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Research Article

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Effect of Surfactant CTAB on the Partial Molar Volumes and Compressibilities of Aqueous Solutions of Sodium Salicylate at 30°C

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ABSTRACT

The partial molar volumes and compressibilities of an anti-inflammatory drug sodium salicylate in aqueous-CTAB solutions have been determined from volumetric and ultrasonic data using standard methods. The refractive indices of these ternary solutions were measured and atomic polarizations were calculated at 30°C. The specific acoustic impedance (Z) and relative association (R_A) of studied solutions are also calculated. Partial molar volumes and compressibilities have been explained in terms of drug-solvent and drug-surfactant interactions. CTAB showed significant effect on the partial molar volumes and compressibilities of aqueous solutions of sodium salicylate.

Keywords: Thermodynamic properties; Anti-inflammatory drug; Surfactant

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INTRODUCTION

Solution behavior of different drugs in aqueous medium has been studied by many researchers [1-7]. Hydration behavior of drug in water is affected by the presence of different co-solutes and many researchers have studied the effect of co-solutes such as amino acids [8,9], salts [10-13], carbohydrates [14] etc. on solvation behavior of drugs and molecular interactions therein. Drug-surfactant interactions have been studied by D. Kaushal et al. and Carlota O Rangel-Yagui et al. [15,16]. This behavior is studied through thermodynamic properties of drug solutions in water and co-solute solutions at defined temperatures. The structure and molecular interactions in drug solution are reflected in thermodynamic properties.

Sodium salicylate (SS, Figure 1) is an anti-inflammatory drug and the apoptosis is induced by it in the cancer cells [17-19]. The cetyl trimethylammonium bromide (CTAB, Figure 1) is cationic surfactant and its cetyltrimethylammonium cation (CTA^+) and salicylate ion (SS^-) form the worm-like micelle. Therefore, in order to understand the interactions between SS and CTAB in water, the systematic study of thermodynamic behavior of SS in aqueous-CTAB solutions is carried out in the present work (Figures 2 and 3).

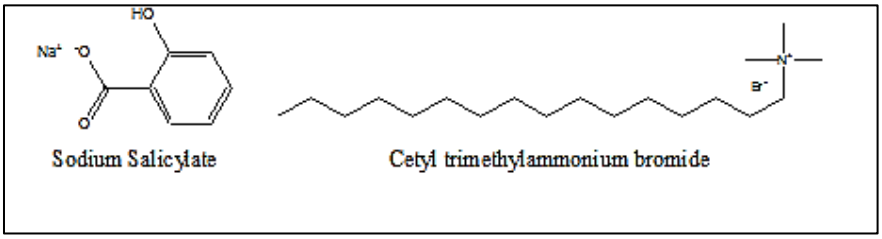

Figure 1: Structures of sodium salicylate and cetyl trimethylammonium bromide

EXPERIMENTAL SECTION

Sodium salicylate (SS) and Cetyl trimethylammonium bromide (CTAB), (S.D. Fine Chemicals Ltd.) have been used. Deionized distilled water (HPLC grade, pH=6.91) obtained from Millipore prefiltration kit (Direct-Q^{TM} system series) was used in present work. Density measurements were performed using single capillary pycnometer (Borosil). Pycnometer was calibrated with benzene and distilled water at 30°C and its volume was corrected for 30°C. Pycnometer was filled with experimental liquids and kept in the constant temperature water bath to attain the thermal equilibrium for 15 min. Three sets of density measurements were performed to get the accurate results. Weighing was done on single pan electronic balance (±0.001 g). Speed of sound (u) was measured using thermostatically controlled ultrasonic interferometer (Model-F05, Mittal, 2 ± 0.0001 MHz). Refractive index measurements were performed on thermostatically controlled Cyber LAB-Cyber Abbe refractometer (Amkette Analytics, ±0.0002). Refractometer was calibrated using standard specimen (n=1.5167). Experimental temperature was maintained by water circulation system surrounding the prism box using water bath. Averages of three readings of density and refractive index are reported.

RESULTS AND DISCUSSION

Densities, apparent molar volumes, refractive indices and atomic polarizations of SS in aqueous and aqueous-CTAB solutions at 30°C are reported in Table 1 and ultrasonic velocities, isentropic compressibilities, specific acoustic impedance, apparent molar isentropic compressibilities and relative associations of SS in aqueous and aqueous-CTAB solutions at 30°C are reported in Table 2.

Density of solutions increases with increase in the drug concentration due to molecular interactions in solution. Apparent molar volumes ($V_{2,\emptyset}$) of SS solutions were calculated from the density data using standard relation [20-22]. They are positive and increases with drug concentration in each system.

