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RESEARCH ARTICLE

Ultrasonic and Thermodynamic Analysis of Molecular Interaction in Sodium Dodecyl Sulphate-Urea-Water Ternary Mixtures at Various Temperatures

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ABSTRACT: This study investigates the ternary mixture of sodium dodecyl sulphate (SDDS) with urea in water through ultrasonic and thermodynamic analyses at temperatures of 303, 308, 313, 318, and 323 K. Experimental values were used to calculate derived parameters such as ultrasonic velocity (U), density (ρ), and viscosity (η). These parameters enabled the computation of acoustic properties, including adiabatic compressibility (βs) and intermolecular free length (Lf). The findings indicate that urea exhibits hydrophilic (structure-breaking, SB) behavior with weak interactions at lower temperatures (303-308 K) and hydrophobic (structure-making, SM) behavior with stronger interactions at higher temperatures (313-323 K). The study demonstrates that ultrasonic velocimetry is a powerful and precise method for characterizing interactions between surfactants and biomolecules. The temperature coefficients of ultrasonic velocity ($\partial U/\partial T$) and adiabatic compressibility ($\partial \beta s/\partial T$) were found to have positive and negative values, respectively, further confirming the temperature-dependent interaction behavior of urea. Additionally, relaxation time analysis revealed that the maximum relaxation time for the binary solution occurs at 312 K and the minimum at 323 K, whereas for the ternary solution, the maximum relaxation time is also at 312 K and the minimum at 320 K. These results have significant implications in fields such as solution chemistry, biochemistry, biosciences, surface science, surfactant chemistry, industrial chemistry, and both physical and chemical sciences.

Keywords: Ultrasonic velocity, Dipole-dipole interaction, Adiabatic compressibility (βs), Sodium dodecyl sulphate (SDDS).

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1. INTRODUCTION

Sodium dodecyl sulphate (SDDS), an anionic surfactant, is a prominent member of the sodium alkyl sulphate family [1]. These surfactants are widely used in various industries due to their effective cleaning properties and relatively low manufacturing costs. SDDS, in particular, finds applications in household and industrial detergents, cosmetics, pharmaceuticals, and food processing. However, despite its widespread use, SDDS poses environmental and health concerns [2]. It is known to be toxic to microorganisms and aquatic life due to its ability to interact with biological membranes, which can disrupt cellular functions depending on its concentration. The biodegradability of SDDS is crucial for minimizing its environmental impact, as persistent surfactants can accumulate in water bodies, affecting aquatic ecosystems and human health [3].

Biomolecules, electrolytes, and water are essential

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components of all living organisms. They play critical roles in numerous cellular processes, including nutrition, growth, reproduction, and response to environmental changes. Biomolecules such as carbohydrates (e.g., glucose, sucrose) and amino acids (e.g., glycine, urea) are particularly significant in biological systems. These molecules are involved in metabolic pathways and contribute to the structural and functional integrity of cells [2]. Urea, for instance, is a vital biomolecule involved in the nitrogen cycle and protein metabolism. Understanding the interactions between biomolecules and electrolytes in aqueous solutions is important because these interactions can influence cellular functions and processes, including aging and apoptosis [3]. The study of solute-solvent and solute-co-solute interactions in ternary systems, which include electrolyte-water-non-electrolyte mixtures, has garnered considerable attention in recent years. These interactions are fundamental to understanding the behavior of solutions in various fields, such as solution chemistry, biochemistry, and microbiology [3, 4]. The structural changes in solvents induced by the addition of ionic or non-ionic solutes can significantly impact the physicochemical properties of the system. Investigating these changes provides insights into the mechanisms governing solute-solvent interactions, which are critical for developing new materials and technologies [5].

The interactions between water, other solvents, and ionic surfactants like SDDS are of particular interest for modeling biological systems, such as liquid membranes and liposomes [6]. These systems are essential for studying biological processes and developing applications in drug delivery, biosensing, and environmental remediation. The physicochemical behavior of ternary systems, such as SDDS-water-urea, can be understood by examining various thermodynamic, absorption, and relaxation parameters [7]. Ultrasonic velocity, viscosity, and density measurements are effective methods for evaluating these parameters and gaining a comprehensive understanding of the system's behavior [8-13].

