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Fused Zinc Chloride
Part II: Some Solubility Measurements

D.H. KERRIDGE and I.A. STURTON
University of Southampton, Southampton, U.K.

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The solubilities of cobalt(II) chloride, zinc sulphate, nickel(II) chloride, chromium(III) chloride and zinc oxide in fused zinc chloride have been measured over a range of temperatures. The latent heats of fusion of the solutes were calculated from the solubility data.

Introduction

Fused zinc chloride has been studied rather more extensively in recent years, much published work being related to aspects of its melt structure and to a lesser extent to its solvent properties. Structural studies have included the influence of temperature, added chloride ion, and Lewis acid (e.g. aluminium chloride) on the melt polymerization, by methods involving, for example, visible–ultra violet spectroscopy using transition metal probe ions, infra red and Raman studies, electrical conductivity and viscosity measurements, and glass transition temperatures. A number of phase diagrams of binary and ternary melts with zinc chloride as one component have been published as well as several incomplete phase diagrams, which also provide information on solubilities in the melt.

In most cases, the phase diagrams were obtained using standard techniques, the "liquidus" curve usually being determined from visual observation of the first appearance of one component (or species), or alternatively from the thermal arrest on cooling, thus defining the solubility of the component at that temperature. An alternative method, utilising continuous stirring to ensure saturation and careful filtration techniques for obtaining samples of melt, has been described recently for determining the solubility of zinc metal in zinc chloride[1], and is considered more satisfactory in the case of this very viscous melt than the standard techniques, which do not employ stirring the saturated melt directly. Extension of the sampling techniques to other solutes is now reported. The solubilities of anhydrous cobalt(II) chloride and zinc sulphate were redetermined, as a check on the published phase diagrams obtained by older methods, and the hitherto unknown solubilities of nickel(II) chloride, chromium(III) and zinc oxide were obtained, in each case over a range of temperatures.

Experimental Section

Materials

B.D.H. zinc chloride (sticks) was purified and dehydrated as previously described[2] (Found: Zn, 48.0; Cl, 51.9. Calc. for $ZnCl_2$, Zn, 48.0; Cl, 52.0%). Anhydrous zinc sulphate was prepared by dehydrating Analar $ZnSO_4.7H_2O$ at 300° C for one hour (Found: Zn, 40.5; SO_4, 59.2 Calc. for $ZnSO_4$: Zn, 40.5; SO_4, 59.5%). Analar zinc oxide was dried at 400° C for one hour. Analar $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CrCl_3.6H_2O$ were dehydrated with thionyl chloride according to the method of Freeman and Smith[3]; the $CrCl_3$ was additionally heated in a current of dry chlorine at 600° C for four hours (Found: a) Co, 45.2; Cl, 54.6. Calc. for $CoCl_2$: Co, 45.4; Cl, 54.6. b) Ni, 44.8; Cl. 54.1. Calc. for $NiCl_2$: Ni, 45.3; Cl, 54.7. c) Cr. 31.8; Cl, 66.9. Calc. for $CrCl_3$: 32.8; Cl, 67.2%).

Procedure

The apparatus and method used were as previously described[1]. The melt containing excess solute was stirred for up to sixty hours. Samples of the melt solutions were withdrawn by suction through a tight glass-wool plug 2 cm long at the lower end of a 6 mm diameter sampling tube. After solidification, the portion above the plug was cut off and analysed.

The solubility was plotted against the time for which the melt was stirred at the given temperature, and the equilibrium values thus determined; these were reached after two to six hours stirring. No solute was found to react in or with zinc chloride in the temperature range studied.

