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Effect of substituents on the Interaction of Some Phenols and Thiophenols with Ketones and Nitrobenzene through Ultrasonic Velocity Measurements

K. GNANASEKARAN* and R. ALAMELU
Department of Chemistry
Annamalai University, Ananamalainagar-608 002, India

Effect of substituents on the intermolecular interactions of phenols with ketones or nitrobenzene has been studied through ultrasonic velocity measurements. *o*- and *p*-Chlorophenols show stronger interaction than phenols which is in agreement with the fact that they are more acidic than phenols. However, *m*-isomer shows abnormal behaviour. In the case of cresols and 2,6-dimethylphenol, the interaction is weak when compared to phenol. Here too, the *m*-cresol does not fall in line with *o*- and *p*-isomers. This study is extended to substituted thiophenols also in place of phenols. A similar trend is seen in the case of chlorothiophenols as found in the case of chlorophenols. In thiocresols, the interaction is so weak that the differences in the strength of interaction among *o*-, *m*- and *p*-isomers do not merit discussion. An explanation based on structural arrangements is offered for the deviation shown by the *m*-isomer from the acidity trend in the strength of interaction.

INTRODUCTION

Measurement of the heats of vaporization[1] of a number of thiophenols indicates the absence or presence of weak hydrogen bonding in thiophenol. Further investigation through magnetic studies[2] reveals that —SH group does not form H-bonding with the $—NO_2$ or the $—\underset{|}{C}O$ group unlike the —OH group of phenol which does interact with ketones or nitrobenzene. This problem has been examined through ultrasonic velocity measurements,[3] which reveal that thiophenol does interact probably through —SH group with ketones or nitrobenzene just as phenol does. However, thiophenol shows weaker interaction than phenol.

EXPERIMENTAL

In the case of phenol, where there is pronounced interaction, the effect of substituents on the intermolecular interactions has been studied. The phenols chosen for the studies are (i) *o*-, *m*- and *p*-chlorophenols, (ii) *o*-, *m*- and *p*-cresols, and (iii) 2,6-dimethylphenol

Ultrasonic velocity measurements were carried out for the binary mixtures of

phenols mentioned above with nitrobenzene of the following ketones namely acetophenone and cyclohexanone.

Measurements were also made with corresponding thiophenols instead of phenol under similar conditions with a view to comparing the behaviour of —OH and —SH groups in intermolecular interaction.

The ultrasonic velocity of the waves in the liquid was measured by using a multifrequency interferometer (Mittal Enterprises, New Delhi). The densities of pure liquids as well as mixtures were measured using low specific gravity bottle. The specific gravity bottles were standardised using doubly distilled carbon dioxide free water.

Calculations

In the components thus chosen, the observed values are compared with the calculated values. The sound velocities were calculated using the following equation[4]:

$$u_{id} = \frac{1}{(\beta_{id}\rho_{id})^{1/2}}$$

The various functions of ideal mixtures may be calculated as

$$\rho_{id} = \phi_1\rho_1 + \phi_2\rho_2$$

$$\beta_{id} = \phi_1\beta_1 + \phi_2\beta_2$$

where ϕ_1, ϕ_2, ρ_1, ρ_2 and β_1, β_2 are the molar volumes, densities and adiabatic compressibilities of the solvent and solute respectively.

To have a clear understanding of the strength of interaction, analysis of other physical parameters such as interaction coefficient (α), percentage deviation ($\Delta U/U$) and adiabatic compressibility (β) has been made.

The non-linear variation of sound velocity and compressibility with respect to mole fraction was studied by Kaulgud and Patil[5], Nambi Narayanan[6] and Misra.[7]

From the ultrasonic data, the compressibility values were calculated using the equation $\beta_{ad} = u^2\rho^{-1}$. The molecular interaction coefficient α which is the deviation of u^2_{exp}/u^2_{id} from unity can be used as an important tool to measure the non-ideality in liquid mixtures. The value of percentage deviation is computed using the equation

$$\frac{\Delta U}{U} = \frac{u_{exp} - u_{ideal}}{u_{exp}} \times 100.$$

RESULTS AND DISCUSSION

In the case of chlorophenols, both *o*- and *p*-isomers show stronger interaction than phenol with ketones or nitrobenzene (Table-1). This is in conformity with the fact that they are more acidic than phenols as evident from their K_a values.[8] However, *m*-chlorophenol shows abnormal behaviour. The strength of interaction of *m*-isomer with nitrobenzene and ketones cannot be explained based on its K_a value.[8]

Compound	K_a *value*
Phenol	1.05×10^{-10}
o-Chlorophenol	77×10^{-10}
p-Chlorophenol	6.3×10^{-10}
m-Chlorophenol	16×10^{-10}

