Ultrasonic Velocity and Allied Parameters in Alcoholic Solutions of Calcium Nitrate

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Ultrasonic velocities at 23 °C have been determined and adiabatic compressibility, intermolecular free length, specific acoustic impedance, molar sound velocity, apparent molal compressibility, and solvation number have been calculated for alcoholic solutions of calcium nitrate in methanol, ethanol, 2-propanol, 1-butanol, and isoamyl alcohol. The results have been discussed in the light of existing theories.

A large amount of experimental data on the ultrasonic velocity and related parameters of aqueous solutions of electrolytes has now been accumulated. The investigations of nonaqueous solutions have received the attention of some workers, but much has not been done. However, mention may be made of the studies of ultrasonic velocity, adiabatic compressibility, and solvation number of some salts in nonaqueous solutions by Fogg (*3*), Allam and Lee (*1*), Subrahmanyam (*11*), Ramabrahmam and Suryanarayana (*9*), Mikhailov et al. (*5*), and Prakash and Prakash (*7*).

We are reporting here the findings of a study of the ultrasonic velocity, adiabatic compressibility, free length, apparent molal compressibility, specific acoustic impedance, molar sound velocity, and solvation number of calcium nitrate in methanol, ethanol, 2-propanol, 1-butanol, and isoamyl alcohol.

Experimental Section

Calcium nitrate (B.D.H. Analar) was used for the preparation of the salt solutions in organic liquids. Calcium nitrate was fused and cooled in a desiccator, and lumps of the fused salts were powdered and reheated in a glass vial up to 175 °C, for about 0.5 h, then cooled and weighed. The process was repeated until the weight became constant and then it was kept in a vacuum desiccator for use. A.R. (B.D.H.) grade organic solvents were purified by standard methods described by Weissberger (*14*) and their densities agreed with those of literature values. The solutions were prepared by dissolving an accurately known weight of the salt in the liquid and kept for some time. The densities were determined pycnometrically with an accuracy of 1 in 10^4. The light diffraction technique (*2*) was employed for the measurement of ultrasonic velocity at 5 MHz. The source of ultrasonic waves was a generator comprising of an oscillator unit and a gold-plated quartz crystal 2.54 cm in diameter as transducer. A glass filter was used to get light of 3657 Å. A suitable glass cell was designed (*8*) for containing the solution during measurements. The diffraction patterns were photographed on Agfa Brovira glossy single weight silver bromide paper. The fringe width for the first-order fringes was measured by a comparator fitted with a traveling microscope and vernier scale reading precisely up to 0.0001 cm. The probable error in the measurements of the velocity was 0.18%. The velocities were determined at 23 °C. The temperature was recorded by a thermometer within ±0.1 °C. The adiabatic compressibility was calculated from $\beta_S = c^{-2}\rho^{-1}$, where c is sound velocity and ρ is density.

Discussion

Ultrasound Velocity. The velocities have been recorded in Table I. It is obvious that the ultrasonic velocity increases with increase in concentration. The explanation can be found from $c = (\beta\rho)^{-1/2}$. If the solute molarity is C, the variation in ultrasound velocity can be expressed as

$$\frac{dc}{dC} = \frac{-c}{2}\left(\frac{1}{\rho}\frac{d\rho}{dC} + \frac{1}{\beta}\frac{d\beta}{dC}\right) \tag{1}$$

As can be seen from the data (Table I) $(1/\rho)(d\rho/dC)$ and $(1/\beta)(d\beta/dC)$ are of opposite sign. Since $-(1/\beta)(d\beta/dC)$ is greater than $(1/\rho)(d\rho/dC)$, dc/dC is positive. In ethanol the velocity does not change much whereas in the other solvents there is an appreciable change. Had it been possible to prepare more concentrated solutions perhaps greater variation would have been noticeable.