Analysis

The samples were, with one exception, analysed by standard volumetric, gravimetric and colorimetric procedures. Chloride was determined volumetrically by Volhard's method, zinc gravimetrically as zinc ammonium phosphate and sulphate gravimetrically as barium sulphate. Cobalt(II), nickel(II) and chromium(III) were determined colorimetrically, cobalt as the $Co(SCN)_4^{2-}$ ion, nickel as the soluble complex formed with an oxidant and dimethylglyoxime (λ_{max} at 465 mμ), and chromium as the violet complex formed with diphenylcarbazide reagent in acid solution after quantitative oxidation to Cr^{VI} with sodium peroxide and sodium carbonate. The solubility of zinc oxide in fused zinc chloride was small. As determination of the zinc and chloride concentrations could only give the zinc oxide content indirectly as a small difference in two large quantities, an analytical procedure was devised to give the solute concentration directly. A known quantity of standardised nitric acid was added to dissolve the zinc oxide and zinc chloride of the sample, and the pH measured. A calibration curve was constructed using standard acid, dried zinc oxide and anhydrous zinc chloride.

Results

The solubility values of the five solutes at various temperatures are given in Figures 1–3.

It was found that the zinc sulphate melt solutions were much more viscous than pure zinc chloride at a given temperature, and formed glasses on cooling.

On cooling the nickel chloride melt solutions, the solute reprecipitated as lustrous yellow spangles, soluble only very slowly in cold water, in contrast to the anhydrous nickel chloride added initially, a hygroscopic powder which dissolved very rapidly in cold water.

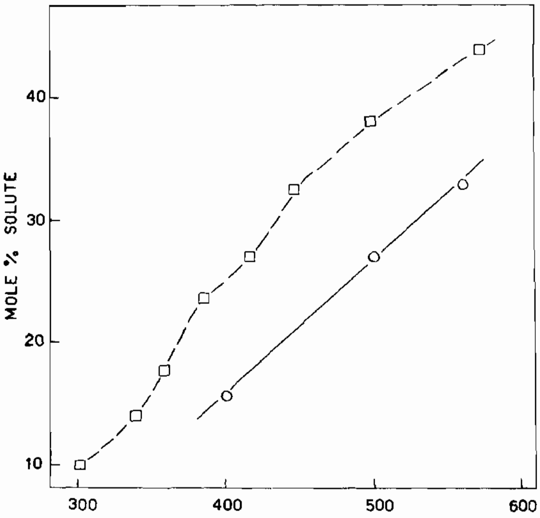

Figure 1. Solubility of zinc sulphate in molten zinc chloride vs. temperature. ○ This work, □ Evseeva and Bergman (ref. 8).

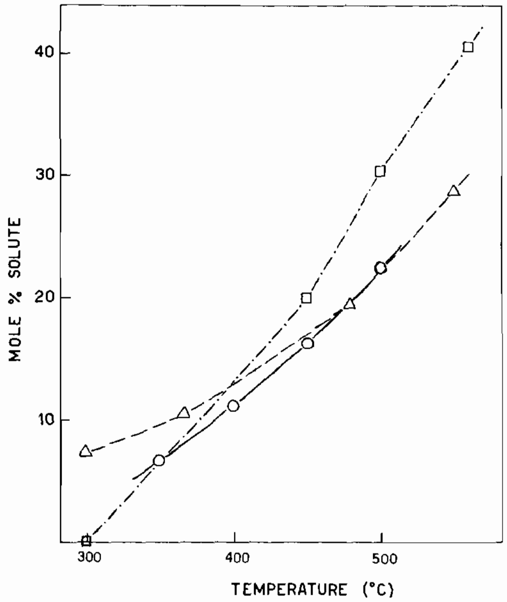

Figure 2. Solubility of cobalt(II) chloride in molten zinc chloride vs. temperature. ○ This work, □ Ferrari and Inganni (ref. 6), △ Bassett and Bedwell (ref. 7).

