

Fluid structure and molecular interaction of acetophenone derivatives

K K GUPTA and P J SINGH

Department of Physics, Government MSJ (PG) College, Bharatpur 321 001, India
E-mail: kkguptakkg@indiatimes.com

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Abstract. Dielectric constants of the binary mixtures of acetophenone, *p*-chloroacetophenone, *p*-methylacetophenone and *o*-hydroxyacetophenone in dilute solutions of benzene and 1,4-dioxane were measured at 303 K and at frequency 100 kHz. The low frequency molecular dynamics of acetophenone and its derivatives have been studied by evaluating the Kirkwood correlation factor g , molar polarization P_2 , excess correlation factor δg and excess free energy ΔG . The dipolar contribution to excess free energy of mixing arising from long-range electrostatic interaction and short-range interaction between identical molecules has been assessed separately. The presence of α - and β -multimers in the above systems was identified. The results have been used to interpret the fluid structure in such mixtures.

Keywords. Kirkwood correlation factor; molar polarization; short-range interaction; excess free energy; α - and β -multimers.

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1. Introduction

To understand the fluid structure of acetophenone and its derivatives it is necessary to determine the various dielectric parameters, which are related with inter and intramolecular association and internal rotation. Study of dielectric behaviour of polar molecules and their mixtures [1–4], under varying conditions of composition and temperatures has evoked considerable interest. Dielectric measurements of acetophenone and its derivatives have been made by various workers [1,5–8]. The Kirkwood correlation factor g is a shape-dependent correlation factor and is a measure of short-range intermolecular force leading to dipole–dipole interaction. The value of g is unity for a normal liquid while it departs from unity in an abnormal or associated liquid. On dilution with non-polar solvent, the value of g undergoes a change, which signifies the change in the nature of multimerization.

Acetophenone is a rigid molecule, the acetyl group being in plane with the benzene ring. Recently, the authors [1] studied some rigid polar molecules and their mixtures and found formation of complexes. Singh and Sharma [7] have studied

the binary mixture of *p*-methylacetophenone with DMSO in dilute solutions. A strong hydrogen bond is expected for an acetyl group ortho to the hydroxy atom, because oxygen is a proton acceptor and because of intramolecular hydrogen bond it is sterically favoured in *o*-hydroxyacetophenone.

Earlier the authors [2] have reported the utility of dielectric measurements while studying the molecular interaction in a binary mixture of liquids by assessing some parameters like Kirkwood correlation factor g , molar polarization P_2 , excess correlation function δg and excess free energy of activation ΔG . Study of g can be used as a tool for the interpretation of liquid structure and intermolecular arrangement. With this in view, the present study is to design to extend our scope of investigation to another aspect of molecular dynamics at a microlevel by exploring the probability of multimers formation due to molecular association, long-range and short-range interaction in acetophenone (ACT), *p*-methylacetophenone (PMA), *p*-chloroacetophenone (PCLA) and *o*-hydroxyacetophenone (OHA) in the presence of benzene and 1,4-dioxane.

2. Experimental methods

The dielectric constant ϵ_0 was measured at 100 kHz using a dipole meter by directly measuring the capacitance and calibrating it for standard liquids. The dielectric constant (ϵ_∞) at optical frequency was obtained by squaring the refractive index for sodium D-lines, measured with the help of an Abbe's refractometer. Using a water-circulating thermostat, the temperature was maintained at 303 K. The accuracy of measurement of ϵ_0 and ϵ_∞ are nearly 0.1% and 0.03% respectively.