Adiabatic Compressibility. The adiabatic compressibility decreases with increase in the concentration of calcium nitrate (column 4) in each case. This behavior is in agreement with the general trend observed in electrolytic solutions. Similar behavior is reported for the aqueous solutions by Roschina and Kaurova (*10*) who demonstrated that in each of the aqueous solutions of $MgCl_2$, $CaCl_2$, and $ZnCl_2$, the adiabatic compressibility decreases with increasing concentration.

The adiabatic compressibility of nitrate solutions is found to obey Bachem's relation $\beta = \beta_0 + AC + BC^{3/2}$, where β and β_0 are the compressibilities of solutions and solvents, respectively, C is the molar concentration, and A and B are constants. When $(\beta - \beta_0)/C$ is plotted against $\sqrt{C}$, a linear variation has been noted in each case studied here (Figure 1). Each line has same sign of the slope. The values of A have been determined from the intercepts on the ordinate, while values of B have been determined from the slopes of the curves. As usual the values of A are negative in sign (Table II).

Intermolecular Free Length. The intermolecular free length is given by $K\sqrt{\beta}$ where K is a temperature dependent constant (*4*) and β is the adiabatic compressibility of the solution. The compressibility decreases with concentration and hence free length is found to decrease with increase in concentration of calcium nitrate (column 5, Table I).

Specific Acoustic Impedance. Specific acoustic impedance Z has been reported in Table I (column 6), which shows the variation of Z with molar concentration. It is obvious that this variation is linear and when plotted the slope of the lines was found to be positive in each case. A linear increase in the value of Z has also been reported in the aqueous and nonaqueous solutions of lithium salts in ethanol, acetone, and methyl ethyl ketone by Ramabrahmam and Suryanarayana (*9*). The specific acoustic impedance Z for the aqueous solutions of inorganic acetates is a linear function of the molar concentration as reported by Suryanarayana (*12*).

Molar Sound Velocity. If n_1 moles of the solute of molecular weight M_1 has been dissolved in n_2 moles of solvent of molecular weight M_2, the molar sound velocity R of the solution is given by

$$R = (\overline{M}/\rho)c^{1/3} \tag{2}$$

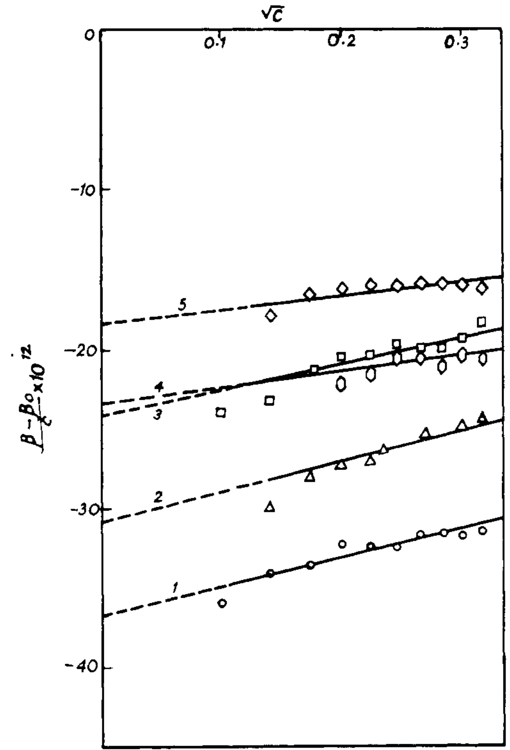
Where $\overline{M} = (n_1M_1 + n_2M_2)/(n_1 + n_2)$ and ρ is the density of the solution. The molar sound velocities for various solutions in-

