Research Paper Chemistry

Acoustical Parameters on Charge Transfer Complexes of Substituted Salicyladehyes with Benzidine in n-Hexane Medium at 303K

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ABSTRACT

Ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for three different salicylaldehyde such as 5-chlorosalicylaldehyde, 4-diethylaminosalicylaldehyde, 3-ethoxysalicylaldehyde with benzidine in n-hexane medium at 303K. From these experimental values, the adiabatic compressibility (β), acoustic impedance (Z), free length (Lf), free volume (Vf), internal pressure (πi), cohesive energy (CE), Lenard Jones Potential formation constant (K), free energy of formation (ΔG), free energy activation (ΔG#) and viscous relaxation time (r) have been discussed in terms of solute- solvent and solvent-co-solute interactions. Formation constant (K) values of the compounds have been determined by using a modified Bhat equation. The values of cohesive energy (CE) and formation constant (K) are found to be high, indicating the presence of charge transfer complex between substituted aldehydes with benzidine in n-hexane medium. The complexes are thermodynamically stable as evidenced from their negative free energy of formation values and high values of molar extinction coefficient identifies the presence of strong complexes (π-π, n-π*) existing in these systems.*

KEYWORDS : Lenard Jones Potential, Cohesive energy (CE), Formation constant (K), Viscous relaxation time(r)

Introduction

Ultrasonic velocity measurements have been successfully employed to detect compute strong and weak interaction between solute and solvent. These interaction are possible in binary [1,2] and ternary [3,4] liquid mixtures. From these measurements may also be identify to form the charge transfer complexes and calculate the stability constant values [5,6]. The charge transfer complexes are mostly formed between electron rich centers and electron deficient compounds. Generally carbonyl group is part of several biologically important molecules. Amines in pure state are self-associated through intermolecular hydrogen bonds. They have both π as well as n-electron donors which allow them to have specific interactions with other electron deficient molecules. Ultrasonic investigations were carried out to detect charge-transfer complexes between aromatic aldehyde such as benzaldehyde, cinnamaldehyde, salicylaldehyde in hexane medium [7]. It is assumed that the hydrogen atom of the aldehyde group has a tendency to form both intra and inter molecular hydrogen bonding [25] but because of polarized C-O-H bond. The newly formed inter molecular hydrogen bond C-O…H has more effect than the intra molecular hydrogen bonding causing the breakage of self associates. The intermolecular interactions influence the structural arrangement in ternary liquid mixtures and these interactions can indicate to complex formation. The structural arrangement can be detected by ultrasonic method [1,6]. It is also used to detect the formation of charge-transfer-complexes by the number of parameters [7, 10]. From the ultrasonic velocity, density and viscosities values, we can calculate the formation constant, viscous relaxation time, free energy of formation and free energy of activation. The present work proved that the three aromatic aldehyde form strong charge-transfer-complex with amine.

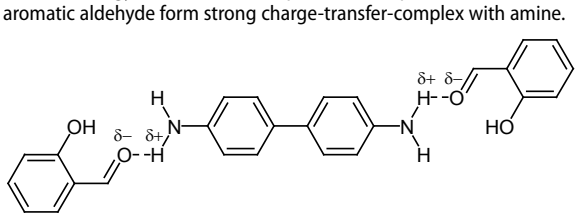


Fig 1 . Possible mechanism for the formation of hydrogen bonding between salicyladehyde with the benzidine.

Materials and Methods

All chemicals used in the physical measurements were analytical reagent grade. 3-ethoxysalicylaldehyde, 4- diethylaminosalicylaldehyde, 5-chlorosalicylaldehyde were purchased from Sigma-Aldrich. Benzidine and n-hexane were received from Merck. A single crystal variable path ultrasonic interferometer (Model F81) operating at 2 MHz frequency supplied by Mittal Enterprises, India was used in the measurement of ultrasonic velocity of liquid mixtures with the accuracy of ± 0.01 ms^{-1}. The density (ρ) of solutions was determined using specific gravity bottles of capacity 10mL. Ostwald's viscometer was used to determine the viscosity, in which the flow time for solutions was measured through a digital stop clock of accuracy ± 0.01s. The temperature was maintained at 303 K during the measurement of ultrasonic velocity, density and viscosity values.

