ULTRASONIC VELOCITIES IN SOME BIVALENT METALLIC SULPHATES

By C. G. BALACHANDRAN

(*Department of Physics, Indian Institute of Science, Bangalore-3*)

Received July 6, 1956

ABSTRACT

Ultrasonic velocities and their variation with concentration up to 1 molar have been measured for aqueous solutions of sulphates of magnesium, cobalt, nickel and cadmium at three different temperatures, *viz.*, 25° C., 40° C. and 60° C. From the values of the velocities, the apparent molar compressibilities have been calculated. The slopes of the apparent molar compressibilities *vs.* square-root of concentration curves are less steep than that predicted by the Debye-Huckel theory. A possible explanation of this behaviour is discussed qualitatively.

1. INTRODUCTION

There is a paucity of data regarding the apparent molar properties of electrolytes of higher valencies. For a few high valence electrolytes studied by Bachem (1936) and Gucker (1933) the slopes of the apparent molar compressibility *vs.* square-root of concentration curves are noticeably less steep than the Debye-Huckel theory demands. The object of the present investigation is mainly to extend the measurements to aqueous solutions of four sulphates of bivalent metals, *viz.*, magnesium, cobalt, nickel and cadmium at all concentrations up to 1 M and temperatures up to 60° C. and study the behaviour of the slopes in all these salts.

2. EXPERIMENTAL DETAILS

Ultrasonic velocities were determined using the Bachem-Hiedemann method of secondary interferences and the ultrasonic interferometer. The experimental details have been described in earlier papers (Balachandran, 1956).

The materials used were pure Merck or Kahlbaum products. Pure double distilled water was used for making up standard solutions, extreme care being taken to prevent contamination.

Density determinations were made at 25° C., 40° C., and 60° C. for solutions of cadmium sulphate, cobalt sulphate and nickel sulphate using a specific gravity bottle. Densities of magnesium sulphate solutions were taken from the I.C. Tables after suitable conversion to weight percentage and interpolation. Using the formula $\beta = 1/v^2 d$, where v is the ultrasonic velocity in metres/second and d the density in gm./c.c., β the adiabatic compressibility was calculated. Apparent molar compressibilities were calculated according to the formula

$$\phi(K) = \frac{1000\,\beta}{C} - \frac{\beta_1}{d_1}\left(\frac{1000d}{C} - M_2\right)$$

where β_1 is the adiabatic compressibility of water at a particular temperature, d_1 the density of water at the same temperature, c the salt concentration in mols/ litre and M_2 the molecular weight of the solute.

3. RESULTS

Graphs showing the variation of apparent molar compressibility with square-root of concentration are given in Figs. 1 to 4.

4. DISCUSSION

The general behaviour is as follows: In all the cases studied the relation between ϕ (K) and $\sqrt{C}$ is linear as pointed out by Gucker (1933). The slopes of the curves are less than that predicted by the Debye-Huckel theory.

Although the thermodynamics of aqueous solutions of cadmium, cobalt, magnesium and nickel sulphates has not been studied very comprehensively, sufficient data are available to indicate that the behaviour of their activity coefficients is of considerable interest. In the first place the freezing point data in dilute solutions show that the activity coefficients of each of these electrolytes have nearly the same value at the same concentration. For instance, at $0 \cdot 1$ M different investigators have obtained values of $0 \cdot 150$ and $0 \cdot 166$ for cadmium and magnesium sulphates. Further, the mean activity coefficients from e.m.f. measurements of LaMer and Parks (1931; 1933) for cadmium sulphate are nearly identical with those of zinc sulphate. Judging from these points the individuality of these salts in every case is poor.

Robinson and Jones (1936) have given the isopiestic vapour pressure data and activity coefficients for the sulphates of magnesium, cadmium and nickel. Their results also substantiate the above views that even in solutions of high concentration the individuality is very much less pronounced than that observed for 1–1 and 2–1 electrolytes. A detailed account of the thermodynamic behaviour of these salts is given by Harned and Owen (1943).