Table I. Values of Parameters in Different Alcohols

Concn (mol l.$^{-1}$)	Density, g ml^{-1}	Ultrasound velocity, m s^{-1}	Adiabatic compressibility ($\times 10^{12}$) (cm^2 dyn^{-1})	Intermolecular free length, Å	Specific acoustic impedance, $Z \times 10^{-5}$ cgs units	Solvation no.
In Methanol						
0.010	0.7918	1134	98.22	0.6165	0.8978	9.02
0.020	0.7929	1135	97.90	0.6155	0.8999	8.53
0.030	0.7941	1136	97.57	0.6145	0.9022	8.46
0.040	0.7952	1137	97.29	0.6137	0.9040	8.08
0.050	0.7966	1138	96.96	0.6125	0.9063	8.12
0.060	0.7977	1139	96.63	0.6115	0.9086	8.15
0.070	0.7986	1140	96.36	0.6106	0.9103	7.96
0.080	0.7998	1141	96.05	0.6096	0.9124	7.91
0.090	0.8009	1142	95.72	0.6085	0.9147	7.99
0.100	0.8021	1143	95.42	0.6077	0.9168	7.89
In Ethanol						
0.010	0.7900	1212	86.30	0.5779	0.9568	6.32
0.020	0.7914	1212	86.02	0.5769	0.9592	5.93
0.030	0.7928	1213	85.78	0.5761	0.9614	5.53
0.040	0.7942	1213	85.53	0.5753	0.9634	5.38
0.050	0.7953	1214	85.27	0.5744	0.9658	5.33
0.055	0.7960	1214	85.17	0.5741	0.9668	5.21
0.072	0.7980	1215	84.80	0.5728	0.9701	5.10
0.090	0.8000	1217	84.39	0.5715	0.9736	4.87
0.100	0.8014	1217	84.18	0.5707	0.9757	4.82
In 2-Propanol						
0.010	0.7862	1231	83.85	0.5696	0.9672	3.73
0.020	0.7875	1232	83.62	0.5689	0.9707	3.65
0.030	0.7885	1233	83.45	0.5682	0.9721	3.31
0.040	0.7897	1233	83.27	0.5676	0.9738	3.18
0.500	0.7910	1234	83.07	0.5669	0.9759	3.18
0.060	0.7922	1234	82.90	0.5663	0.9773	3.11
0.070	0.7933	1234	82.69	0.5657	0.9795	3.11
0.080	0.7945	1235	82.50	0.5650	0.9813	3.09
0.090	0.7955	1235	82.35	0.5645	0.9828	2.90
0.100	0.7966	1236	82.22	0.5640	0.9842	2.90
In 1-Butanol						
0.100	0.8111	1317	71.14	0.5247	1.0680	4.13
0.020	0.8120	1318	70.89	0.5237	1.0700	3.98
0.030	0.8126	1319	70.68	0.5230	1.0730	3.72
0.040	0.8131	1320	70.53	0.5224	1.0740	3.45
0.050	0.8137	1321	70.33	0.5218	1.0760	3.31
0.060	0.8143	1323	70.18	0.5211	1.0770	3.14
0.070	0.8148	1324	69.98	0.5204	1.0790	3.06
0.080	0.8154	1326	69.72	0.5194	1.0810	3.23
0.090	0.8162	1327	69.56	0.5188	1.0830	3.14
0.100	0.8167	1329	69.33	0.5180	1.0850	3.18
In Isoamyl Alcohol						
0.010	0.8130	1290	73.84	0.5346	1.0490	2.36
0.020	0.8141	1291	73.67	0.5339	1.0510	2.24
0.030	0.8151	1291	73.53	0.5334	1.0530	2.07
0.040	0.8161	1292	73.38	0.5328	1.0540	2.02
0.050	0.8171	1293	73.23	0.5323	1.0560	1.99
0.060	0.8181	1293	73.07	0.5318	1.0580	1.99
0.070	0.8191	1294	72.91	0.5311	1.0600	1.99
0.080	0.8202	1294	72.76	0.5307	1.0620	1.98
0.090	0.8214	1295	72.59	0.5301	1.0640	1.99
0.100	0.8227	1296	72.40	0.5293	1.0660	2.03

Table II. Constants A and B of Bachem's Relation, Apparent Molal Compressibility at Zero Concentration, $\phi_{0(k)}$, and Solvation Number from Wada's Relation

