

Similarly the molar volume of oil (V_m) was determined from the following relation:

$$\log V_m = \log (h\, N_A - C) \qquad (9)$$

Here h, N_A and C respresent Planck's constant, Avogadro number and intercept of the plot of log η versus 1/T respectively. The values of energy of activation (ΔE_v) and latent heat of vaporization (ΔL_v) get increased with increase in oil concentration whereas change in molar volume of oil (V_m) is irregular with concentration. The numbers of molecules of oil are greater at higher concentration. The aggregation of molecules produces hindrance in the mobility of molecules. This makes difficult to provide vacant sites in the solvent matrix resulting high energy of activation (ΔE_v) and latent heat of vaporization (ΔL_v). The molar volume of oil (V_m) generally decreases with increase in concentration of oil. Table 8 shows the observations obtained in the presence of electrolytes. These results reveal that addition of electrolyte affects the mobility of oil solution. The concentration of electrolyte generally increases the activation energy (ΔE_v) and latent heat of vaporization (ΔL_v). Increase or decrease of molar volume (V_m) is not regular in the values obtained in the presence of NaCl but electrolytes HCl and NaOH gives the values which get decreased with the increment of electrolyte concentration.

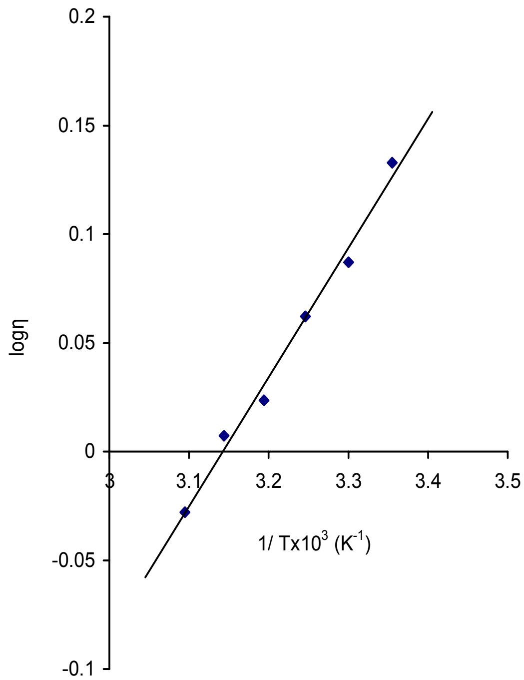

Fig 6: Plot of log η versus 1 / T (K^{-1}) of 5% Canola oil in 1,4-dioxane.

Conclusion: In brief the unsaturation of fatty acid present in canola oil causes the changes of various parameters determined in the presence and absence of strong electrolytes. The behavior of electrolytes on the viscosity of canola oil solution was dealt with Jones-Dole equation in terms of ion-ion and ion-solvent interactions and concluded that electrolytes like HCl, NaOH and NaCl behave as structure breaker in oil-1,4-dioxane system.

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