3. Theory

The Kirkwood correlation factor g has been calculated by the modified Kirkwood-Fröhlich [9] equation for dilute solutions in non-polar solvent.

$$g\mu^2 = \frac{9KT(2\epsilon_m + \epsilon_\infty)^2}{4\pi N f_2 (\epsilon_\infty + 2)^2 (2\epsilon_m + 1)} \times \left[\frac{V(\epsilon_m - 1)}{\epsilon_m} - \frac{3V_1 f_1 (\epsilon_1 - 1)}{2\epsilon_m + \epsilon_1} - \frac{3V_2 f_2 (\epsilon_\infty - 1)}{2\epsilon_m + \epsilon_\infty} \right]. \quad (1)$$

Here ϵ_m is the static dielectric constant of the solution, ϵ_∞ is the square of refractive index at the frequency of D-lines of sodium for pure solute, ϵ_1 is the static dielectric constant of pure solvent, f_1 is the mole fraction of the solvent, f_2 is the mole fraction of the solute, V , V_1 and V_2 are the molar volume of solution, pure solvent and pure solute respectively. K , T and N are Boltzmann's constant, absolute temperature and Avogadro's number respectively. Molar polarization of solutions is

$$P = f_1 P_1 + f_2 P_2 \quad (2)$$

from which the molar polarization of the solute is

$$P_2 = P_1 + \left\{ \frac{(P - P_1)}{f_2} \right\}, \quad (3)$$

where P and P_1 are the molar polarization of the solution and solvent, which are given by

$$P = \left\{ \frac{(\varepsilon_m - 1)}{(\varepsilon_m + 2)} \right\} V; \quad P_1 = \left\{ \frac{(\varepsilon_1 - 1)}{(\varepsilon_1 + 2)} \right\} V_1. \quad (4)$$

The excess Gibb's free energy of mixing ΔG is given by [10]

$$\begin{aligned} \Delta G &= -\frac{N}{2} [f_2 \mu_2^2 (R_2 - R_2^0) + f_2^2 \mu_2^2 (g - 1) (R_2 - R_2^0)] \\ &= \Delta G_0 + \Delta G_{rr}. \end{aligned} \quad (5)$$

The first term ΔG_0 represents the excess dipolar energy due to long-range electrostatic interaction and the second term ΔG_{rr} gives the excess dipolar energy due to short-range interaction between identical molecules.

The terms R_2^0 and R_2 which give the reaction field parameters in the pure liquid and in the mixture respectively, are given by

$$R_2^0 = \frac{8\pi N}{9V_2} \frac{(\varepsilon_2 - 1)(\varepsilon_\infty + 2)}{(2\varepsilon_2 + \varepsilon_\infty)} \quad \text{and} \quad R_2 = \frac{8\pi N}{9V_2} \frac{(\varepsilon_m - 1)(\varepsilon_\infty + 2)}{(2\varepsilon_m + \varepsilon_\infty)},$$

where ε_2 is the dielectric constant for pure solute.

The excess correlation function δg in the binary mixture is given by

$$\delta g = g - (g_1 f_1 + g_2 f_2). \quad (6)$$

4. Results and discussion

The dielectric constants of ACT, PMA, PCLA and OHA in two non-polar solvents, benzene and 1,4-dioxane, measured at 303 K are presented in tables 1 and 2. The experimental data were used to compute the values of the various parameters and their relevant trends are displayed graphically in figures 1–4. Figures 1 and 2 show the Kirkwood correlation factor g plotted against percentage mole fraction of solute in the dilute solutions of benzene and 1,4-dioxane respectively at 303 K. The observed g values greater than and less than unity show that these molecules associate to form multimers with parallel dipole moment and also with antiparallel dipole moment. The observed value of g for all the substances increases with increase of concentration of the solute in benzene environment, while decreases in the case of 1,4-dioxane, which may be due to the fact that in the 1,4-dioxane-rich region the intermolecular H-bonding between the solute molecules and the 1,4-dioxane molecules is strong and as the dilution decreases the H-bonding weakens and hence decreases the g values. Figures 1 and 2 show that the g values are in the order OHA > PCLA > ACT > PMA. Since Cl group is strongly electronegative, it will presumably become negatively charged with respect to benzene ring, while CH_3 group is electron repelling, it will become positively charged with respect to

