



**STUDIES ON THE MOLECULAR INTERACTIONS IN THE MIXTURES OF
ANTIFUNGAL, PHARMACEUTICAL INTERMEDIATE AND DISINFECTANT
THROUGH DIELECTRIC PARAMETERS**

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ABSTRACT

The molecular interactions of the binary mixtures of anti-fungal - caprylic acid and pharmaceutical intermediate - valeric acid in disinfectant- o-cresol are studied by determining the dielectric parameters such as Kirkwood correlation factor, Excess permittivity, Bruggemann factor and Dipolar excess free energy. These parameters have been calculated from the experimentally measured values of capacitance and refractive index of mixtures, at temperatures 303K, 313K and 323K. In the above studied systems, existence of short and long range, homo and hetero interactions are identified. These interactions are found to be concentration and temperature dependent. The hetero interaction results in the formation linear as well as closed multimers in the mixture. Due to the existing interactions, structural changes are found to take place.

KEYWORDS: candida albicans, fungal yeast, antifungal, disinfectant, pharmaceutical intermediate, caprylic acid, valeric acid.

INTRODUCTION

Many people are plagued by yeast infections, called as Candida Albicans. They may occur in the mouth, digestive tract, or really anywhere that's accommodating to fungus.^[1] It presents naturally in the human gut; Our gut is also full of natural bacteria that feed on the yeast and so keep levels to a low number and stop it from becoming a problem. The yeast becomes problematic when it grows beyond normal levels and spreads throughout the gastrointestinal tract, into the bloodstream and from there throughout the body. The yeast then does something remarkable into fungus. This fungus now settles itself into the tissue and a fungal colony quickly spreads. The risk for the Candida fungus is the human immune system. In this study, o-cresol has been used as a solvent and caprylic acid and valeric acid as solute. Caprylic Acid is a potent antifungal that kills Candida cells, as well as restoring your stomach acidity to its normal levels. Natural antifungals like caprylic acid work best in combination, as this prevents the Candida yeast from adapting to a single treatment. So we can combine Caprylic Acid with other natural antifungals like oregano oil, garlic and grapefruit seed extract. o-cresol is used as a solvent, disinfectant, and chemical intermediate.^[2] It is also used in the preparation of antioxidant and muscle relaxant, called as carvacrol^[3] and Mephenesin. Both are derived from alkylation of o-cresol with propylene.^[4] The chemical intermediate valeric acid is used to manufacture flavors and perfumes,

synthetic lubricants, agricultural chemicals, and pharmaceuticals.^[5,6] so that, compounds used as medicines are most often mixture of organic compounds. Therefore it is seemed important to examine the molecular interaction studies on the mixture of organic liquids. Dielectric studies are of great help in the assignment of the molecular structure or configurations, particularly those of organic compounds and also helps to detect the formation and composition of complexes in them. The molecular complex formation can be investigated by studying static permittivity (ϵ_{om}), the static permittivity at high frequency ($\epsilon_{\infty m}$), often represented by the square of refractive index corresponding to sodium D-line, Kirkwood correlation factor (g), Excess permittivity (ϵ^E), Bruggemann factor (f_b) and Dipolar excess free energy (ΔF^E).^[7] The objective of this paper is to investigate the molecular interaction between acid and alcohol molecules through dielectric study at temperatures 303K, 313K and 323K. It makes one to understand the solute-solvent interaction and liquid structure.

THEORY

The determination of the structure and properties of associated liquids could provide deeper insight into the phenomena of the molecular interactions and is of great importance in Biology and Chemical Physics. The IR and NMR spectroscopic methods were extensively used

for determining the nature of association. However, these methods could give only circumlocutory information regarding the alignment of neighboring molecules. This vital information could be obtained from dielectric measurements by virtue of its influence on the correlation between the permanent dipole moments in such a molecule. There are various mixture formulae with which one can correlate dielectric parameters with molecular activities in liquid.

