828. Solvation of Calcium Nitrate and of Lithium Perchlorate in Acetone Solution measured by an Ultrasonic Method.

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Evidence for the formation of complexes when calcium nitrate or lithium perchlorate is dissolved in acetone has been obtained by measuring the ultrasonic velocity in the solutions. Spectroscopy has yielded additional evidence for the formation of acetone–calcium nitrate complexes in solution. A simple instrument for measuring the velocity of sound in liquids is described.

THE degree of solvation of a salt can be related to the compressibility of the solution and hence to the velocity of sound in the solution, by Passynsky's method.[1] The degrees of hydration of numerous salts have been so measured;[2] the values obtained are comparable with those obtained by other methods.[3] There is spectroscopic evidence for solvation of salts in non-aqueous solutions[4] but there have been few quantitative measurements of degrees of solvation.

The degree of solvation of lithium perchlorate and of calcium nitrate at various concentrations in acetone has now been measured.

EXPERIMENTAL

Materials.—Hydrated calcium nitrate (B.D.H.) was dehydrated at 170°. Lithium perchlorate was prepared from lithium carbonate (B.D.H.) by neutralising it with a slight excess of " AnalaR " 72% perchloric acid. The mixture was digested on a hot-plate until evolution of carbon dioxide ceased and a clear solution resulted. Excess of acid and water were removed by heating *in vacuo* at 150°. " AnalaR " acetone was dehydrated by anhydrous calcium sulphate.

Apparatus.—The velocity of sound in different liquids was compared by use of an acoustic interferometer in which the surface of the liquid serves as reflector (see Figure). A similar method has been used previously.[5]

A quartz crystal *A* of fundamental frequency *ca.* 1000 kc./sec. is made to oscillate by a circuit of the Pierce type. Changes in the power needed cause changes in the anode current of the valve in the oscillating circuit which are measured by a mirror galvanometer in a potentiometer circuit. The crystal is fixed in a holder of the Gutmann type[6] (not shown in detail) which is screwed into a brass cylinder with uniform bore. The joint is sealed by a gasket. The cylinder is securely clamped so that the crystal is level. Liquid under test can be run into the cylinder from a burette *B* with an elongated tip. The top of the cylinder is fitted with a rubber bung and drying tube *C*. The burette is also fitted with a drying tube.
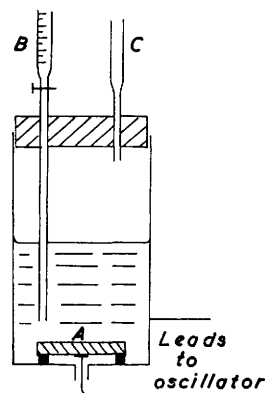
Sound waves are reflected from the surface of the liquid and at certain levels of liquid the anode current reaches a sharp maximum. This occurs when the distance between liquid surface and crystal surface is equal to $\frac{1}{2}n\lambda + \frac{1}{4}\lambda$ where n is an integer and λ the wavelength of the sound. The distance between two such positions is equal to $\lambda/2$.

Twenty consecutive burette readings r for maximum current are recorded. The average

[1] Passynsky, *Acta Physicochim. U.R.S.S.*, 1938, **8**, 835.
[2] Giacomini and Pesce, *Ricerca sci.*, 1940, **11**, 605.
[3] Bockris, " Modern Aspects of Electrochemistry," Butterworths Scientific Publications, London, 1954, p. 62; Bell, *Endeavour*, 1958, **17**, 31.
[4] Pullin and Pollock, *Trans. Faraday Soc.*, 1958, **54**, 11.
[5] Hunter and Fox, *J. Acoustical Soc. Amer.*, 1950, **22**, 239.
[6] Gutmann, *J. Sci. Instr.*, 1947, **24**, 276.

difference between two consecutive readings, which is proportional to $\lambda/2$, is calculated from the relation:

$$\text{Average} = \left(\sum_{n=11}^{n=20} r - \sum_{n=1}^{n=10} r \right)/100$$

Measurements are reproducible to about 1 part in 2000, showing that the frequency remains constant. Velocities of sound in different liquids are therefore proportional to the difference between two consecutive readings.

An ordinary density bottle was used to measure densities of liquids.

The room temperature was maintained at $17° \pm 0.1°$.