Ultrasonic velocity and related acoustical properties of solutions are useful to understand the thermodynamic and solution behavior [23,24]. These properties are further useful to collect the information about molecular interactions in solution [25-29]. Pharmacological properties [30] of drugs are highly dependent on the solution behavior. Ultrasonic velocity (Figure 4) and refractive index increases with drug concentration in each system which is due to increase in the compactness of the solution as result of strong molecular interactions among components of solution. Variation in the refractive index and atomic polarization of drug solutions is in agreement with the volumetric and compressibility data and observations made from it.

The apparent molar isentropic compressibility ($K_{s,2,\emptyset}$) of SS solutions were calculated from the density and ultrasonic velocity data using standard relation [21,22]. They are negative and increases with drug concentration (becomes less negative) in each system.

Further, from the plots of concentration dependence of $V_{2,\emptyset}$, the limiting partial molar volumes ($V°_{2,\emptyset}$) were determined by extrapolating each lines, Figure 5 [21,22]. And from the plots of concentration dependence of $K_{s,2,\emptyset}$, the limiting partial molar isentropic compressibilities ($K°_{s,2,\emptyset}$) were determined by extrapolating each lines, Figure 6 [21,22]. The $V°_{2,\emptyset}$ and $K°_{s,2,\emptyset}$ values are reported in Table 3. The positive values of $V°_{2,\emptyset}$ and negative values of $K°_{s,2,\emptyset}$ are attributed to the strong drug-solvent interactions [31]. The electrolyte solutes show negative $K°_{s,2,\emptyset}$ values due to electrostriction [32]. Variation in $V°_{2,\emptyset}$ and $K°_{s,2,\emptyset}$ values also suggests that these interactions strengthens till 0.0010 mol · dm^{-3} CTAB.

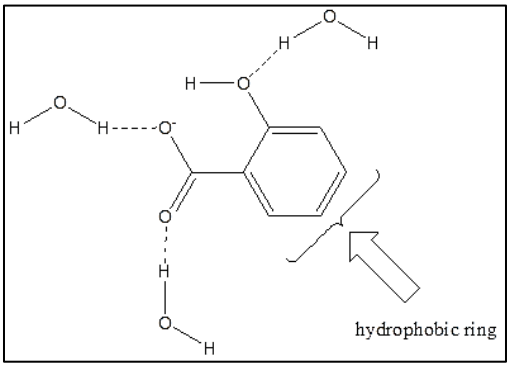

Figure 2: Hydrogen bonding interactions between salicylate ion and water molecules

Table 1: Molar concentrations, densities, apparent molar volumes, refractive indices and atomic polarizations of SS in aqueous and aqueous-CTAB solutions at 30°C

c	ρ	$V_{2,\phi}$	n	P_a
0.0000 mol · dm^{-3} CTAB				
0	995.7	-	1.331	1.8601
0.02	997	95.1	1.3321	1.8632
0.04	998.27	95.74	1.3325	1.8643
0.06	999.57	96.42	1.3332	1.8663
0.08	1000.79	96.91	1.334	1.8685
0.1	1002	97.26	1.3347	1.8705
0.0005 mol · dm^{-3} CTAB				
0	995.24	-	1.331	1.8601
0.02	996.61	91.58	1.3318	1.8624
0.04	998	92.65	1.3325	1.8643
0.06	999.35	92.46	1.3335	1.8671
0.08	1000.64	93.87	1.3342	1.8691
0.1	1001.89	95.05	1.335	1.8713
0.0010 mol · dm^{-3} CTAB				
0	994.61	-	1.3315	1.8615
0.02	996.19	80.98	1.332	1.8629
0.04	997.8	82.05	1.3327	1.8649
0.06	999.3	82.86	1.3338	1.868
0.08	1000.71	85.25	1.3345	1.8699
0.1	1002.17	86.12	1.3352	1.8719
0.0020 mol · dm^{-3} CTAB				
0	995.4	-	1.3318	1.8624
0.02	996.87	86.53	1.3322	1.8635
0.04	998.39	86.98	1.333	1.8657
0.06	999.77	88.15	1.3342	1.8691
0.08	1001.07	90.54	1.3347	1.8705
0.1	1002.42	91.41	1.3355	1.8727

Φοοτ νοτε: ρ=κγ•μ^{-3}, $V_{2,\phi}$ =·10^{-6} μ^3•μολ^{-1}.

The graphical values of $V°_{2,Ø}$ and $K°_{s,2,Ø}$ shows the trend as: $V°_{2,Ø}$ in Water > $V°_{2,Ø}$ in 0.0005 mol · dm^{-3} CTAB > $V°_{2,Ø}$ in 0.0020 mol · dm^{-3} CTAB > $V°_{2,Ø}$ in 0.0010 mol · dm^{-3} CTAB.

