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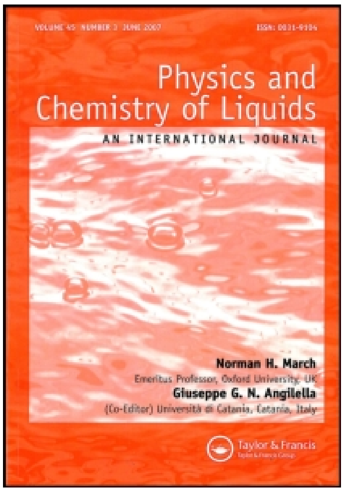

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Anil Kumar[a]
[a] Department of Chemistry, Institute of Basic Sciences, Agra University, Agra, India

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THEORETICAL EVALUATION OF SOUND VELOCITY AND OTHER ACOUSTIC PARAMETERS FOR AQUEOUS SOLUTIONS OF SODIUM DODECYL SULPHATE (NaDS) AT 298.15 K

ANIL KUMAR

Department of Chemistry, Institute of Basic Sciences, Agra University, Khandari Road, Agra-282002, India.

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The intermolecular free length L_f has been evaluated employing thermodynamic approach of Eyring and Hirschfelder while free length theory (FLT) of Jacobson has been used to compute the theoretical values of ultrasonic velocity. Subsequently, the theoretical values of other acoustic parameters were calculated. The results of theoretically calculated parameters have been compared with those derived from experimental ultrasonic velocity data. Both, v_{theo} and v_{exp} differ by 0.20% and $v_{\text{theo}} > v_{\text{exp}}$. The results for $\phi_{K\ \text{theo}}$ and $\phi_{K\ \text{exp}}$ show the maximum variation (62%) while data for R_{theo} and R_{exp} change by minimum (0.07%) and $R_{\text{theo}} > R_{\text{exp}}$.

KEY WORDS: Sound velocity, sodium dodecyl sulphate, free length theory, acoustic parameters.

INTRODUCTION

Theoretical values of sound velocity have been evaluated in many binary liquid mixtures[1-3] employing various empirical and semi-empirical theories[4-6]. Good agreement has been found[7-9] between the theoretical values of the parameters and those obtained experimentally.

The present study embodies a relatively different approach to previous investigation[10] in that the ultrasonic velocity and derived parameters were computed theoretically and compared with their experimental values for binary system i.e. water-NaDS at 298.15 K.

EXPERIMENTAL

Sodium dodecyl sulphate NaDS (Fluka puriss) was crystallised twice in ethanol and dried under vacuum for at least 24 h before use. All solutions were prepared by twice redistilling good distilled water over alkaline $KMnO_4$. The solutions were kept at a constant temperature for about 2 h in a thermostat. The densities used (Table 1) were taken from Ref. 11. These were reportedly measured using a vibrating tube flow densimeter[11] (Sodev Inc; model 03 D) sensitive to 3 ppm.

Table 1 Thermodynamic and acoustic parameters for NaDS in water at 298.15 K.