A Perkin-Elmer model 21 spectrometer was used to investigate the spectra of calcium nitrate solutions.

RESULTS AND DISCUSSION

Results are tabulated. Values for the velocity of sound and the compressibility are relative to those for pure acetone at the same temperature.

The adiabatic compressibility β is related to the density d and the velocity of sound v by the equation $\beta = 1/v^2d$. On account of electrostriction, molecules in the solvation sheath will be highly compressed so that these molecules will be less compressible than those in the bulk of the solution when an external pressure is applied. Hence the bulk compressibility of the solution is less than that of the pure solvent. Passynsky[1] assumed that molecules very near to the ion in the primary solvation sheath have zero compressibility. If the bulk compressibility of the solvent is represented by β_0, the compressible volume of the solution by V, and the incompressible volume of the solvation sphere by u, then

$$\beta_0 = \frac{1}{V-u}\left(\frac{\partial(V-u)}{\partial P}\right)_T = \frac{1}{V-u}\left(\frac{\partial V}{\partial P}\right)_T$$

and

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Hence $\beta/\beta_0 = (V-u)/V = (V-\alpha V)/V$ where $\alpha = u/V$

or $\alpha = 1 - \beta/\beta_0$

If there are n_2 moles of solute and n_1 moles of solvent there are $\alpha n_1/n_2$ moles of incompressible solvent per mole of solute. This may be identified with the primary solvation number of the salt.

Concn. (M)	Velocity of sound	d (g./c.c.)	β	Solvation no.	Concn. (M)	Velocity of sound	d (g./c.c.)	β	Solvation no.
		Calcium nitrate					*Lithium perchlorate*		
0·0136	0·999	0·8204	0·972	2·03	0·0142	1·014	0·8140	0·951	3·40
0·0317	1·001	0·8522	0·932	2·00	0·0336	1·028	0·8364	0·900	2·87
0·0549	1·002	0·8950	0·885	1·97	0·0619	1·057	0·8742	0·814	2·83
0·0891	1·030	0·9576	0·782	2·06	0·1169	1·111	0·9518	0·738	2·44
0·1601	1·113	1·0784	0·594	2·12	0·1847	1·176	1·0314	0·558	1·95
					0·2181	1·207	1·0836	0·504	1·78
					0·3348	1·253	1·2196	0·416	1·16

The solvation number of calcium nitrate is 2, to the nearest whole number, and does not vary significantly with concentration. This is in accord with the formation of a stable complex with two molecules of acetone associated with one calcium ion. Crystals of an acetone complex will gradually settle from a concentrated solution of calcium nitrate in acetone. Some of these crystals were filtered off in a dry atmosphere, dried between filter papers, and analysed by finding the proportion of acetone lost *in vacuo*. The molar ratio acetone : salt was 1·9. A little bound acetone may have been lost during filtration and drying.

The solvation number of lithium perchlorate varies from 1·2 to 3·4 in the concentration range studied. This is in accord with the existence of an equilibrium mixture of unsolvated ions, acetone molecules, and ions of different degrees of solvation. The results show that at infinite dilution the solvation number would be about 4.

A preliminary investigation of the infrared absorption spectra of calcium nitrate solutions showed that the 1225 cm.$^{-1}$ acetone band is split into two components at about 1224 cm.$^{-1}$ and 1237 cm.$^{-1}$ and that the 1715 cm.$^{-1}$ band becomes complex in saturated solution and in 0·1334M-solution. The relative intensity of the 1237 cm.$^{-1}$ band is greater in the saturated than in the weaker solution. Similar changes of these acetone bands have been reported by Pullin and Pollock [4] in the spectra of silver perchlorate and lithium perchlorate solutions. They have been explained as being due to the formation of acetone complexes. The changes in the spectra of calcium solutions are probably also due to complex formation.

Pullin and Pollock have shown that, in 0·3M-lithium perchlorate solution, the acetone is almost completely associated, presumably as $Li^+(acetone)_2$ (solvation no. 2). Interpolation of the results quoted above gives a solvation number of 1·35 at this concentration. This difference may show that the neglect of the compressibility of complexes in concentrated solutions is not completely justified.

The fact that lithium ions appear to be more solvated than calcium ions at infinite dilution may be related to a difference in mode of formation of complexes in the two cases. Another possibility is that perchlorate ions are solvated in these solutions although anions are not usually solvated.

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