The Kirkwood model

The Kirkwood correlation factor is a measure of the short- range interaction between the components in the liquid mixtures. For pure liquids and liquid mixtures, it can be described by the following expression.^[8-11]

$$\frac{4\pi N \mu^2 \rho}{9kTM} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (1)$$

$$\frac{4\pi N \left(\frac{\mu_A^2 \rho_A}{M_A} X_A + \frac{\mu_B^2 \rho_B}{M_B} X_B \right) g^{eff}}{9kT} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (2)$$

$$\frac{4\pi N \left(\frac{\mu_A^2 \rho_A g_A}{M_A} X_A + \frac{\mu_B^2 \rho_B g_B}{M_B} X_B \right) g_f}{9kT} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (3)$$

Where μ is the dipole moment in the gas phase, ρ is the density at temperature T , M is the molecular weight, k is the Boltzmann constant, N is the Avogadro's number, ϵ_0 is the static permittivity and ϵ_∞ is the static permittivity at high frequency, often represented by the square of refractive index corresponding to sodium D-line. X is the volume fraction and suffices m , A and B represents mixture, liquid A and liquid B respectively. The departure of Kirkwood correlation factor from unity is an indication for the molecular association. It means that if $g > 1$ indicates the parallel orientation among the dipoles, $g < 1$ indicates the anti - parallel orientation among the dipoles and $g = 1$ represents an equilibrium between the multimers or non - association among the dipoles.

Excess permittivity (ϵ^E)

The excess static permittivity is used to explain the formation of multimers in the mixture.^[12-13] It is defined as,

$$\epsilon^E = (\epsilon_{0m} - \epsilon_{\infty m}) - [(\epsilon_{0A} - \epsilon_{\infty A}) X_A + (\epsilon_{0B} - \epsilon_{\infty B}) X_B] \quad (4)$$

The excess permittivity provides qualitative information about multimer formation in the mixture as given below. If $\epsilon^E = 0$ indicates that there is no interaction between the unlike molecules.

$\epsilon^E < 0$ indicates the interaction between the molecules in such a way that the effective dipoles get reduced. The two liquids mix in such way that the mixture may form multimers leading to the less effective dipoles.

$\epsilon^E > 0$ indicates that the two liquids interact in such a way that the effective dipoles increase. This may be due to the formation of monomers and dimers.

Bruggeman factor (f_B)

The Bruggeman factor is another parameter which may be used as an indicator of hetero interaction. The Bruggeman factor f_B is given by^[14],

$$f_B = \left[\frac{\epsilon_{0m} - \epsilon_{0B}}{\epsilon_{0A} - \epsilon_{0B}} \right] \left[\frac{\epsilon_{0A}}{\epsilon_{0m}} \right]^{1/2} = (1 - X_B) \quad (5)$$

From equation (5), a linear relationship is expected when plotted f_B against X_B . Any deviation from this linear relation indicates molecular interactions. It is practically observed that in our experimental data for binary mixtures do not fit well with equation (5). To fit the experimental data, the equation (5) has been modified

$$f_B = 1 - [a - (a - 1)X_B] X_B \quad (6)$$

Where a is a numerical fitting parameter known as Bruggeman parameter. The value of a contains, information regarding the nature of interaction between solute and solvent, as follows.

$a > 1$ indicates that the effective microscopic volume of solvent gets more than actual volume. The solute exerts a repulsive force in the system.

$a < 1$ indicates that the effective microscopic volume of solvent gets less than actual volume. The solvent exerts an attractive macroscopic force in the system.

$a = 1$ indicates no change in effective microscopic volume of the system and corresponds to the ideal Bruggeman mixture factor.