Previous studies have extensively examined the interactions and thermodynamic behavior of ternary systems consisting of electrolytes, water, and non-electrolytes. The pioneering work of Robinson and Stokes laid the foundation for understanding electrolyte-solvent-non-electrolyte systems [6]. Various physicochemical techniques, including conductometry and viscometry, have been employed to investigate these systems' properties and behaviors [14-16]. These studies have highlighted the importance of solute-solvent interactions and their impact on the physicochemical properties of the solutions.

This study focuses on the interactions of SDDS with urea in water, analyzed through thermodynamic, absorption, and relaxation parameters. Urea, an organic additive and biomolecule, plays a crucial role in many physiological processes. Despite the significance of anionic surfactants and their interaction with biomolecules, a comprehensive and systematic ultrasonic investigation of such systems has been lacking. Ultrasonic velocimetry is a highly accurate and sensitive technique that can be used to explore solute-solvent interactions and the structural effects within ternary mixtures of SDDS-water-urea.

The present research aims to investigate the ultrasonic velocity and related parameters of SDDS-water-urea ternary mixtures at various temperatures (303, 308, 313, 318, and 323 K). By providing detailed insights into the physicochemical properties of these systems, this study contributes to a better understanding of solute-solvent interactions and their potential applications in fields such as biochemistry, material science, and industrial chemistry. The findings can help in designing new materials and improving existing technologies that rely on the unique properties of ternary mixtures involving surfactants and biomolecules.

2. EXPERIMENTAL DETAILS

2.1. Materials and Preparation

Sodium dodecyl sulphate (SDDS) of analytical reagent (A.R.) grade from Qualigen and urea from S.D. Fine Chemicals were used without further purification. An aqueous solution of SDDS with a constant molarity of 0.5 mM was prepared using distilled de-ionized water (specific conductance k = 2.48 μmhos, pH = 7.8). Similarly, a 0.5 M aqueous solution of urea was prepared using the same distilled de-ionized water, which served as the solvent for preparing the ternary mixture.

2.2. Measurement of Ultrasonic Velocity, Viscosity, and Density

The ultrasonic velocity, viscosity, and density of the freshly prepared 0.5 mM SDDS solution in water and the 0.5 M urea solution were measured at various temperatures (303 K, 308 K, 313 K, 318 K, and 323 K). A variable path interferometer using a single crystal ultrasonic interferometer (Mittal Enterprises, New Delhi, Model F-81) operating at 1.5 MHz was used for measuring ultrasonic velocity. Viscosity was measured using an Ostwald viscometer, and density was determined using a pyknometer.

To ensure accurate measurements, the constant temperature of the solutions was maintained by circulating water from a thermostat controlled by a mercury contact thermometer with an accuracy of ±0.1 K. The ultrasonic velocity, viscosity, and density data were accurate within ±0.2%, ±0.3%, and ±0.02%, respectively.

2.3. Calibration of Instruments

The instruments were calibrated before use with pure water, benzene, and carbon tetrachloride at different temperatures. Ultrasonic velocity measurement is based on accurately determining the wavelength (λ) of the ultrasonic waves in the medium. The measuring cell was connected to the output

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terminal of a high-frequency generator via a shielded cable and filled with the solution. The generator was switched on, and the micrometer was slowly moved until maxima in the anode current of the high-frequency generator were observed. Several maxima readings (n) were obtained as the micrometer moved a distance (d). The ultrasonic velocity (U) was calculated using the below relation [17]:

$$U = \lambda \times f$$

where the wavelength (λ) was determined from the total distance (d) moved by the micrometer using the below equation:

$$d = n \times \lambda/2$$

2.3. Theoretical Formulation

Various ultrasonic parameters were computed from the velocity and density data using the following equations [18-22]:

Adiabatic Compressibility (βs):

$$\beta s = \rho^{-1} U^{-2}$$

Intermolecular Free-Length (Lf):

$$L_f = K U^{-1} \rho^{-1/2} = K \beta s^{1/2}$$

where K is Jacobson's empirical constant, temperature-dependent (K = 642 x 10^{-6} at 313 K).

