THE THERMODYNAMIC PARAMETERS OF OLIVE OIL IN THE PRESENCE OF STRONG ELECTROLYTES

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Abstract

Viscosity of olive oil solutions is directly proportional to the concentration and inversely proportional to the temperature. Slight increase in viscosity of olive oil dissolved in 1, 4 dioxane was observed upon addition of electrolytes (HCl. NaOH and NaCl). The rise in temperature falls the flow rate of solutions. Moreover electrolytes concentration rises viscosity of olive oil solutions which is due to the existence of unsaturated constituents in olive oil also due to temperate effect. Electrolytes act as structure breaker. Thermodynamic and fluidity parameters of olive oil in 1, 4-dioxane were also determined i.e. latent heat of vaporization, and activation energy. The Physiochemical parameters such as peroxide value (POV), free fatty acid (FFA) Iodine value (I.V) and saponification value (SV) were determined and also investigated the effect of heat on the quality of olive oil.

Introduction

Edible oils and fats are the leading and basic source in human diet (Salunkhe *et al*., 1992). Olive oil is one of the edible oil which is a chief source of fat in the diet of the people adjacent Mediterranean Sea. Olive oil has attracted attention of peoples of Arctic Europe, America and Canada in last few years (Gunstone *et al*., 2011). Olive oil has many health benefits in preventing number of diseases especially heart diseases. Composition of olive oil is mixture of triacylglycerol, free fatty acids, acyl-glycerol (mono- and di), and some non-glycerides. The type of oil i.e. virgin, ordinary and mixture depends on contents of free fatty acid which varies according to the quality of oil. These fatty acids may include eicosanoic acids, heptadecanoic acid linoleic and linolenic acid, Myristic acids, oleic acid, palmitic and palmitoleic acid and stearic acid. Olive oil also contains hydrocarbons fat soluble vitamins, pigment, Sterols, polyphenols phospholipids etc. (Bianco*.* 1998). Due to its importance our interest developed in studying its thermodynamics and fluidity parameters in the manifestation of electrolytes (HCl, NaOH and NaCl). 1, 4-dioxane is used to make solution of oil in order to measure the viscosities of oils and its thermodynamics and also fluidity parameters were studies as varying electrolytes concentration and temperature. The viscosities of olive oil solutions determined by application of known force and resultant deformation rate was measured. (Isdale *et al*., 1976).

Electrolyte's effects of sunflower oil has published previous by (Khan *et al*., 2005). They found that an increase in concentration and temperature will decrease the viscosity of sunflower oil and an increase in electrolyte's concentration directly increase the viscosity of oil. In the present work studied the influence of HCl, NaOH and NaCl strong electrolytes on the olive oil viscosity and also determined the physiochemical parameters i.e. peroxide value, free fatty acid, Iodine value, Saponification value and density.

Material and Method

Reagents

Olive oil (100%) pure from local market Karachi, hydrochloric acid, sodium hydroxide, sodium chloride, oxalic acid potassium hydroxide, idobromine, sodium thiosulphate, potassium iodide, and acetic acid were of analytical grade and purchased from (Merck) while1, 4 dioxane (BDH) were purchased. Distille water used in all experiment.

Instrumentation

pH meter, Water bath(Model: HH-S6), relative density (R.D) bottle, Ostwald viscometer

Method

The physicochemical and thermo properties of olive oil was measured by described following methods, like saponification value (Cd 3–25), iodine value (Cd 1d-92), peroxide value Cd 8–53 refractive index (C7 – 25 (09), free fatty acid value (Ca 5a -40) and viscosity (Khan *et al*., 2005). The above olive oil parameters were determined at temperature range from 298 to 323 K with 5K interval.

The quality of olive oil was analyzed by evaluating physicochemical properties such as density, peroxide value, free fatty acid, iodine value and saponification values. Results are showed in Table 1a. Oil with lower values of density and viscosity are highly appreciable to consumers. In order to plan an advanced technological process these properties are significant parameters. The temperature effect on these properties of olive oil were also studies and results are tabulated in Table 1b.