Dipolar excess free energy (ΔF^E)

The excess Helmholtz free energy of mixing ΔF^E is given by^[15],

$$\Delta F^E = -\frac{N}{2} \left[\sum_{i=A,B} \mu_i^2 X_i (R_{ij} - R_{j0}) + \sum_{i=A,B} \mu_i^2 X_i^2 (g_{ii} - 1)(R_{ij} - R_{j0}) + X_A X_B \mu_A \mu_B (g_{AB} - 1)(R_{ij} + R_{ji} - R_{j0} - R_{i0}) \right] \\ = \Delta F_0^E + \Delta F_{rr}^E + \Delta F_{ab}^E \quad (7)$$

This first term ΔF_0^E in equation (7) represents the excess dipolar energy due to long-range electrostatic interaction. The second term ΔF_{rr}^E gives the excess dipolar energy due to short-range interaction between identical molecules and The third term ΔF_{ab}^E gives the excess dipolar energy due to short-range interaction between dissimilar molecules.

The term R_{fro} and R_{fr} which give the reaction field parameters in the pure liquid and in the mixture, are given by,

$$R_{fro} = \frac{8\pi N}{9Vr} \frac{(\epsilon_r - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_r + \epsilon_{\infty r})} \\ R_{fr} = \frac{8\pi N}{9Vr} \frac{(\epsilon_r - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_{0m} + \epsilon_{\infty r})}$$

It gives excess thermodynamic functions in binary mixtures that take into account the contribution due to both short-range and long-range dipolar interactions between both like and unlike molecules is adopted for polar-nonpolar mixtures.

MATERIALS AND METHODS

Compounds used in the present study were of AR grade and were all procured from SRL, India. The static permittivity ϵ_{om} at 1 KHz was measured using a digital VLCR-7 meter supplied by M/S Vasavi electronics, India, after calibrating it for standard liquids like carbon tetrachloride, benzene, toluene and chlorobenzene. The permittivity at optical frequency ϵ_{om} was obtained by squaring the refractive Index for sodium D-line, which was measured with the help of an Abbe's refractometer. The uncertainties in static permittivity, refractive index and density were ± 0.0005 , ± 0.0002 and ± 0.0001 g/cc respectively. All measurements were made at 303 ± 1 K,

and 323 ± 1 K using a water circulating thermostat arrangement.

RESULTS AND DISCUSSION

The values of dielectric parameters such as static permittivity (ϵ_{om}), the static permittivity at high frequency (ϵ_{om}), often represented by the square of refractive index corresponding to sodium D-line, Kirkwood correlation factor (g), Excess permittivity (ϵ^E), Bruggemann factor (f_B) and Dipolar excess free energy (ΔF^E) for the binary mixtures caprylic acid + o-cresol and valeric acid + o-cresol are reported in Tables 1-2 at 303K, 313K and 323K. Persual of the tables 1-2 shows that static permittivity value increases with the increasing concentration of the alcohols.

Table 1: Values of ϵ_{om} , ϵ_{om} , g^{eff} , g_f , ϵ^E , f_B , ΔF_0^E , ΔF_{rr}^E , ΔF_{ab}^E and ΔF^E of binary mixtures of Caprylic Acid with o-cresol as a function of mole fraction at 303K, 313K and 323K.