Results and discussion

The calculated values of ultrasonic velocity, density and viscosity at equimolar concentration of aromatic aldehyde (acceptor) and aromatic amine (donor) in n-hexane medium at 303K are given in table -1. Ultrasonic velocity (U) increases with the concentration of three substituted salicylaldehydes indicates there was a stronger interaction between donor and acceptor systems. The increase in velocity may be attributed to strong solute-solute interactions. It was proved that the strength of molecular interactions becomes high where the velocity maximum occurs [16]. The increase in velocity showed dipole-dipole interaction and strong complex formation through intermolecular hydrogen bond [17].Adiabatic compressibility (β) and free length (L_f) influence the structural arrangements of the molecule. Adiabatic compressibility shows the formation or dissociation of intermolecular bond. β and L_f values showed the reverse trend that the existence strong interaction between benzidine and substituted salicylaldehyde. The gradual decrease in adiabatic compressibility (β) and free length (L_f) suggest the increasing compactness of the system [18].The internal pressure increases as the concentration increases in all the system. This parameter also used to detect the intermolecular interaction in ternary liquid mixtures. The internal pressure is also used to assess the force of attraction and force of repulsion in the liquid mixtures. A reverse trend showed in the change of free volume (V_f). The decreasing free volume observed that the increasing in solute-solute interaction and strong intermolecular hydrogen bonds between substituted salicylaldehyde and benzidine.Cohesive energy (CE) were calculated and presented in tables.Cohesive energy is higher in 3-ethoxysalicylaldehyde than 4-diethylsalicylaldehyde and 5-chloro-2-nitrobenzaldehyde. It proved that the CE increases as well as the intermolecular forces also increases. The magnitude of CE shows that the presence of strong dipole-dipole interaction in the intermolecular hydrogen bonding for ternary system. LJP increases with the concentration of three substituted salicylaldehydes indicates there was a extent of complexation for all the system. It is also presented in tables.

Table 1
Ultrasonic velocity (U), Density (ρ), Viscosity (η), Free length (L_f) , Acoustic Impendence(Z), Internal Pressure (π_i), Free volume (V_f), Cohesive Energy (CE) and and Lenard Jones potential values for 5- chlorosalicyladehyde with benzidine in n- hexane at 303k.

Concentration x10^{-4} M	U	ρ	η	β	L_f	z	π_i	Vf	CE	LJP
1	891.4	1.46	4.61	8.39	1.83	13.01	1565.9307	2.43	9.24	0.55
2	894.6	1.47	4.78	8.39	1.81	13.15	1889.2967	2.32	11.08	0.61
3	899.7	1.47	4.8	8.29	1.8	13.22	2135.7166	2.32	12.53	0.71
4	934.4	1.48	4.93	7.74	1.73	13.82	2326.7831	2.36	13.56	1.42
5	939.8	1.48	5.07	7.65	1.72	13.9	2505.9732	2.28	14.61	1.54
6	943.7	1.49	5.21	7.64	1.71	14.06	2699.8898	2.21	15.64	1.63
7	948.9	1.49	5.36	7.56	1.7	14.13	2838.7929	2.13	16.45	1.74
8	955.2	1.5	5.49	7.51	1.68	14.32	2977.9838	2.08	17.14	1.89

Table 2
Ultrasonic velocity (U), Density (ρ), Viscosity (η), Free length (L_f) , Acoustic Impendence(Z), Internal Pressure (π_i), Free volume (V_f), Cohesive Energy(CE) and Lenard Jones potential values for 4- diethylamniosalicyladehyde with benzidine in n- hexane at 303k.

