Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 90, Number 6, December 1981, pp. 511–517.
© Printed in India.

Hydration numbers of some metal acetates, monochloroacetates and trichloroacetates in solution from ultrasonic velocity and compressibility measurements

D K KOPPIKAR, M V LELE† and S SOUNDARARAJAN*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

† Central Instruments and Servicing Laboratory, Indian Institute of Science, Bangalore 560 012, India

MS received 9 July 1981 ; revised 16 October 1981

Abstract. Ultrasonic velocities in aqueous solutions of some metal acetates, monochloroacetates and trichloroacetates, and the respective acids have been measured at 1 MHz frequency using the pulse technique. The ultrasonic velocity, adiabatic compressibility and apparent molal compressibility were measured as a function of concentration. The apparent molal compressibility values at infinite dilution were calculated and used to determine the hydration numbers. The hydration numbers obtained are, CH_3COOH (HP) = 3·1, NiP_2 = 15·0, CuP_2 = 8·6, LaP_3 = 18·3, PrP_3 = 20·3, NdP_3 = 16·5, $ClCH_2COOH$ (HQ) = 3·5, NiQ_2 = 14·0 CuQ_2 = 7·6, MgQ_2 = 9·3, CaQ_2 = 9·4, BaQ_2 = 17·5, LaQ_3 = 19·5, PrQ_3 = 18·5, NdQ_3 = 18·0, YQ_3 = 20·5, Cl_3CCOOH (HR) = 6·3, NiR_2 = 11·5, CuR_2 = 6·3, MgR_2 = 8·8, CaR_2 = 9·8, BaR_2 = 13·0, LaR_3 = 28·8, PrR_3 = 30·0, NdR_3 = 27·8 and YR_3 = 31·3. The low hydration numbers obtained for most of the salts of divalent metal ions are probably due to incomplete dissociation in solution.

Keywords. Ultrasonic velocities ; compressibilities ; hydration numbers ; metal acetates ; metal monochloroacetates ; metal trichloroacetates.

1. Introduction

Ultrasonic velocity measurements in aqueous solutions of a number of electrolytes have been carried out (Hall and Yeager 1973 ; Stuehr and Yeager 1965). However, data concerning rare-earth electrolytes are limited (Saraswathi *et al* 1974 ; Spedding and Atkinson 1959 ; Satya Prakash *et al* 1966 ; Bockris and Saluja 1972 ; Jezowska-Trzebiatowska *et al* 1976*a*, *b*, 1977). The velocity and hydration number data for lanthanum, cerium, praseodymium and neodymium perchlorates, lanthanum nitrate and ammonium ceric nitrate have been reported earlier from this laboratory (Saraswathi *et al* 1974). The present paper deals with the measurement of ultrasonic velocities in aqueous solutions of lanthanum,

* To whom correspondence should be made.

praseodymium, neodymium, yttrium, magnesium, calcium, barium, copper and nickel trichloroacetates and monochloroacetates, and of lanthanum, praseodymium, neodymium, copper and nickel acetates. The velocities have also been measured in aqueous solutions of acetic, monochloroacetic and trichloroacetic acids. These measurements in combination with the density data have been used to determine the various parameters like adiabatic compressibility, apparent molal compressibility, hydration number, acoustic impedance, relative association and molar sound velocity. All the measurements were made at 30° C and in the concentration range 0·02 to 0·6 M. Although data are available for the velocity and compressibility in aqueous solutions of some acetates like those of alkali metals, alkaline earth metals, etc. (Suryanarayana 1962; Suryanarayana and Ramabrahmam 1963) data for the monochloroacetates and trichloroacetates are lacking.

2. Experimental

2·1 *Preparation of the salts*

Except cupric acetate, all the other salts investigated were prepared in the laboratory. Nickel acetate and the rare-earth salts were prepared starting with the corresponding hydroxides. For the rest of the salts the corresponding carbonates were used. The hydroxide or the carbonate was added in excess to an aqueous solution of the acid. After allowing the mixture to stand for about 15 hr the excess hydroxide or carbonate was removed by filtration. The clear solution was evaporated at room temperature to obtain the solid salts.

2·2 *Analysis*

The rare-earths and copper were estimated by EDTA titrations using xylenol orange as the indicator. Magnesium, calcium and barium, and nickel were also estimated similarly using Eriochrome black T, methylthymol blue, and murexide, respectively, as indicators.

2·3 *Physical measurements*

The ultrasonic velocities in aqueous electrolyte solutions at 1 MHz frequency were measured using the ultrasonic pulse interferometer constructed in this laboratory (Lele *et al* 1976). The principle of measurement is based on the Carstensen's velocity difference method (Carstensen 1954). The densities were measured with a density bottle fitted with a thermometer. All the measurements were made at 30° C.