T/K	X ₂	ϵ_{om}	ϵ_{om}	g^{eff}	g_f	ϵ^E	f_B	ΔF_0^E /Jmole ⁻¹	ΔF_{rr}^E /Jmole ⁻¹	ΔF_{ab}^E /Jmole ⁻¹	ΔF^E /Jmole ⁻¹
303	0.00	6.6380	2.3553	1.30	1.00	0.0000	1.00	0.00	0.00	0.00	0.00
	0.10	6.3410	2.3137	1.23	1.05	0.1345	0.95	-51.83	12.08	-3.15	-42.90
	0.20	6.1250	2.2258	1.22	1.17	0.3875	0.90	-126.71	37.38	-18.06	-107.39
	0.30	5.0450	2.1963	0.92	1.00	-0.2592	0.69	-58.47	65.88	-0.36	7.05
	0.40	4.5860	2.1653	0.79	1.00	-0.2992	0.59	-75.34	94.26	0.25	19.18
	0.50	4.3430	2.1421	0.72	1.06	-0.1404	0.54	-135.75	132.12	-2.78	-6.40
	0.60	3.8570	2.1243	0.58	1.02	-0.2128	0.42	-112.53	144.92	-0.07	32.32
	0.70	3.5330	2.0817	0.49	1.08	-0.1052	0.34	-121.17	158.67	2.11	39.61
	0.80	3.2360	2.0301	0.42	1.20	0.0391	0.26	-124.14	160.09	9.18	45.12
	0.90	2.8580	1.9954	0.31	1.23	0.0725	0.16	-115.34	133.05	9.36	27.07
1.00	2.3450	1.9449	0.15	1.00	0.0000	0.00	0.00	0.00	0.00	0.00	
313	0.00	6.5570	2.3247	1.35	1.00	0.0000	1.00	0.00	0.00	0.00	0.00
	0.10	6.2600	2.3077	1.25	1.03	0.0969	0.94	-47.59	12.51	-1.86	-36.95
	0.20	6.0440	2.2210	1.24	1.14	0.3336	0.90	-117.33	35.93	-14.11	-95.52
	0.30	4.9370	2.1954	0.92	0.96	-0.3541	0.67	-41.00	66.06	2.79	27.85
	0.40	4.5320	2.1633	0.80	0.96	-0.3524	0.58	-59.80	90.37	2.12	32.69
	0.50	4.3160	2.1369	0.74	1.02	-0.1788	0.53	-118.76	122.07	-1.00	2.31
	0.60	3.8030	2.1214	0.58	0.96	-0.2924	0.40	-86.05	130.02	-0.25	43.71
	0.70	3.5060	2.0779	0.50	1.02	-0.1702	0.32	-95.19	139.16	0.55	44.52
	0.80	3.2090	2.0275	0.43	1.10	-0.0402	0.24	-93.14	134.54	5.22	46.62
	0.90	2.8310	1.9895	0.31	1.08	-0.0193	0.13	-77.20	99.44	3.62	25.86
1.00	2.4260	1.9421	0.19	1.00	0.0000	0.00	0.00	0.00	0.00	0.00	
323	0.00	6.4220	2.3080	1.36	1.00	0.0000	1.00	0.00	0.00	0.00	0.00
	0.10	6.1520	2.2970	1.27	1.03	0.1005	0.94	-46.04	11.96	-1.69	-35.77
	0.20	5.9900	2.1972	1.28	1.16	0.3861	0.91	-116.45	33.14	-15.49	-98.80
	0.30	4.9100	2.1659	0.96	0.98	-0.2841	0.67	-40.10	63.26	1.13	24.29
	0.40	4.5050	2.1430	0.83	0.97	-0.3092	0.58	-55.12	85.81	1.36	32.05
	0.50	4.2890	2.1263	0.76	1.02	-0.1641	0.53	-109.58	113.93	-0.84	3.51
	0.60	3.7760	2.0840	0.61	0.98	-0.2671	0.39	-73.30	119.70	-0.25	46.15
	0.70	3.4790	2.0332	0.54	1.03	-0.1550	0.31	-78.37	125.28	1.18	48.09
	0.80	3.1820	1.9954	0.45	1.09	-0.0549	0.23	-72.11	116.92	4.80	49.61
	0.90	2.7770	1.9875	0.30	0.96	-0.1101	0.10	-41.30	70.98	-1.70	27.98
1.00	2.4800	1.9402	0.22	1.00	0.0000	0.00	0.00	0.00	0.00	0.00	

Table 2: Values of ϵ_{0m} , $\epsilon_{\infty m}$, g^{eff} , g_f , ϵ^E , f_B , ΔF_0^E , ΔF_{rr}^E , ΔF_{ab}^E and ΔF^E of binary mixtures of Valeric Acid with o-cresol as a function of mole fraction at 303K, 313K and 323K.

