

ULTRASONIC VELOCITIES IN CADMIUM AND ZINC HALIDES

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ABSTRACT

Ultrasonic velocities and their variation with concentration at different temperatures, *viz.*, 25° C., 40° C., 50° C. and 60° C., have been measured for solutions of cadmium chloride, cadmium bromide, cadmium iodide and zinc iodide. From the values of the velocities, the partial molal compressibilities have been calculated. The effect of associated ions on the partial molal compressibility indicates a deviation from the conclusions based on the Debye-Huckel theory for the three cadmium halides in the concentration range studied. On the other hand solutions of zinc iodide are found to obey the theory up to a concentration of 0.5 N.

1. INTRODUCTION

The abnormalities of the solutions of cadmium and zinc halides have long been a subject of great interest (Harned and Fitzgerald, 1936; Bates, R. G., 1938, 1939, 1941; Robinson and Wallace, 1942). All investigations indicate the existence of ion association in these solutions although the nature and concentration of the complex species are in general unknown. One of the important thermodynamic quantities, *viz.*, the partial molal compressibility has been calculated from measured ultrasonic velocities and densities of these solutions and the results presented in this paper confirm the general conclusions regarding the solutions of the three cadmium halides and of zinc iodide.

2. EXPERIMENTAL DETAILS

In the present investigations the method of secondary interferences due to Bachem and Hiedemann (1936) has been employed for the determination of ultrasonic velocities. The fringe system obtained, by focussing on a plane containing the convergence lines, was made as sharp and parallel as possible by adjusting a parallel reflector facing the radiating quartz crystal. The interference pattern was photographed and the average fringe width of fifty fringes was measured using a comparator. The cell containing the salt solution was maintained successively at different temperatures, *viz.*, 25° C., 40° C., 50° C. and 60° C. by circulating water around it from a thermostatically controlled water-bath. Temperature was maintained constant to within $\pm 0.1^\circ$ C. up to 60° C. The actual temperature of the ultrasonic cell under control was determined by a thermometer attached to it. Velocity determinations were made as accurate as possible by taking photograph of the interference pattern for distilled water,