Magnesium Sulphate.—Ultrasonic velocity measurements in solutions of this salt are found to be in substantial agreement with those of others (Bachem, 1934; Bachem and Falkenhagen, 1935; Szalay, 1934). The slope of the apparent molar compressibility *vs.* square-root of concentration curve is less than the theoretically predicted value (theoretical value $50 \cdot 3 \times 10^{-10}$; experimental value $40 \cdot 6 \times 10^{-10}$).

This may be caused by complex formation or incomplete dissociation evidence for which can be obtained from other physical properties.

Activity coefficients have been computed and they show a slight disagreement with the Debye-Huckel theory at extreme dilution (Young and Seligman, 1938). Harned and Owen (1943) also point out the fact that the value of mean ionic diameter calculated by Bjerrum from activity data is much less than that for a 2–2 valence electrolyte and this has been attributed to the incomplete dissociation of this salt. It may be mentioned that ultrasonic absorption in this salt solution
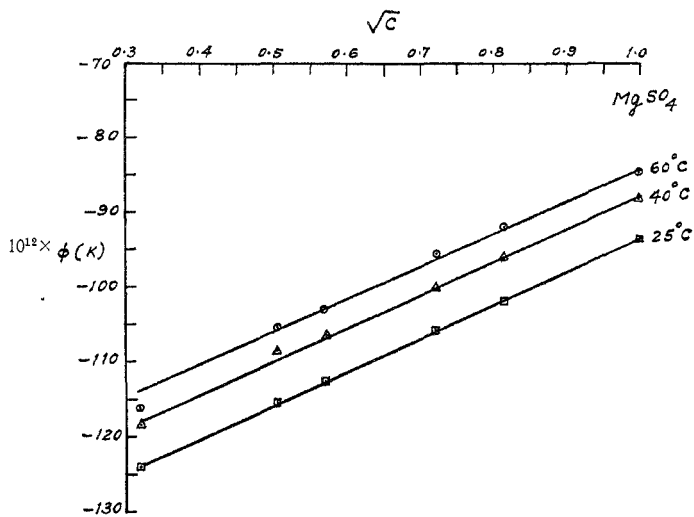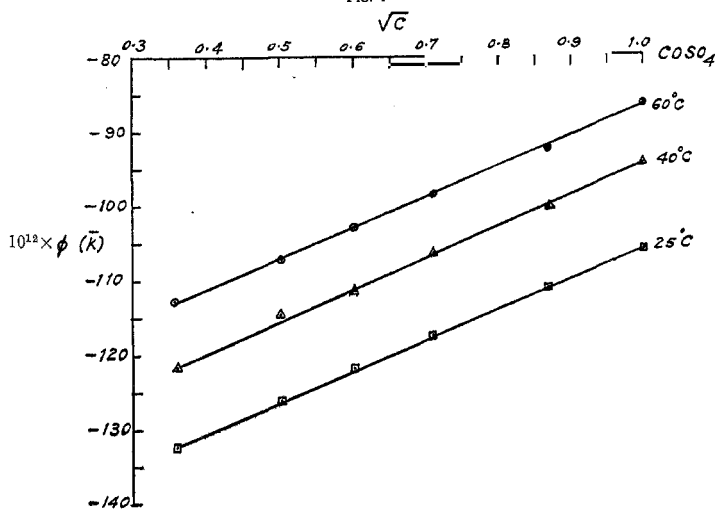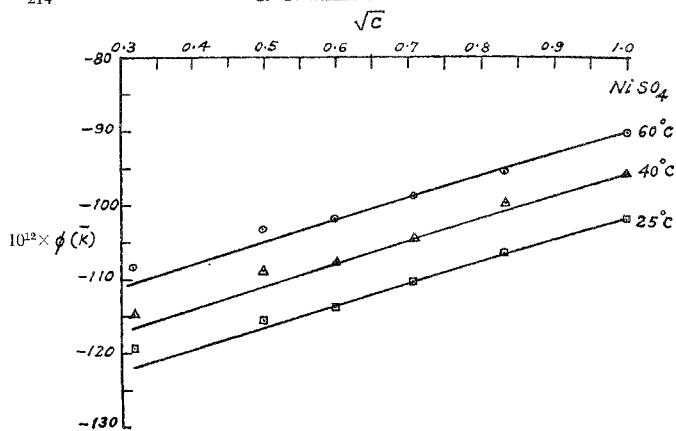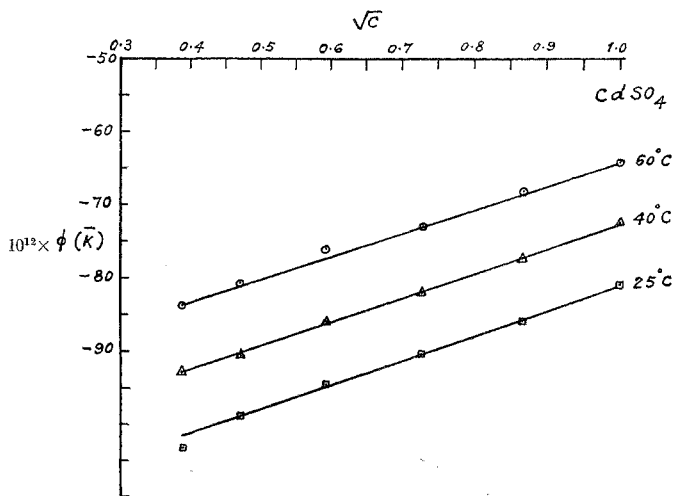
FIG. 1