Conc. *(C)* *Mole* Kg^{-1}	*Density* (ρ) $Kg\ m^{-3}$	*Molar Volume* $(V_T \times 10^6)$ $m^3 mole^{-1}$	*Available Volume* $(V_a \times 10^6)$ m^3	*Surface Area per Mole* $(Y \times 10^{-3})$ m^2	*Intermolecular free Length* $L_{f\ theo} \times 10^{10})$ *m*	*Adiabatic Compressibility* $(\beta_{theo} \times 10^{10})$ m^2N^{-1}	*Ultrasonic Velocity* (v_{theo}) ms^{-1}	*Specific Acoustic Impedance* $(Z_{theo} \times 10^{-5}$ $Kg\ m^2s^{-1}$	*Solvation Number* (Sn_{theo})	*Molar Sound Velocity* $(R_{theo} \times 10^2)$ m^3mole^{-1} $(N/m^2)^{1/3}$	*Apparent Molal Compressibility* $(-\phi_{K theo} \times 10^9)$ $m^5\ N^{-1}mole^{-1}$
0.00861	997.467	289.11	296.81	159.22	37.28	2.612	1959	19.54	7.41	361.75	34.87
0.01427	997.683	289.05	296.74	159.20	37.28	2.612	1959	19.54	5.96	361.67	28.03
0.02860	998.234	288.89	296.58	159.14	37.27	2.610	1959	19.55	5.20	361.47	24.47
0.04880	999.014	288.66	296.34	159.06	37.26	2.609	1959	19.57	4.35	361.19	20.47
0.07487	999.997	288.38	296.06	158.95	37.25	2.608	1958	19.58	3.97	360.78	18.67
0.10700	1001.193	288.04	295.71	158.83	37.24	2.606	1958	19.60	3.77	360.34	17.73
0.13870	1002.349	287.70	295.36	158.70	37.22	2.603	1958	19.63	3.83	359.93	18.00
0.18930	1004.168	287.18	294.82	158.51	37.20	2.601	1957	19.65	3.59	359.22	16.87
0.22010	1005.246	286.88	294.52	158.40	37.19	2.599	1956	19.66	3.57	358.77	16.78
0.25720	1006.528	286.51	294.14	158.27	37.17	2.596	1956	19.69	3.55	358.31	16.69
0.32460	1008.784	285.87	293.06	158.03	37.09	2.585	1956	19.73	3.92	357.51	18.46
0.37090	1010.277	285.45	293.05	157.88	37.12	2.590	1955	19.75	3.37	356.92	15.87
0.39460	1010.999	285.24	292.83	157.80	37.11	2.588	1955	19.76	3.39	356.67	15.93
0.54970	1015.818	283.89	291.45	157.30	37.06	2.581	1953	19.84	3.16	354.85	14.88
0.98450	1027.445	280.68	288.15	156.11	36.92	2.562	1949	20.02	2.84	350.60	13.37

A multifrequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi), operating at a frequency of 4 MHz, was used to measure the ultrasonic velocity of the aqueous solutions of NaDS at a constant temperature i.e. 298.15(± 0.01)K. The maximum uncertainty of velocity results was ± 0.02%.

METHOD OF CALCULATION

The intermolecular free length L_f has been evaluated by the thermodynamic method of Eyring and Hirschfelder[12] using the following equations:

$$L_f = (2\,Va)/Y \tag{1}$$

$$Va = V_T - V_0 \tag{2}$$

$$V_0 = V_T[1 - (T/T_c)^{0.3}] \tag{3}$$

where Va is the available volume, V_T is the molar volume at temperature T, T_c is the critical temperature and Y is the surface area per mole given by:

$$Y = [36\pi N V_0^2]^{1/3} \tag{4}$$

where N is Avogadro's number and V_0 is the molar volume at 0 K. The theoretical values of adiabatic compressibility and ultrasonic velocity were then computed:

$$\beta = L_f^2 K \tag{5}$$

$$v = \left[\frac{1}{\beta\rho}\right]^{1/2} \tag{6}$$

where K is the temperature dependent Jacobson's constant[13] and ρ is density of the solutions.

The theoretical and experimental values of several other acoustic parameters viz. specific acoustic impedance Z, solvation number Sn, molar sound velocity R and apparent molal compressibility ϕ_K, have been evaluated using the following well-known relationships:

$$Z = \rho v \tag{7}$$

$$\mathrm{Sn} = -\phi_K / V_0\beta_0 \tag{8}$$

$$R = \frac{M}{\rho}(v)^{1/3} \tag{9}$$

$$\phi_K = \frac{1000}{C\rho_0}(\rho_0\beta - \beta_0\rho) + \frac{\beta_0 M}{\rho_0} \tag{10}$$

where V_0, β_0, ρ_0 are the molar volume, adiabatic compressibility, density of solvent and M is the molar weight of the solute.