Table 1. Values of $\epsilon_0, g, P_2, \delta g, \Delta G_0, \Delta G_{rr}$ and ΔG with concentration in benzene at 303 K

f_2	ϵ_0	g	P_2 (CC)	δg	ΔG_0	ΔG_{rr}	ΔG (J/mol)
Acetophenone (ACT)							
0.01518	2.347	0.42	113.76	-0.58	65.53	0.07	65.60
0.04405	2.550	0.49	125.20	-0.52	177.37	0.59	177.96
0.07322	2.765	0.51	126.62	-0.50	274.73	1.51	276.25
0.11228	3.115	0.55	130.67	-0.46	377.71	3.19	380.90
0.16159	3.865	0.69	145.75	-0.32	438.48	5.33	443.81
0.21895	4.795	0.78	148.45	-0.23	467.18	7.69	474.87
0.28934	5.685	0.79	139.69	-0.23	499.38	10.86	510.24
<i>p</i> -chloroacetophenone (PCLA)							
0.02139	2.36	0.52	103.51	-0.49	53.11	0.90	54.01
0.06756	2.62	0.61	112.05	-0.44	153.60	8.27	161.87
0.08944	2.74	0.73	125.14	-0.33	195.54	13.94	202.89
0.11481	3.096	0.82	132.13	-0.27	224.57	20.55	245.12
0.16447	3.680	0.95	140.46	-0.17	271.51	35.59	307.10
0.22701	4.500	1.07	143.15	-0.11	301.37	54.53	355.90
0.26657	4.984	1.10	141.05	-0.11	313.72	66.65	380.39
<i>p</i> -methylacetophenone (PMA)							
0.01332	2.330	0.35	111.68	-0.65	54.31	0.11	54.42
0.04018	2.49	0.40	119.57	-0.61	155.03	0.98	156.02
0.06087	2.64	0.43	125.45	-0.58	223.42	2.14	225.56
0.09272	2.920	0.49	133.77	-0.52	311.16	2.55	315.71
0.13176	3.28	0.53	137.02	-0.49	396.54	8.23	404.78
0.18246	4.180	0.69	155.65	-0.33	428.21	12.31	440.53
0.23316	4.880	0.74	153.57	-0.30	458.73	16.86	475.59
<i>o</i> -hydroxyacetophenone (OHA)							
0.01565	2.340	0.53	106.09	-0.47	45.43	0.40	45.83
0.041694	2.56	0.75	134.64	-0.27	114.56	2.68	117.24
0.075049	2.825	0.77	135.27	-0.26	189.26	7.91	197.17
0.105815	3.340	1.05	159.39	-0.01	223.46	13.27	236.72
0.136264	3.94	1.23	171.59	0.16	243.27	18.60	261.87
0.164738	4.36	1.26	168.25	0.18	263.39	24.34	287.74
0.191380	4.98	1.38	171.62	0.27	262.23	28.15	290.38

benzene ring. Therefore, substituting the chloro and methyl groups in the para position on the acetophenone molecules increases the g value of PCLA, while it decreases the g value of PMA as compared to ACT values. The group moments for chloro and methyl linkage with C are -1.5 D and $+0.4$ D respectively [11], which again support the above conclusion. In the case of OHA, the hydroxy group on the ortho position is capable of forming intramolecular hydrogen bond with acetyl group. Also since oxygen is a proton acceptor, the intramolecular hydrogen bond is sterically favoured in OHA [12]. The observed g values for all the molecules under investigation are higher in 1,4-dioxane than in benzene. This may be due to the fact that in 1,4-dioxane environment oxygen atom establishes hydrogen bonding with the acetyl group of acetophenone and its derivatives.

Figures 1 and 2 also show that the g values in dilute solutions of benzene are less than 1 for ACT and PMA indicating the formation of β -multimers only, while in

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Table 2. Values of ϵ_0 , g , P_2 , δg , ΔG_0 , ΔG_{rr} and ΔG with concentration in 1,4-dioxane at 303 K.

