

Comparative study of intermolecular interactions by acoustic properties of α -bromoacetophenones and coumaran-3-ones in ethanol and dioxane solvents

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Abstract : Ultrasonic velocity and density measurement of 2-hydroxy-3-*H*/substituted-5-methyl- α -bromoacetophenones and 2-(4'-*H*/chloro)benzylidene-5-methyl-7-*H*/substituted coumaran-3-ones were carried out in two different solvents, ethanol and dioxane respectively for investigating solute-solvent, solute-solute interactions. These interactions were also performed in presence of Cu^{II} and Fe^{III} metal ions at 303.15 K. The data obtained during the study is used for determining the most significant acoustic parameters like adiabatic compressibility (β) and relative association (R_A). These parameters explore solute-solute and solute-solvent interactions in different solvents. In this investigation, the comparative study of effect of solvents, effect of metal ions and effect of substituents in the solute are studied on molecular interaction of the matter.

Keywords : Acoustic, interferometry, α -bromoacetophenone.

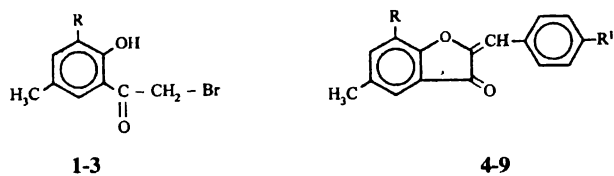
Ultrasonic waves have acquired the status of an important probe for the study of structure and properties of matter¹. In the basic sciences, these waves are used to provide information on the behaviour of microscopic particle of matter². The unique feature of sound wave property is that it gives direct and precise information of adiabatic properties of solution. The use of ultrasound is one of the well recognized approaches for the study of molecular interactions in fluids. Ultrasonic velocity plays an important role in the investigation of intermolecular interactions. The structural arrangements are influenced by the shape of the molecules as well as by their mutual interactions. The ultrasonic velocity and adiabatic compressibility can be measured with great accuracy and consequently provides a powerful tool for the prediction of intermolecular interaction. In view of the analytical, medicinal, agricultural, industrial, pharmaceutical significance³⁻¹¹ α -bromoacetophenones and coumaran-3-ones it is of interest to investigate the acoustic parameters such as adiabatic compressibility (β) and relative association (R_A) in ethanol and dioxane solvent respectively along with the effect of Cu^{II}/Fe^{III} metal ion on the above systems by ultrasonic interferometric technique in order to discuss intermolecular interactions.

Literature survey shows that much work has been done in water and organic solvent mixtures¹²⁻¹⁸, but scanty work is found in pure ethanol or dioxane solvent and comparison of interactions in these different solvents. Also the review does not reveal any attempt made on ultrasonic interferometric study of α -bromoacetophenones and coumaran-3-ones. Hence, we intended to analyze comparative study of these solutes in ethanol and dioxane solvents, specially related to protic-aprotic nature, polarity-nonpolarity, hydrogen bonding, dielectric constant and density of solvent on solute-solvent, ion-solvent and ion-ion interactions. Therefore in this present investigation, attempt is made to understand behaviour of 2-hydroxy-5-methyl- α -bromoacetophenone (**1**), 2-hydroxy-3-bromo-5-methyl- α -bromoacetophenone (**2**), 2-hydroxy-3-nitro-5-methyl- α -bromoacetophenone (**3**), 2-benzylidene-5-methylcoumaran-3-one (**4**), 2-benzylidene-5-methyl-7-bromocoumaran-3-one (**5**), 2-benzylidene-5-methyl-7-nitrocoumaran-3-one (**6**), 2-(4'-chloro)benzylidene-5-methylcoumaran-3-one (**7**), 2-(4'-chloro)benzylidene-5-methyl-7-bromocoumaran-3-one (**8**), 2-(4'-chloro)benzylidene-5-methyl-7-nitrocoumaran-3-one (**9**) compounds in ethanol and dioxane solvents separately and also by addition of Cu^{II} and Fe^{III} metal ion solutions

respectively with respect to adiabatic compressibility and relative association.

