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Acoustical Properties of Monochloroacetic Acid-Acetone-Water System at Different Temperatures

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Ultrasonic velocities in solutions of monochloroacetic acid(MCAA) in aqueous acetone mixtures were measured at 25°C and 30°C by using a single crystal interferometer at a frequency of 1.5 MHz. The ultrasonic velocity, density and concentration were used to calculate adiabatic compressibility, apparent molar compressibility, intermolecular free length, specific acoustic impedance, relative association and solvation number. Bachem and Gucker's laws have been found to be valid.

INTRODUCTION

Accurate thermodynamic data on dilute electrolyte solutions are frequently needed. The sound velocity is a thermodynamic function. Many other thermodynamic properties of electrolyte solutions are determined from sound velocity[1-3]. In recent years ultrasonic velocity studies in many of the aqueous and nonaqueous electrolytic solutions have led to new insight into the process of ion-ion and ion-solvent interactions. Very little experimental data on the solvation behaviour of ions are available in mixed solvents. Ultrasonic velocity and adiabatic compressibility are quite sensitive to changes in ionic concentrations. Either or both of them can be used to detect ionic interactions inclusive of complex formation. Adiabatic compressibility, apparent molar compressibility, intermolecular free length, specific acoustic impedance, relative association and solvation number are functions of ultrasonic velocity. As these parameters are a more accurate measure of ion–ion and ion–solvent interactions, an ultrasonic study on solutions of monochloroacetic acid (MCAA) in aqueous acetone has been made at different temperatures.

EXPERIMENTAL

Monochloroacetic acid (MCAA) was recrystallised from hot benzene and dried in vacuum as described previously[4]. Melting point determination revealed the alpha form of the acid. The purified form of the acid was stored in a desiccator under vacuum. The desiccator was fully covered with black paper to prevent even the slightest amount of photolysis of the acid. Acetone purified by the method adopted by Ruostesuo *et al*[5], and triply distilled water were mixed (by weight)

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to give mixtures of different compositions. Solutions of different molarities were prepared by dissolving accurately known weights of the acid in solvent mixtures and kept for some time. A pycnometer mounted in temperature controlled bath to 25–30 ± 0.01°C was used for density measurements. The maximum uncertainty in density readings was ± 0.00005 units. The velocities of ultrasonic waves of frequency 1.5 MHz were measured with the multifrequency interferometer (Mittal's M–81 instrument) at different temperatures in the range 25–30 ± 0.01°C as reported earlier[6]. The error in velocity measurements is ± 0.1%.

RESULTS AND DISCUSSION

Different thermodynamic parameters such as adiabatic compressibility (β_{ad}), apparent molar compressibility (ϕ_k), intermolecular free length (L_f), specific acoustic impedance (Z), relative association (R_A) and solvation number (S_n) have been calculated at 25 and 30°C using ultrasonic velocity (U) and density (ρ) of these solutions with the help of following equations presented in an earlier paper[7].

$$\beta_{ad} = \frac{1}{U^2\rho} \tag{1}$$

$$\phi_k = (\rho_0\beta_{ad} - \rho\beta^0_{ad})\frac{1000}{C \times \rho_0} + \frac{\beta^0_{ad}M_2}{\rho_0} \tag{2}$$

$$L_f = K\sqrt{\beta_{ad}} \tag{3}$$

$$Z = U \times \rho \tag{4}$$

$$R_A = \frac{\rho}{\rho_0}\left(\frac{U_0}{U}\right)^{1/3} \tag{5}$$

$$S_n = \frac{n_1}{n_2}\left(1 - \frac{\beta_{ad}}{\beta^0_{ad}}\right) \tag{6}$$

$$S_n = -\phi^0_k(M_2/\rho_0) \tag{7}$$

$$S_n = \frac{\phi^0_k - \phi^0_k(d)}{\phi^0_v(\beta_{ad} - \beta^0_{ad})} \tag{8}$$