f_2	ϵ_0	g	P_2 (CC)	δg	ΔG_0	ΔG_{rr}	ΔG (J/mol)
Acetophenone (ACT)							
0.03337	2.98	1.61	319.38	0.61	116.99	0.29	117.65
0.05234	3.41	1.56	298.51	0.56	161.35	0.64	161.99
0.07125	3.92	1.58	288.16	0.58	190.47	1.02	191.49
0.09602	4.47	1.52	263.74	0.51	222.25	1.60	223.85
0.14720	5.60	1.44	228.52	0.43	259.10	2.87	261.98
0.20566	6.54	1.31	195.31	0.29	292.59	4.52	297.11
<i>p</i> -chloroacetophenone (PCLA)							
0.03997	2.92	1.96	264.46	0.94	82.53	2.63	85.16
0.08107	3.68	1.90	240.94	0.84	133.82	8.65	142.48
0.12399	4.445	1.84	219.12	0.74	166.93	16.50	183.43
0.17593	5.284	1.75	196.99	0.61	192.60	27.01	219.61
0.22856	5.84	1.60	175.45	0.42	219.66	40.02	259.69
0.27663	5.60	1.59	165.31	0.36	281.08	61.97	343.06
<i>p</i> -methylacetophenone (PMA)							
0.0470	3.12	1.27	276.98	0.26	148.35	1.10	149.45
0.0938	4.04	1.22	246.32	0.20	228.40	3.37	231.77
0.1225	4.38	1.10	219.71	0.08	273.02	5.27	278.29
0.1602	4.94	1.05	201.77	0.03	310.62	7.84	318.46
0.18068	5.24	1.03	194.08	-0.04	326.03	9.28	335.31
0.21335	5.68	1.00	183.05	-0.03	347.45	11.68	359.13
<i>o</i> -hydroxyacetophenone (OHA)							
0.03179	2.92	2.27	318.19	1.24	77.82	1.38	79.20
0.06163	3.58	2.13	284.88	1.09	124.21	4.29	128.51
0.08964	4.42	2.25	277.97	1.20	144.45	7.24	151.69
0.11691	4.86	2.04	246.08	0.98	168.87	11.07	179.94
0.14104	5.36	1.99	230.54	0.91	180.78	14.30	195.08
0.18856	6.28	1.72	196.24	0.62	215.94	22.72	238.67

the case of OHA and PCLA up to 10 and 18% mole concentration respectively, g values are less than 1 indicating the predominance of β -multimers with antiparallel orientation of dipoles and above this concentration β -multimers are converted into α -multimers with parallel dipolar orientation. In the case of dilute solutions in 1,4-dioxane, for all the substances the g values are greater than one indicating the formation of α -multimers only.

Molar polarization P_2 vs. percentage mole fraction plots (figures 3 and 4) in dilute solution of benzene and 1,4-dioxane show that P_2 follows the similar trend as Kirkwood correlation factor g with the variation of concentration and confirms our earlier conclusions. At higher values of g , molar polarization is large while for lower values of g it is small. P_2 values are higher in the 1,4-dioxane solutions than that for benzene solutions suggesting the presence of hydrogen bonding between the solute molecules under investigation and 1,4-dioxane molecules and this bonding becomes more intense in the case of OHA along with intramolecular bonding. Similar results were obtained by other workers [13,14].

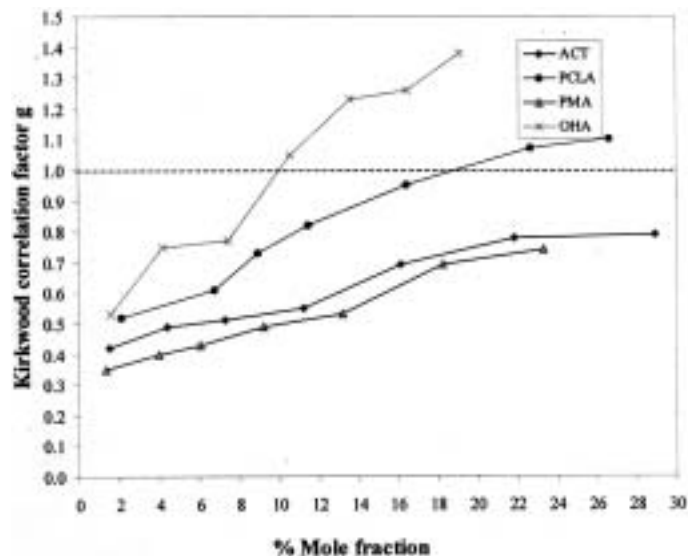


Figure 1. Variation of Kirkwood correlation factor (g) with % mole fraction of solute in benzene solution.