Molar Sound Velocity (R):

$$R = (M/\rho)\, U^{1/3}$$

where M is the effective molecular weight of the ternary solution, given by: $M = \frac{n1M1+n2M2+n3M3}{n1+n2+n3}$ and n_1, n_2, n_3 are the number of moles of water, glycine, and SDDS respectively; M_1, M_2, and M_3 are their respective molecular weights.

Specific Acoustic Impedance (Z):

$$Z = \rho\, U$$

Relative Association (RA):

$$R_A = \rho / \rho^0 \, (U^0/U)^{1/3}$$

where U^0 and ρ^0 are the ultrasonic velocity and density of the solvent, respectively.

This comprehensive methodology ensures the precise determination of various thermodynamic and acoustic parameters, providing valuable insights into the interactions within the ternary mixtures of SDDS, urea, and water.

3. RESULTS AND DISCUSSION

The experimentally determined values of ultrasonic velocity, viscosity, density, and other acoustic parameters for the ternary system of sodium dodecyl sulphate (SDDS), water, and urea at different temperatures (303 K, 308 K, 313 K, 318 K, and 323 K) are presented in Figure 1-4 and Tables 1-2. These measurements are used to assess molecular interactions in the ternary system across the temperature range.

The solute-solvent and solute-co-solute interactions in aqueous ternary systems consisting of electrolyte-water-non-electrolyte, as well as the structural properties of solutes in aqueous solutions, are evaluated in terms of various thermodynamic, absorption, and relaxation parameters derived from ultrasonic velocity, viscosity, and density measurements. These parameters in electrolyte solutions like SDDS generally exhibit linearity with temperature at a constant milli-molarity (0.5 mM) of surfactant (solute). However, non-linearity has also been observed. The departure of sound velocity from linearity with temperature may indicate various interactions in the system being investigated.

Figures 1-4 display the temperature dependence of the ultrasonic velocity of 0.5 mM SDDS in water and 0.5 M aqueous urea solution. The temperature at which the curves intersect indicates that the behavior of both solutions (binary and ternary systems) is similar.

Figure 1 represents the plots of ultrasonic velocity of 0.5 mM SDDS in water and 0.5 M aqueous urea solution versus temperature. Different trend curves are obtained in the binary and ternary solutions of the same milli-molarity of SDDS. The velocity exhibits nonlinearity with temperature in both solutions. The ultrasonic velocity versus temperature curve for the binary solution of SDDS exhibits a negative slope in the low-temperature range (303 K to 308 K) and almost zero slope in the higher temperature range (313 K to 323 K). The curve for the ternary solution of SDDS in 0.5 M urea also displays non-rectilinear behavior with temperature. Ultrasonic velocity reaches a minimum at 313 K, which may be considered the minimum velocity temperature. The nonlinear curve for the ternary solution also exhibits a distinct break at 313 K, where the temperature coefficient of ultrasonic velocity (∂U/∂T) has positive and negative values. The positive (∂U/∂T) indicates hydrophilicity, and the negative (∂U/∂T) indicates the hydrophobicity of urea. The (∂U/∂T) remains negative and positive within the temperature ranges of 303 K to 308 K and 313 K to 323 K, respectively, and acquires zero value (∂U/∂T) = 0 at 313 K. This reveals that urea is hydrophilic within the temperature range of 303 K to 308 K and hydrophobic within the temperature range of 313 K to 323 K.

The plots of adiabatic compressibility (βs) of 0.5 mM SDDS in water and 0.5 M aqueous urea biomolecular

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solution versus temperature are depicted in Figure 2. Different curve trends are obtained in binary and ternary solutions. The plots of adiabatic compressibility versus temperature for SDDS are different from the ultrasonic velocity profile, as depicted in Figure 1. The compressibility displays non-linearity with temperature. The non-linearity curve for the binary solution exhibits a positive slope at 308 K and almost zero slope in the higher temperature range of 313 K to 323 K. The curve for the ternary solution of SDDS in 0.5 M urea displays maximum adiabatic compressibility at 313 K, which may be marked as the temperature of maximum compressibility [23].