where ρ, ρ_0 and U, U_0 are the densities and ultrasonic velocities of solution and solvent, respectively; M_2 is the molecular weight of the solute; β^0_{ad} and β_{ad} are the adiabatic compressibilities of solvent and solution; K, Jacobson constant; C, concentration in mol/litre; n_1 and n_2 are the number of moles of solvent and solute respectively; ϕ^0_k and $\phi^0_k(d)$ are partial molar adiabatic compressibilities of solvated and desolvated solute; ϕ^0_v is the partial molar volume of the solute. The value of $\phi^0_k(d)$ is generally assumed to be zero.

The variation of ultrasonic velocity in a solution depends on the intermolecular free length on mixing. On the basis of a model for sound propagation proposed

TABLE 1

ULTRASONIC VELOCITY (U) AND INTERMOLECULAR FREE LENGTH (L_f) OF MCAA SOLUTIONS AT 25°C AND 30°C.

Concentration mol/lit	U (m/s)	L_f (Å)	U (m/s)	L_f (Å)	Concentration mol/lit	U (m/s)	L_f (Å)	U (m/s)	L_f (Å)
	25°C		30°C			25°C		30°C	
	10 Wt % Acetone					30 Wt % Acetone			
0.0000	1551.0	0.4064	1554.6	0.4099	0.0000	1572.0	0.4071	1569.0	0.4124
0.0006	1551.2	0.4063	1554.8	0.4098	0.0074	1572.6	0.4064	1569.7	0.4118
0.0073	1552.9	0.4059	1556.4	0.4093	0.0116	1573.8	0.4061	1570.8	0.4115
0.0102	1553.5	0.4057	1557.7	0.4089	0.0208	1575.9	0.4054	1572.8	0.4108
0.01095	1555.8	0.4051	1561.3	0.4079	0.0460	1581.3	0.4039	1578.0	0.4092
0.0403	1560.0	0.4038	1563.3	0.4072	0.0605	1583.7	0.4032	1580.4	0.4085
0.0810	1566.0	0.4021	1570.5	0.4051	0.0725	1586.1	0.4025	1582.8	0.4079
0.1053	1563.0	0.4000	1572.9	0.4043	0.0950	1588.5	0.4018	1585.3	0.4072
	50 Wt % Acetone					70 Wt % Acetone			
0.0000	1495.5	0.4364	1491.0	0.4430	0.0000	1430.0	0.4685	1418.0	0.4786
0.0223	1488.3	0.4382	1483.8	0.4449	0.0185	1418.2	0.4723	1403.5	0.4832
0.0291	1483.5	0.4395	1479.0	0.4462	0.0213	1417.0	0.4727	1402.7	0.4835
0.0319	1482.2	0.4398	1477.7	0.4466	0.0370	1413.5	0.4736	1398.2	0.4847
0.0413	1480.5	0.4403	1476.0	0.4471	0.0426	1412.1	0.4740	1397.0	0.4851
0.0507	1478.5	0.4408	1474.0	0.4477	0.0546	1409.0	0.4748	1394.0	0.4864
0.0596	1475.1	0.4417	1470.6	0.4484	0.0796	1403.0	0.4766	1391.0	0.4868
0.0685	1471.2	0.4428	1466.7	0.4494	0.0897	1400.0	0.4775	1388.0	0.4876
0.0926	1468.0	0.4434	1463.5	0.4510	0.1054	1397.0	0.4785	1385.0	0.4885
0.1075	1467.2	0.4435	1462.7	0.4512					

