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Ultrasonic Studies on Metal Halides in Aqueous Lactose Solution at Different Temperatures

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Abstract: ***To investigate the solute-co-solute, solute-solvent interaction, the volumetric, viscometric and compressibility behavior of potassium bromide, potassium fluoride in aqueous lactose solutions (5%, 10% and 15% wt of lactose) at 303, 308 and 313 K have been studied. Using the measured values of density, viscosity and ultrasonic velocity the acoustical parameters such as adiabatic compressibility (β), free length (L_f), relative association (R_A), acoustic impedance (Z), relaxation time (τ), classical absorption coefficient (α / f^2), apparent molal volume (ϕ_v), limiting apparent molal volume (ϕ_v°), adiabatic compressibility (β), apparent molal compressibility (ϕ_k), limiting apparent molal compressibility (ϕ_k°), Falkenhagen coefficient (A), Jones-Dole coefficient (B), hydration number (H_n) have been calculated to study the molecular interaction of potassium bromide, potassium fluoride in aqueous lactose solutions.***

Keywords: ***Ultrasonic velocity, Adiabatic Compressibility, Relative Association, Apparent Molal Volume, Hydration Number***

1. INRODUCTION

The study of saccharides and carbohydrates has become a subject of increasing interest because of the multidimensional, physical, biomedical, and industrially useful properties of these compounds. The thermodynamic properties of biological molecules in aqueous solutions are important for studies. Studies involving density and ultrasonic velocity measurements are important for elucidation of ion-solvent, ion-ion and solute-solvent interactions in the mixed solvent systems. Interactions of electrolytes with saccharides are very important in exploring the stability of polysaccharides in biological systems as well as in the chemical industry of saccharides.

The study of the liquid states properties using spectroscopic and acoustical methods provides valuable information for their varied usage. Acoustics is a field widely used in recent years to study various molecular interactions. Ultrasonics has become a valuable tool in medical and biological sciences, engineering, geophysics, etc. Ultrasonics studies in organic liquids have been the subject of extensive research recently. These parameters are discussed in terms of various solute-co solute interactions in aqueous solutions; thus the study contributes to a better understanding of the interactions taking place between solute and solvent.

2. MATERIALS AND METHODS

The aqueous lactose solutions 5%, 10%,15%, mass percentage of lactose, were prepared using distilled water and these were used as solvents and metal halides (potassium bromide and potassium fluoride) were added as solute of six different molar concentrations (ranging from 0to 2.5 in steps of 0.5). The density of all compounds was measured by 10 ml specific gravity bottle calibrated with distilled water and acetone. The ultrasonic velocity was measured by a single crystal interferometer with a high degree of accuracy operating at a frequency 2 MHz (Model F-05, with digital micrometer) at 303, 308 and 313K. The viscosity was measured by Ostwald's Viscometer. An electronically operated constant temperature water bath was used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature.

The density, viscosity and ultrasonic velocity of the varying concentration of metal halides at different composition were measured at 303, 308, 313 K.

3. THEORY AND CALCULATIONS

Using the measured data, some acoustical parameters such as acoustical impedance, relaxation time, classical absorption coefficient, hydration number, apparent molal volume, apparent molal compressibility, limititing apparent molal volume, limiting apparent molal compressibility and viscosity A & B coefficients were studied and evaluated by using the standard equations.

4. RESULTS AND DISCUSSION

The experimental values of acoustical impedance, relaxation time and classical absorption coefficient for different molal compositions of potassium bromide in 15 wt. % lactose at different temperatures (i.e., 303K, 308K, and 313K).

Acoustical impedance (Z), Relaxation time (τ) and Classical absorption coefficient (α/f^2)

Table 1 and 2, the gradual increase in acoustic impedance with increase in concentration predicts the strong intermolecular association complexes between the saccharide, metal halides and water molecules. The increase of metal halide (potassium bromide and potassium fluoride) is accompanied by an increase of relaxation time as observed by Eyring and Kincaid (1938). The interaction between solute and solvent molecules is responsible for the increase in relaxation time.