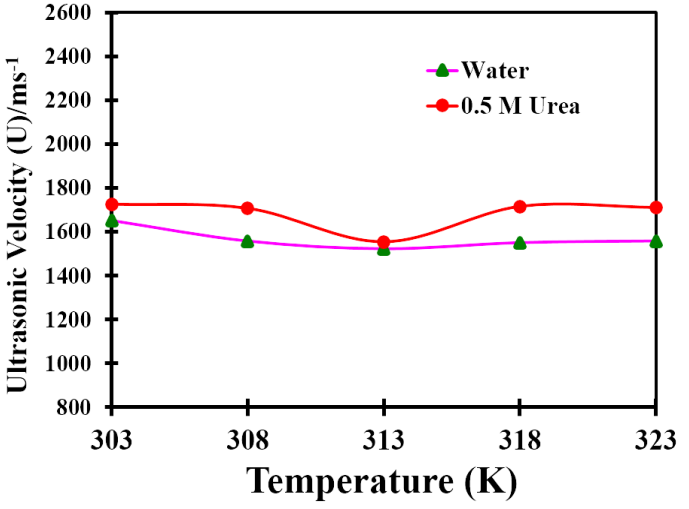

Fig. 1. Temperature dependence of ultrasonic velocity (U) for a 0.5 mM solution of Sodium Dodecyl Sulphate (SDDS) in water and a 0.5 M aqueous urea solution.

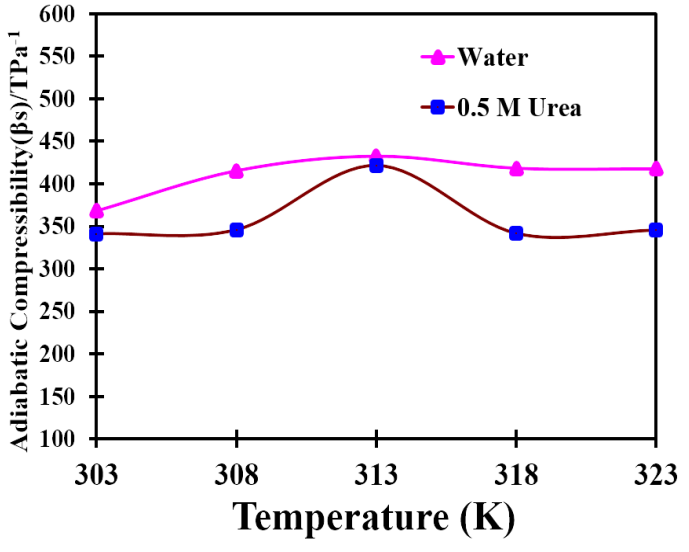

Fig. 2. Effect of temperature on the adiabatic compressibility (βs) of a 0.5 mM solution of SDDS in water and a 0.5 M aqueous urea solution. The graph illustrates the temperature-induced changes in compressibility for both systems.

This curve also exhibits a distinct break at 313 K, where the temperature coefficient ($\partial\beta s/\partial T$) has positive and negative values. A negative ($\partial\beta s/\partial T$) within the temperature range of 313 K to 318 K indicates the hydrophilicity of urea. This further confirms that urea behaves both as hydrophobic and hydrophilic in a ternary solution of SDDS [24].

Figure 3 depicts the effect of temperature on classical water absorption and 0.5 M aqueous urea solution. Different curve trends are obtained in binary and ternary solutions. Both plots are almost similar, as exhibited by the adiabatic compressibility profile of SDDS in Figure 2. The curves for both binary and ternary solutions show a general increase in absorption with temperature. This indicates that the interaction between SDDS and water or urea molecules increases with temperature, leading to higher absorption values. The similarity in the trend between the binary and ternary solutions suggests that the presence of urea does not significantly alter the absorption behavior of SDDS, but rather enhances it in a predictable manner [25].