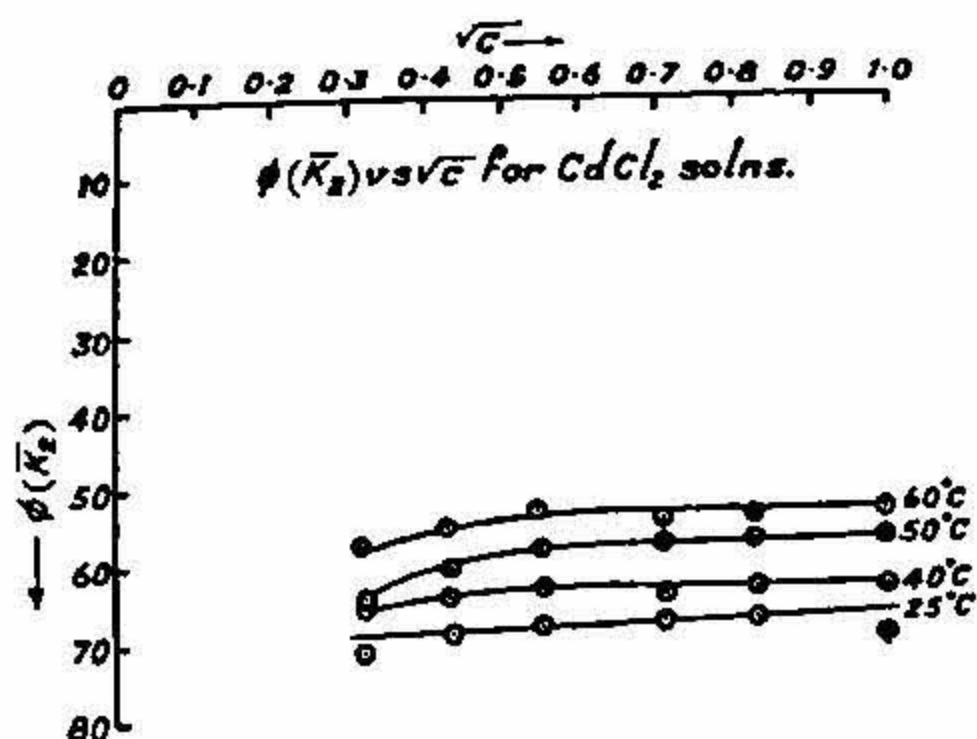


FIG. 1

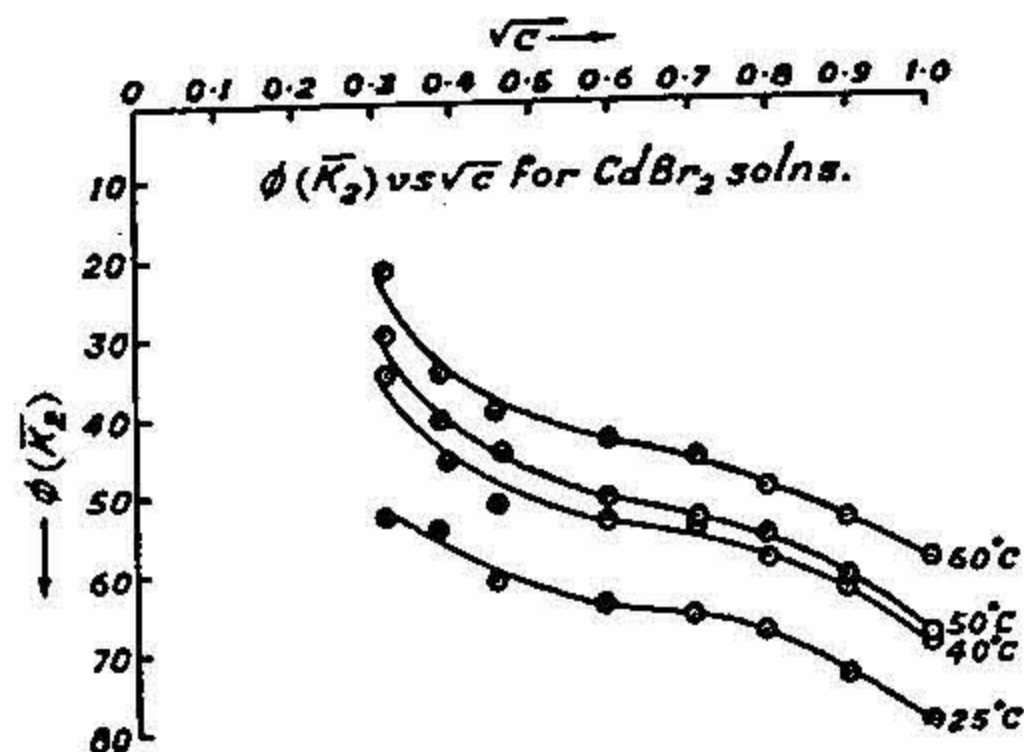


FIG. 2

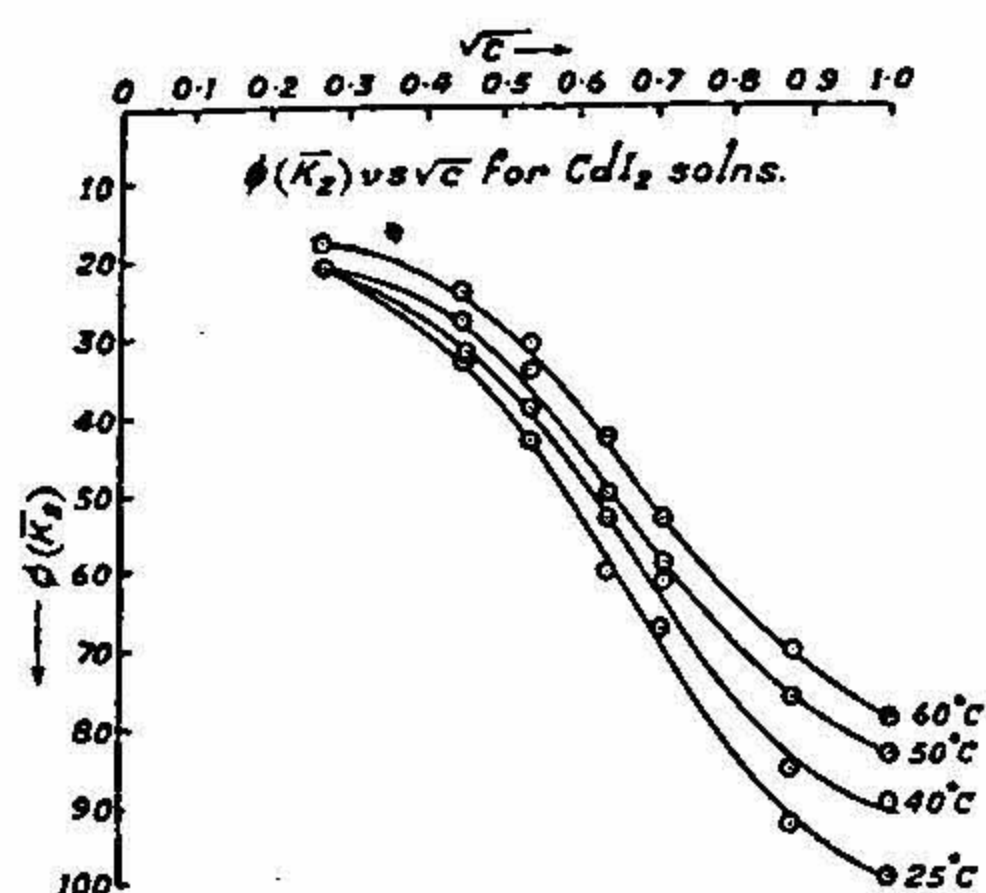


FIG. 3

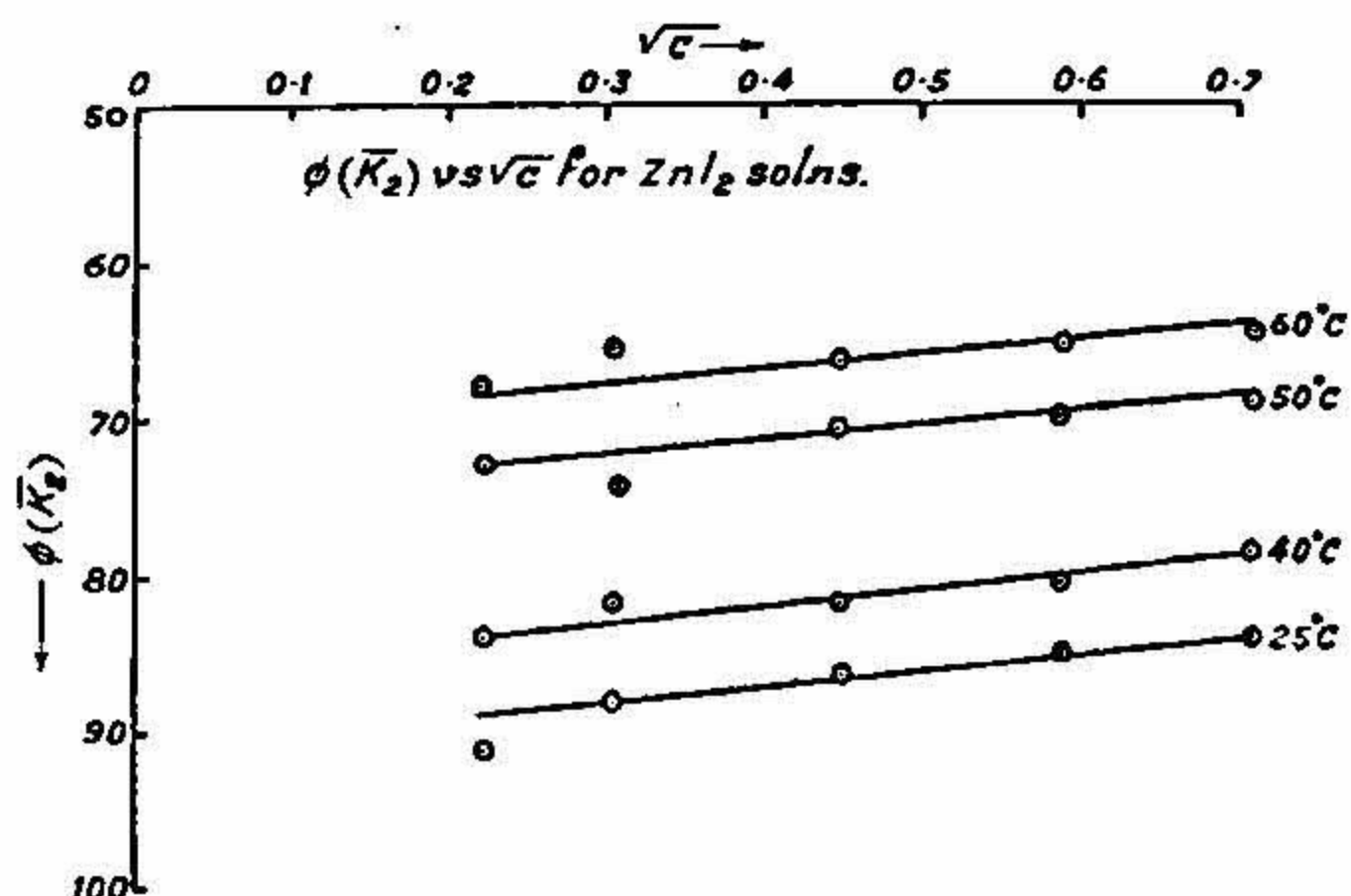


FIG. 4

on the same photographic plate. The frequency of the electron coupled 807 valve oscillator generating the ultrasonic waves was determined by a BC 221 heterodyne wavemeter.

All the three cadmium halides were Merck products and zinc iodide was a Kahlbaum product. Densities of the solutions at different temperatures were taken from *International Critical Tables*. Using the formula $\beta = 1/\rho v^2$, where ρ is the density in gm./c.c. and v the ultrasonic velocity in metres/second, β the adiabatic compressibility was calculated. The partial molal compressibilities were calculated according to the formula

$$\phi(\bar{K}_2) = \frac{1000\beta}{c} - \frac{\beta_1}{d_1} \left(\frac{1000d}{c} - M_2 \right)$$

where β_1 is the adiabatic compressibility of water at a particular temperature, d_1 the density of water at the same temperature, d the density of the salt solution, c the salt concentration in mols/litre of the solute, and M_2 the molecular weight of the solute. All partial molal compressibility values were reduced to the first place. Plots of $\phi(\bar{K}_2)$ vs. \sqrt{c} are given in the accompanying graphs.