	90 Wt % Acetone			
0.0000	1287.0	0.5321	1266.0	0.5428
0.0160	1281.9	0.5334	1260.8	0.5443
0.0229	1280.0	0.5339	1258.7	0.5449
0.0369	1275.9	0.5353	1254.8	0.5462
0.0567	1270.5	0.5372	1249.5	0.5481
0.0787	1265.3	0.5391	1244.2	0.5502
0.0885	1263.0	0.5401	1242.0	0.5512
0.1098	1257.2	0.5422	1236.4	0.5537

by Eyring and Kincaid[8], ultrasonic velocity increases on decrease of free length and vice versa. Intermolecular free length is a predominant factor in determining the variation of ultrasonic velocity in fluids and their solutions. In the present investigation, it has been observed that intermolecular free length decreases linearly on increasing concentration of MCAA in 10 and 30 wt% (Table 1) acetone mixtures and hence increase in ultrasonic velocity with concentration of MCAA. This indicates significant interaction between ion and solvent molecules, suggesting a structure promoting behaviour of the added electrolyte. However, intermolecular free length increases linearly on increasing the concentration of MCAA which results in a decrease of ultrasonic velocity in solutions in 50, 70, 90 and 100 wt % (Table 1) solvent mixtures. This implies a decrease in the number of free ions and hence occurrence of ionic association due to strong ion-ion interactions.

Solutions in 10 wt % solvent mixtures show increase in ultrasonic velocity with increase in temperature suggesting the weakening of ion-solvent interaction with rise in temperature. However, solutions of MCAA in 30, 50, 70, 90 and 100 wt % solvent mixtures show decrease in ultrasonic velocity with increase in temperature favouring strong ion-ion interactions.

As expected, β_{ad} decreases with increase of concentration of MCAA in solutions in 10, 30 wt % solvent mixtures and may be due to aggregation of solvent molecules around ions[9], supporting strong ion-solvent interactions. On the other hand, β_{ad} increases with increase of concentration in solutions in 50, 70, 90 and 100 wt % acetone, indicating a strong ion-ion interaction in these solutions.

Generally value of acoustic impedance, Z, increases while β_{ad} decreases[10], if U increases with temperature and vice versa. The behaviour observed in the present study is perhaps due to much weaker interactions at higher temperatures.

The adiabatic compressibility of solutions studied here are found to obey Bachem's relation[11]

$$\beta_{ad} = \beta_{ad}^{0} + AC + BC^{3/2} \tag{9}$$

where A and B are constants obtained as slopes and intercepts of linear plots of $\frac{\beta_{ad} - \beta_{ad}^{0}}{C}$ versus $C^{1/2}$ respectively. The values of constants A and B are listed in Table 2.

TABLE 2

BACHEM'S CONSTANTS A AND B, ϕ_k^0 AND S_k VALUES FOR MCAA IN AQUEOUS ACETONE

Acetone	$A \times 10^{12}$	$B \times 10^{12}$	$\phi_k^0 \times 10^9$	$S_k \times 10^9$	$A \times 10^{12}$	$B \times 10^{12}$	$\phi_k^0 \times 10^9$	$S_k \times 10^9$
	25°C				30°C			
10	–18.5	26.00	–16.6	22.25	–23.5	40.20	–16.2	22.6
30	–21.9	35.20	–31.3	76.40	–20.3	30.45	–28.2	64.5
50	30.2	–48.35	31.9	–42.25	19.4	–20.35	23.4	–19.5
70	46.8	–73.65	57.7	–117.53	68.4	–133.25	67.8	–112.3
90	22.2	10.55	13.2	50.50	24.8	8.25	15.5	46.0
100	19.6	60.55	10.2	96.50	15.8	58.65	11.2	88.8