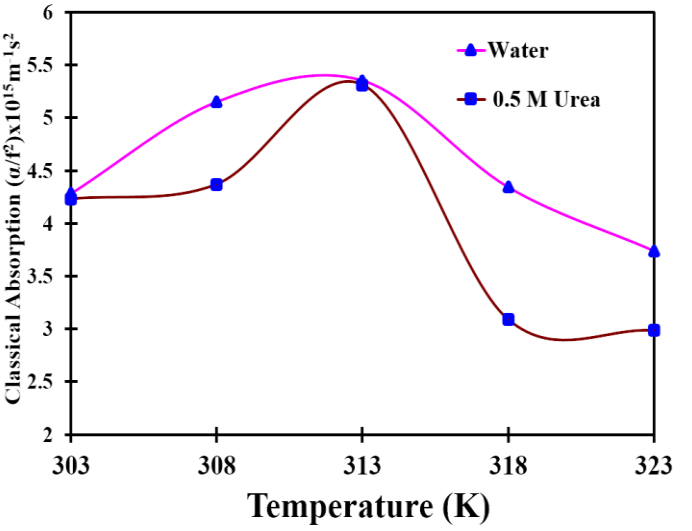

Fig. 3. Temperature dependence of classical absorption (α/f^2) for a 0.5 mM solution of SDDS in water and a 0.5 M aqueous urea solution.

Figure 4 represents the temperature dependence of the relaxation time of 0.5 mM SDDS in water and in 0.5 M aqueous urea solution. This curve for the binary solution shows the maximum relaxation time at 312 K and minimum relaxation time at 323 K, while the ternary solution shows the maximum relaxation time at 312 K and minimum relaxation time at 320 K. The relaxation time is indicative of the time required for the system to return to equilibrium after a disturbance. The observed maxima at 312 K suggest that this temperature is critical for the relaxation processes in both binary and ternary solutions. The slight difference in the temperature of minimum relaxation time between the binary and ternary solutions indicates that urea affects the relaxation dynamics of SDDS solutions, likely due to its interaction with the surfactant molecules [26].

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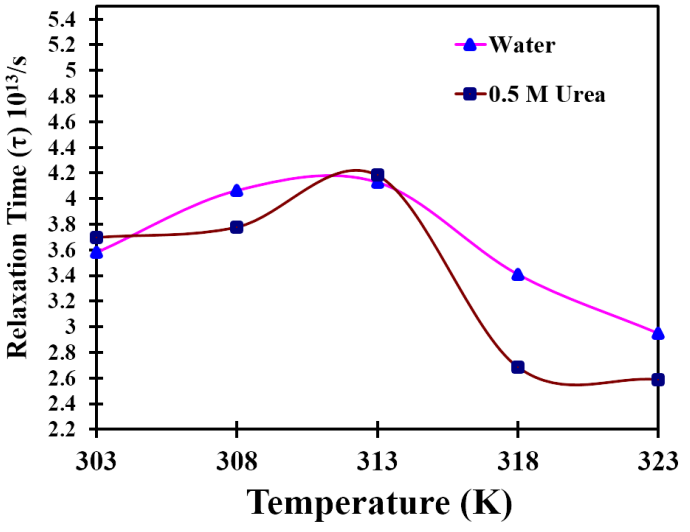

Fig. 4. Temperature dependence of relaxation time (τ) for a 0.5 mM solution of SDDS in water and a 0.5 M aqueous urea solution. The figure shows the variation in relaxation time with temperature for both solutions.

Tables 1 and 2 report the data of other parameters. These tables examine similar results for solutes, anionic surfactants, and biomolecules, as obtained graphically in Figures 1-4. The data in these tables provide detailed insights into the behavior of SDDS in aqueous urea solutions across different temperatures. The non-linearities in ultrasonic velocity, adiabatic compressibility, and other parameters highlight the complex molecular interactions and structural transitions occurring in the system.

The data presented in these tables confirm the graphical observations and provide detailed insights into the behavior of SDDS in aqueous urea solutions across different temperatures.