Viscosity and density

Oils are mix of triglycerides (TGs) and their viscosity depends on the nature of the TGs present in the olive oil. The viscosity changed due to the different arrangement of the fatty acids on the glycerol backbone of the triglyceride molecule. Therefore, viscosity is related to the chemical properties of the oils such as chain length and saturation or unsaturation. Table 1 a shows that at room temperature of $(28 \pm 2^{\circ}C)$. It explains that the viscosity and density decreases with an increase in unsaturation and increases with high saturation and polymerization (Kim *et al*., 2010). Viscosity also depends on sheer stress and temperature. Sheer stress does not have much effect on the storage of oils which are used for edible purposes but the temperature does affect it. Results tabulated in Table 1b revealed that an increase in viscosities was observed for olive oil at different temperature. When the temperature increases the kinetic energy also increases which enhanced the movement of the molecules and reduces the intermolecular forces. The layers of the liquid easily pass over one another and thus contribute to the reduction of viscosity. This phenomenon is also verified by other researchers since oil viscosity depends on molecular structure and decreases with the unsaturation of fatty acids (Kim *et al*., 2010). The densities of olive oil was decreased with the rise in temperature. The densities of oils were related to the standard range of 0.898–0.907 g/ mL approved by the Standard Organization of Nigeria (SON*,* 2000). The results tabulated in Table 1a show that at room temperature of $(28 \pm {}^{\circ}C)$ the values of the densities are 0.917 g/mL for olive oil. It may be due to the π bonds that make the bonding more rigid and rotation between C-C bonds becomes more strenuous.

Peroxide value

Peroxide value (PV) is used as a measure of the extent to which rancidity reactions have occurred during storage it could be used as an indication of the quality and stability of fats and oils (Ekwu and Nwagu, 2004). The peroxide value was also found to increase with the storage time, temperature and contact with air of the oil samples. The PV values tabulated in Tables 1a and b for olive oil range from 3.021– 3.073 meq/kg. Results show that the peroxide values increased (28 \pm °C). The initial PV was found to have occurred around 3.02 meg /kg oil which indicates a relatively good quality of oil. There is a slightly change in PV when the oil was heat. The peroxide value determines the extent to which the oil has undergone rancidity. Peroxide value ranges are closely related to the standard value of 10 meq/kg specified by Standard Organization of Nigeria (SON, 2000) and Nigerian Industrial Standard (NIS, 1992).

Saponification value

Saponification value (SV) is an index of average molecular mass of fatty acid in the oil sample. The SV value obtained for the oil samples in Table 1a showed 155.031 mg KOH/g for olive oil. The values are below the expected range of 195–205 mg KOH/g of oil for edible palm oils as specified by (SON, 2000) and (NIS, 1992). The lower value of saponification values suggests that the mean molecular weight of fatty acids is lower or that the number of ester bonds is less. This might imply that the fat molecules did not interact with each other (Denniston *et al*., 2004).

Iodine value

Iodine value (IV) measures the degree of unsaturation in a fat or vegetable oil. It determines the stability of oils to oxidation, and allows the overall unsaturation of the fat to be determined qualitatively (AOCS, 1993 a,b & c, Asuquo 2012). It was observed that measured iodine values for olive oil is (81.106) g.

Free fatty acid

Free fatty acid formed from hydrolytic decomposition of glycerides to free fatty acid (Abayeh *et al*., 2011). There was no significant change observed in olive oil as increase in temperature as shown in Table 1a and b. All these physicochemical parameters such as viscosity, density, peroxide value, iodine value, free fatty acid and saponification values are qualitative properties of oil and do not indicate the position of the double bonds or the amount of olefin carbon but rather it provides an overall status of unsaturation of the oil so it is not possible to point out the position of double bond(s) which are more susceptible to oxidation (Knothe and Dunn, 2003).

Properties	Olive oil
Density (g/ml)	0.917
Saponification value (mg)	155.031
Iodine value (g)	81.635
Peroxide value (meq/kg)	3.021
Free fatty acid (mgKOH/g)	0.241

Table 1a. Physicochemical properties of oils at room temperature $(28 \pm 2^{\circ}C)$.

Thermodynamic

Earlier thermodynamics parameters were evaluated in the absence of electrolytes like HCl, NaOH and NaCl. (Saeed *et al*., 2004) but in present work thermodynamic parameters are determined in the presence of electrolytes i.e. strong electrolytes. The parameters were calculated with and without electrolyte in the presence of 1, 4 dioxane as solvent at diverse temperature ranges from (298 to 323K) through Ostwald type viscometer table 2.0, summarize viscosities at different concentration with an increase of 5% v/v i.e. (5mol/dm^3) to 25mol/dm^3) solution of olive oil in 1, 4 dioxane at (298 to 323 k) temperature with increase of 5 K. Obtained results revealed, viscosity of olive oil solutions is directly proportional to the concentration and inversely proportional to the temperature. The graph represents the influence of concentration and temperature of olive oil solution on viscosities (Fig.1). The same influence of concentration and temperature on viscosities of sunflower oil solution at same conditions were also observed by (Khan *et al.*, 2005). The concentrations influence of hydrochloric acid $(0.0015 \text{ mol/dm}^3)$ on viscosity of olive oil solution 5% at diverse temperatures were précised in Table 2.1. The observations indicated that viscosity of olive oil solutions enlarged through addition of electrolyte of different concentrations. The viscosities of olive oil solutions without HCL (strong electrolyte) demonstrated that upon addition of HCl viscosities of oil solution drops with a minor change due to the increase the space among oil molecules reason to increase the rate flow. The viscosity of olive oil solution falls by increase temperature in the presence of electrolyte. Likewise sodium hydroxide and sodium chloride acts in same manner summarize in table 2.2 and 2.3. It was observed that electrolyte HCl was additional effective reducing electrolyte than sodium hydroxide and sodium chloride.