Systems	A	B	$\phi_{0(k)}$	Slope of $\phi_{(k)}$ vs. $\sqrt{C}$	Solvation no. (eq 2)
$Ca(NO_3)_2$ in methanol	−36.75	18.75	−33.00	25.00	8.27
$Ca(NO_3)_2$ in ethanol	−31.00	20.00	−29.25	27.77	5.83
$Ca(NO_3)_2$ in 2-propanol	−24.25	17.05	−21.50	25.00	3.34
$Ca(NO_3)_2$ in 1-butanol	−23.50	10.71	−17.50	23.33	2.91
$Ca(NO_3)_2$ in isoamyl alcohol	−18.50	9.14	−15.25	16.16	1.94



$\frac{\beta-\beta_0}{C}$ vs $\sqrt{C}$, $Ca(NO_3)_2$ in methanol(1), ethanol(2), iso-propanol(3), n-butanol(4) and iso-amyl' alcohol (5)

Figure 1.

vestigated have been calculated and are found to vary linearly with the concentration of calcium nitrate (Figure 2). The value of *R* increases in the case of calcium nitrate solutions in methanol, ethanol, and 1-butanol and decreases in 2-propanol and isoamyl alcohol. There is very little change when 2-propanol is the solvent.

Apparent Molal Compressibility. For all the alcoholic calcium nitrate solutions studied here it is found that the apparent molal compressibility $\phi_{(k)}$ varies linearly as the square root of the molar concentration *C*. Graphs of $\phi_{(k)}$ vs. $\sqrt{C}$ for these alcoholic solutions are shown in Figure 3. The values of $\phi_{(k)}$ are negative for all the solutions. With increase in concentration $\phi_{(k)}$ increases in every case but the magnitudes are different. For isoamyl alcohol, the rate of increase of $\phi_{(k)}$ with concentration becomes small.

The linear increase in $\phi_{(k)}$ with $\sqrt{C}$ is similar to that observed in aqueous solutions of electrolytes. Also, the slope of the lines changes below a certain concentration as required by the theory. For all the solutions investigated here, the slopes of $\phi_{(k)}$ vs. $\sqrt{C}$ and intercepts $\phi_{0(k)}$ are given in Table II.

Solvation. The values of $\phi_{0(k)}$ were evaluated by extrapolating the graphs of $\phi_{(k)}$ vs. $\sqrt{C}$ to infinite dilution and these values of $\phi_{0(k)}$ of the salt have been used to calculate the solvation number by Wada's relation (*13*).

$$S_n = V_n/\text{molar volume} \quad (3)$$

Where V_n is the volume of primary alcohols of solvation for the solute molecules and the value of V_n is obtained from the following relation

$$\phi_{(k)\lim C\to 0} = -\beta_0 V_n \quad (4)$$

Where β_0 is the compressibility of the pure solvent.

Passynsky (*6*) assumed that the ions in the first solvation zone are incompressible. He developed the following equation for the calculation of solvation numbers.

$$n_s = -\frac{n_1}{n_2}\left(1 - \frac{V\beta}{n_1 V_1^0 \beta_0}\right) \quad (5)$$