Concentration x10^{-4} M	U	ρ	η	β	L_f	z	π_i	Vf	CE	LJP
1	943.1	1.104	4.08	10.18	1.99	10.41	1263.47	3.18	9.86	1.61
2	956.7	1.109	5.91	9.85	1.95	10.7	1513.8938	1.86	11.7	1.92
3	961.4	1.114	7.6	9.71	1.94	10.7	1717.1656	1.29	13.29	2.03
4	972.1	1.119	9.29	9.45	1.91	10.87	1893.093	0.96	14.59	2.29
5	980.8	1.122	10.845	9.26	1.89	10.9	2039.3162	0.86	15.68	2.5
6	990.4	1.125	12.535	9.06	1.87	11.1	2185.049	0.63	16.76	2.75
7	1090.4	1.128	13.943	7.45	1.7	12.29	2199.51	0.62	16.83	5.84
8	1123.4	1.131	15.318	7.01	1.65	12.7	2274.6266	0.57	17.36	7.14

Table 3
Ultrasonic velocity (U), Density (ρ), Viscosity (η), Free length (L_f) , Acoustic Impendence(Z), Internal Pressure (π_i), Free volume (V_f),Cohesive Energy (CE) and and Lenard Jones potential values for 3- ethoxysalicyladehyde with benzidine in n- hexane at 303k.

Concentration x10^{-4} M	U	ρ	η	β	L_f	z	π_i	Vf	CE	LJP
1	1038.3	1.151	5.09	8.05	1.77	11.95	4373.1071	2.63	25.8	4.09
2	1041.7	1.159	5.21	7.95	1.75	12.07	4436.2027	2.56	26	4.20
3	1054.4	1.168	5.34	7.7	1.73	12.31	4485.7734	2.51	26.3	4.60
4	1061.4	1.171	5.46	7.58	1.71	12.42	4527.2463	2.45	26.3	4.82
5	1072.3	1.175	5.58	7.4	1.69	12.59	4562.3542	2.41	26.6	5.19
6	1083.1	1.179	5.72	7.24	1.67	12.76	4605.2058	2.36	26.6	5.57
7	1092.4	1.181	5.85	7.09	1.66	12.9	4641.1792	2.31	26.8	5.91
8	1104.7	1.184	5.97	6.92	1.64	13.07	4668.8095	2.28	26.8	6.38

Thermodynamic parameter:

The thermodynamic stability of the donor-acceptor complexes formed between the aldehyde and aromatic amine can be compared by calculating the stability constants of these complexes. By applying Kannappan equation from the measured values of ultrasonic velocity, the values of stability constants were calculated for all the system at 303K. The stability constant of the hydrogen bonded complexes increases in the order 3-ethoxysalicylaldehyde, 4- diethylaminosalicylaldehyde, 5-chloro salicylaldehyde. The complex formed between carbonyl oxygen of substituted salicylaldehyde and hydrogen of imino group in benzidine. The presence of electron releasing ethoxy group in the salicylaldehyde improves the nucleophilic character of carbonyl oxygen and thus favours complex formation in the case of 3-ethoxy salicylaldehyde through strong hydrogen bond formation. In case of 5-chloro-salicylaldehyde the presence of electron withdrawing group in the carbonyl group weakens the hydrogen bond. This shows the smaller value of K for this complex. The viscous relaxation time values were similar for all the system. This suggests that the same type of complexes were formed between aromatic amine and aldehyde.The negative values of free energy of formation indicate that the charge transfer interaction is exothermic and strong interaction. It is noted from the table 4 that the systems with 3-ethoxy salicylaldehyde have more exothermic than 5-chloro salicylaldehyde.

Table 4
Formation constant, free energy of formation, free energy of activation and viscous relaxation time values of donor acceptor complexes of certain aldehydes with benzidine in n- hexane 303K.

Compound	K / mol^{-1}	ΔG / $kJmol^{-1}$	ΔG^* / ($kJmol^{-1}$)	Γ' / $10^{-13}s$
5-chlorosalicylaldehyde	174.94	-3.4	8.6	5.2
4-diethyl salicylaldehyde	279.07	-3.4	8.4	5.3
3-ethoxy salicylaldehyde	405.7	-3.4	8.6	5.5

Figure 1. Plots of ultrasonic velocity vs various concentration of salicyladehyde-benzidine in n-hexane at 303K

