

The corresponding equations for ions with a d^2 or d^7 configuration in an octahedral field, or with a d^3 or d^8 configuration in a tetrahedral field, are given below.

For example, d^7 (octahedral field) where v_2 is ${}^4T_{1g}(F) - {}^4A_{2g}$, and v_3 is ${}^4T_{1g}(F) - {}^4T_{1g}(P)$,

$$340Dq^2 + 18(v_3 - 2v_2)Dq + v_2^2 - v_2v_3 = 0 \quad (3)$$

$$B = \frac{v_3 - 2v_2 + 30Dq}{15} \quad (4)$$

Table 1 records examples of Dq and B calculated using equations (1)–(4) together with those reported previously, for some octahedral and tetrahedral compounds of cobalt (II) and nickel (II).

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Ultrasonic Absorption in Aqueous Solutions of Certain Inorganic Sulphates

It is well known¹ that for a salt solution the relationship between adiabatic compressibility, β , and molarity, c , is given by the expression:

$$\beta = A + Bc + Cc^{3/2}$$

Recently², the variation of compressibility with concentration, for aqueous solutions of various inorganic sulphates (lithium sulphate, magnesium sulphate, sodium sulphate, potassium sulphate, etc.), was reported; differences in the behaviour of each solution were related to differences in the cations—as the sulphate ion was common to all, the differences were considered to be due to differences in the ionic radius of the cations.

When the ionic radius increases, the compressibility decreases; if it is assumed that the hydration of the sulphate ion is the same in each solution for a given con-

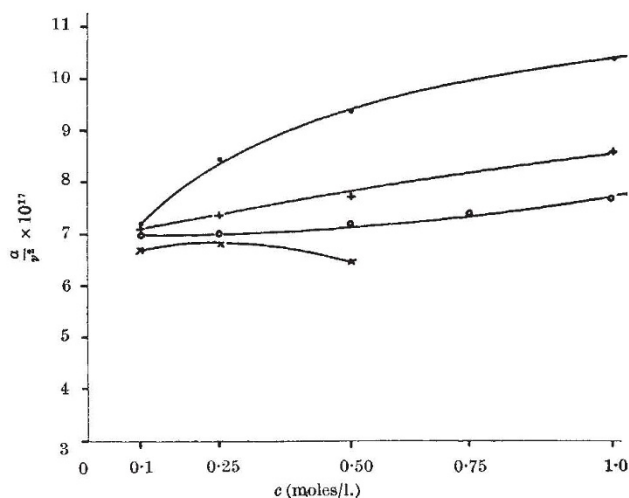


Fig. 1. Plot of ultrasonic absorption against molarity for the sulphates of magnesium (●), lithium (+), sodium (○) and potassium (×)

centration, it would seem that a larger ionic radius would lead to greater solvation which would result in a lower compressibility.

It is necessary to take into account the fact that the radius of Li^+ ions ($r = 0.60 \text{ \AA}$)³ has a greater effect on compressibility in lithium sulphate than does the radius of the Mg^{++} ion ($r = 0.65 \text{ \AA}$) in magnesium sulphate.

It is possible that a larger number of water molecules is bound by the two Li^+ ions than by the single doubly charged Mg^{++} ion. We can obtain values for ultrasonic absorption ($\frac{\alpha}{v^2} \times 10^{17}$) (ref. 4) from the expression:

$$\frac{\alpha}{v^2} = \frac{8}{3} \frac{\eta^2}{\rho V^3}$$

where V is the ultrasonic velocity, ρ is the density (20°C), and η is the viscosity (Ostwald) 20°C .

In liquids, as we know, the contribution of the thermic conductivity to the ultrasonic absorption is negligible; thus, because $\alpha_{\text{class}} = \alpha_\eta + \alpha_{\text{cond}}$, $\alpha_{\text{class}} = \alpha_\eta$.

Table 1 gives $\frac{\alpha}{v^2} \times 10^{17}$ values, molarity, density and viscosity coefficient, and Fig. 1 a plot of ultrasonic absorption against molarity, for the sulphates of magnesium, lithium, sodium and potassium.

For a given value of concentration, we can see that $\frac{\alpha}{v^2} \times 10^{17}$ is largest for a solution of magnesium sulphate, and that it decreases in the order lithium sulphate, sodium sulphate, potassium sulphate.

Because dissociation of magnesium sulphate only results in one Mg^{++} ion ($r = 0.65 \text{ \AA}$), while dissociation of lithium sulphate, sodium sulphate and potassium sulphate results in two Li^+ , Na^+ and K^+ ions, respectively, (the radii of which are 0.60, 0.90 and 1.33 \AA , respectively), when ionic radius increases, the ultrasonic absorption decreases. It is thus necessary to take into account the fact that there is a lower effect for doubly charged Mg^{++} ion than for Li^+ and other ions. This could well confirm the hypothesis that the number of water molecules bound to ions in solution is responsible for the different behaviours of η , β , V in various solutions, that is, the larger the number of water molecules bound by ions of large ionic radius, the lower the value of ultrasonic absorption.

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Magnesium sulphate in water		Mg^{++} ($r = 0.65 \text{ \AA}$)	
c molarity	ρ (20°C) g/cm ³	η centipoise 20°C	$\frac{\alpha}{v^2} \times 10^{17}$
0.10	1.0105	1.0670	7.1650
0.25	1.0291	1.1724	8.4508
0.50	1.0501	1.3785	9.41864
1.00	1.1014	1.944	10.4159
2.00	1.1990	3.908	15.9238
$\text{Li}_2\text{SO}_4 \rightleftharpoons 2\text{Li}^+ + \text{SO}_4^{--}$			
Lithium sulphate in water		Li^+ ($r = 0.60 \text{ \AA}$)	
0.10	1.0080	1.0565	7.2888
0.25	1.0215	1.1416	7.3513
0.50	1.0440	1.296	7.7399
1.00	1.0874	1.670	8.5892
Sodium sulphate in water		Na^+ ($r = 0.95 \text{ \AA}$)	
0.10	1.0111	1.0890	6.9970
0.25	1.0279	1.1050	6.9801
0.50	1.0606	1.2260	7.2065
0.75	1.0891	1.2730	7.4120
1.00	1.1179	1.5700	7.7200
Potassium sulphate in water		K^+ ($r = 1.33 \text{ \AA}$)	
0.10	1.0325	1.0545	6.7050
0.25	1.0125	1.022	6.860
0.5	1.0734	1.109	6.4651