The classical absorption coefficient is a characteristic of the medium and it depends on the external condition like temperature, pressure and frequency of measurement as reported by Das et al. (1999). From the Table 1 and 2, it is understood that the absorption coefficient increases with increase in the mole fraction of the component, while it decreases slightly as the temperature increases in all mixtures.

Table 1 Values of acoustical impedance (Z), relaxation time (τ) and classical absorption coefficient (α/f^2) of potassium bromide in aqueous lactose mixture (05, 10 and 15% by weight of lactose) at 303,308 and 313K

Molality (mol/Kg)	$Z \times 10^{-6}$ Kgm^{-2}S^{-1}			$\tau \times 10^{-12}$ sec			$\alpha/f^2 \times 10^{-11}$ Ns^{2}m^{-1}		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
Lactose –Water (05 : 95%)									
0	1.5481	1.5483	1.5500	2.1064	1.9082	1.7805	4.1536	3.7629	3.5111
0.02	1.5579	1.5574	1.5638	2.0965	1.9177	1.7825	4.1343	3.7817	3.5150
0.04	1.5654	1.5654	1.5675	2.1267	1.9181	1.8352	4.1937	3.7824	3.6189
0.06	1.5737	1.5760	1.5796	2.3615	1.9400	1.8540	4.6566	3.8256	3.6560
0.08	1.5817	1.5807	1.5834	2.3795	1.9574	1.8744	4.6922	3.8599	3.6962
0.1	1.5839	1.5862	1.5907	2.4162	2.1400	1.8992	4.7646	4.2199	3.7451
Lactose –Water (10 : 90%)									
0	1.5829	1.5817	1.5870	2.2982	2.0016	1.8471	4.5320	3.9471	3.6424
0.02	1.5894	1.5903	1.5928	2.3014	2.0354	1.9168	4.5382	4.0137	3.7798
0.04	1.6002	1.6000	1.6041	2.3173	2.0273	1.9044	4.5695	3.9977	3.7554
0.06	1.6087	1.6078	1.6126	2.4028	2.0460	1.9339	4.7383	4.0345	3.8136
0.08	1.6160	1.6135	1.6180	2.4270	2.0908	1.9295	4.7860	4.1230	3.8049
0.1	1.6252	1.6249	1.6271	2.4053	2.0718	1.9580	4.7431	4.0854	3.8611
Lactose –Water (15 : 85%)									
0	1.6160	1.6168	1.6242	2.4454	2.1139	1.9488	4.8222	4.1685	3.8430
0.02	1.6249	1.6307	1.6357	2.4111	2.1167	1.9451	4.7546	4.1741	3.8355
0.04	1.6334	1.6372	1.6399	2.4148	2.1281	1.9423	4.7619	4.1965	3.8302
0.06	1.6383	1.6429	1.6485	2.4243	2.1352	1.9727	4.7805	4.2105	3.8901
0.08	1.6423	1.6475	1.6538	2.4419	2.1639	2.0181	4.8153	4.2671	3.9795
0.1	1.6559	1.6581	1.6592	2.5525	2.1868	2.0590	5.0333	4.3122	4.0603

Table 2 Values of acoustical impedance (Z), relaxation time (τ) and classical absorption coefficient (α/f^2) of potassium fluoride in aqueous lactose mixture (05, 10 and 15% by weight of lactose) at 303, 308 and 313K

