

Investigations in Acoustic Parameters of Substituted Thiocarbamidoacetophenones

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ABSTRACT

Ultrasonic velocity and density measurements have been carried out for solutions of 2-hydroxy-3-nitro-5-methyl- α -thiocarbamidoacetophenone (6a) and 2-hydroxy-3-nitro-5-methyl- α -phenylthiocarbamidoacetophenone (6d) in ethanol and dioxane solvents and also after the addition of Co(II) and Cr(II) metal ion solutions at 303.15 K and frequency 2MHz. This data have been used to determine various acoustic/thermodynamic parameters viz. adiabatic compressibility (β), apparent molar compressibility (ϕ_{κ}), apparent molar volume (ϕ_{ν}), intermolecular free length (L_f), relative association (R_A) and specific acoustic impedance (Z). These properties are used to interpret weak molecular solute-solvent, solute-solute interactions in the system.

Keywords: Ultrasonic velocity, Acoustical properties, Molecular interactions.

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INTRODUCTION

Determinations of ultrasonic velocity and absorption coefficient have furnished methods for studying molecular and structural properties of liquids and the study of molecular interactions in liquids provides valuable information regarding internal structure, molecular association, complex formation, internal pressure etc. In recent years, Ultrasonic waves have acquired the status of an important probe for the study of structure and properties of matter.

Ultrasonic technique reveals very weak intermolecular interactions due to its useful wavelength range. Many workers have studied the acoustical parameters by the measurement of density and ultrasonic velocity of different aqueous and non-aqueous systems at different temperatures, different concentrations of solute and in different percentage of organic solvents [1-8]. In recent years, ultrasonic velocity and absorption studies in case of electrolyte solutions have led to new insight into the process of ion-association and complex formation. Density, ultrasonic velocity and viscosity measurements of pharmacologically significant drugs in methanol at 25°C have been studied by D. V. Jahagirdar et al [9]. Ultrasonic Velocity and Compressibility in Aqueous Solutions of Alkali Metal Chlorides have been studied by Hisashi Uedaira and Yasuko Suzuki [10]. Deosarkar et al studied the acoustical behavior of these pyrazoles in 0.01M concentration in different percentage of dioxane-water mixture to discuss the interactions of unlike molecule of solvents in presence of solute [11]. S. R. Aswale et al studied molecular interaction in paracetamol solution at different concentrations [12]. From literature survey it is clear that much work has been done in water and organic solvent mixtures, but scanty work is found in pure ethanol or dioxane solvent and comparison of interactions in these different solvents. Hence, we intended to analyze comparative study of ethanol and dioxane solvents with 2-hydroxy-3-nitro-5-methyl- α -thiocarbamidoacetophenone (6a) and 2-hydroxy-3-nitro-5-methyl- α -phenylthiocarbamidoacetophenone (6d), the effect of these solvents specially related to protic-aprotic nature of solvent, polarity-non-polarity of solvent and hydrogen bonding in solvent, dielectric constant, density, viscosity and surface tension of solvent on solute-solvent, ion-solvent and ion-ion interactions in this investigation.

MATERIALS AND METHODS

All the chemicals used were of AR grade. The solvents (1,4-dioxane and ethanol) were purified by standard procedure [13]. The double distilled water is used for preparation of metal solutions of Co(II) and Cr(II). Densities were measured with the help of density bottle. Solutions of ligands in ethanol and dioxane solvent and 0.01 M solutions of Co(II) and Cr(II) were prepared separately. Weighing was made on CCB – 4 digital electronic balance, with an accuracy of ± 0.001 gm. For measuring the ultrasonic velocity and density a special thermostatic arrangement was made, in which continuous stirring of water was carried out with the help of electric stirrer and temperature variation was maintained within $\pm 0.1^\circ\text{C}$. The Borosil make density bottle (25ml) was used for this study. Single crystal interferometer (Mittal Enterprises, Model F-81) with accuracy of $\pm 0.03\%$ and frequency 2 MHz was used.

Theory and Calculations

Ultrasonic velocities measurements are extensively used to study the intermolecular interactions. The structural arrangements are influenced by the shape of molecules as well as by their mutual interactions.