3. Results and discussions

The measurements show that the velocity increases with concentration for all the solutions. The variation is linear for most of the salts of monochloroacetic acid and trichloroacetic acid. The plot is not linear for a few of the trichloroacetates (Cu, La and Nd) and monochloroacetates (Y and Pr), and for all the acetates studied in the present investigation.

The adiabatic compressibility (β) was obtained from the relation, $\beta = 1/u^2\rho$, where u is the ultrasonic velocity and ρ the density of the solution. For all the salts studied in the present investigation, β decreases with concentration (figures 1 to 3) and is lower than that of pure water at all concentrations. It has been shown that the variation in β of aqueous salt solutions with concentration at a given temperature must be compatible with the equation,

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

where β_0 is the adiabatic compressibility of the solvent, β that of the solution at concentration C, and A and B are constants. Accordingly, the trichloroacetates of La^{3+}, Pr^{3+}, Nd^{3+} and Cu^{2+}, the monochloroacetates of Pr^{3+} and Y^{3+}, and the acetates of La^{3+} and Pr^{3+} deviate from linearity of the plot at higher concentrations. However, in most cases, the constant B is small and the variation of β with concentration is linear as found for the rest of the salts in the present study. The slopes of the plots determined at low concentrations increase with an increase in the valency of the cation for salts with a common anion. When the slopes for the salts with the same cation are compared, the general trend observed is,

trichloroacetates > monochloroacetates > acetates.

From this it appears that the solvation of the anions increases in the same order.

The limiting hydration numbers (n) for the electrolytes were obtained from the relation (Wada *et al* 1950)

$$n = -\varphi_k^0/(\beta_0 M_0/\rho_0).$$

where φ_k^0 is the apparent molal compressibility at infinite dilution, and M_0 and ρ_0 are the molecular weight and the density of water, respectively. φ_k^0 was determined by calculating the apparent molal compressibility (φ_k) at different concentrations (Saraswathi *et al* 1974) and extrapolating the plot of φ_k versus $C^{1/2}$ to infinite dilution. Since φ_k is the difference between two large quantities, deviations from linearity occur at very low concentrations (Stuehr and Yeager 1965 ; Gucker 1933; Marks 1960). This behaviour has been observed by other workers also (Satyanarayanamurthy and Krishnamurthy 1963). The straight line portions of the plots were used for extrapolation to infinite dilution. The φ_k^0 values and the hydration numbers determined have been tabulated in table 1. The hydration numbers obtained for the salts of the divalent cations are generally very low. This suggests that these salts are not completely dissociated in solution. Cation-anion association or complexation in solution is possible for salts of these metal ions with carboxylate anions. The effect of association is the displacement of water molecules from the primary hydration sheath of the ions. It is well-known that copper acetate and monochloroacetate conform to a bridge structure in the solid state and the bridges are only partially broken in solution (Cotton and Wilkinson 1969). The monochloroacetates of the divalent ions are also known to have a bridge structure in the solid state (Warrier and Narayanan 1967). In view of these facts it is not surprising that low hydration numbers are obtained for these salts. It must, therefore, be remembered that the hydration numbers obtained for these salts do not represent the true hydration numbers. These numbers are useful only in suggesting incomplete dissociation of the salts in solution.

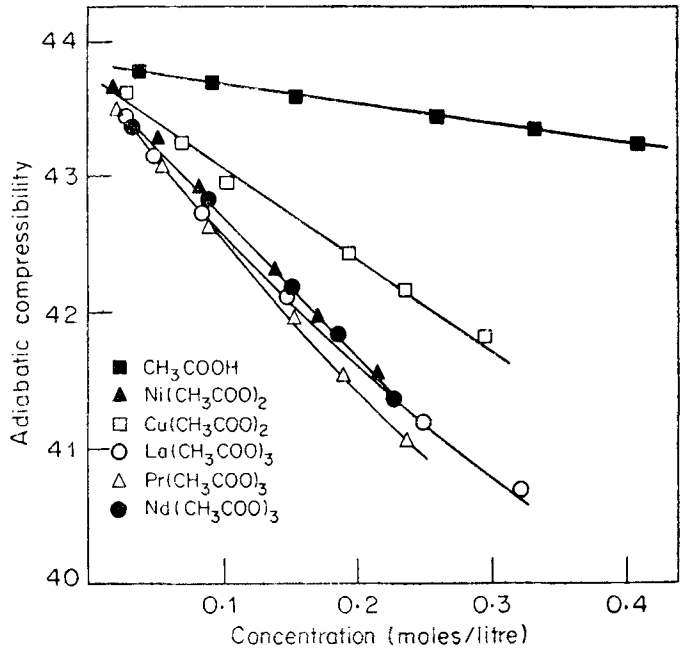

Figure 1. Variation of adiabatic compressibility with concentration.