Molality (mol/Kg)	$Z \times 10^{-6}$ $Kgm^{-2}S^{-1}$			$\tau \times 10^{-12}$ sec			$\alpha/f^2 \times 10^{-11}$ Ns^2m^{-1}		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
Lactose –Water (05 : 95%)									
0	1.5481	1.5483	1.5500	2.1064	1.9082	1.7805	4.1536	3.7629	3.5111
0.02	1.5848	1.5855	1.5880	2.2259	1.9120	1.7704	4.3893	3.7703	3.4911
0.04	1.5863	1.5884	1.5905	2.3710	1.9414	1.8127	4.6755	3.8284	3.5746
0.06	1.5898	1.5921	1.5944	2.4764	1.9950	1.8306	4.8834	3.9341	3.6098
0.08	1.5937	1.5948	1.5961	2.6150	2.0709	1.9404	5.1565	4.0837	3.8264
0.1	1.6025	1.6071	1.6080	2.6730	2.0670	1.9607	5.2711	4.0761	3.8664
Lactose –Water (10 : 90%)									
0	1.5829	1.5817	1.5870	2.2982	2.0016	1.8471	4.5320	3.9471	3.6424
0.02	1.6216	1.6220	1.6234	2.5479	1.9753	1.8464	5.0244	3.8952	3.6410
0.04	1.6243	1.6247	1.6273	2.6509	2.1086	1.9393	5.2274	4.158	3.8241
0.06	1.6291	1.6289	1.6292	2.7121	2.2503	1.9808	5.3481	4.4375	3.906
0.08	1.6329	1.6316	1.6328	2.7904	2.3036	2.0878	5.5026	4.5426	4.1171
0.1	1.6414	1.6401	1.6417	2.8615	2.3156	2.1454	5.6427	4.5662	4.2307
Lactose –Water (15 : 85%)									
0	1.6160	1.6168	1.6242	2.4454	2.1139	1.9488	4.8222	4.1685	3.8430
0.02	1.6513	1.659	1.6622	2.3918	2.0912	1.9540	4.7165	4.1237	3.8531
0.04	1.6627	1.6660	1.6636	2.4815	2.1755	2.0024	4.8934	4.2900	3.9485
0.06	1.6670	1.6675	1.6672	2.5803	2.2752	2.0532	5.0881	4.4865	4.0489
0.08	1.6763	1.6740	1.6759	2.6424	2.3527	2.0835	5.2107	4.6394	4.1085
0.1	1.6793	1.6778	1.6795	2.7081	2.4017	2.1756	5.3402	4.7361	4.2902

Hydration Number (H_n), Apparent Molal Volume (ϕ_V) and Apparent Molal Compressibility (ϕ_k)

From the Table 3 and 4, the positive hydration number values indicate an appreciable salvation of solutes reported by Mehra et al. (2001). This result provides added support for the structure-promoting nature of the solute and water molecules. The values of hydration number suggest that the compressibility of the solution will be less than that of the pure solvent. As a result, solutes will gain mobility and have a greater probability of contacting solvent molecules. This greater probability may enhance the interaction between solute and solvent. From the Table 3 & 4, the values of hydration number decreases with increasing concentration of solute. This shows that potassium bromide and potassium fluoride have a dehydration effect on aqueous lactose solution at 303, 308 and 313K.
The following observations have been made in ϕ_V and ϕ_k from the Tables 3 and 4

- The values of ϕ_v and ϕ_k are all negative over the entire range of molality and temperature although their magnitudes are different.
- The negative values of parameters, ϕ_v and ϕ_k are found to be increased with increasing molalities of solute.
- For different salts studied here, a non-linear relation between ϕ_v, ϕ_k and solute has been observed throughout the concentration range.

The above observation of ϕ_v and ϕ_k clearly suggests the existence of solute-solvent interaction in the solution. The negative values indicate the presence of hydrophilic-ionic interactions occurring in these liquid systems. The increasing values of apparent molal compressibility (ϕ_k) and apparent molal volume (ϕ_v) with addition of solute and solvent contents reveal the strengthening of the solute and solvent interaction.