In the case of cresols and 2,6-dimethylphenol, the ability of —OH group to enter into intermolecular interactions is reduced when compared to phenol (Table-1). This is in agreement with the fact that they are less acidic than phenol.[9]

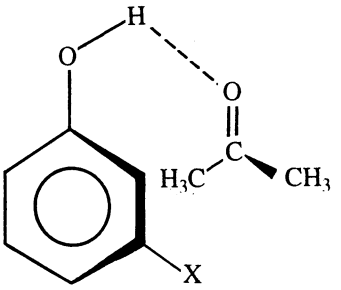
TABLE-1
EXCESS ULTRASONIC VELOCITY, INTERACTION COEFFICIENT, PERCENTAGE DEVIATION AND EXCESS ADIABATIC COMPRESSIBILITY VALUES OF PHENOLS WITH CYCLOHEXANONE SYSTEM AS 50% MOLE FRACTION

Phenols	Mole fraction of phenols	Excess ultrasonic velocity in m/sec Δu	Interaction coefficient α	Percentage deviation $\Delta U/U$	Excess adiabatic Compressibility $\beta^E \times 10^9\ m^2\ N^{-1}$
Phenol	0.5000	27.50	0.0405	1.9677	–0.0181
o-Chlorophenol	0.5114	34.84	0.0539	2.5930	–0.0327
p-Chlorophenol	0.5089	32.09	0.0488	2.3561	–0.1258
m-Chlorophenol	0.4997	30.40	0.0461	2.2291	–0.0173
o-Cresol	0.4604	14.97	0.0217	1.0691	–0.0110
p-Cresol	0.5061	18.27	0.0251	1.2295	–0.0800
m-Cresol	0.5078	16.16	0.0236	1.1589	–0.0133
2,6-Dimethylphenol	0.5006	10.02	0.0145	0.7216	–0.0101

Compound	K_a *(mol dm*$^{-3}$*)*
Phenol	1.05×10^{-10}
o-Cresol	5.25×10^{-11}
m-Cresol	8.32×10^{-11}
p-Cresol	7.24×10^{-11}
2,6-Dimethyl phenol	2.50×10^{-11}

Here too *m*-cresol does not fall in line with *o*- and *p*-isomers. It is found that whether it is chlorophenol or cresol, the *m*-isomer shows deviation. Anbanathan[10] has also reported a weaker interaction for *m*-isomer than *o*- and *p*-isomers in the ultrasonic studies of the binary systems of dioxane with *o*- or *m*- or *p*-toluic acid. Electronic effects fail to explain the observed deviation. The deviation shown by the *m*-isomer from the acidity trend in the strength of interaction may be due to some structural arrangements in the complex formation. If parallel approach is visual-

ized, then substituents at *o*- or *m*-position may offer steric hindrance. Geometric consideration shows that substituents at *p*-position are unlikely to offer any steric hindrance.



Further, from the K_a values it is seen that *o*-chlorophenol is about 75 times as acidic as phenol. This is not reflected in the interactions. A possible reason could be steric hindrance of *o*-substituent.

The study of the effect of substituents on the interaction has also been carried out with substituted thiophenols. A similar trends is seen in the case of chlorothiophenols as found in the case of chlorophenols (Taable-2). In thiocresols, the interaction is so weak that the differences in the strength of interaction among *o*-, *m*- and *p*-isomers do not merit discussion.

The values (α, ΔU/U, β and ΔU) recorded in Tables 1 and 2 are for the binary systems of phenols or thiophenols with cyclohexanone as a specimen. Further, for the comparative study, the values are reported at about 50% by mole, since for all the systems studied, the interaction is maximum at about 50%. As an example we have reported the values for the *p*-chlorophenol-acetophenone system at all concentrations and it is seen that the interaction is maximum at about 50% (Table-3; Fig. 1 and Fig. 2).

TABLE-2
EXCESS ULTRASONIC VELOCITY, INTERACTION COEFFICIENT, PERCENTAGE DEVIATION AND EXCESS ADIABATIC COMPRESSIBILITY VALUES OF THIOPHENOLS WITH CYCLOHEXANONE SYSTEM AS 50% MOLE FRACTION.

Thiophenols	Mole fraction of thiophenols	Excess ultrasonic velocity in m/sec Δu	Interaction coefficient α	Percentage deviation ΔU/U	Excess adiabatic compressibility $\beta^E \times 10^9$ m^2 N^{-1}
Thiophenol	0.5010	8.20	0.0123	0.6083	–0.0228
o-Chlorothiophenol	0.4806	8.40	0.0127	0.6276	–0.0103
m-Chlorothiophenol	0.5023	7.63	0.0115	0.5706	–0.0094
o-Thiocresol	0.5003	4.11	0.0061	0.3039	–0.0043
p-Thiocresol	0.4632	7.90	0.0088	0.5877	–0.0237
m-Thiocresol	0.4769	4.73	0.0071	0.3546	–0.0094

Table-3
ULTRASONIC VELOCITY, INTERACTION COEFFICIENT, PERCENTAGE DEVIATION AND ADIABATIC COMPRESSIBILITY VALUES OF *p*-CHLOROPHENOL-ACETOPHENONE SYSTEM.