RESULTS AND DISCUSSION

Theoretical values for intermolecular free length $L_{f\,\mathrm{theo}}$ have been computed by the thermodynamic method of Eyring and Hirschfelder[12] employing Eqs (1-4). The theoretical values for ultrasonic velocity v_{theo} were then evaluated from free length theory (FLT) of Jacobson using Eqs (5) and (6). The values for these parameters are recorded in Table 1. Employing Eqs (7-10), the theoretical and experimental values for several other acoustic parameters were subsequently determined.

The variation of ultrasonic velocity with concentration (dv/dC) depends on the concentration derivatives of density and adiabatic compressibility:

$$\frac{dv}{dC} = -\frac{v}{2}\left(\frac{1}{\rho}\frac{\partial \rho}{\partial C} + \frac{1}{\beta}\frac{\partial B}{\partial C}\right) \tag{11}$$

The derivatives $\partial\rho/\partial C$ and $\partial\beta/\partial C$ are opposite in sign with the latter negative and numerically larger. Thus the velocity usually increases with increasing concentration. However, the data for both theoretical and experimental velocity decrease with increasing NaDS concentration (Figure 1). The mathematical explanation for the decrease in velocity with concentration lies in the fact that the magnitudes of the terms $(\partial\rho/\partial C)$ and $(\partial\beta/\partial C)$ are such that the velocity decreases. The studies[14–16] explicitly show that the ultrasonic velocity of salts involving heavy metal cations decreases with concentration.

It is found that theoretical velocity v_{theo} decrease linearly while experimental velocity v_{exp} show a dip at 0.390 moles Kg^{-1} in velocity versus concentration curve for aqueous solutions of NaDS at 298.15 K (Figure 1). Similar dip in the vicinity of 0.390 moles Kg^{-1} is observed when theoretical data for both adiabatic compressibility β_{theo} and intermolecular free length $L_{f\,\mathrm{theo}}$ were plotted as a function of surfactant concentration (Figure 1). These plots (Figure 1) when extrapolated to zero NaDS concentration gave pure solvent values ($v_0 = 1960\ \mathrm{ms}^{-1}$, $\beta_0 = 2.614 \times 10^{-10}\ \mathrm{m}^2\ \mathrm{N}^{-1}$) in accordance with their experimental values ($v_0 = 1960\ \mathrm{ms}^{-1}$, $\beta_0 = 2.613\ \mathrm{m}^2\ \mathrm{N}^{-1}$) indicating that NaDS molecules do not aggregate to an appreciable extent below 0.390 moles Kg^{-1}. Both the velocity data (Figure 1) differ by 0.20% and $v_{\mathrm{theo}} > v_{\mathrm{exp}}$. On the other hand, the theoretical and experimental adiabatic compressibility vary by 0.39% while a variation of 0.27% is observed between theoretical and experimental data for intermolecular free length. The experimental data for both adiabatic compressibility and intermolecular free length are higher than their respective theoretical values i.e. $\beta_{\mathrm{exp}} > \beta_{\mathrm{theo}}$ and $L_{f\,\mathrm{exp}} > L_{f\,\mathrm{theo}}$.

Apparent molal compressibility ϕ_K, apparent molar volume ϕ_v and adiabatic compressibility β are all related to the solute concentration C by the following well-known relationships:

$$\phi_K = \phi_K^{\circ} + S_K C^{1/2} \tag{12}$$

$$\phi_v = \phi_v^{\circ} + S_v C^{1/2} \tag{13}$$

$$\beta = \beta_0 + AC + BC^{3/2} \tag{14}$$

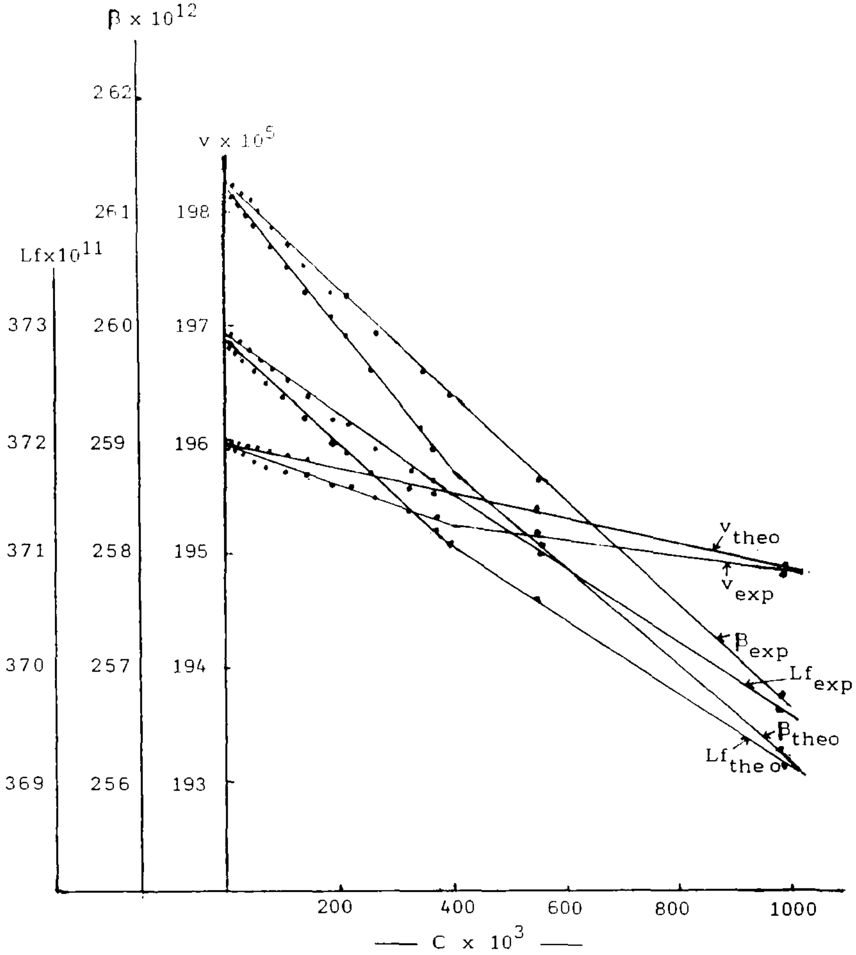

Figure 1 Plots of theoretical and experimental data for ultrasonic velocity, intermolecular free length and adiabatic compressibility as a function of concentration of aqueous solutions of NaDS at 298.15 K.

where S_K (1.0 × 10^{-6}), S_v (60.4) and B (13.6 × 10^{-11}) are the slopes of ϕ_K versus $C^{1/2}$, ϕ_v versus $C^{1/2}$ and $(\beta_{\text{theo}} - \beta_0)/C$ versus $C^{1/2}$ plots while ϕ_K° (-40.6×10^{-9}), ϕ_v° (237.70) and $A(-31.2 \times 10^{-12})$ are their intercepts (Figure 2). The values of constant A and $B(-31.2 \times 10^{-12}$ and $13.6 \times 10^{-11})$ obtained for NaDS at 298.15 K are consistent with $A = (\phi^{\circ}_K - \beta_0\phi_v) \times 10^{-3}$ and $B = (S_K - \beta_0 S_v) \times 10^{-3}$, since it follows from thermodynamics that $\beta = \beta_0$ for dilute solutions.