Experimental

All the chemicals used were of A.R. grade. 2-Hydroxy-5-methyl- α -bromoacetophenone (**1**), 2-hydroxy-3-bromo-5-methyl- α -bromoacetophenone (**2**), 2-hydroxy-3-nitro-5-methyl- α -bromoacetophenone (**3**), 2-benzylidene-5-methylcoumaran-3-one (**4**), 2-benzylidene-5-methyl-7-bromocoumaran-3-one (**5**), 2-benzylidene-5-methyl-7-nitrocoumaran-3-one (**6**), 2-(4'-chloro)benzylidene-5-methylcoumaran-3-one (**7**), 2-(4'-chloro)benzylidene-5-methyl-7-bromocoumaran-3-one (**8**), 2-(4'-chloro)benzylidene-5-methyl-7-nitrocoumaran-3-one (**9**) were synthesized in our laboratory¹⁹ (Scheme 1). Compounds (**1-3**) are recrystallized from acetic acid and water mixture, whereas compounds (**4-9**) are recrystallized from alcohol



1-3		4-9		
Compd.	R	Compd.	R	R'
1	H	4	H	H
2	Br	5	Br	H
3	NO ₂	6	NO ₂	H
		7	H	Cl
		8	Br	Cl
		9	NO ₂	Cl

Scheme 1

and water. The solvents (1,4-dioxane and ethanol) were purified by standard procedure²⁰. The double distilled water is used for preparation of metal solutions of Cu^{II} and Fe^{III}. Densities were measured with the help of bicapillary pycnometer. 0.01 M solutions of Cu^{II} and Fe^{III} in distilled water and 0.01 M solutions of ligands in ethanol and dioxane solvents were prepared separately. Weighing was made on Mechaniki Zaktady Precyzyjnej Gdansk Balance, made in Poland (± 0.001 g). A special thermostatic arrangement was done for density and ultrasonic velocity measurements. Elite thermostatic water bath was used; in which continuous stirring of water was carried out with the help of electric stirrer and temperature variation was maintained within ± 0.1 °C. Single crystal interferometer (Mittal Enterprises, Model MX-3) with accuracy of $\pm 0.03\%$ and frequency 1 MHz was used in the present work. The working of the ultrasonic interferometer was checked by measuring ultrasonic

velocity of pure water at 303.15 K. The measured value 1505 m s⁻¹ is in good agreement with literature²¹ value 1510 m s⁻¹. The densities and ultrasonic velocities of ligands (**1** to **9**) in ethanol solvent were measured at 303.15 K. Then 10 ml of each ligand solution in ethanol was mixed with 2 ml metal ion [Cu^{II}/Fe^{III}] solution in water and densities, ultrasonic velocities of these solutions also were measured. Similar measurements were carried out in dioxane solvent also.

Results and discussion

In the present investigation, measurements of densities and ultrasonic velocities of ligands in solvent and ligands and metal ions in solvent have been made, and given in Tables 1-6. The adiabatic compressibility (β) can be evaluated by using Laplace's equation.

$$\beta = 1/v^2.d \quad (1)$$

Relative association is a function of ultrasonic velocity and is computed by the equation,

$$R_A = \frac{d_s}{d_0} \left(\frac{v_0}{v_s} \right)^{1/3} \quad (2)$$

where, v_0 and v_s are ultrasonic velocities in solvent and solution.

Table 1. Acoustic parameters for ligands in ethanol at 303.15 K

Ligand	v (m s ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (Pa ⁻¹)	R_A
Ethanol	1167.59	777.5	9.4340	
1	1199.99	780.00	8.9030	0.9941
2	1199.87	780.83	8.8960	0.9952
3	1199.50	778.33	8.9300	0.9921
4	1200.50	775.83	8.9430	0.9887
5	1197.25	779.17	8.9540	0.9938
6	1200.01	777.50	8.9320	0.9909
7	1168.06	760.83	9.6330	0.9784
8	1133.89	764.17	10.180	0.9925
9	1133.56	760.83	10.230	0.9883

From Table 1 and Figs. 1 and 2, it can be noted that the values of β of α -bromoacetophenones (**1-3**) in alcohol are slightly less than coumaran-3-ones (**4-9**) in alcohol while these values continuously increase from (**1**) to (**9**), but the increment is quite notable in (**7**), (**8**) and (**9**), which can be explained on the basis of structure and nature of ligand where the benzylidene moiety of nucleus has electronegative chlorine atom at *para* position. The smaller values of β of acetophenones may be due to benzenoid cyclic nature and higher values in coumaran-