FIG. 2

FIG. 3

FIG. 4

shows an anomalous behaviour and this has been explained on the basis of a perturbation in the chemical equilibrium involving the ions (Liebermann, 1948).

Cobalt Sulphate.—In this case also the slope of the apparent molar compressibility *vs.* square-root of concentration curve is less steep than the theoretical value (theoretical value $50 \cdot 3 \times 10^{-10}$; experimental value $39 \cdot 6 \times 10^{-10}$). The partial molar volume of this salt has been studied by Cantelo and Phifer (1932) and they find a slope less steep than the value predicted by the Debye-Huckel theory. The transference numbers of the salt found by Cantelo and Payne (1937) deviate largely from the value calculated for zero concentration from equivalent conductance data of Cantelo and Berger (1930). These results indicate that with increasing concentration either there is a very great change in the mobilities of cobalt and sulphate ions or there is the appearance of complex ions in increasing number as the solution increases in stoichiometrical concentration. A tentative assumption may be that the decreased slope of the ϕ (K) *vs.* $\sqrt{C}$ curve may be due to the formation of complex ions in aqueous solutions of this salt at higher concentrations.

Nickel Sulphate.—The experimental slope of the ϕ (K) *vs.* $\sqrt{C}$ curve is less than the theoretical value for this salt solution also (theoretical value $50 \cdot 3 \times 10^{10}$; experimental value $30 \cdot 0 \times 10^{-10}$). Here again the formation of ion pairs or intermediate ions may be a contributory factor. In fact activity measurements by Robinson and Jones (1936) do indicate the ion pair formation. The possibility of the formation of nickel sulphate complexes has been discussed by Pfanhauser (1901). He found in a saturated solution of nickel ammonium sulphate in a concentration cell, the nickel moved entirely towards the anode in the form of complex ions $Ni^{++} (SO_4^{--})_2$. The formation of such complex ions can also be expected to affect the slopes of the curves.