3. RESULTS AND DISCUSSION

It is found that the velocities in solutions of cadmium bromide, cadmium iodide and zinc iodide are always less than that of water. The existing data on

partial molal compressibilities particularly of Bachem (1936) and Gucker (1939) have shown excellent agreement with Debye-Huckel theory for most metallic salts of 1-1, 1-2 valence type in that the partial molal compressibility varies linearly with the square-root of concentration over a wide range of concentrations and at all temperatures with a slope characteristic of the valence type of the salt under investigation. But the present measurements with cadmium chloride, cadmium bromide and cadmium iodide reveal a complete departure from the above type of behaviour. The partial molal compressibility goes on decreasing with increasing concentration; at all temperatures studied, which has not been observed so far in any case. The shapes of the curves are also unusual. The anomalies observed in the concentration range studied are probably due to the existence of associated ionic complexes, and the change in the degree of association taking place in the salt solution during the passage of the sound wave. These curves indicate the largest degree of association for cadmium iodide and the least for cadmium chloride. This is also the order indicated by the other thermodynamic properties of these salts (Harned *et al.*, 1936; Bates, R. G., 1939, 1941; Robinson *et al.*, 1942). So it may be said that the presence of particles other than the simple anions and cations in these salt solutions are to a large extent responsible for the abnormal behaviour of these salts as revealed by the partial molal compressibility vs. square-root of concentration curves.

In the case of zinc iodide the behaviour is perfectly normal in the region of concentrations studied. Higher concentrations could not be studied since the solution was coloured and the coloration rapidly increased with increasing salt concentration. The dependence of partial molal compressibility on the square-root of concentration is linear and the slope is also of the same order as that of any other normal bi-univalent electrolyte. The abnormalities of incomplete dissociation and complex ion formation are of no significant influence in this concentration range. This is quite in conformity with the earlier observation on other thermodynamic properties of this salt (Bates, R. G., 1938).

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