That is the $V°_{2,Ø}$ and $K°_{s,2,Ø}$ values decreases till 0.0010 mol · dm^{-3} CTAB and then increases in 0.0020 mol · dm^{-3} CTAB but still are smaller than $V°_{2,Ø}$ and $K°_{s,2,Ø}$ values in water. This is a very interesting behavior of SS in aqueous-CTAB solutions where the thermodynamic properties $V°_{2,Ø}$ and $K°_{s,2,Ø}$ shows variations in their values as CTAB concentration changes. The $V°_{2,Ø}$ and $K°_{s,2,Ø}$ values of SS in water are in good agreement with the values obtained by TS Banipal et al. [32].

This behavior of SS in aqueous-CTAB solutions could be explained on the basis of molecular interactions between SS and CTAB micelle. Around 0.0010 mol · dm^{-3} CTAB in water the CTAB forms micelle (cmc) and the salicylate ion fits into the CTAB micelle (Figure 3) and hence relatively contraction in the $V°_{2,Ø}$ value and reduction in the compressibility of solutions. The volumetric and compressibility data indicates that the better fitting and strong interactions among salicylate-cetyltrimethylammonium are observed in 0.0010 mol · dm^{-3} aqueous-CTAB solutions.

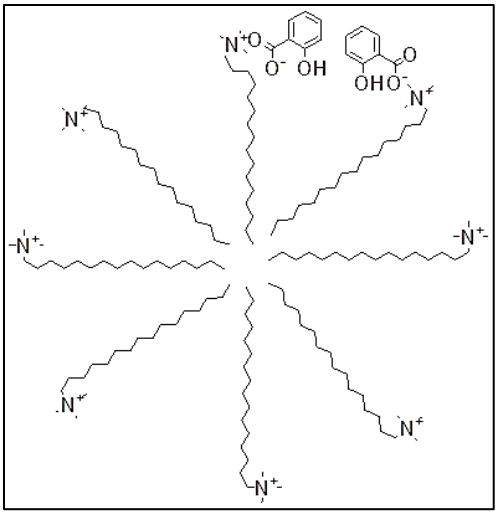

Figure 3: Proposed interactions between salicylate and cetyltrimethylammonium ions

Table 2: Molar concentrations, ultrasonic velocities, isentropic compressibilities, specific acoustic impedance, apparent molar isentropic compressibilities and relative associations of SS in aqueous and aqueous-CTAB solutions at 30°C

c	u	K_s	Z	$K_{s,2,\phi}$	R_A
0.0000 mol · dm^{-3} CTAB					
0	1510.21	4.403	1.504	-	1
0.02	1512.21	4.386	1.508	-4.549	1.0009
0.04	1514.16	4.369	1.512	-4.41	1.0017
0.06	1516.15	4.352	1.515	-4.258	1.0026
0.08	1517.96	4.336	1.519	-4.107	1.0034
0.1	1519.67	4.321	1.523	-3.95	1.0042
0.0005 mol · dm^{-3} CTAB					
0	1502.22	4.453	1.495	-	1
0.02	1504.29	4.434	1.499	-5.158	1.0009
0.04	1506.37	4.416	1.503	-4.914	1.0019
0.06	1508.39	4.398	1.507	-4.913	1.0028
0.08	1510.56	4.38	1.512	-4.808	1.0036
0.1	1512.71	4.362	1.516	-4.7	1.0043
0.0010 mol · dm^{-3} CTAB					
0	1512.65	4.394	1.504	-	1
0.02	1514.93	4.374	1.509	-6.595	1.0011
0.04	1517.34	4.353	1.514	-6.503	1.0022
0.06	1519.51	4.334	1.518	-6.302	1.0032
0.08	1522.14	4.313	1.523	-6.264	1.004
0.1	1524.71	4.292	1.528	-6.247	1.0049
0.0020 mol · dm^{-3} CTAB					
0	1516.48	4.368	1.51	-	1
0.02	1518.69	4.349	1.514	-5.844	1.001
0.04	1520.94	4.33	1.518	-5.689	1.002
0.06	1523.14	4.311	1.523	-5.595	1.0029
0.08	1525.55	4.292	1.527	-5.454	1.0037
0.1	1527.98	4.273	1.532	-5.423	1.0045

Foot note: u, m·s^{-1}, κ_s= ×10^{-10} m^{-2}·N^{-1}, Z=× 10^{6} kg·m^{-2}·s^{-1}, $K_{S,2,\phi}$ ×10^{-14} m^{3}·mol^{-1}·Pa^{-1}