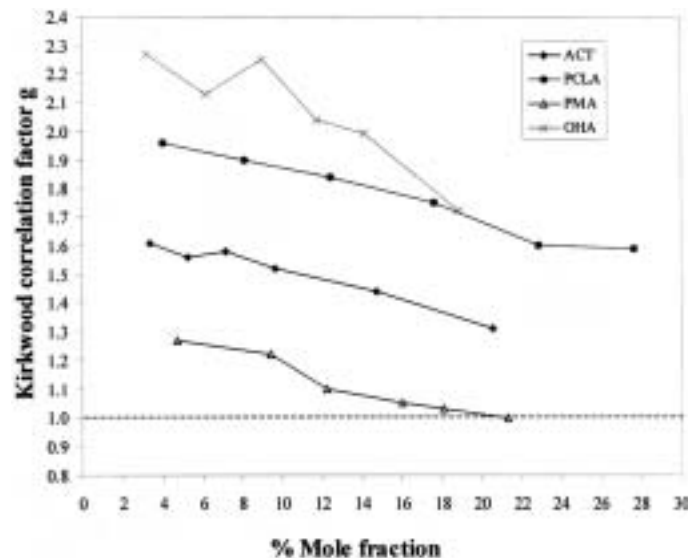


Figure 2. Variation of Kirkwood correlation factor (g) with % mole fraction of solute in 1,4-dioxane solution.

Davis and Douheret [15] introduced a parameter called excess correlation factor δg to represent the departure from ideality. δg values are reported in tables 1 and 2 for the molecules under investigation. Negative δg values indicate the lack of cooperative angular correlation. The δg values for ACT, PCLA, PMA are all negative

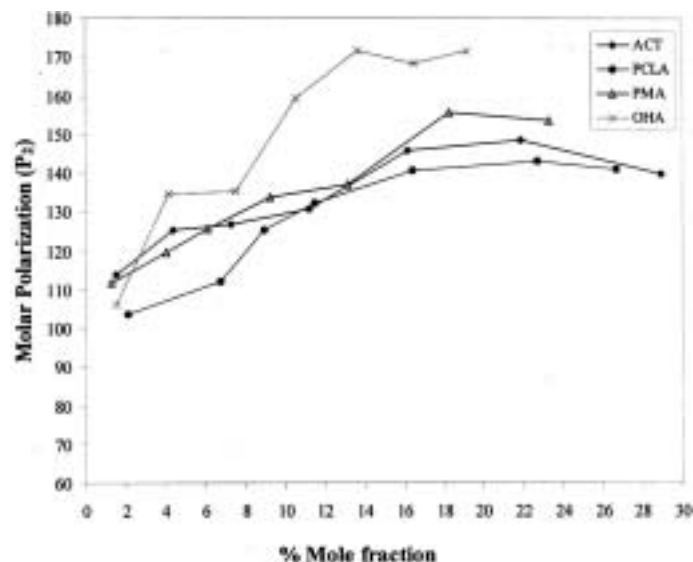


Figure 3. Variation of molar polarization (P_2) with % mole fraction of solute in benzene solution.

and for OHA up to 0.106 mole fraction are negative in dilute solutions of benzene that signify near complete destruction of angular correlation (β -cluster) while for OHA onwards 0.13 mole fraction in benzene and for all molecules in 1,4-dioxane solution δg values are positive, indicating reinforcement of angular correlation (α -cluster).

The excess free energy (ΔG) values for all the compounds under investigation are given in tables 1 and 2. The values of ΔG are observed to be minimum for OHA in both the environments. This support our earlier finding that interaction of OHA is stronger in both the environments than that of other solutes. In dilute solutions the ΔG values reflect the total picture taking into account the excess dipolar energy due to long-range electrostatic interaction and due to the short-range interaction between identical and dissimilar molecules. The ΔG values are positive for all the systems under investigation and increases with the increase in the concentration of the solutes. Swain [16] discussed these long-range and short-range interactions on the basis of ΔG_0 and ΔG_{rr} values for the associated and non-associated molecules. In the present study, ΔG is mainly contributed by ΔG_0 values, which are positive, exhibiting the long-range electrostatic interaction between identical molecules. ΔG_{rr} values are small and positive, which show that anti-parallel alignments in the short-range interaction in identical molecules exist but since ΔG_0 values dominate the ΔG_{rr} values, for the present molecules under investigation long-range interaction in identical molecules predominates.