ϕ_k values show linear relationship with $C^{1/2}$ within the concentration range studied at both temperatures. The partial molar compressibility at infinite dilution (ϕ_k^0) obtained as intercept of linear plots and slope (S_k) are presented in Table 2. The ϕ_k^0 values are positive in solutions in 50, 70, 90 and 100 wt % acetone, while these are negative in solutions in 10 and 30 wt % acetone at all temperatures. The negative ϕ_k^0 values are interpreted[12] in terms of loss of compressibility of solvent due to strong electrostrictive force in the vicinity of ions, causing electrostrictive solvation of ions. The monochloroacetic acid anion carries a negative charge centre and also is lyophobic in nature[7], and hence negative ϕ_k^0 manifests both electrostrictive and lyophobic solvation effect. The nearly constant $\phi_k^0(T)$ values show that the electrostriction is relatively insensitive to rise in temperature. It is thus reasonable to assume the validity of Frank and Wen[13] model for interactions of ions with solvent molecules, resulting in three regions of the solvent, namely A (highly electrostricted), B (partially disordered) and C (normal bulk). The near constancy of negative ϕ_k^0 means that the A region is firmly held even at elevated temperature and structural changes and B and C regions undergo such changes with rising temperature, which nearly compensate each other, leaving ϕ_k^0 relatively unaffected.

The positive ϕ_k^0 values are mainly due to B and C regions of Frank and Wen model, while A has negligible contribution. Positive ϕ_k^0 are also insensitive to temperature variation. S_k values represent ion-ion interactions[9–14]. The positive slopes (S_k) of ϕ_k versus $C^{1/2}$ in solutions in 10, 30, 90 and 100 wt % acetone show that ion-ion interaction increases with concentration, which is also evident from the decrease of S_n with increase in concentration. Figs. 1 and 2 show the behavior of L_f, β_{ad}, Z and S_n as functions of MCAA concentration in 10 and 70 wt % acetone respectively at 25°C. The negative slopes (S_k) in solutions in 50 and 70 wt % acetone show that ion-ion interaction decreases with concentration as observed from the increase in S_n with increase in concentration.

Relative association is influenced by two factors: (i) the breaking up of the solvent molecules on addition of electrolyte to it, and (ii) the solvation of ions that are simultaneously present; the former resulting in decrease and latter increase of relative association. In the present investigation, relative association increases with concentration and temperature in all solvent mixtures, as was indicated in a representative plot at 25°C (not shown), while the behaviour is implied at other temperatures.

The increase of R_A with concentration suggests that solvation of ions predominates over the breaking up of the solvent aggregates (water-water, water-acetone) on addition of MCAA. As the temperature of solution rises, the aggregates of solvent molecules break down, resulting in increased solvation of ions by free solvent molecules and thereby increase in R_A with increase in temperature.

Solvation number (S_n) calculated using Passynski[15], Wada *et al.*[16] and Nomura *et al.*[17] equations are listed in Table 3. These are positive in solutions in 10 and 30 wt % acetone, suggesting appreciable solvation of ions; here added electrolyte behaves as structure promoter. The values of S_n in 50, 70, 90 and 100 wt %