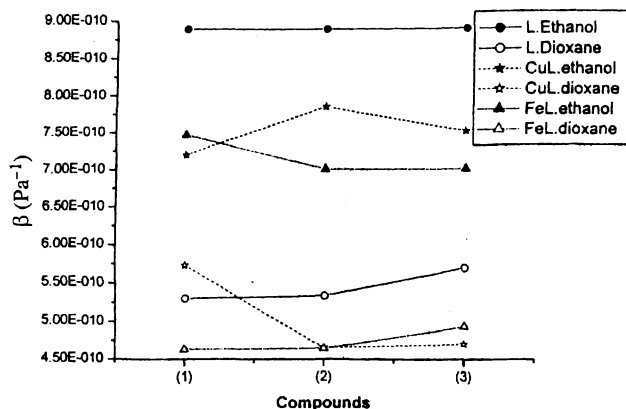


Fig. 1. Adiabatic compressibility (β) of α -bromoacetophenones.

3-ones may be due to their heterocyclic nature. The nature and size of ring may be directly affecting the β values. Similar trend is observed in dioxane solvent also, as can be seen by inspection of Table 2 and Figs. 1 and 2.

Table 2. Acoustic parameters for ligands in dioxane at 303.15 K

Ligand	ν (m s^{-1})	d (kg m^{-3})	$\beta \times 10^{-10}$ (Pa^{-1})	R_A
Dioxane	1353.59	1022.44	5.3380	
1	1353.18	1028.57	5.3100	1.0065
2	1349.14	1026.53	5.3520	1.0055
3	1302.66	1028.57	5.7290	1.0194
4	1317.26	1029.59	5.5980	1.0166
5	1316.53	1029.59	5.6040	1.0168
6	1320.57	1031.63	5.5580	1.0178
7	1316.74	1029.59	5.6020	1.0167
8	1320.63	1031.63	5.5580	1.0178
9	1279.87	1030.11	5.9260	1.0269

By comparing the values of β in alcohol (Table 1) and dioxane (Table 2) it is clearly observed that the β values in dioxane medium are considerably and notably smaller than in alcohol medium. This may be due to nature of solvents. The parameters of solvents, which directly affect the values of β , are aprotic nature, non-polarity, low dielectric constant (2.2) and higher density of dioxane as compared with protic nature, polarity, high dielectric constant (24.6) and lower density of ethanol. In ethanol, hydrogen bonding is possible while it is not observed in dioxane.

Similar trends (Tables 3–6) and patterns (Figs. 1 and 2) of β values are seen after the addition of metal ion solutions [Cu^{II} and Fe^{III} in water] to each of the above solution. But the adiabatic compressibilities are lower for Cu^{II} and lowest for Fe^{III} as compared with ligands in both the solvents.

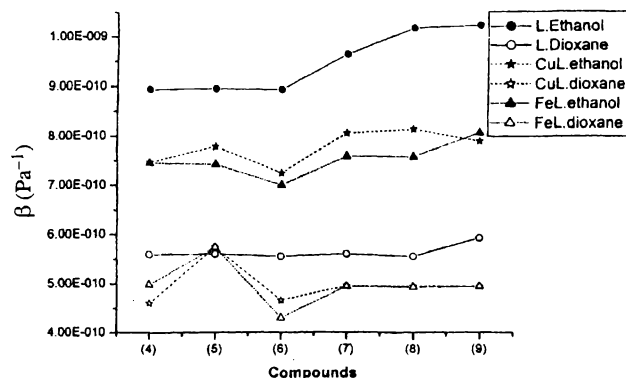


Fig. 2. Adiabatic compressibility (β) of coumaran-3-ones.

Thus it may be generalized that the β values for all ligands (1 to 9) in alcohol solvent are higher than those in dioxane solvent and in both the solvents the values of ligands in pure solvent are higher than after addition of Cu^{II} solution [Cu^{II} -L-solvent] and lowest in case of Fe^{III} solution [Fe^{III} -L-solvent].

L-ethanol > L-dioxane and

L-solvent > Cu^{II} -L-solvent > Fe^{III} -L-solvent

With solute (1) in alcohol, the combination forms polar-polar molecules and as such the interaction between solute and solvent is a polar-polar interaction with resulting compressibility which is of higher value.