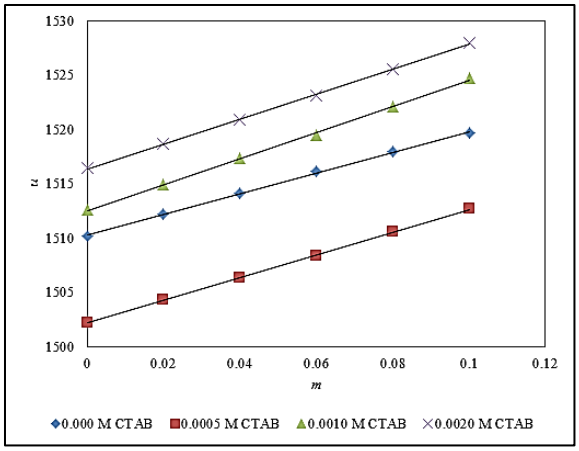

Figure 4: Variation in the ultrasonic velocity with drug concentration in aqueous and aqueous-CTAB solutions at 30°C

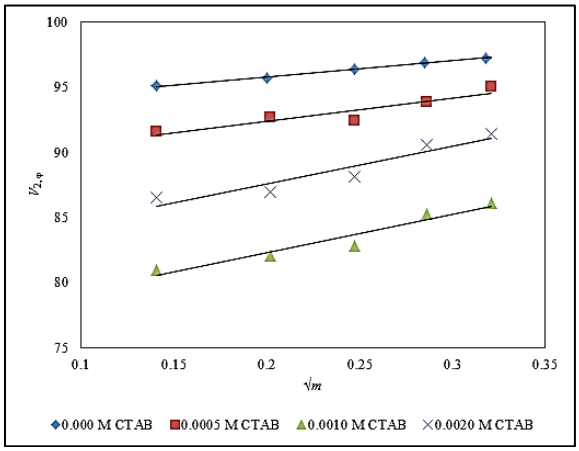

Figure 5: Variation in the apparent molar volumes with drug concentration in aqueous and aqueous-CTAB solutions at 30°C

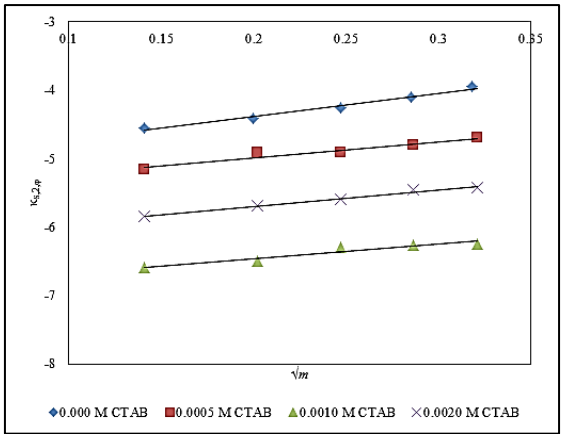

Figure 6: Variation in the apparent molar isentropic compressibility with drug concentration in aqueous and aqueous-CTAB solutions at 30°C

Table 3: Partial molar volumes and compressibilities of SS in aqueous and aqueous-CTAB solutions at 30°C

System	$V°_{2,\phi}$	S_v	$K°_{s2,\phi}$	S_k
0.0000 mol · dm^{-3} CTAB	93.3	12.49	-5.056	3.363
0.0005 mol · dm^{-3} CTAB	88.84	17.85	-5.455	2.324
0.0010 mol · dm^{-3} CTAB	76.34	29.68	-6.893	2.133
0.0020 mol · dm^{-3} CTAB	81.76	29.07	-6.183	2.434

Foot note: $V_2°_{,\phi}$ =×10^{-6} m^3·mol^{-1}, S_v=10^{-6} m^3·$mol^{-3/2}$·$kg^{1/2}$, $K_s°_{2,\phi}$ =× 10^{-14} m^3·mol^{-1}·Pa^{-1}, S_k=10^{-14} m^3·$mol^{-3/2}$·Pa^{-1}·$kg^{1/2}$

The S_v and S_k values (experimental slopes) obtained from the plots of concentration dependence of $V_{2,\emptyset}$ and $K_{s,2,\emptyset}$ are found to be positive which suggests that there exist ion-ion interactions along with the ion-solvent interactions. Other ultrasonic properties such as specific acoustic impedance (Z) and relative association (R_A) are also calculated. Both Z and R_A increase with increase in the SS concentration in each system which is due to increase in the salicylate-cetyltrimethylammonium interactions.

CONCLUSION

From the partial molar volumes and compressibilities of aqueous solutions of sodium salicylate in aqueous and aqueous-CTAB solutions at 30°C, it is concluded that there exists strong solute-solvent interactions which are affected by the presence of surfactant CTAB in solution. Around the cmc value (0.0010 mol · dm^{-3} CTAB) of CTAB, the solute-solvent interactions modifies which is due to relatively strong salicylate-cetyltrimethylammonium interactions. The results of volumetric and ultrasonic properties and contraction in the volume and reduction in the compression in 0.0010 mol · dm^{-3} CTAB solution indicates interactions of drug anion with cationic part of CTAB in its micelle.

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