Table 3 Values of hydration number (H_n), apparent molal volume (ϕ_V) and apparent molal compressibility (ϕ_k) of potassium bromide in aqueous lactose mixture (05, 10 and 15% by weight of lactose) at 303, 308 and 313K

Molality (mol/Kg)	H_n			$-\phi_V$ m^3mol^{-1}			$-\phi_k \times 10^{10}$ m^2N^{-1}		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
Lactose –Water (05 : 95%)									
0	-	-	-	-	-	-	-	-	-
0.02	22.37	21.86	32.71	211.45	177.43	266.75	2677.00	2485.82	3708.69
0.04	22.60	21.69	21.44	127.85	138.00	153.13	2347.37	2311.47	2345.08
0.06	20.49	22.47	23.51	155.72	164.28	181.12	2298.92	2486.87	2629.67
0.08	21.38	20.33	20.19	127.85	129.37	146.96	2252.37	2169.97	2222.82
0.1	17.89	18.77	19.87	114.08	124.20	136.34	1915.96	2023.57	2153.33
Lactose –Water (10 : 90%)									
0	-	-	-	-	-	-	-	-	-
0.02	15.38	22.43	13.39	106.28	101.65	106.59	1684.00	2234.68	1511.75
0.04	22.09	22.53	21.90	106.28	128.27	104.07	2234.00	2359.60	2189.70
0.06	21.58	21.85	20.78	109.50	111.33	121.01	2207.30	2236.32	2170.87
0.08	20.64	20.07	19.37	105.07	96.81	96.81	2114.01	2032.20	1958.90
0.1	33.58	22.38	20.26	86.96	89.06	92.93	3093.18	2188.72	2015.21
Lactose –Water (15 : 85%)									
0	-	-	-	-	-	-	-	-	-
0.02	21.00	32.10	23.81	119.06	195.55	219.80	2203.65	3414.12	2801.82
0.04	22.04	24.72	16.44	80.96	112.09	140.96	2142.98	2481.93	1896.60
0.06	17.29	20.04	17.42	100.01	116.06	135.38	1828.73	2115.37	1955.32
0.08	15.30	17.45	16.29	85.72	106.12	112.29	1608.38	1863.03	1772.89
0.1	19.63	19.49	15.43	77.15	95.39	105.12	1932.17	1988.50	1674.96

Table 4 Values of hydration number (H_n), apparent molal volume (ϕ_V) and apparent molal compressibility (ϕ_k) of potassium fluoride in aqueous lactose mixture (05, 10 and 15% by weight of lactose) at 303, 308 and 313K

Molality (mol/Kg)	H_n			$-\phi_V$ m^3mol^{-1}			$-\phi_k \times 10^{10}$ m^2N^{-1}		
	Temperature (K)								
	303	308	313	303	308	313	303	308	313
Lactose –Water (05 : 95%)									
0	-	-	-	-	-	-	-	-	-
0.02	77.58	77.13	76.51	9.98	53.82	119.04	9717.35	9822.74	9976.48
0.04	62.47	64.38	62.78	14.95	36.89	79.54	5045.94	5278.61	5307.55
0.06	44.27	45.74	44.90	29.89	44.56	73.04	3666.81	3836.90	3872.69
0.08	35.89	36.26	34.81	32.38	38.41	59.78	2999.87	3047.55	3009.34
0.1	33.96	36.03	34.63	29.89	42.71	59.84	2839.80	3051.73	2999.06
Lactose –Water (10 : 90%)									
0	-	-	-	-	-	-	-	-	-
0.02	75.19	78.14	70.35	50.56	59.37	60.51	9748.82	10155.15	9102.94
0.04	62.35	64.66	60.44	35.06	39.49	40.03	5204.84	5408.06	5024.32
0.06	45.56	46.48	41.74	36.43	39.40	33.23	3857.13	3942.68	3501.21