The non-linearities in ultrasonic velocity, adiabatic compressibility, and other parameters highlight the complex molecular interactions and structural transitions occurring in the system. The ultrasonic velocity data shows a distinct transition at 313 K, which is supported by changes in adiabatic compressibility and relaxation parameters. This transition is indicative of a structural change in the ternary solution, likely related to the role of urea as a structure-breaker (SB) at lower temperatures and a structure-maker (SM) at higher temperatures. The varying temperature coefficients ($\partial U/\partial T$ and $\partial \beta s/\partial T$) further confirm this behavior, showcasing the dynamic nature of molecular interactions in the system.

The presented study provides comprehensive insights into the physicochemical properties of the SDDS-water-urea ternary system, highlighting the significant role of temperature in influencing molecular interactions and structural characteristics. These findings have implications for various applications, including biochemistry and industrial chemistry, where understanding solute-solvent interactions is crucial. The insights gained from this study can aid in the design and optimization of processes involving similar ternary systems, contributing to advancements in areas such as drug delivery, detergent formulation, and environmental remediation.

Table 1. Ultrasonic Parameters of 0.5 mM SDDS in 0.5 M Aqueous Urea Solution at Different Temperatures.

Temperature (K)	Density ($\rho \times 10^{-3}$ kg/m^3)	Ultrasonic Velocity (U, m/s)	Adiabatic Compressibility (βs, TPa^{-1})	Free Length (Lf, pm)	Molar Sound Velocity ($R \times 10^6$ m$^{10/3}$s$^{-11/3}$) mol^{-1})	Acoustic Impedance ($Z \times 10^{-6}$ kg/m^{2}s)	Free Volume (Vf, m^3)
303	0.9850	1725.0	341.2	36.86	213.9	1.699	0.0540
308	0.9934	1706.1	345.8	37.40	213.1	1.695	0.0525
313	0.9826	1554.0	421.4	41.68	206.6	1.527	0.0527
318	0.9949	1715.1	341.7	37.88	213.5	1.706	0.0868
323	0.9899	1710.0	345.5	38.32	213.3	1.693	0.0929

Table 2. Absorption & Relaxation Parameters of 0.5 mM SDDS in Aqueous Urea Solution at Different Temperatures.

Temperature (K)	Classical Absorption ($\alpha/f^2 \times 10^{15}$ m^{-1}s^2)	Relaxation Time ($\tau \times 10^{13}$ s)	Viscosity (η, Pa-s)	Relaxation Strength (γ)	Attenuation Coefficient ($\alpha \times 10^{-8}$ m^{-1})
303	4.2320	3.698	0.8129	-0.1624	7.619
308	4.3710	3.778	0.8193	-0.1370	7.758
313	5.3133	4.183	0.7444	0.0567	7.692
318	3.0900	2.685	0.5893	-0.1978	10.858
323	2.9870	2.587	0.5617	-0.1422	11.302

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4. CONCLUSIONS

The study demonstrates that ultrasonic velocimetry is a highly effective and precise technique for investigating intermolecular interactions within the SDDS-water-urea ternary system. The experimental results reveal significant insights into the nature of these interactions. The temperature coefficients of ultrasonic velocity ($\partial U/\partial T$) and adiabatic compressibility ($\partial \beta s/\partial T$) exhibit both positive and negative values, indicating varying degrees of hydrophilicity and hydrophobicity of urea across different temperature ranges. Specifically, urea shows hydrophilic behavior within the temperature range of 303 K to 308 K and transitions to hydrophobic behavior within the temperature range of 313 K to 323 K. The relaxation time measurements indicate that for the binary solution, the maximum relaxation time is observed at 312 K, with a minimum at 323 K. In the ternary solution, the maximum relaxation time is similarly observed at 312 K, while the minimum relaxation time occurs at 320 K. These results highlight the influence of urea on the relaxation dynamics of the system. The findings of this study provide valuable information for various fields including solution chemistry, biochemistry, biosciences, surface science, surfactant chemistry, and industrial chemistry. The ability of ultrasonic velocimetry to accurately characterize these interactions underscores its importance in advancing our understanding of complex molecular systems and their thermodynamic behaviors.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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