By measuring ultrasonic velocity (v) and density (d) experimentally, the adiabatic compressibility (β) can be evaluated by using Laplace's equation-

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

Apparent molar compressibility (ϕ_k) is an acoustic property which is determined by measuring density and ultrasonic velocity.

$$\phi_k = [1000 (\beta_s d_o - \beta_o d_s) / m d_s d_o] + (\beta_s M / d_s) \quad (2)$$

Where, β_s = adiabatic compressibility of solution, β_o = adiabatic compressibility of pure solvent, d_s = density of solution, d_o = density of pure solvent, M = molecular weight of solute, and m = molality of solution

Intermolecular free length has been calculated from adiabatic compressibility (β) by Jacobson's formula, [14,15]

$$L_f = K \cdot \sqrt{\beta_s} \quad (3)$$

where, K is the temperature dependent constant known as Jacobson's constant and is independent of the nature of liquid.

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

$$R_A = \frac{d_s}{d_o} \left(\frac{v_o}{v_s} \right)^{1/3} \quad (4)$$

where, v_o and v_s are ultrasonic velocities in solvent and solution respectively.

From the measurement of ultrasonic velocity and density Specific acoustic impedance (Z) is determined by formula,

$$Z = v_s \cdot d_s \quad (5)$$

Interactions between solute and solvent may be interpreted in terms of acoustic impedance.

The apparent molar volume was determined by the relation,

$$\phi_v = [1000 (d_o - d_s) / m d_s d_o] + (M/d_s) \quad (6)$$

Table-1:Acoustic parameter for ligand in ethanol at 303.15K [Freq.=2MHz]

ligand	v (m/sec ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (pa ⁻¹)	ϕ_v (m ³ mol ⁻¹)	ϕ_k ((m ³ mol ⁻¹ pa ⁻¹)	L_f (A)	R_A	$Z \times 10^4$ (kg m ⁻² sec ⁻¹)
6a	1180.22	783.45	9.1635	0.4849	-1.0365	0.0191	0.9895	92.46
6d	1185.45	783.98	9.0767	0.4954	-2.1384	0.0190	0.9887	92.94

Table-2:Acoustic parameter for ligand in dioxane at 303.15K [Freq.=2MHz]

ligand	v (m/sec ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (pa ⁻¹)	ϕ_v (m ³ mol ⁻¹)	ϕ_k ((m ³ mol ⁻¹ pa ⁻¹)	L_f (A)	R_A	$Z \times 10^4$ (kg m ⁻² sec ⁻¹)
6a	1215.25	1075.41	5.9393	-1.8538	9.3018	0.0154	1.083	134.56
6d	1259.05	1066.00	5.9178	-1.1028	9.6299	0.0153	1.071	134.21

Table-3:Acoustic parameter for Cr(II)-ligand in ethanol at 303.15K [Freq.=2MHz]

ligand	v (m/sec ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (pa ⁻¹)	ϕ_v (m ³ mol ⁻¹)	ϕ_k ((m ³ mol ⁻¹ pa ⁻¹)	L_f (A)	R_A	$Z \times 10^4$ (kg m ⁻² sec ⁻¹)
6a	1186.69	799.56	8.8813	-2.0938	-6.9394	0.0187	1.008	94.88
6d	1185.44	820.47	8.6720	-5.1679	-1.222	0.0186	1.0347	97.26

Table-4:Acoustic parameter for Cr(II)- ligand in dioxane at 303.15K[Freq.=2MHz]

ligand	v (m/sec ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (pa ⁻¹)	ϕ_v (m ³ mol ⁻¹)	ϕ_k (m ³ mol ⁻¹ pa ⁻¹)	L _f (A)	R _A	Z x10 ⁴ (kg m ⁻² sec ⁻¹)
6a	1313.56	1054.87	5.4942	-0.1076	6.1486	0.0148	1.0454	138.56
6d	1315.84	1072.20	5.3866	-1.5740	4.3363	0.0146	1.0619	141.08

Table-5:Acoustic parameter for Co(II)-ligand in ethanol at 303.15K [Freq.=2MHz] T

ligand	v (m/sec ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (pa ⁻¹)	ϕ_v (m ³ mol ⁻¹)	ϕ_k (m ³ mol ⁻¹ pa ⁻¹)	L _f (A)	R _A	Z x10 ⁴ (kg m ⁻² sec ⁻¹)
6a	1180.42	811.25	8.8465	-3.9033	-8.9750	0.0188	1.0245	95.76
6d	1210.34	790.42	8.6363	-0.5475	-8.6759	0.0185	0.9899	95.67