0.08	36.34	36.49	33.31	42.00	39.35	39.63	3122.23	3122.49	2841.03
0.1	33.64	33.93	31.47	41.43	35.40	39.55	2905.13	2902.18	2696.59
Lactose –Water (15 : 85%)									
0	-	-	-	-	-	-	-	-	-
0.02	65.70	76.97	68.60	15.61	43.66	68.61	8522.76	10060.08	8987.15
0.04	63.81	66.81	53.26	84.99	89.46	82.71	5596.69	5846.20	4655.56
0.06	45.74	45.48	37.87	69.52	66.08	74.50	4056.18	4009.96	3380.50
0.08	39.90	38.05	33.38	71.44	64.05	80.08	3573.46	3381.83	3030.12
0.1	33.14	32.12	28.29	64.86	58.97	71.81	2993.80	2878.45	2586.82

Limiting Apparent Molal Compressibility ($\Phi_k^\circ)\Phi_k^\circ)$ and slope (S_k)

The limiting apparent molar compressibility $\Phi_k^\circ\Phi_k^\circ$ and the constant S_k for each electrolyte solutions have been evaluated by least square method using the relation obtained Gucker (1933) from Debye Huckel Theory (1923). $\Phi_k^\circ\Phi_k^\circ$ provides information regarding solute-solvent interactions and S_K provides information regarding solute-solute interactions in the mixtures observed by Massan (1929). The value of $\Phi_k^\circ\Phi_k^\circ$ is a measure of the protection against compression, which the solute molecules impart to water molecules Jha & Jha (1990) The appreciable negative values of $\Phi_k^\circ\Phi_k^\circ$ for all the systems reinforce about the existence of ion-solvent interactions.

From Tables 3 and 4, the $\Phi_k^\circ\Phi_k^\circ$ values are negative indicates strong electrostrictive solute-solvent interaction with increasing concentration. The negative $\Phi_k^\circ\Phi_k^\circ$ values may be due to loss of compressibility of solvent because of strong electrostrictive forces of ions Lankfort and Criss (1987). The electrostriction makes the solvent molecules considerably less compressible than bulk solvent due to the formation of rigid structure of solvent molecules around the solute molecules as reported by Rajkotia & Parsania (1999). The magnitude of the values of $\Phi_k^\circ\Phi_k^\circ$ is greater in potassium fluoride salts than potassium bromide because of the larger ionic size, which indicates a large number of water molecules bounded loosely and shows greater tendency towards complex formation.

The values of S_k exhibit both negative and positive. This behavior indicates the existence of ion-ion or solute-solute interaction. It is well known that solutes causing electrostriction leads to decrease in the compressibility of the solution. This is reflected by the negative values of $\Phi_k^\circ\Phi_k^\circ$ in the systems reported Palani (2004).

Limiting Apparent Molal Volume ($\Phi_v^\circ)\Phi_v^\circ)$ and slope (S_v)

The $\Phi_v^\circ\Phi_v^\circ$ reflects the effect of solute-solvent interaction and its magnitude relates the solute-solute interactions. As seen in Tables 3 and 4, the values of $\Phi_v^\circ\ \Phi_v^\circ$ shows negative values for all the electrolytic solutions at all the temperatures indicating the presence of weak solute interaction between the ions and solvent Parmer et al. (1989). The decrease in the Φ_v° values with increasing temperature may be attributed to the increase in salvation. The molecular interaction in the solvent

system increases due to the extensive hydrogen bonding against the solvent molecules as observed by Shashikant & Rekha Kumari (1995).

S_v is a measure of solute-solute interaction Radha Rani Gupta & Mukhtar Singh (2007). It is evident from the Tables 3 and 4, that the constant S_v exhibits the positive values predict strong solute-solute interaction in the systems.

CONCLUSION

The measurements of density, viscosity and ultrasonic velocity in aqueous solutions containing (5, 10 and 15% weight of lactose) at different temperatures of electrolytic systems reveal that

i) The presence of solute-solute and solute-solvent interaction exists in all the systems.
ii) The existence of ion-solvent or solute-solvent interactions resulting in attractive forces which promote the structure making tendency, while solute-solute interaction resulting dipole-dipole, dipole-induced dipole and electrostrictive forces enhance the structure breaking properties of metal halides.

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