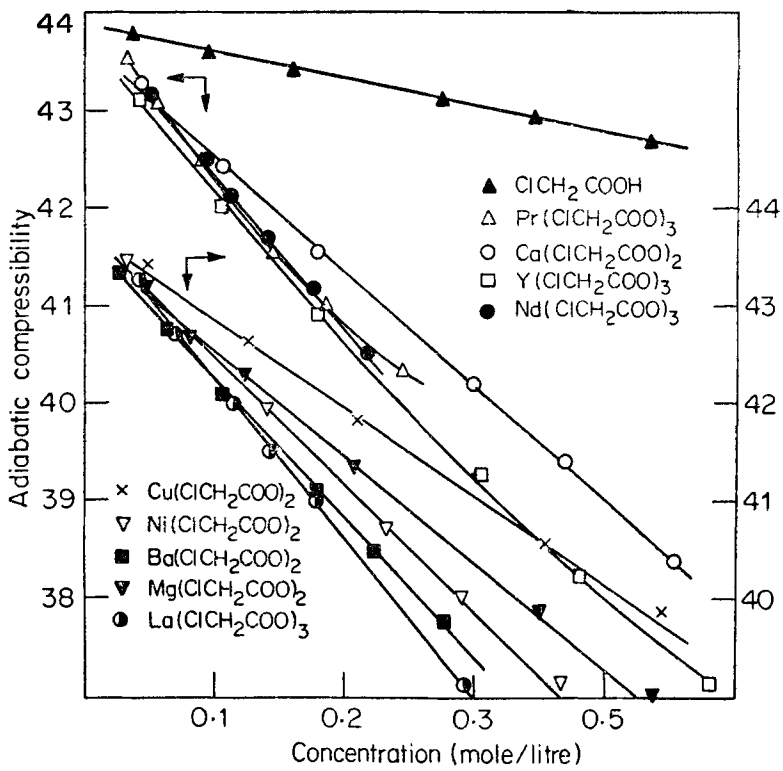

Figure 2. Variation of adiabatic compressibility with concentration.

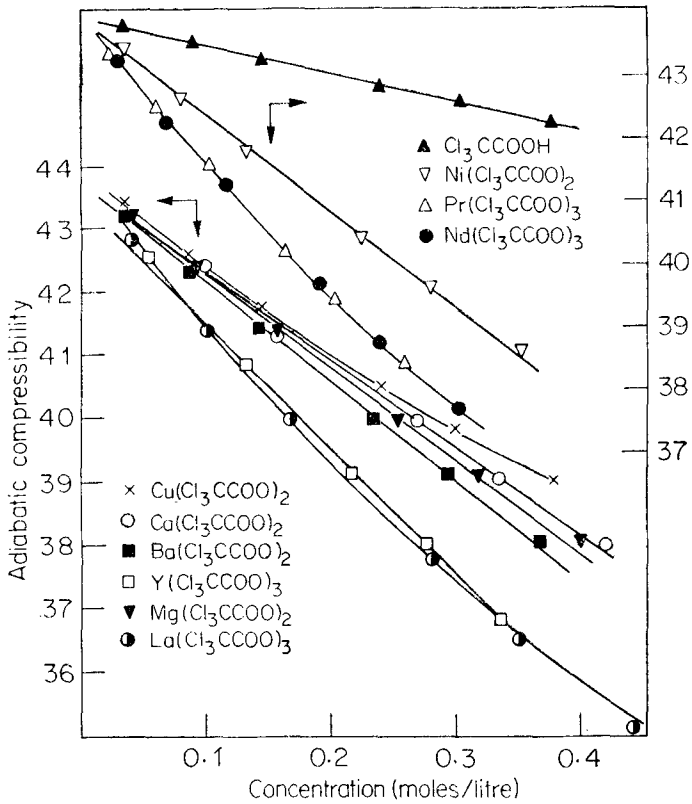

Figure 3. Variation of adiabatic compressibility with concentration.

Table 1. Apparent molal compressibilities at infinite dilution and hydration numbers.

	$-\varphi_k^0$			Limiting hydration numbers		
	Ac^-	$MCAc^-$	$TCAc^-$	Ac^-	$MCAc^-$	$TCAc^-$
H^+	25	28	50	3·1	3·5	6·3
Ni^{2+}	120	111	92	15·0	14·0	11·5
Cu^{2+}	69	61	50	8·6	7·6	6·3
Mg^{2+}	..	74	70	..	9·3	8·8
Ca^{2+}	..	75	78	..	9·4	9·8
Ba^{2+}	..	140	104	..	17·5	13·0
La^{3+}	146	156	230	18·3	19·5	28·8
Pr^{3+}	162	148	240	20·3	18·5	30·0
Nd^{3+}	132	143	222	16·5	18·0	27·8
Y^{3+}	..	164	250	..	20·5	31·3

Ac^- = acetate : $MCAc^-$ = monochloroacetate : $TCAc^-$ = trichloroacetate.