Table-6:Acoustic parameter for Co(II)- igand in dioxane at 303.15K

ligand	v (m/sec ⁻¹)	d (kg m ⁻³)	$\beta \times 10^{-10}$ (pa ⁻¹)	ϕ_v (m ³ mol ⁻¹)	ϕ_k (m ³ mol ⁻¹ pa ⁻¹)	L _f (A)	R _A	Z x10 ⁴ (kg m ⁻² sec ⁻¹)
6a	1371.24	1056.98	5.0316	-0.2974	1.6563	0.0142	1.0326	144.98
6d	1377.17	1056.09	4.9926	-0.1455	1.3619	0.0141	1.0302	145.44

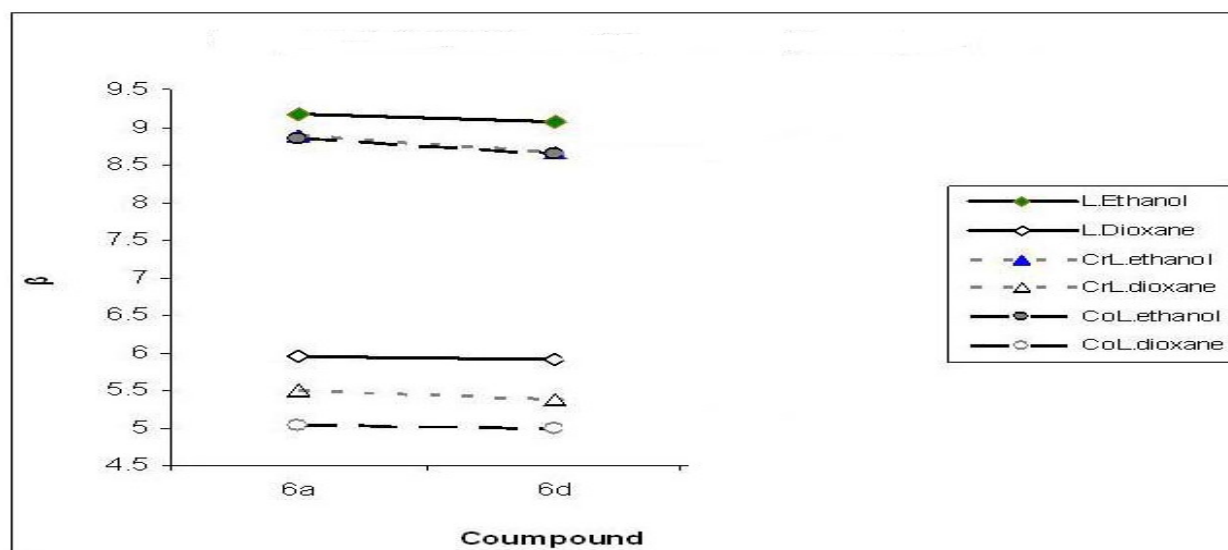


Fig.-1: Adiabatic compressibility of 6a, 6d

RESULTS AND DISCUSSION

Measurement of ultrasonic velocity is the best tool to investigate solute-solvent, solute-solute and ion-solvent interactions. Therefore, in last four decades ultrasonic interferometric study created its own identity for determining solute-solvent interactions. By this study, β , ϕ_k , L_f , R_A , Z etc. acoustic properties are determined which explain how these interactions occur and responsible for breaking and making of the structure in the solution. So in the present work these acoustic parameters were studied for newly synthesized ligands, which are used as solutes.

Literature survey reveals that the comparative study of these acoustic parameters is not done in between dioxane and ethanol, so our aim in this work was to find out how the property of solvent interferes in breaking and making of structure of solvent. From this study it is clear that properties, which are directly or indirectly responsible for this are protic-aprotic nature of solvents, dielectric constant, polarity, density, tendency of forming hydrogen bonding, surface tension, viscosity of solvent etc.