It is observed that these plots (Figure 2) are not linear. The departure from linearity predicted by Eqs (12-14) may be ascribed to the stepwise dissociation or association of NaDS in water at the experimental temperature. Khare[17] ascribed the change in slope of ϕ_k versus $C^{1/2}$ plots for $NaHSO_4$ to the further dissociation of HSO_4 into H^+

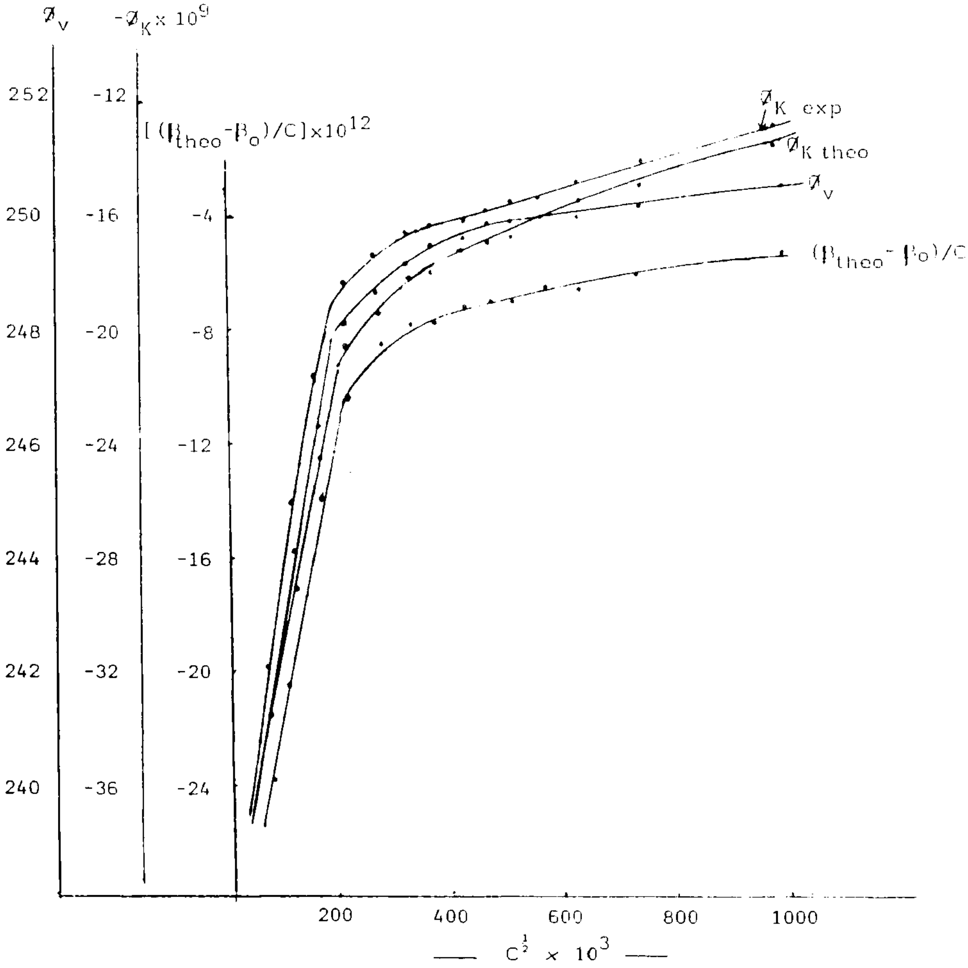

Figure 2 Plots of theoretical and experimental data for apparent molal compressibility and $(\beta_{theo} - \beta_0)/C$ as a function of square root of concentration of aqueous solutions of NADS at 298.15 K.

and SO_4^{2-} at low concentrations and not to a gradual shift predicted by Debye-Hückel theory. The decrease in β and increase in ϕ_K (Table 1) with concentrations may be explained on the basis of close-packing of ionic head groups in the micelles, resulting in an increase in ionic repulsion and, finally, internal pressure. The theoretical and experimental molal compressibility (Figure 2) may vary by 62%.