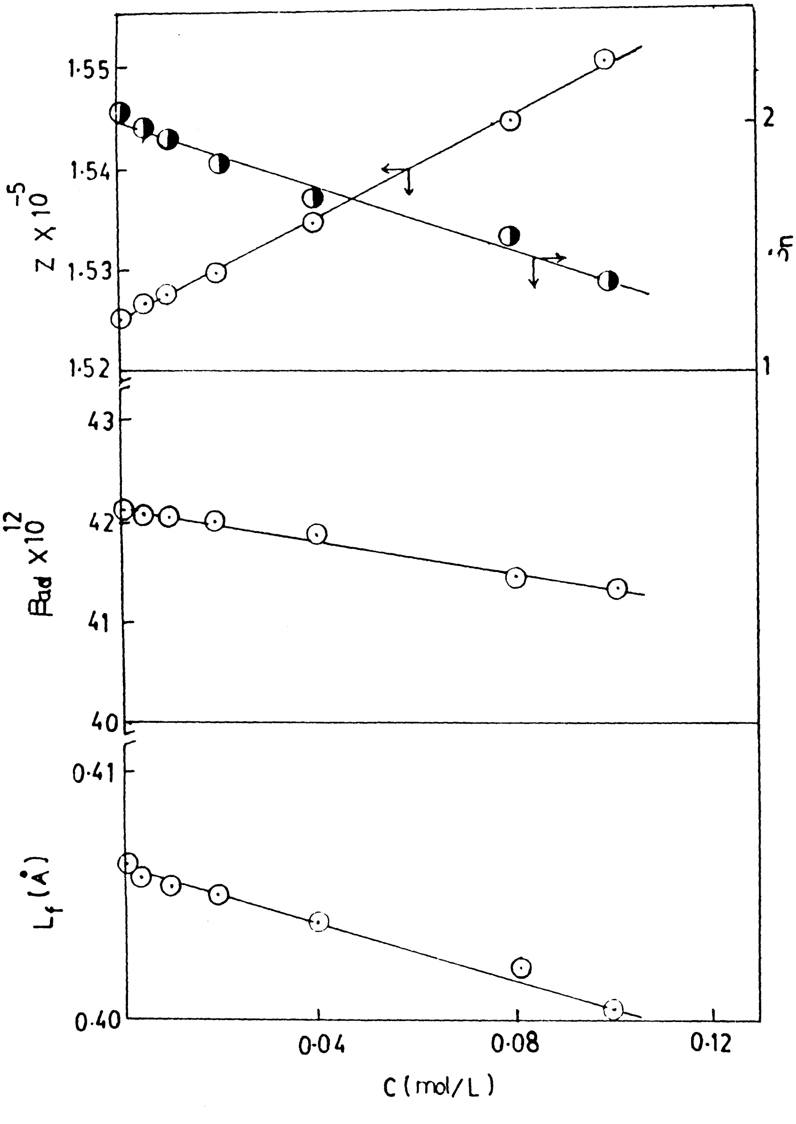

Fig. 1 L_f, β_{ad}, Z and S_n as functions of MCAA concentration in 10 wt % acetone at 25°C