The hydration numbers obtained for the rare-earth salts indicate that there is not much complexation in solution. Y^{3+} seems to be more hydrated than the other rare-earth ions. The hydration number obtained for acetic acid in the present study is greater than that reported earlier (Allam and Lee 1966). Obviously, this is because the measurements made herein are at concentrations lower than those reported earlier. The hydration numbers are in general highest for the trichloroacetates and lowest for the acetates. This means that the hydration number of the acetate ion is increased by substitution of the hydrogens by chlorine atoms. Chlorosubstitution, thus, seems to increase the "structure promoting" ability of the acetate ion. Similar "structure promoting" ability has been observed for cations of large size like the tetraalkylammonium ions (Diamond 1963).

From the velocity and density data other parameters like acoustic impedance (Z), relative association (RA) and molar sound velocity (R) were also determined in the same way reported earlier (Saraswathi *et al* 1974). Z and RA showed a linear variation with concentration as expected (Marks 1959, 1960). R showed a linear variation with mole fraction (C_m) of the electrolyte. It has been shown (Rao 1940, 1941 ; Langeman and Corry 1942 ; Langeman and Dunbar 1945) that R in unassociated liquids is an additive property of the atoms and bonds constituting the molecule. In the present study, the R versus C_m plots for the three acids were extrapolated to 100% concentration to obtain the R values for the pure components. The values so obtained are 657, 757 and 1057 for acetic, monochloroacetic and trichloroacetic acids, respectively. Interestingly, these values show good agreement with the R values, 648, 782·5 and 1051·5, predicted for the three acids on the basis of atomic increment values. The values predicted on the basis of bond increments are slightly less being 609·4, 744·2 and 1013·8 for the three acids.

Acknowledgement

One of the authors (DKK) thanks the UGC (India) for financial assistance during the course of this work.

References

Allam D S and Lee W H 1966 *J. Chem. Soc.* Sect. A p. 426

Bockris J O'M and Saluja P P S 1972 *J. Phys. Chem.* **76** 2140

Carstensen E L 1954 *J. Acoust. Soc. Am.* **26** 858

Cotton F A and Wilkinson G 1969 *Advanced inorganic chemistry* 2nd edition (New Delhi : Wiley Eastern) p. 904

Diamond R M 1963 *J. Phys. Chem.* **67** 2513

Gucker F T 1933 *J. Am. Chem. Soc.* **55** 2709

Hall C and Yeager E 1973 *Techniques of electrochemistry* (eds. E Yeager and A J Salkind) (New York : Wiley) 2 399

Jezowska-Trzebiatowska B, Ernst S, Legendziewicz J and Oczko G 1976a *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **24** 997

Jezowska-Trzebiatowska B, Ernst S, Legendziewicz J and Oczko G 1976b *Int. Symp. Specific Interact. Mol. Ions (Proc.) 3rd* **1** 245

Jezowska-Trzebiatowska B, Ernst S, Legendziewicz J and Oczko G 1977 *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **25** 649
Langeman R T and Corry J E 1942 *J. Chem. Phys.* **10** 759
Langeman R T and Dunbar W S 1945 *J. Phys. Chem.* **49** 428
Lele M V, Chary S L V and Soundararajan S 1976 *Indian J. Pure Appl. Phys.* **14** 294
Marks G W 1959 *J. Acoust. Soc. Am.* **31** 936
Marks G W 1960 *J. Acoust. Soc. Am.* **32** 327
Rao M R 1940 *Indian J. Phys.* **14** 109
Rao M R 1941 *J. Chem. Phys.* **9** 682
Saraswathi N, Koppikar D K, Soundararajan S and Lele M V 1974 *Indian J. Pure Appl. Phys.* **12** 509
Satyanarayanamurthy M and Krishnamurthy Bh 1963 *Indian J. Pure Appl. Phys.* **1** 234, 332
Satya Prakash, Som Prakash and Shobhaya Laxmi 1966 *Bull. Chem. Soc. Jpn.* **39** 2114
Spedding F H and Atkinson G 1959 *Structure of electrolytic solutions* (ed. Hamer W) (New York : Wiley) p. 319
Stuehr J and Yeager E B 1965 *Physical acoustics* (ed. W Mason) (New York : Academic Press) **2A** 351
Suryanarayana M 1962 *J. Sci. Ind. Res. (India)* **B21** 57
Suryanarayana M and Ramabrahmam K 1963 *Indian J. Pure Appl. Phys.* **1** 406
Wada Y, Shibo S and Oda M 1950 *J. Acoust. Soc. Am.* **22** 880
Warrier A V R and Narayanan P S 1967 *Spectrochim. Acta* **A23** 1061