The increase in the values of specific acoustic impedance Z with NaDS concentration, can be explained on the basis of hydrophobic interaction between NaDS and water molecules, which increases the intermolecular distance, leaving relatively wider gaps between the molecules and thus becoming the main cause of obstruction to the propagation of ultrasound waves. It is observed that theoretical and experimental acoustic impedance (Figure 3) may vary by 0.22%.

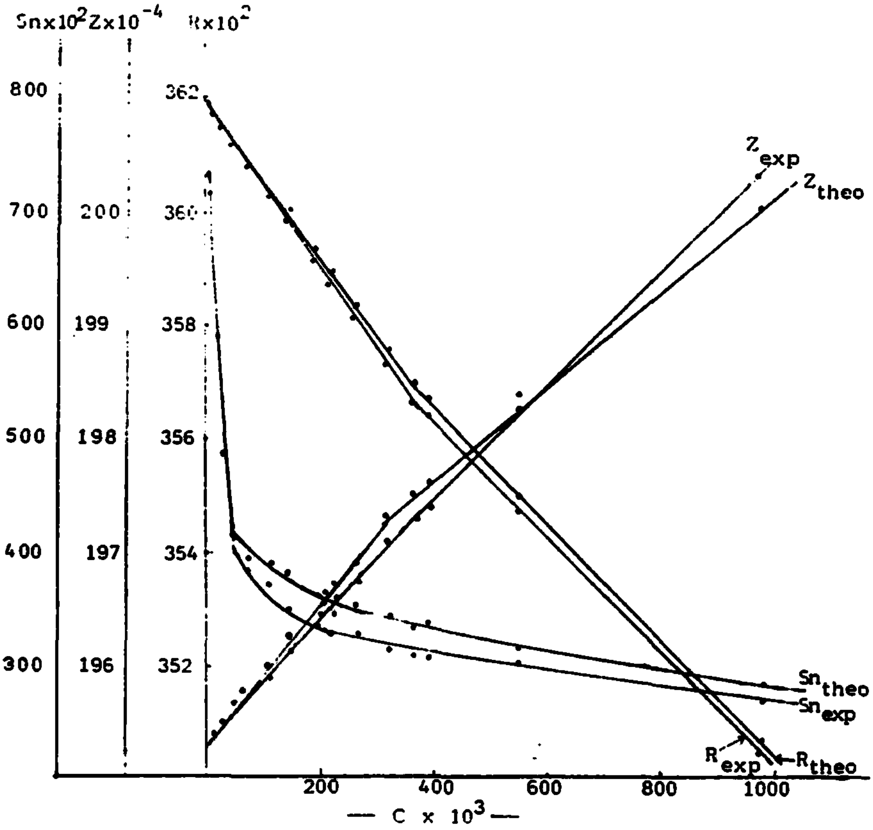

Figure 3 Plots of theoretical and experimental data for specific acoustic impedance, molar sound velocity and solvation number as a function of concentration of aqueous solutions of NaDS at 298.15 K.

The molar sound velocity R decreases with concentration and the value for the ratio: $\rho(v_0)^{1/3}/\rho_0(v)^{1/3}$, evaluated at 298.15 K for NaDS in water increases linearly with concentration (the ratio varies from 5.50×10^{-6} to 6.33×10^{-4} over the entire range of NaDS concentration) in accordance with the results found for several sulphates[18] and hydroxides[19]. Similar results were observed by Subrahamanyam *et al*[15]. The increase in the ratio: $\rho(v_0)^{1/3}/\rho_0(v)^{1/3}$, produced by the ionic solutes was ascribed to the strong interaction of the ions with the solvent molecules. Both theoretical and experimental molar sound velocity (Figure 3) differ by 0.07% and $R_{\text{theo}} > R_{\text{exp}}$.

The values of Sn (Table 1) correspond to the number of water molecules in the primary hydration sheaths of the ions. The values of Sn are in good agreement with other hydration numbers in the literature[16,18,20–22]. It is found (Figure 3) that both theoretical and experimental data for solvation number may differ by 62%.

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