In the present study, interaction of metal ions with ligands and solvents were investigated. The aim during the investigation was to study effect of ionic size, oxidation state, electronegativity of metal ion in solute-solvent interaction etc. The above two studied properties of solvent and metal ions are not the only prime factors which influence the interactions but the properties of ligand viz. resonance stability of ligand, size of ligand, structure of

ligand, heterocyclic nature of ligand and different substituents like electron donating/withdrawing groups in ligands also will have influence on interactions.

CONCLUSIONS

It can be concluded from above study that interferometric technique requires minimum efforts, solutions and is somewhat a direct method and has its own identity and significance in material sciences, which can give idea about effectiveness of solvent. By knowing these parameters the selection of solvent during synthesis in organic and coordination chemistry can be predicted. The acoustic parameters studied in the present work are in pure solvents and interactions are interpreted.

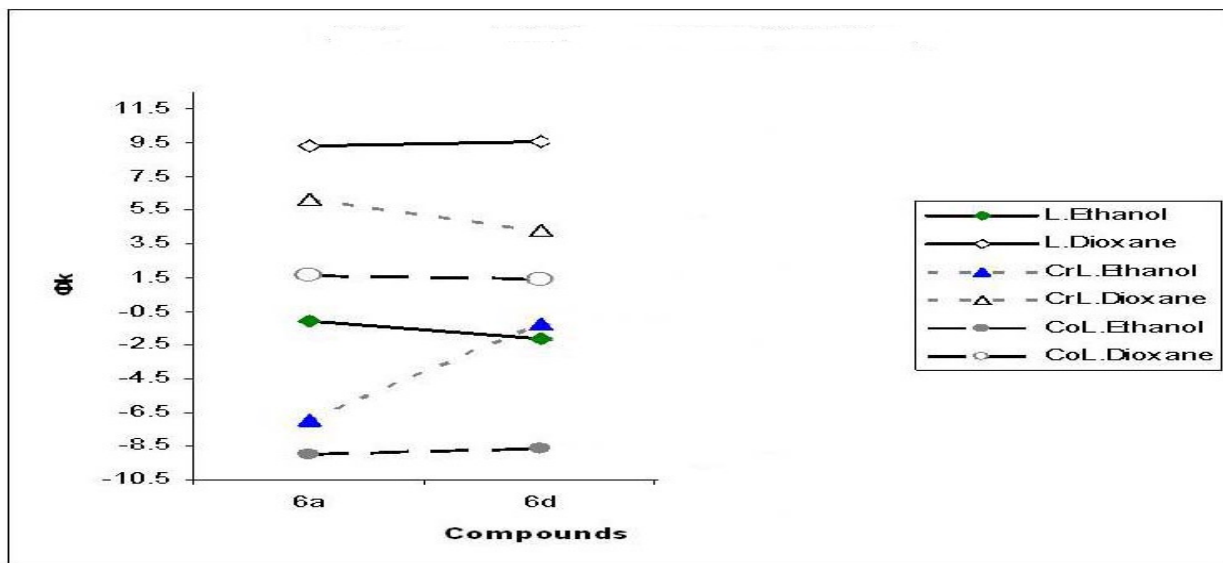


Fig.-2: Apparent molar compressibility

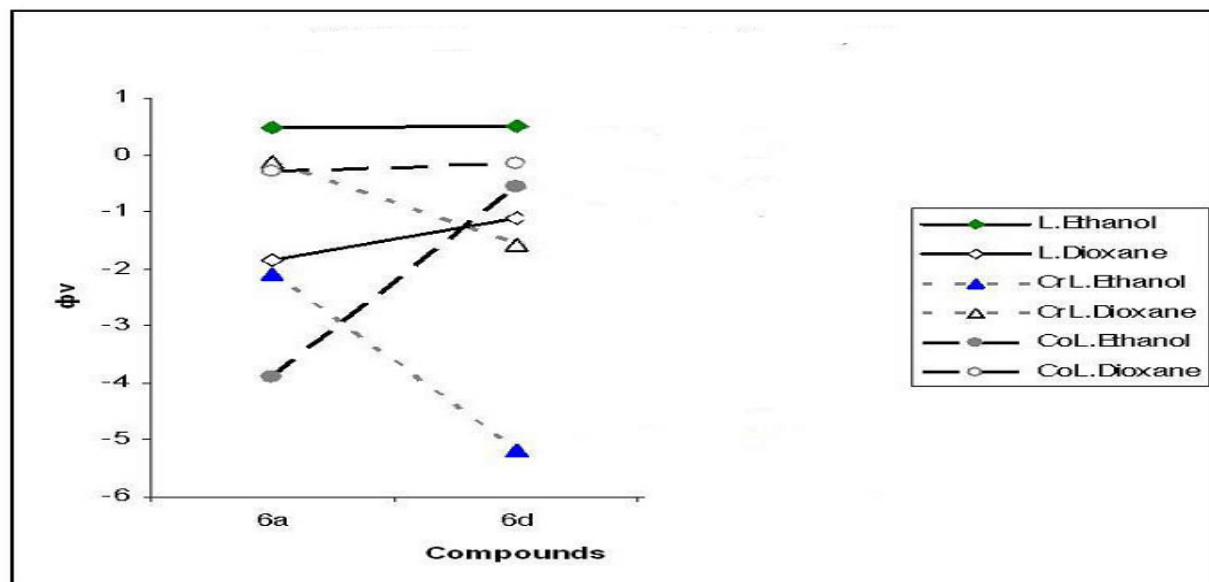


Fig.-3: Apparent Molar Volume of 6a, 6d

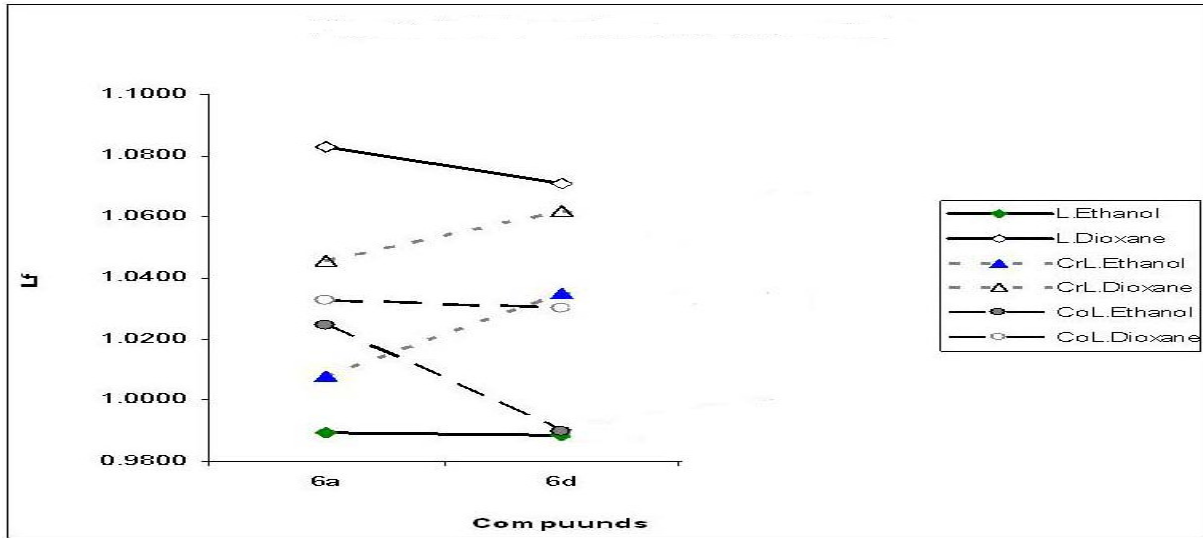


Fig-4: Intermolecular free Length

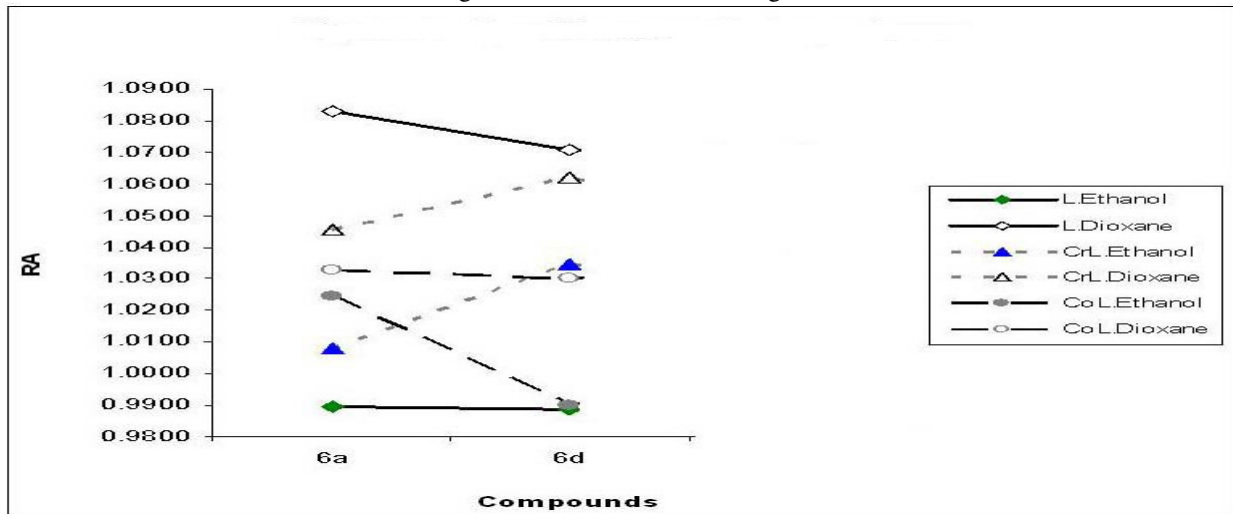


Fig-5: Specific Acoustic Impedance

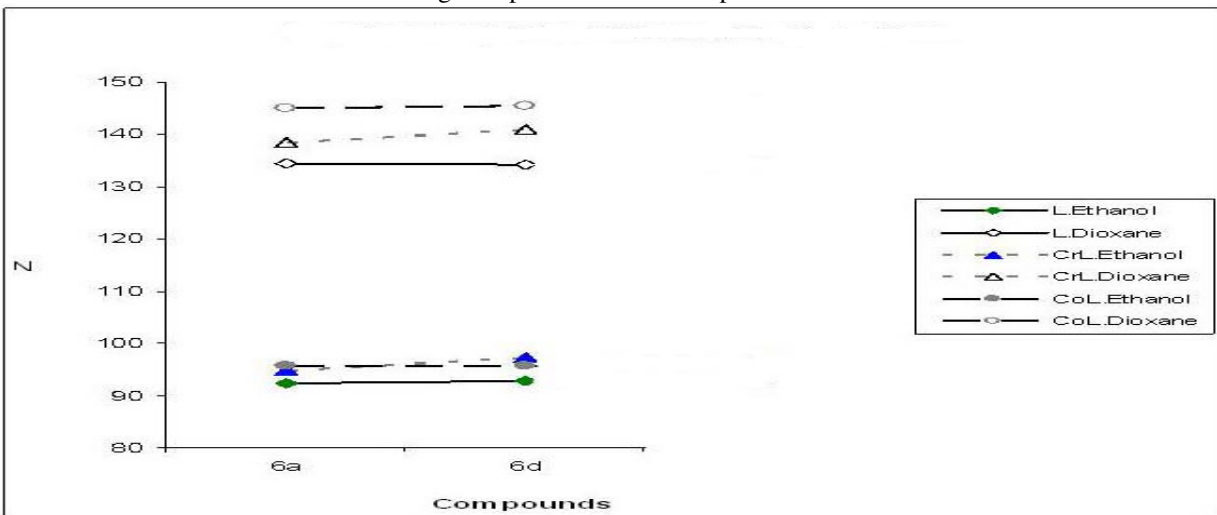


Fig-6: Specific Acoustic Impedance

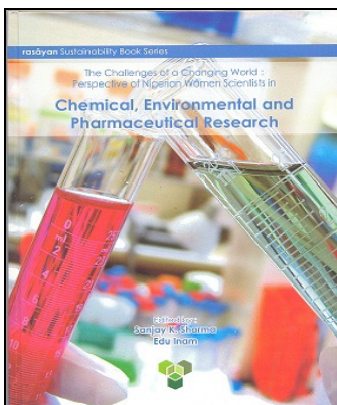
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