Mole fraction of *p*-Chlorophenol	Experimental ultrasonic velocity m/sec	Ideal ultrasonic velocity m/sec	Excess ultrasonic velocity m/ sec (ΔU)	Interaction cofficient (α)	Percentage deviation ($\Delta U/U$)	Density kg/m^3	Aldiabatic compressibility $10^9 m^2 n^{-1}$		
							Experimental	Additive $(\beta)^E$	Excess
0.1009	1438.0	1436.30	1.70	0.0023	0.1182	979.33	0.4938	0.5012	-0.0074
0.2058	1427.6	1426.88	0.72	0.0010	0.0543	1052.70	0.4661	0.4935	-0.0274
0.3545	1454.7	1379.85	74.85	0.1114	5.1454	1085.86	0.4352	0.4827	-0.0475
0.3765	1475.6	1401.98	73.62	0.1078	4.9892	1091.28	0.4209	0.4817	-0.6080
0.5106	1497.0	1373.76	123.24	0.1875	8.2325	1123.90	0.3970	0.4712	-0.0742
0.6062	1460.2	1370.82	89.38	0.1347	6.1211	1148.38	0.4084	0.4642	-0.0558
0.7037	1433.0	1367.84	65.16	0.0975	4.5471	1173.70	0.4149	0.4571	-0.0422
0.7879	1409.7	1376.66	33.04	0.0486	2.3438	1215.67	0.4139	0.4510	-0.0371
0.8997	1399.8	1368.84	30.96	0.0457	2.2212	1224.41	0.4168	0.4428	-0.0260

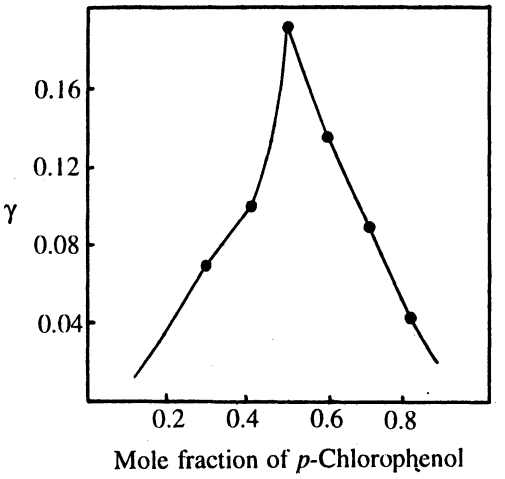


Fig. 1. *p*-chlorophenol-acetophenone

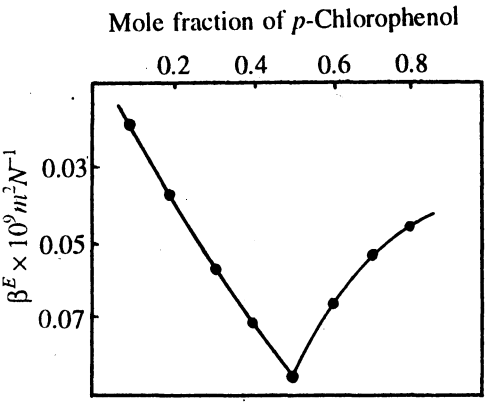


Fig. 2. *p*-chlorophenol-acetophenone

REFERENCES

1. V. Balaiah and K. Gnanasekaran, *Indian J. Chem.*, **25A**, 673 (1986).
2. V. Balaiah, K. Ganapathy and K. Gnanasekaran, *Indian J. Chem.*, **28A**, 67 (1989).
3. R. Alamelu, Ph.D. Thesis, Annamalai University (1994).
4. N. Manoharamurthy and G. Nagabushanam, *J. Acoust. Soc. Ind.*, **1**, 32 (1984).
5. M.V. Kaulgud and K. Patil, *J. Acoustica*, **28**, 130 (1973).
6. T.K. Nambinarayanan, *Indian J. Pure and Appl. Phys.*, **16**, 711 (1978).
7. M. Misra, R.N. Gupta and R.C. Pandey, *J. Pure and Appl. Phys.*, **10**, 539 (1972).
8. R.T. Morrison and R.N. Boyd, Organic Chemistry, Prentice-Hall of India Pvt. Ltd., New Delhi, 3rd Edition, p. 788.
9. I.L. Finar, Organic Chemistry, ELBS, 2nd Edition, p. 665 (1971).
10. D. Anbanathan, *J. Acoust. Soc. Ind.*, **7**, 4 (1979).

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