As against this when the solvent contains Cu^{II} and solute (1) both solute being polar, the resulting interaction between polar solutes and polar solvent is bound to be an enhanced one, resulting in decreased compressibility as can be seen from Fig. 1. Further in case of Fe^{III} -L₁ the Fe^{III} is more polar the resulting combination with increased polarity is bound to reflect in greater polar-polar interaction, giving rise to a further decrement in compressibility. These physical occurrences of solute-

Table 3. Acoustic parameters for Cu^{II} -ligands in ethanol at 303.15 K

Ligand	ν (m s^{-1})	d (kg m^{-3})	$\beta \times 10^{-10}$ (Pa^{-1})	R_A
1	1303.88	815.83	7.2100	1.0114
2	1249.77	814.17	7.8640	1.0237
3	1276.98	811.67	7.5550	1.0132
4	1281.85	814.17	7.4750	1.0151
5	1253.75	816.69	7.7900	1.0258
6	1300.81	815.00	7.2510	1.0112
7	1249.09	795.83	8.0540	1.0008
8	1242.02	796.67	8.1370	1.0038
9	1253.28	806.67	7.8920	1.0133

Table 4. Acoustic parameters for Cu^{II}-ligands in dioxane at 303.15 K

Ligand	ν (m s ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (Pa ⁻¹)	R_A
1	1300.38	1029.66	5.7430	1.0211
2	1446.08	1027.20	4.6550	0.9832
3	1437.35	1028.55	4.7060	0.9865
4	1452.06	1030.02	4.6050	0.9845
5	1300.34	1029.97	5.7420	1.0214
6	1441.36	1032.03	4.6640	0.9889
7	1400.73	1030.10	4.9480	0.9965
8	1398.02	1033.67	4.9500	1.0006
9	1401.49	1030.43	4.9410	0.9966

Table 5. Acoustic parameters for Fe^{III}-ligands in ethanol at 303.15 K

Ligand	ν (m s ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (Pa ⁻¹)	R_A
1	1278.94	817.50	7.4780	1.0200
2	1321.47	815.00	7.0260	1.0059
3	1321.06	813.33	7.0450	1.0039
4	1280.80	817.50	7.4570	1.0195
5	1281.98	819.17	7.4280	1.0213
6	1322.34	816.67	7.0030	1.0077
7	1281.01	803.33	7.5860	1.0018
8	1278.79	806.67	7.5810	1.0065
9	1239.18	807.50	8.0650	1.0182

solvent interactions are reflected in the decrease in compressibility.

The lower values in case of Fe^{III}-L-solvent than Cu^{II}-L-solvent may also be interpreted in terms of smaller size and high charge by radius ratio of Fe^{III} than Cu^{II}. Because of the smaller size and polar-polar interaction due to high positive charge on Fe^{III} close packing will occur and compressibility will decrease. It may also be interpreted in terms of electrostriction²². When the ligand is added to ethanol electrostriction increases, since the ligand is polar and solvent is also polar having hydrogen bonding. Consequently the adiabatic compressibility will decrease.

Ethanol is a polar solvent having profuse hydrogen bonding and hence the structural property like water may be there. Because of hydrogen bonding, the molecules must be arranged such that the void spaces may be available due to which the solvent is more compressible (Table 1). In this solvent when polar solutes are added the association of solute and solvent molecules occurs resulting in close packing and clinging of molecules. Therefore the solution becomes less compressible and thereby decreasing the β values.

On the other hand dioxane is a non-polar solvent having higher density and no hydrogen bonding. Therefore, already packing of dioxane molecules occurs in the structure and hence it becomes less compressible (Table 2). After the addition of polar solute the association, in other words, packing or clinging of molecules increases, resulting in less compressible nature of solution. Further addition of metal ions still increases the polar-polar interactions, thereby increasing the compactness of solution resulting in further decrease in compressibility, as is clearly indicated by inspection of Table 2 and Figs. 1 and 2 where the β values in dioxane solvent are considerably

lower and go on decreasing with the addition of Cu^{II} and Fe^{III} solutions.

It is clearly observed from Figs. 1 and 2 that when atoms like bromine and chlorine are present in the molecules attached to phenyl ring the compressibilities are increased meaning thereby decrease in compactness, in spite of their polar nature and high electronegativity. The reason for this may be looked into the negative inductive and positive mesomeric effects of these groups which are operating simultaneously but in opposite directions, neutralizing the effect of negative charge on the halogen atom. So, the close packing at these ends may not be possible leaving voids between molecular species, i.e. making the solution more compressible. Similarly decrease in compressibility because of close packing due to polar nitro group may be explained.

