Ultrasonic and spectroscopic studies on hydrogen bonded complexes of aromatic amine and aryl ketones in n-hexane at 303.15 K

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ABSTRACT

Viscometric and ultrasonic studies have been carried out in n-hexane solutions, containing equimolar concentration from 0.02 to 0.2 M of aromatic ketones and N-methylaniline (NMANI), at 303.15 K and at atmospheric pressure. The ketones studied in the present investigation are acetophenone (ACP), 4-chloroacetophenone (ClACP) and 4-methylacetophenone (MACP). The behaviour of measured ultrasonic velocity (u), density (ρ) and viscosity (η) and also the computed acoustic parameters provide strong evidence for the presence of strong solute–solute interactions in the three ternary systems. Excess molar volume and excess thermo acoustic parameters reveal the existence of hydrogen bonded complexes between the solute molecules, ketones and secondary amine. The variation of these parameters with the concentration shows that the existing interactions are influenced by the structure of components and functional groups of the components involved. An attempt has been made to confirm the formation of 1:1 complexes in these systems through UV–visible spectroscopic method at 303.15 K. The calculated values of formation constants of the charge transfer complexes both by acoustic and optical methods agree satisfactorily. The variation in the values of formation constant reveals that electron releasing substituent in the acetophenone molecule enhances the stability while electronegative substituent decreases the stability of the complex. The negative values of free energy of formation of these three complexes indicate that these complexes are thermodynamically stable.

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1. Introduction

Charge transfer interaction plays a vital role in various fields [1–3]. The interaction between polar groups such as carbonyl group of ketones and amino group in non-polar environment is significant in practical applications. Carbonyl group which is a part of several biologically important molecules such as protein, lipids and hormones, has electron deficient carbon that can function as electrophile. The carbonyl oxygen is electron rich and it can form hydrogen bond. Ketones can interact strongly with amines and alcohols due to the presence of active hydrogen in these molecules. Thus, the formation of donor–acceptor complexes can be expected between ketones and primary and secondary amines. It is reported that amines can form charge transfer complexes with ketones [4]. The formation of charge transfer complexes of ketones with aniline in n-hexane [5] and iodine monochloride with ethers in different solvents [6] by ultrasonic method have been reported.

In the present investigation, three aromatic ketones, acetophenone, 4-chloroacetophenone and 4-methylacetophenone were mixed separately with equimolar concentrations of N-methylaniline in n-hexane. The values of ultrasonic velocity (u), density (ρ) and viscosity (η) were measured for these solutions at 303.15 K. From these values, acoustic parameters and excess parameters were computed. The stability constants of the donor–acceptor complexes were calculated using Kannappan equation (ultrasonic method) and Benesi–Hildebrand equation (optical method) at ambient temperature and the results are discussed. The stability constant values were used to calculate free energy of formation (ΔG) of these complexes. The results are interpreted in terms of molecular interactions between the components of the system.

2. Material and methods

All compounds used in the present work were of Analar grade samples and they were purified before use in accordance with the procedure described elsewhere [7,8]. The estimated purity was >99.8%. Ultrasonic sound velocities were measured in a single crystal variable path ultrasonic interferometer operating at 2 MHz frequency supplied by Mittal Enterprises, India, Model F81, at 303.15 K. The

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Table 1
The values of ultrasonic velocity u, density ρ, viscosity η, adiabatic compressibility κ, free length L_f, molar volume V, free volume V_f, interaction parameter α, Lenard Jones Potential LJP and internal pressure $π_i$ for equimolar concentration 'C' of acetophenone and N-methylaniline in n-hexane at 303.15 K.

C	u/ (ms^{-1})	ρ/ (kgm^{-3})	η/ (10^{-4} Nsm^{-2})	κ/ (npa^{-1})	L_f/ (A^0)	V/ 10^{-4}(m^3 mol^{-1})	V_f/ 10^{-7}(m^3 mol^{-1})	α	LJP/ (Jmol^{-1})	$π_i$/ (10^2 Mpa)
0.02	1064.1	672.1	3.394	1.314	0.7250	1.284	5.028	−0.0024	4.914	2.489
0.04	1065.9	673.1	3.392	1.308	0.7232	1.285	5.058	−0.0033	4.974	2.484
0.06	1067.9	674.1	3.406	1.301	0.7213	1.285	5.053	−0.0037	5.042	2.484
0.08	1070.3	677.0	3.478	1.289	0.7182	1.281	4.926	−0.0033	5.123	2.510
0.1	1071.2	677.7	3.451	1.286	0.7172	1.282	5.002	−0.0057	5.154	2.496
0.12	1072.5	679.1	3.450	1.280	0.7156	1.281	5.025	−0.0073	5.199	2.493
0.14	1074.9	680.9	3.460	1.271	0.7131	1.280	5.031	−0.0068	5.282	2.494
0.16	1076.5	682.4	3.515	1.265	0.7112	1.279	4.936	−0.0078	5.338	2.511
0.18	1076.9	683.3	3.519	1.262	0.7105	1.279	4.942	−0.0109	5.352	2.510
0.2	1078.4	685.1	3.507	1.255	0.7086	1.278	4.989	−0.0119	5.405	2.504

instrument was calibrated by measuring the velocity of triple distilled water, carbon tetra chloride and dimethyl sulfoxide. The sound velocities are accurate to 0.02%. The densities of the solutions were determined using a 10 ml specific gravity bottle and a digital balance of accuracy $±10^{-6}$ kg. Viscosity measurements were made with an Ostwald's viscometer in which the flow time for solutions was measured through a digital stop clock of accuracy ±0.01 s. Digitally controlled and well-stirred thermostatic water bath with a temperature T = (303.15 ± 0.1) K was used for all the measurements. UV–visible spectra were recorded on a Shimadzu UV-1650 model spectrophotometer with quartz cell of 1 cm optical path length. The solvent (n-hexane) was used for base line correction. The absorbance spectra were recorded in the region of 200–700 nm at a scanning rate of 0.2 nm/s and a slit width of 1 cm.