Cadmium Sulphate.—Again the slope of the apparent molar compressibility *vs.* square-root of concentration curve is less steep than the theoretical Debye-Huckel value (theoretical value $50 \cdot 3 \times 10^{-10}$; experimental value $34 \cdot 4 \times 10^{-10}$). The existence of ion pairs or the formation of intermediate complexes in this salt solution can be considered. Evidence for the formation of such complexes is given below.

Low values of activity coefficient suggest the formation of complexes. This is substantiated by the discrepancy in the transference number values of Wolten and King (1949) compared with those of Jahan and others (1910). According to Masaki and Ikkatai (1932), Bray (1927) and LaMer and Parks (1931) the activity coefficients of both zinc and cadmium sulphates are about $0 \cdot 08$ in a $0 \cdot 3$ molal solution. This is approximately the concentration above which the results indicate negative cationic transference numbers. It has also been shown on the basis of conductivity measurements by McBain and Van Rysselberghe (1930) that cations in solutions of magnesium, zinc and cadmium sulphates form negatively charged complexes in the presence of excess alkali sulphate.

Lange, Monheim and Robinson (1933) observe that 2-2 valence type electrolytes indicate larger deviation from the limiting law at the lowest concentration measured. Dunkelberger and Robinson (1938) have found out the heats of dilution and heat content of cadmium sulphate over the concentration range from 0·8 to 0·0001 m. at 10°, 15° and 20° C. and extrapolated to infinite dilution to obtain integral heat of dilution. No definite approach is indicated at the lowest concentration measured.

The results of the present experiments are probably to be explained in terms of complex formation. It may be mentioned that complex formation in general can be expected to influence the valence factor, which enters in the slope derived on the basis of the Debye-Huckel theory of complete dissociation. The calculation of the magnitude of the change is of necessity complicated since the fraction of the complexes formed and even their exact nature is unknown. But such an effect can be generally expected.

REFERENCES

1.	Bachem	..	*Zeit. f. Physik.*, 1936, **101**, 544.
2.	—— and Falkenhagen	..	*Zeit. f. Elektro-chemie*, 1935, **41**, 510.
3.	Balachandran	..	*J. Ind. Inst. Sci.*, 1956, **38** (1), 10.
4.	Bray	..	*J. Am. Chem. Soc.*, 1927, **49**, 2372.
5.	Cantelo and Phifer	..	*J. Phys. Chem.*, 1932, **36**, 1845.
6.	—— and Payne	..	*J. Am. Chem. Soc.*, 1937, **55**, 1333.
7.	—— and Berger	..	*Ibid.*, 1030, **52**, 2648.
8.	Dunkelberger and Robinson		*Ibid.*, 1938, **60**, 1301.
9.	Gucker	..	*Chem. Revs.*, 1933, **13**, 113.
10.	Harned and Owen	..	*Am. Chem. Soc. Monograph Series*, 1943, No. 95.
11.	Jahan	..	*Z. Physik. Chem.*, 1910, **58**, 649.
12.	LaMer and Parks	..	*J. Am. Chem. Soc.*, 1931, **53**, 2040.
13.	——————	..	*Ibid.*, 1933, **55**, 4545.
14.	Lange, Monheim and Robinson		*Ibid.*, 1933, **55**, 4737.
15.	Liebermann	..	*J. Acous. Soc. Am.*, 1948, **20**, 868.
16.	Masaki and Ikkatai	..	*Bull. Chem. Soc. Japan*, 1932, **7**, 238.
17.	McBain and Van Rysselberghe		*J. Am. Chem. Soc.*, 1930, **52**, 2326.
18.	Pfanhauser	..	*Z. f. Elektro-chemie*, 1901, **7**, 698.
19.	Robinson and Jones	..	*J. Am. Chem. Soc.*, 1936, **58**, 959.
20.	Szalay	..	*Physikal Zeits.*, 1934, **35**, 639.
21.	Wolten and King	..	*J. Am. Chem. Soc.*, 1949, **71**, 576.
22.	Young and Seligman	..	*Ibid.*, 1938, **60**, 2379.