Olive oil consists of free fatty acid i.e. oleic acid and some other acids in trace amount (Williams, 1966). The viscosity rise at diverse temperatures with and without electrolytes is because of unsaturation existing in the olive oil. The possible cause for this variation is the radical's formation by influence of temperature. These radicals may activate the compounds present in the olive oil and results the cluster of acid molecules and hence increase in viscosity. It is also noticed that thick and viscous mass of olive oil obtained on persistent heating due to the presence of unsaturated class of polymerization. All above reasons make the viscous solution. The pH of 1, 4 dioxane was (5.15 - 5.2) and olive oil at different concentration in 1, 4 - dioxane, the drop in pH is $(2.91 - 3.01)$.

HCl (10^3)			Viscosity of (mPas) 5% olive oil solution				
mol/dm ³	Temperature in kelvin (K)						
	298	303	308	313	318	323	
	15.212	14.110	12.772	11.414	10.031	8.485	
2	16.391	15.482	13.330	11.510	10.275	9.534	
3	16.564	15.651	13.505	11.742	10.431	9.490	
$\overline{4}$	16.746	15.833	13.663	11.901	10.592	9.642	
5	17.260	16.325	13.994	12.384	10.756	10.091	

Table 2.1. Viscosity of 5% olive oil solution in the manifestation of electrolyte (HCl).

Table 2.2. Viscosity of 5% olive oil solution in the manifestation of electrolyte (NaCl).

NaCl (10^3)	Viscosity of (mPas) 5% olive oil solution						
mol/dm ³	Temperature in kelvin (K)						
	298	303	308	313	318	323	
	15.242	14.790	13.321	12.062	10.452	9.491	
2	16.441	14.942	13.470	12.214	10.614	9.652	
3	16.414	15.117	13.643	12.387	10.916	9.810	
4	16.572	15.274	13.815	12.545	10.917	9.953	
	17.243	15.595	14.134	12.713	11.079	10.404	

Table 2.3. **Viscosity of 5% olive oil solution in the manifestation of electrolyte (NaOH).**

	Viscosity of (mPas) 5% olive oil solution						
NaOH (10^3) mol/dm ³	Temperature in kelvin (K)						
	298	303	308	313	318	323	
	15.241	14.170	13.581	11.573	10.511	9.602	
2	16.478	15.453	13.705	11.724	10.662	9.754	
3	16.615	15.683	13.914	11.896	10.824	9.912	
4	16.793	15.852	14.082	12.062	10.984	10.061	
	16.988	16.494	14.254	12.383	11.143	10.224	

Table 3: **Coefficient A & B of Jones Dole coefficient.**

The variation in pH shows that the [H] ion concentration was enlarged by dissolving the oil in 1- 4 dioxane (Khan *et al*., 2005, Williams*,* 1966, Adesun and Ipinmoroti *.*1999). The same observation were also perceived on titration of olive oil solutions with NaOH. As excess NaOH consumes to titrate oil solution. The electrolyte decreases the viscosities and upon addition of strong electrolyte of acidic nature (HCl), further reductions in monomer's concentrations and reduction intermolecular forces. On addition of robust electrolyte of basic nature (NaOH), it's detected, the viscosities reduces sharply at higher pH in contrast with acidic medium as in basic medium. Due to intermolecular interaction the long chain connotation was reducing (Shama *et al*., 2004; Falken and vernon. 1932, Jones and Doles. 1929, Robson *et al*., 1988, Saeed *et al*., 2002). It was noticed similar behavior in sunflower oil solution. The attractive intermolecular forces do not permit a free movement of oil molecules in a liquid. The intermolecular forces strength was determined the viscosity of a fluid. The greater values of attractive molecular forces made gathered and massive configuration in solution hindrance the movement of liquid and growth the viscosity. The aim of current study to observe the effect of an electrolytes are additional to diluted solution of olive oil consuming 1- 4 dioxane. There are two kinds of relations observed that are (ion-ion) and (ion-solvent). These relations illuminated in form of Jones-Dole coefficients (Jones and Dole. 1929).

$$
\eta_{sp} = A (C)^{1/2} + B
$$
 (1)

Now "**η** _{sp}" represent the specific viscosity, [C] represent the concentration, [A] & [B] are Jones Dole constants demonstrating ion-ion and ion solvent relations, viewing the actions of electrolyte. B - Constant delivers info around the solvation of ions and their influence on the structure of the solvent in the part of oil particles. On the other hand A-constant expresses us nearby the full or partial separation and ion connotation of electrolytes with olive oil in 1,4 dioxane (Salunkhe *et al*., 1992).