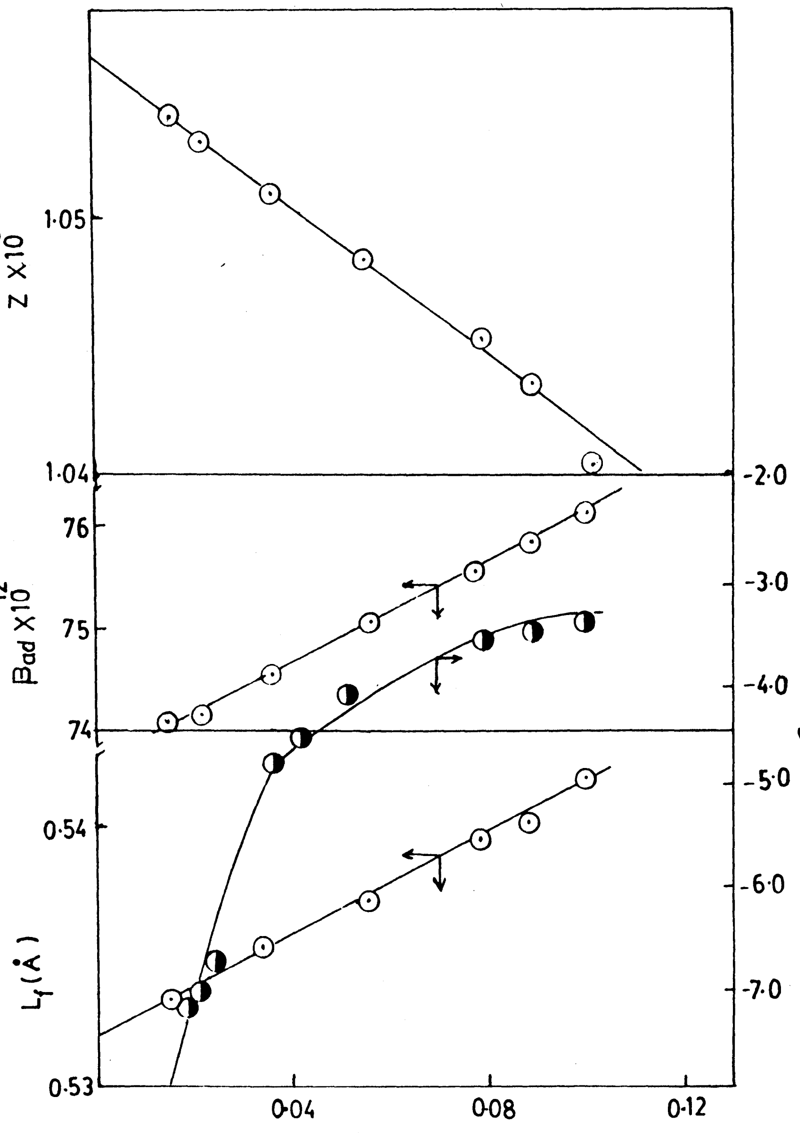

Fig. 2 L_f, β_{ad}, Z and S_n as functions of MCAA concentration in 70 wt % acetone at 25°C.

acetone are negative, indicating the structure breaking tendency of MCAA in these solvent mixtures[18].

TABLE 3
VARIATION OF SOLVATION NUMBER (S_n) WITH COMPOSITION OF SOLVENT MIXTURES AT 25°C

Acetone wt %	Concentration mol/litre	Solvation number		
		a	b	c
10	0.1053	1.53	2.49	0.00027
30	0.0950	5.27	2.50	0.00047
50	0.1057	–6.15	–4.90	–0.00033
70	0.1057	–3.42	–5.72	–0.00040
90	0.1098	–3.32	–0.73	–0.000045
100	0.1133	–0.99	–6.14	–0.000034

[a] By using Passynski equation.
[b] By using Wada *et al.* equation.
[c] By using Nomura *et al.* equation.

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REFERENCES

1. V.F. Nozdrev, Applications of Ultrasonics in Molecular Physics, Gordon and Breach, New York (1963).
2. S.J. Synder and J.R. Synder, *J. Chem. Eng. Data*, **19**, 270 (1974).
3. G.W.J. Marks, *J. Acoust. Soc. Am.*, **31**, 936 (1959).
4. P.S. Nikam and Mehdi Hasan, *J. Chem. Eng. Data*, **33**, 165 (1988).
5. P.A. Ruostesuo and P.L. Pirila-Honkanen, *J. Chem. Eng. Data*, **32**, 303 (1987).
6. P.S. Nikam and Mehdi Hasan, *Indian J. Pure and Appl. Phys.*, **24**, 502 (1986).
7. P.S. Nikam and A.R. Hiray, *Indian J. Pure and Appl. Phys.*, **29**, 601 (1991).
8. H. Eyring and J.F. Kincaid, *J. Chem. Phys.*, **6**, 620 (1938).
9. J.D. Pandey, A. Shukla, R.D. Rai and K.J. Mishra, *J. Chem. Eng. Data*, **34**, 29 (1989).
10. Pankaj and C. Sharma, *Indian J. Pure & Appl. Phys.*, **27**, 32 (1989).
11. C.H. Bachem, *Z. Phys. A.*, **101**, 541 (1936).
12. V.B. Corey, *Phys. Rev.*, **64**, 350 (1943).
13. H.S. Frank and W.Y. Wen, *Disc. Faraday Soc.*, **24**, 133 (1957).
14. A. Shukla, Aradhana and R.K. Shukla, *Acoust. Letter*, **7**, 161 (1984).
15. A. Passynski, *Acta Phys. Chim.*, **8**, 385 (1938).
16. Y. Wada, S. Shimbo and H. Oda, *J. Acoust. Soc. Am.*, **22**, 880 (1950).
17. S. Koda, K. Matsumoto, R. Nishimura and H. Nomura, *J. Chem. Soc. Trans.*, **87**, 1287 (1991).
18. M. Woldan, *Z. Physik Chemie*, **269**, 628 (1988).

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