T/K	X ₂	ϵ_{0m}	$\epsilon_{\infty m}$	g^{eff}	g_f	ϵ^E	f_B	ΔF_0^E /Jmole ⁻¹	ΔF_{rr}^E /Jmole ⁻¹	ΔF_{ab}^E /Jmole ⁻¹	ΔF^E /Jmole ⁻¹
303	0.00	6.6380	2.3553	1.30	1.00	0.0000	1.00	0.00	0.00	0.00	0.00
	0.10	6.5030	2.3262	1.33	1.08	0.2810	0.97	-2.48	3.12	-1.24	-0.60
	0.20	6.3950	2.2308	1.51	1.21	0.5934	0.95	-28.22	6.18	-9.08	-31.11
	0.30	6.1250	2.2070	1.56	1.27	0.6945	0.89	-36.11	11.71	-13.77	-38.17
	0.40	5.9360	2.1851	1.62	1.38	0.8909	0.85	-45.81	15.43	-19.32	-49.71
	0.50	5.8010	2.1515	1.74	1.53	1.1459	0.82	-63.35	18.97	-26.30	-70.67
	0.60	5.3150	2.1278	1.70	1.57	1.0356	0.71	-59.99	23.68	-17.73	-54.04
	0.70	4.7210	2.0955	1.57	1.57	0.8407	0.57	-43.29	25.43	-4.34	-22.21
	0.80	4.4780	2.0604	1.69	1.75	0.9729	0.51	-69.32	27.29	1.09	-40.94
	0.90	4.0190	2.0224	1.62	1.87	0.9084	0.39	-74.06	25.69	7.87	-40.50
1.00	2.7500	2.0215	0.74	1.00	0.0000	0.00	0.00	0.00	0.00	0.00	
313	0.00	6.5570	2.3247	1.35	1.00	0.0000	1.00	0.00	0.00	0.00	0.00
	0.10	6.4490	2.3137	1.37	1.08	0.2860	0.98	-4.56	2.91	-1.17	-2.81
	0.20	6.2600	2.2302	1.52	1.18	0.5033	0.94	-23.99	7.78	-7.39	-23.59
	0.30	5.9360	2.2031	1.55	1.22	0.5508	0.87	-27.59	14.17	-10.52	-23.94
	0.40	5.7740	2.1824	1.61	1.33	0.7697	0.83	-39.34	17.16	-15.92	-38.10
	0.50	5.6390	2.1486	1.73	1.48	1.0217	0.80	-57.08	20.05	-22.22	-59.25
	0.60	5.0450	2.1255	1.63	1.45	0.7999	0.66	-44.70	24.58	-10.86	-30.97
	0.70	4.5050	2.0947	1.50	1.46	0.6542	0.53	-30.19	25.50	-0.64	-5.34
	0.80	4.1540	2.0595	1.53	1.56	0.6757	0.43	-47.68	24.77	5.57	-17.34
	0.90	3.6140	2.0195	1.37	1.55	0.5290	0.28	-43.44	19.70	9.17	-14.57
1.00	2.7230	2.0141	0.74	1.00	0.0000	0.00	0.00	0.00	0.00	0.00	
323	0.00	6.4220	2.3080	1.36	1.00	0.0000	1.00	0.00	0.00	0.00	0.00
	0.10	6.3950	2.3037	1.41	1.09	0.3494	0.99	-10.84	0.91	-1.41	-11.34
	0.20	6.1520	2.2293	1.53	1.17	0.4940	0.94	-25.13	7.57	-7.12	-24.69
	0.30	5.7740	2.1981	1.54	1.20	0.4816	0.86	-23.56	15.09	-9.15	-17.62
	0.40	5.5850	2.1806	1.59	1.29	0.6599	0.81	-32.79	18.11	-13.23	-27.92
	0.50	5.3420	2.1398	1.65	1.40	0.8007	0.76	-42.10	21.20	-15.71	-36.60
	0.60	4.6670	2.1220	1.49	1.31	0.4825	0.59	-19.93	25.08	-3.68	1.47
	0.70	4.1540	2.0932	1.35	1.29	0.3512	0.45	-4.13	24.58	3.20	23.66
	0.80	3.9650	2.0581	1.45	1.46	0.5249	0.40	-35.99	22.78	6.59	-6.61
	0.90	3.3710	2.0181	1.22	1.36	0.3140	0.22	-23.93	15.60	7.69	-0.64
1.00	2.6960	2.0034	0.75	1.00	0.0000	0.00	0.00	0.00	0.00	0.00	

Table 3: Values of Bruggeman factor a for the systems at 303K, 313K and 323K.