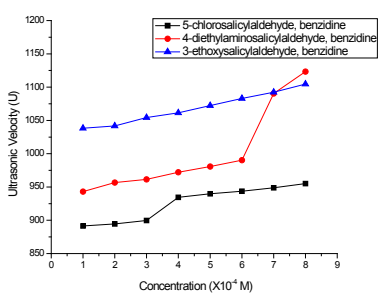


Figure 2. Plots of adiabatic compressibility vs various concentration of salicyladehyde-benzidine in n-hexane at 303K

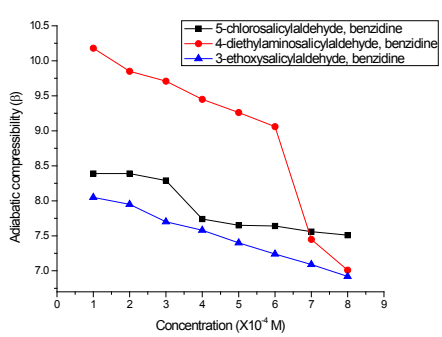


Figure 3. Plots of free length vs various concentration of salicyladehyde-benzidine in n-hexane at 303K

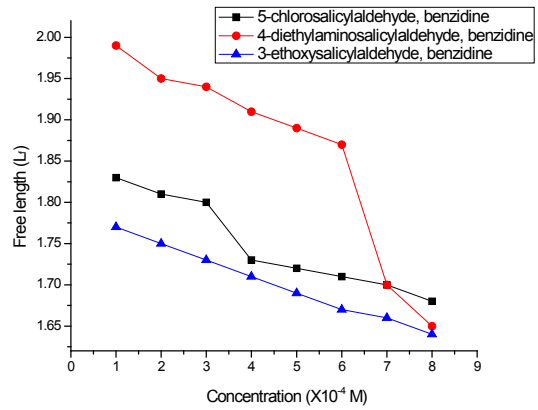


Figure. 4. Plots of internal pressure vs various concentration of salicyladehyde-benzidine in n-haxane at 303K

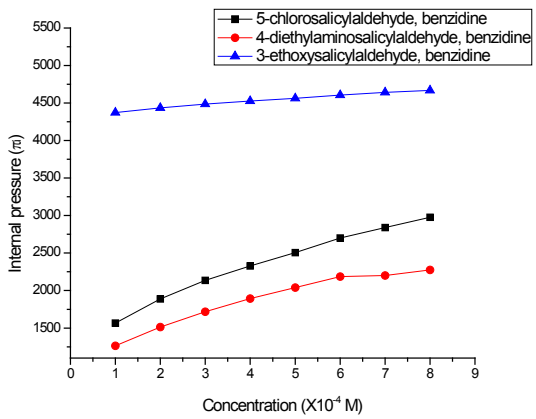
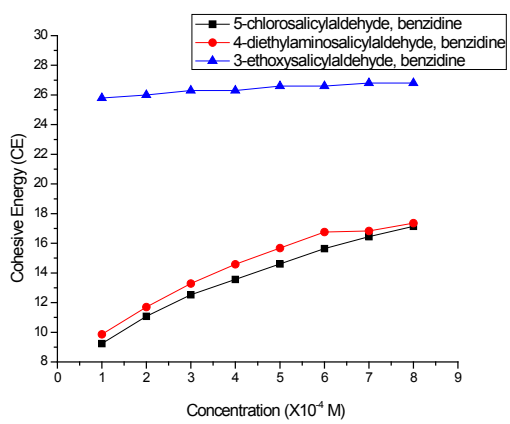


Figure. 5. Plots of cohesive energy vs various concentration of salicyladehyde-benzidine in n-hexane at 303K



Conclusion

Aldehyde with electron deficient carbonyl carbon form thermodynamically stable charge transfer complex with benzidine. The formation constants of these complexes indicate the presence of electron releasing group in acceptor molecule increases the tendency of complex formation. Thus the formation constant value of 5-chloro-2-nitro-salicylaldehyde with benzidine is lesser than the 3-ethoxy-salicylaldehyde and 4-diethyl-salicylaldehyde with benzidine. Due to the –I effect group with carbonyl double bond, the 5-chloro-2-nitro-salicylaldehyde-diethylamine complex has less formation constant.

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