The standard relations used to calculate the various acoustic and excess thermo acoustic parameters using the measured values of ultrasonic velocity (u), density (ρ) and viscosity (η) were taken from literature [9–11]. The stability constants of the complexes were computed from 'u' values by employing Kannappan equation and using the absorbance values of UV–vis spectra by employing Benesi–Hildebrand equation as reported in our earlier work [12].

3. Results and discussion

3.1. Acoustical parameters

The measured values of ultrasonic velocity (u), density (ρ) viscosity (η) and the computed values of various acoustic parameters for the three ternary systems at 303.15 K are presented in Tables 1–3. The variation of adiabatic compressibility (κ) and internal pressure ($π_i$) with concentration of amine and ketones (equimolar) are shown in Figs. 1 and 2. Perusal of Tables 1–3 reveals that the measured parameters for the three ternary systems increase with the increase in the solute concentrations. The trend in the ultrasonic velocity is almost similar for all the systems. The increase in velocity may be attributed to strong solute–solute interactions. It was reported that the strength of molecular interaction in liquid mixtures becomes maximum where the velocity maxima occur [13]. This may probably be due to molecular association and complex formation through hydrogen bonding [14]. The mixing of ketones, with secondary amine, N-methylaniline breaks the hydrogen bonds in NMANI releasing several molecules of the component liquids for mutual interaction, possibly through (new) hydrogen bonds between –COCH$_3$ group of ketone with –NHCH$_3$ group of NMANI.

Table 2
The values of ultrasonic velocity u, density ρ, viscosity η, adiabatic compressibility κ, free length L_f, molar volume V, free volume V_f, interaction parameter α, Lenard Jones Potential LJP and internal pressure $π_i$ for equimolar concentration 'C' of 4-chloroacetophenone and N-methylaniline in n-hexane at 303.15 K.

C	u/ (ms^{-1})	ρ/ (kg m^{-3})	η/ (10^{-4} Nsm^{-2})	κ/ (npa^{-1})	L_f/ (A^0)	V/ 10^{-4}(m^3 mol^{-1})	V_f/ 10^{-7}(m^3 mol^{-1})	α	LJP/ (Jmol^{-1})	$π_i$/ (10^2 Mpa)
0.02	1064.5	671.2	3.379	1.315	0.7252	1.287	5.073	−0.0015	4.927	2.478
0.04	1066.6	673.6	3.447	1.305	0.7225	1.286	4.958	−0.0016	4.998	2.498
0.06	1068.0	677.0	3.445	1.295	0.7197	1.283	4.991	−0.0029	5.045	2.497
0.08	1069.5	678.5	3.479	1.289	0.7179	1.284	4.948	−0.0040	5.096	2.503
0.1	1071.1	681.0	3.516	1.280	0.7155	1.282	4.900	−0.0049	5.151	2.513
0.12	1072.6	683.1	3.508	1.272	0.7134	1.282	4.946	−0.0060	5.203	2.506
0.14	1074.2	684.8	3.525	1.266	0.7115	1.282	4.940	−0.0068	5.258	2.507
0.16	1075.4	687.1	3.553	1.258	0.7095	1.280	4.908	−0.0083	5.300	2.514
0.18	1077.4	689.1	3.567	1.250	0.7072	1.280	4.910	−0.0083	5.370	2.515
0.2	1078.9	691.2	3.604	1.243	0.7051	1.279	4.862	−0.0092	5.423	2.524

Table 3
The values of ultrasonic velocity u, density ρ, viscosity η, adiabatic compressibility κ, free length L_f, molar volume V, free volume V_f, interaction parameter α, Lenard Jones Potential LJP and internal pressure $π_i$ for equimolar concentration 'C' of 4-methylacetophenone and N-methylaniline in n-hexane at 303.15 K.

C	u/ (ms^{-1})	ρ/ (kg m^{-3})	η/ (10^{-4} Nsm^{-2})	κ/ (npa^{-1})	L_f/ (A^0)	V/ 10^{-4}(m^3 mol^{-1})	V_f/ 10^{-7}(m^3 mol^{-1})	α	LJP/ (Jmol^{-1})	$π_i$/ (10^2 Mpa)
0.02	1064.7	668.9	3.379	1.319	0.7263	1.292	5.074	−0.0013	4.934	2.472
0.04	1066.2	671.1	3.447	1.311	0.7241	1.289	4.946	−0.0027	4.984	2.496
0.06	1068.0	672.8	3.445	1.303	0.7220	1.289	4.978	−0.0035	5.045	2.492
0.08	1069.6	674.1	3.479	1.297	0.7202	1.289	4.931	−0.0046	5.100	2.499
0.1	1071.7	676.2	3.516	1.288	0.7177	1.287	4.882	−0.0048	5.171	2.509
0.12	1073.4	678.0	3.508	1.280	0.7156	1.287	4.925	−0.0057	5.230	2.503
0.14	1075.1	679.9	3.525	1.272	0.7134	1.285	4.915	−0.0065	5.289	2.506
0.16	1076.6	681.6	3.553	1.266	0.7116	1.285	4.881	−0.0076	5.342	2.513
0.18	1078.8	682.9	3.567	1.258	0.7094	1.285	4.881	−0.0074	5.419	2.513
0.2	1080.6	685.4	3.604	1.249	0.7070	1.282	4.832	−0.0079	5.483	2.525