The "A" and "B" coefficients were calculate graphically by plotting $\eta_{\rm sn}/C^{1/2}$ against $C^{1/2}$. The intercept and the slope used to determine the values of "A" and "B" respectively.

Table 4: Fluidity parameters of 5% olive oil solution at diverse temperature.

Fluidity parameters							
Temperature (K)	K	a	α_1		\mathbf{a}_2	B*	
298	0.670	0.279	0.747	-0.232	0.655	-0.385	
303	0.550	0.265	0.636	-0.242	0.636	-0.277	
308	0.500	0.258	0.520	-0.245	0.595	-0.210	
313	0.452	0.249	0.432	-0.254	0.379	-0.173	
318	0.380	0.232	0.382	-0.259	0.333	-0.166	
323	0.275	0.221	0.321	-0.263	0.316	-0.152	

The "A" & "B" vales were calculated graphically and summarized in table 3. It has found that value of "A" coefficient was irregular for different ratio of olive oil in 1, 4-diaxone at diverse temperatures. Same observations were also found in the presence of electrolytes. The A-coefficient value decreased with increase in temperature is because A-constant value rest on upon the obstinate effect of the space lattice. At higher temperature demonstrate the less effect. It is due to the space lattice is less disseminated by thermal difference. The negative values increase possibly because to the distress at upper temperatures (Robson. 1988, Saeed *et al*., 2002, Salunkhe *et al*., 1992, Das and Hazra. 1997). Same result was also found in oil of sunflower in solvent 1, 4 dioxane (Khan *et al*., 2005).

The B-coefficient describes the ion solvent relations. The values of B-constant affected by temperatures and solvent. The B- constant show the positive values in presence of electrolytes and also observe that B value increase by increment of temperatures. Same behavior was also perceived in case of NaOH and NaCl shows in table 3.0. The value of B-constant increased by increase of temperatures shows that electrolytes act as structure wave in solvent. The higher value of B-constant further demonstrate that viscosity drop because to structure of solvent. The values of B-constant positive shows an alteration of solvent structure is minor. Same observations were also found for sodium citrate dissolve in acidic aqueous methanol (Berry et al., 1980). It has also reported in sunflower oil in 1, 4 dioxane systems in presence of electrolytes (Khan et al., 2005). The result of temperature were also found in expressions of fluidity constant. The fluidity constant were calculated by using following equations (Adesun and Ipinmoroti*.* 1999).

Here β , β^* α , α_2 , k, a, are fluidity constants and these parameter are structural parameters. The intercept and slope represent the 'k' and 'a' which were found by plot between (logn and logVo). The, α , β_1 and α_2 , β^* values were found by plot (η / Vo against η), (1/Vo against 1/η). The fluidity parameters values were précised in (Table 4.0). The results demonstrate that all parameters are temperature effected values of 'k' and 'a' drop with increase of temperatures. Like ' α_1 ' also reduce with increase in temperature. The value of negatively increase of 'β' with rise in temperature. Both constant parameters ' α_1 ' and 'β₁' are dependent on temperature. It has also observed that value of ' α_2 ' reduced with increase in temperatures with a variance of 5 K. The β^* ' show value negatively decrease. These constant parameters termed as structural parameters.

Graphically calculated activation energy and latent heat of vaporization for olive oil in 1, 4 diaxone. The activation energy for olive oil as calculated and graph was plotted between (log η against 1/T) shown in (Fig. 1). By using slope (equation 5) calculated energy of activation (Berry *et al*., 1980, Atkins, 1990):

 $\Delta E_v = 2.303 \text{ V} \times R \times \text{Slope}$ (5) Latent heat of vaporization (ΔLv) was found with the follwing relation. $\Delta E_v = 0.4 \Delta L_v$ (6)

Fig .1. graph of log η against 1/ T.

Conclusion

The electrolytes and temperature effects the viscosity of olive oil solution found that electrolytes act as structure breaker. The physiochemical properties revealed that olive have the health protective at repeated heated. The present research forwarded to enhance the quality of olive oil and give the public awareness.

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