System	Value of a		
	303K	313 K	323 K
O-Cresol+Caprylic acid	-0.23	-0.08	0.002
O-Cresol+Valeric acid	0.97	1.04	1.05

This implies that the interaction between acid molecule and alcohol molecule is such that, on adding alcohol, spherical aggregates are converted into ellipsoidal aggregates. This results in structural change. Results on similar lines are reported by Shirke et al.^[16] for methyl acetate – alcohol mixtures. Similar conclusions have been drawn by Liakthalikhan^[17] for the mixture of acrylic esters with alcohols. The extent of non-linearity changes from system to system. The extent of non – linearity implies the strength of the hetero interaction is not the same in all the studied systems. In acid – alcohol mixtures value of g^{eff} decreases with increasing concentration of the acids. In pure state, alcohol

molecules exist in multimer state. But when Caprylic acid is added to it, value of g^{eff} increases with increasing concentration of the acid. This implies that interaction is existing between acid and alcohol molecules. In pure state Valeric acid molecules exist as dimers. When Valeric acid is added to alcohol, due to the hetero interaction between acid and alcohol, the dimeric acid molecules got broken up. This may enhance the parallel orientation among the dipoles which is reflected by the increasing value of g^{eff} . This trend seems to be reversed in the mixture of Valeric acid with alcohols. In the mixture of Valeric acid - alcohols, on adding the acid component, value of g^{eff} decreases. In the alcohol rich

region, value of g^{eff} is greater than unity, which goes to confirm the parallel orientation among the dipoles. In acid regions, the hetero interaction is such that value of g^{eff} is less than unity. This implies that the existence of anti-parallel orientation of the dipoles. In Valeric acid mixtures, the interaction between the components is such that the anti-parallel orientations are more favoured. Values of g_f are greater than unity indicating the existence of parallel orientation among the dipoles with increased dipole moment. According to Thenappan et al.^[18], value of g_f less than unity implies that the effective number of dipoles in the mixture is less than the corresponding average value in pure liquids. This suggests that the unlike molecules in the mixtures may form multimer structures through hydrogen bonding in such a way that the effective dipole moment gets reduced. Value of g_f greater than unity suggests that the effective number of dipoles in the mixture is greater than the average number of dipoles in pure liquids. This also implies that the molecules in mixture may form multimer structures through the formation of hydrogen bonding between the unlike molecules in such a way that the effective dipole moment gets increased. Thus deviation of g_f value from unity confirms the association between the unlike molecules. Value of excess free energies were obtained from equation 7. Values of ΔF_0^E , ΔF_{tr}^E , ΔF_{ab}^E and ΔF^E for all the systems taken for investigation at three temperatures are reported in tables 1-2. The contribution to excess free due to various interactions are given in equation 7. Value of ΔF_0^E describes the long range dipole-dipole interaction. Value of ΔF_{tr}^E reflects the short interaction between the molecules due to hydrogen bonding. ΔF_{ab}^E gives information on the hetero association. In alcohol-acid systems, value of ΔF_{tr}^E is positive at all concentrations and varies with concentration of the acids. The variations are shown in figures 1-2. Positive value of ΔF_{tr}^E implies the rupture of H-bondings between the dipoles. As acid concentration increases, value of ΔF_{tr}^E increases. This implies that with increasing concentration, the number of rupture of H-bonds also increases. This may be due to the interaction between acid and alcohol molecules. Results on similar lines have been reported by Thenappan et al.^[19] With increase of temperature, value of ΔF_{tr}^E varies marginally. This may be due to a small change in the random orientation of the dipoles.^[20] In case of alcohol-acid mixtures, in all systems, negative value of ΔF_{ab}^E is observed in the alcohol rich regions and positive value of ΔF_{ab}^E is observed in acid rich regions. This implies that in alcohol rich regions, interaction between the unlike molecules is such that the formation of linear multimers dominate. In acid rich regions, the heterogeneous interaction may lead to the formation of cyclic structures. The magnitude of ΔF_{ab}^E value is a measure of the strength of hetero interaction. Small magnitude of ΔF_{ab}^E indicates that the strength of the hetero interaction is small and is found to be concentration dependent. For caprylic acid + O-Cresol system, at 303K and 313K, value of a is found to be negative. Positive value of a