5. Conclusions

- The extent of hydrogen bonding in different molecules varies with concentration.

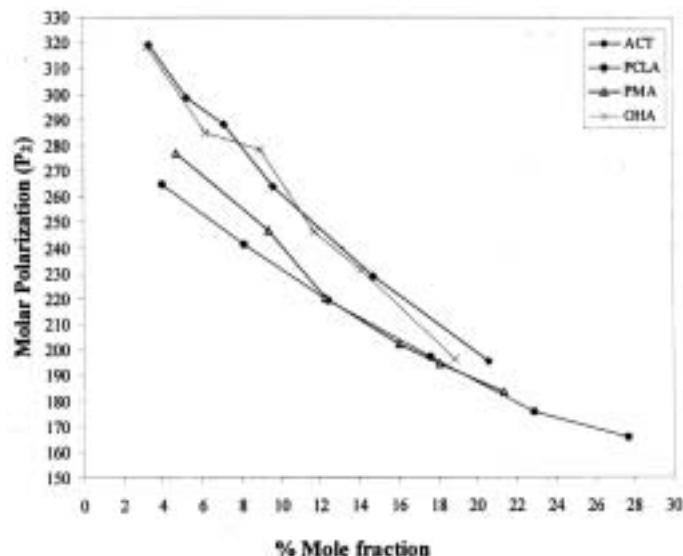


Figure 4. Variation of molar polarization (P_2) with % mole fraction of solute in 1,4-dioxane solution.

- Comparatively higher inter and intramolecular hydrogen bonding is found in *o*-hydroxyacetophenone in dilute solutions of 1,4-dioxane.
- Presence of α - and β -multimers is noticed in all the molecules.
- The positive values of excess free energy suggest that long-range interaction in identical molecules predominates.

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References

- [1] K K Gupta, A K Bansal, P J Singh and K S Sharma, *Indian J. Pure Appl. Phys.* **41**, 57 (2003)
- [2] K K Gupta and P J Singh, *Indian J. Phys.* **B77**, 299 (2003)
- [3] P J Singh and K S Sharma, *Pramana - J. Phys.* **46**, 259 (1996)
- [4] K K Gupta, A K Bansal, P J Singh and K S Sharma, *J. Mol. Liquids* **108**, 79 (2003)
- [5] S L Abd-El Messieh, *J. Mol. Liquids* **105**, 37 (2003)
- [6] R K Khanna and A Bhatnagar, *J. Mol. Liquids* **38**, 63 (1988)
- [7] P J Singh and K S Sharma, *Indian J. Pure Appl. Phys.* **34**, 1 (1996)
- [8] A C Kumbharkhane, S M Puranik, C G A Kode and S C Mehrotra, *Indian J. Phys.* **A74**, 471 (2000)
- [9] C J F Böttcher, *Theory of electric polarization* (Elsevier, Amsterdam, 1973) vol. 1, p. 261

Studies on acetophenone derivatives

- [10] J Winkelmann and K Quitzsch, *Z. Phys. Chemie.* **257**, 746 (1976)
- [11] S Glasstone, *Text book of physical chemistry*, second edition (McMillan India Ltd., 1990) p. 552
- [12] A A Antony and C P Smyth, *J. Am. Chem. Soc.* **86**, 156 (1964)
- [13] R J Sengwa and K Kaur, *J. Mol. Liquids* **82**, 231 (1999)
- [14] R J Sengwa, *Polym. Int.* **45**, 202 (1998)
- [15] M I Davis and G Douheret, *Thermochim. Acta* **104**, 203 (1986)
- [16] B B Swain, *Acta Chim. Hungarica* **118**, 321 (1985)