Relative association is an acoustic property of understanding interaction, which is influenced²³ by two opposing factors :

- (i) Breaking of solvent structure on addition of solute to it and
- (ii) solvation of the solutes that are simultaneously present by the free solvent molecules.

The former effect results in the decrease in R_A values while the latter resulting in increase of R_A values.

From the Tables 1–6 and Figs. 3 and 4, it can be easily seen that the R_A values in dioxane are higher than in alcohol for the ligands, which is a reverse trend than that is observed for β . The general trend can be shown as

L-dioxane > L-ethanol,

L-dioxane > Fe^{III}-L-dioxane > Cu^{II}-L-dioxane and

L-ethanol < Fe^{III}-L-ethanol < Cu^{II}-L-ethanol.

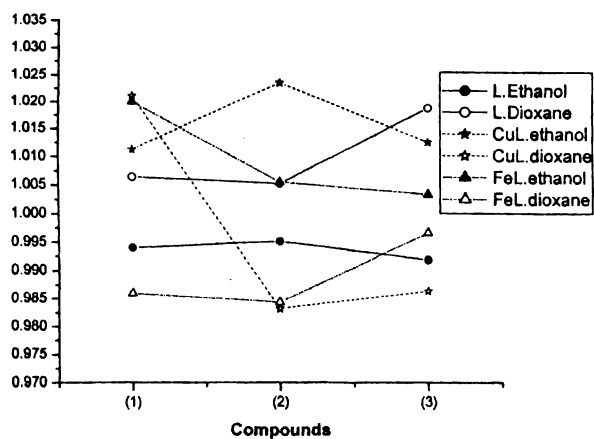
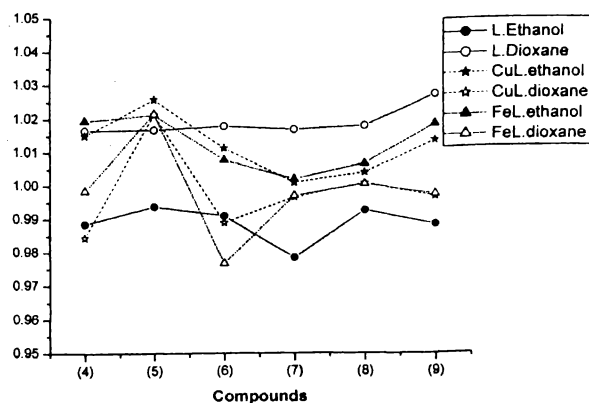
Table 6. Acoustic parameters for Fe^{III}-ligands in dioxane at 303.15 K

Ligand	ν (m s ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (Pa ⁻¹)	R_A
1	1447.86	1030.54	4.6290	0.9860
2	1446.97	1028.60	4.6430	0.9843
3	1400.92	1030.61	4.9440	0.9969
4	1395.78	1030.89	4.9790	0.9984
5	1300.33	1030.14	5.7410	1.0215
6	1499.27	1032.72	4.3080	0.9766
7	1401.43	1030.69	4.9400	0.9969
8	1400.30	1033.98	4.9320	1.0003
9	1400.89	1030.91	4.9430	0.9972

In ethanol, increase in R_A on addition of M ion suggests that solvation of solute is predominant over the breaking of solvent structure, whereas, in dioxane decrease in R_A suggests that breaking of solvent structure predominates over the solvation of solute due to non-polar nature of dioxane.

The alcohol molecules are well known to be associated as compared to dioxane, which are not associated due to hydrogen bonding. As soon as solute is added to alcohol as well as dioxane, the probability of solute forming association with alcohol will be lesser as compared to dioxane. This is evident because the existing association in alcohol will render less probability of alcohol forming association with solute than dioxane. This is actually observed in case of relative association as shown in Figs. 3 and 4.

With the addition of Fe^{III} and Cu^{II} to alcohol naturally the tendency of association should increase which is evident from our experimental observations, where R_A is increased as compared to that with the solvent alone. Similar effect

**Fig. 3.** Relative association (R_A) of α -bromoacetophenones.**Fig. 4.** Relative association (R_A) of coumaran-3-ones.

is observed in case of compressibility.

In case of solute Fe^{III} and Cu^{II} added to dioxane the interaction/association of dioxane molecules is almost absent and Fe^{III} and Cu^{II} will have almost negligible association with dioxane molecules due to the charged neutrality and zero dipole moment of the dioxane molecule. Thus overall association of solute in dioxane will be further reduced as compared to pure dioxane.

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