indicates that there is more number of dipoles in pure liquids than in the mixture. Negative value of a indicates that the effective number of dipoles is greater in the mixture than in pure liquids. Thus the study of Kirkwood correlation factor gives information on the hetero interaction and confirms the resultant H-bonding association between the unlike molecules.

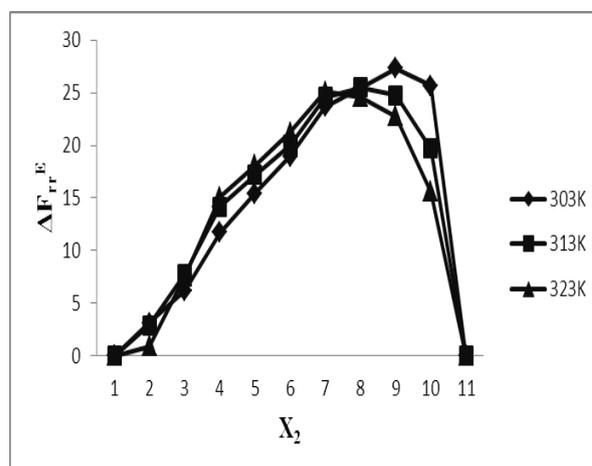


Fig. 1.

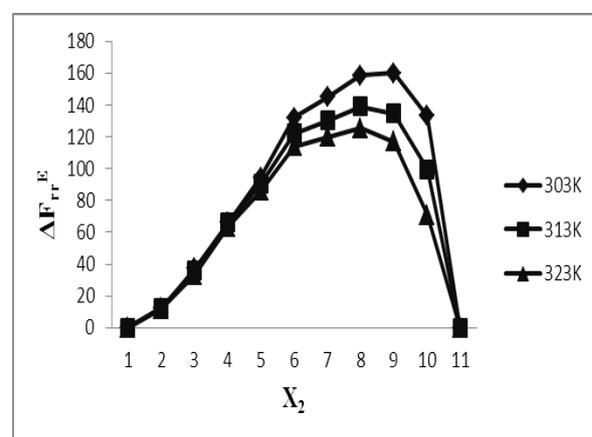


Fig. 2.

CONCLUSIONS

In all the studied systems, at all the range of concentrations studied and at all the three studied temperatures, existence of short and long range, homo and hetero interactions are identified. These interactions are found to be concentration and temperature dependent. The hetero interaction results in the formation linear as well as closed multimers in the mixture. Due to the existing interactions, structural changes are found to take place.

REFERENCES

1. Marcos-Arias C, Eraso E, Madariaga L, Quindós G. In vitro activities of natural products against oral *Candida* isolates from denture wearers. *BMC Complement Altern Med.*, 2011; 11: 119.
2. Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Cresols. Public