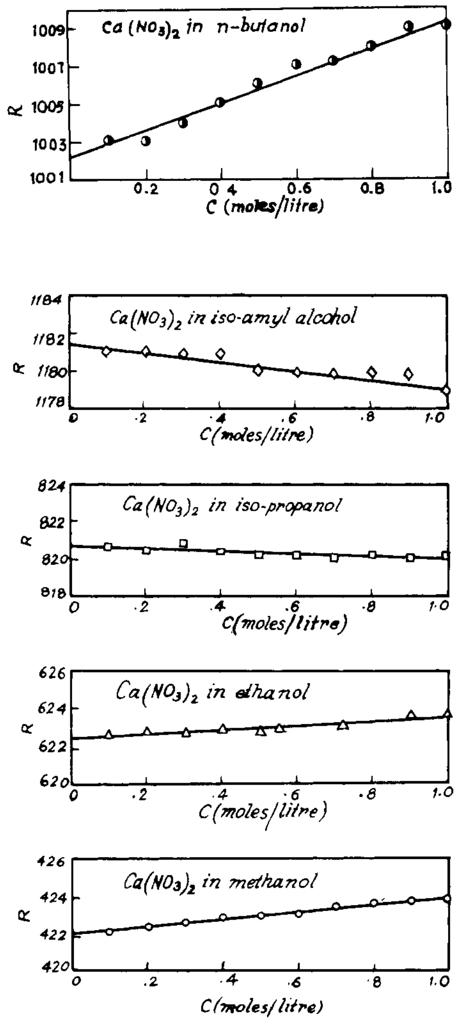
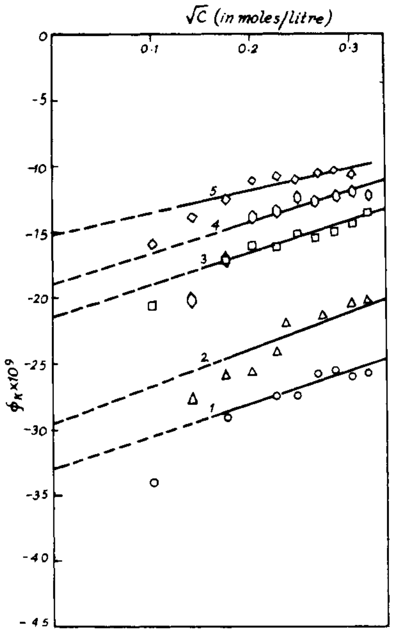


Figure 2.



ϕ_K vs $\sqrt{C}$, $Ca(NO_3)_2$ in methanol(1), ethanol(2), iso-propanol(3), n-butanol(4), iso-amyl alcohol(5)

Figure 3.

Where *V* is the volume of solution containing n_2 moles of solute, V_1^0 is the molar volume of solvent whose number of moles is n_1, and β and β_0 are the adiabatic compressibilities of solution and solvent, respectively.

Equations 3 and 5 have been used to calculate the solvation numbers. It is remarkable that the values of solvation numbers as calculated from the equation (5) in Table I and those from Wada's relation (3) in Table II agree very closely with each other.

The progressive decrease in solvation numbers with concentration is usually ascribed to the change over to the secondary solvation. However, this situation is not observed in these cases because with the change in concentration there is very small variation in the values of the solvation numbers as is evident from the results given in Table I.

Glossary

C	concentration, mol $l.^{-1}$
β	adiabatic compressibility of solution
β_0	adiabatic compressibility of solvent
Z	specific acoustic impedance
R	molar sound velocity
$\phi_{(k)}$	apparent molal compressibility
n_s	solvation number
c	sound velocity, m s^{-1}
ρ	density, g cm^{-3}
n_1	number of moles of solvent
n_2	number of moles of solute
V	volume of solution
V_1^0	molar volume of solvent

Literature Cited

(1) Allam, S. D., Lee, W. H., *J. Chem. Soc.*, supplement 2, 6049 (1964).
(2) Debye, P., Sears, F. W., *Proc. Natl. Acad. Sci. U.S.A.*, **18**, 410 (1932).
(3) Fogg, P. G. T., *J. Chem. Soc.*, 4111 (1958).
(4) Jacobson, B., *Acta Chem. Scand.*, **6**, 1485 (1952).
(5) Mikhailov, I. G., Rozina, M. V., Shutilov, V. A., *Akust. Zh.*, **10** (2), 213 (1964).
(6) Passynsky, A., *Acta Phys. Chim. URSS*, **8**, 835 (1930).
(7) Prakash, S., Prakash, O., *Acustica*, **32** (4), 279 (1975).
(8) Prakash, S., Prakash, S., *J. Phys. Chem.*, **70**, 3325 (1966).
(9) Ramabrahmam, K., Suryanarayana, M., *Ind. J. Pure Appl. Phys.*, **6**, 422 (1968).
(10) Roschina, G. P., Kaurova, A. S., *Akust. Zh.*, **12** (1), 118 (1966).
(11) Subrahmanyam, S. V., *Phys. Lett.*, **1**, 20 (1962).
(12) Suryanarayana, M., *J. Sci. Ind. Res., Sect. B*, **21**, 57 (1962).
(13) Wada, Y., Shimbo, S., Oda, M., *J. Acoust. Soc. Am.*, **22**, 880 (1950).
(14) Weissberger, A., "Techniques of Organic Chemistry", Vol. 7, Interscience, New York, N.Y., 1959.