- Health Service, U.S. Department of Health and Human Services, Atlanta, GA., 1990.
- Kulisi T, Krisko A, Dragovi-Uzelac V, Milos M, Pifat G. The effects of essential oils and aqueous tea infusions of oregano (*Origanum vulgare* L. spp. *hirtum*), thyme (*Thymus vulgaris* L.) and wild thyme (*Thymus serpyllum* L.) on the copper-induced oxidation of human low-density lipoproteins. *Int J Food Sci Nutr.*, 2007; 58(2): 87-93.
 - Helmut Fiegein "Cresols and Xylenols" in *Ullmann's Encyclopedia of Industrial Chemistry* 2007; Wiley-VCH, Weinheim.
 - Valeric Acid Technical Data Sheet, The Dow Chemical Company, Form No. 327-00048-0812.
 - Campbell, Princess, Science Assessment for Valeric Acid, U.S. Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances, Washington, D.C., June 1, 2005; 2.
 - Prathima A, Karthikeyan S, Prabhakaran M, Thenappan T. Studies on structural properties of the binary mixtures of pharmaceutical intermediates through dielectric investigations. *Int J Pharm Sci and Res.*, 2013; 4(7): 2753-2760.
 - Ajay Chaudhari, Anita Das, Garigipati Raju, Harish Chaudhari, Prakash Khirade, Navinkumar Narain, and Suresh Mehrotra: Complex permittivity spectra of binary mixture of ethanol with nitrobenzene and nitro toluene using time domain technique. *Proceedings of the National Science Council, Republic of China, Part A*, 2001; 25(4): 205-210.
 - Hosamani MT, Fattepur RH, Dhasepande DK, and Mehrotra SC: Temperature and frequency dependent dielectric studies of p-fluorophenyl – acetonitrile – methanol mixtures using time domain reflectometry. *Journal of Chemical Society, Faraday Transactions*, 1995; 91(4): 623-626.
 - Kumbharkane AC, Puranik SM, and Mehrotra SC: Structural of amide – water mixtures using dielectric relaxation technique. *Journal of Molecular Liquids*, 1992; 51: 261-277.
 - Pawar VP and Mehrotra SC: Dielectric relaxation study of liquids having chlorogroup with associate liquids II – 1, 2 dichloroethane with methanol, ethane and 1-propane. *Journal of Solution Chemistry*, 2002; 31: 577-588.
 - Pawar VP, Patil AR and Mehrotra SC: Time – dependent dielectric relaxation study of chlorobenzene with n-methyl formamide from 10MHz to 20GHz. *Journal of Molecular Liquids*, 2005; 121(23): 88-93.
 - Kumbharkane AC, Puranik SM and Mehrotra SC: Dielectric relaxation studies of aqueous N, N dimethyl formamide solution through dielectric relaxation parameters using picosecond time domain technique. *Journal of Solution Chemistry*, 1993; 22: 219-228.
 - Ajay Chaudhari, Harish Chaudhari and Suresh Mehrotra: Temperature dependent dielectric relaxation in solvent mixture at microwave frequencies. *Journal of Chinese Chemical Society*, 2002; 49: 489-494.
 - Dubal SS, Sayyad SB, Patil SS, Khirade PW: Microwave dielectric characterization of diethylene glycol monomethyl ether with N, N-dimethylformamide. *International Journal of Multidisciplinary Research*, 2011; 1(4): 4-10.
 - Shrike RM, Ajay Chaudhari, More NM, Patil PB, Dielectric measurement on methyl-acetate-alcohol mixtures at 288,298,308 and 318k using time domain technique, *J. Chem. Engg. Data*, 2000; 45: 917-919.
 - Liakthalikhan F, FTIR and Dielectric studies of acrylic esters with alcohols and phenol derivatives – Ph.D. thesis – Annamalai University – 2007.
 - Thenappan T and Parthipan G: Dielectric and thermodynamic studies on a binary mixture of anisole with butyric acid (or) caprylic acid, *Philosophical Magazine Letters*, 2008; 88(2): 125-136.
 - Thenappan, T. and Sankar, U., "Study of correlation factors and dipolar excess free energies of esters in benzene," *Journal of Molecular Liquids*, 2006; 126: 1-3, 23-28.
 - Parthipan G and Thenappan T: Studies on molecular interactions and fluid structure of anisole with 2-ethyl- 1-hexanol and decyl alcohol. *Journal of Molecular Liquids*, 2007; 133(1): 1-6.