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Molal Volumes of Lithium, Sodium, and Potassium Chloride in Multicomponent Electrolyte Solutions (LiCl–NaCl–KCl–Aqueous Dioxane)

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Molal volumes of LiCl, NaCl, and KCl have been evaluated in multicomponent solutions of aqueous dioxane (30%, 50%, 70%) from the density data of the system LiCl–NaCl–KCl–aqueous dioxane, at different temperatures. The results have been interpreted in terms of ion–solvent interaction.

During the recent years considerable activity has been noticed regarding thermodynamic and transport properties of multicomponent electrolyte solutions (*4*, *7*). Studies in mixed solvents have so far been restricted to one or two salt systems only. Mixed solvent multicomponent systems are important as they approach very close to biological fluids. In aqueous dioxane it is considered that dioxane acts more or less like an inert dilutent (*7*) and water takes part in the equilibrium process as in pure water. However, at higher content of dioxane in aqueous dioxane solvent, viz., as the dielectric constant of the mixed solvent decreases, the interionic forces are strong enough to lead to some form of ion pairing (*4*). These types of ion–ion or ion–solvent interactions can be interpreted by the partial molar volume studies.

Experimental Section

The alkali chlorides used in this experiment were of Analar grade and they were used without further purification. Conductivity water prepared by the usual method (*3*) was used for making the aqueous dioxane mixture by weight. Dioxane (G.R.) was purified by refluxing over sodium metal for 5-6 h followed by distillation.

The densities were measured with the help of an apparatus similar to the hydrostatic balance described by Ward and Millero (*10*). A 116-g glass float of volume 26.17 cm^3 was suspended into a glass sample cell of 200 cm^3 capacity. The cell has a bakelite top with a hole in the center and is placed in a temperature bath controlled to better than ±0.025 °C. The densities of the solutions were calculated from the equation:

$$d - d^0 = (W^0 - W)/V_f \qquad (1)$$

where d and d^0 are the densities of the solution and pure water, respectively, W and W^0 are the weights of the float in the solution and pure water, respectively, and V_f is the volume of the float. The accuracy was checked by measuring density of pure dioxane at 30 °C. Our value $d = 1.022\ 46$ is in excellent agreement with the literature value (*9*) $d = 1.022\ 30$. The difference in weight of the float in water and dioxane was $\pm 3.0 \times 10^{-5}$ g and it gives a good precision in the measurement of the density.

Results and Discussion

The densities of the following systems were measured in 50% aqueous dioxane at 30, 40, and 50 °C: I, LiCl (C_i) + NaCl (0.01 N) + KCl (0.01 N) + aqueous dioxane; II, LiCl (0.01 N) + NaCl (C_i) + KCl (0.01 N) + aqueous dioxane; III, LiCl (0.01 N) + NaCl (0.01 N) + KCl (C_i) + aqueous dioxane; where C_i is the concentration of the respective salt. Densities were also measured for the systems I, II, and III in 30 and 70% aqueous dioxane at 40 °C. The densities as a function of concentration C_i are given in Tables I–III.

The partial molar volumes $\bar{V}_i$ for the ith salt in these systems have been calculated by using eq 2

$$\bar{V}_i = \frac{M_i - 1000H_i}{\rho - \sum_{j=1}^{q} H_jC_j} \qquad (2)$$