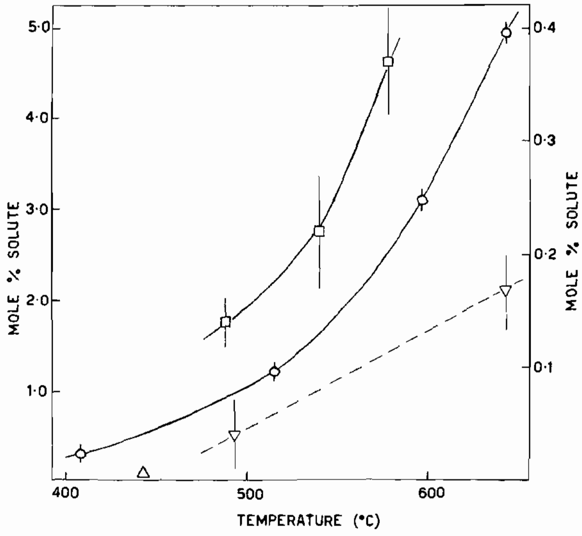

Figure 3. Solubility in molten zinc chloride vs. temperature. ○ Nickel(II) chloride (left hand scale), □ chromium(III) chloride (right hand scale), ▽ zinc(II) oxide (left hand scale), △ zinc(II) oxide from ref. 12 (left hand scale).

Assuming that the solutions are ideal the heat of fusion of each solute has been calculated from a plot of log solubility against 1/T°K, using the integrated form of the Clapeyron–Clausius equation, and the values are reported in Table I.

TABLE I.

Solute	L_f (kcal/mole)	
	Present work	From ref.
$CoCl_2$	8.0	7.2[4]
$ZnSO_4$	5.0	–
$NiCl_2$	15.1	18.47[5]
$CrCl_3$	13.6	–
ZnO	18.0[a]	–

[a] Evaluated using present results, and solubility value at 450° from reference 12.

Discussion

Cobalt(II) Chloride

The present results were in excellent quantitative agreement with solubility values reported by earlier workers[6,7], although these had been obtained by the cooling curve method. Particularly close agreement would, of course, be anticipated when the solute dissolved and reprecipitated very easily, as was found for cobalt chloride.

Zinc Sulphate

The present results were of the same order of magnitude as those reported by Evseeva and Bergman[8], but quantitative agreement was less satisfactory, as their solubilities were approximately 12 mole % higher at a given temperature. In view of the uncertainty attached to these authors' figures, due to the difficulty of satisfactorily nucleating a very viscous melt, it is considered that the present results provide a more reliable representation of the solubility.

Nickel(II) Chloride

The results reported here for nickel chloride are the first obtained by any method. It is surprising that no phase studies of the nickel chloride–zinc chloride system have previously been reported, as the spectrum of Ni^{II} dissolved (as nickel chloride) in zinc chloride melts has been the object of extensive investigation.

The low solubility level of nickel chloride compared with cobalt chloride (of the same crystal lattice and very similar lattice parameters[9]) is attributed to two factors: (a) the lattice energy (and melting point) of nickel chloride is considerably higher than for cobalt chloride, because of a larger contribution from the octahedral Ligand Field Stabilisation Energy and (b) in going from the solute crystal into solution, the Co^{II} and Ni^{II} must change (at least partly) from octahedral to tetrahedral coordination and this change is more favoured for Co^{II} because of a larger contribution from the tetrahedral LF SE.

Chromium(III) Chloride

The results reported here for chromic chloride are again the first reported by any method. The very low solubility is in contrast to the limited data reported for other $M^{III}Cl_3/ZnCl_2$ systems, where fairly complete miscibility has been found. For example, complete miscibility has been reported at 200° C for the aluminium chloride–zinc chloride system between the limits 38.5 $AlCl_3$/61.5 $ZnCl_2$ and 68.5 $AlCl_3$/31.5 $ZnCl_2$,[10] while at 692° 1 mole of zinc chloride will dissolve 2 moles of cerium(III) chloride[1] (m.pt. 794°). Chromic chloride does not fall into this pattern, probably because of its very high lattice energy, and because of the extreme reluctance of Cr^{III} to accept a tetrahedral environment, the implicit requirement for solution in fused zinc chloride.

A system described as a "5.5 mole % solution of chromic chloride in zinc chloride" has been mentioned in a study of ESR in solid and liquid salt mixtures[11]. This level of solubility is one or two orders of magnitude greater than that found in the present work; however, as the "solution" was prepared by heating the salts in vacuo at 200° and then melting without any reported stirring, sampling or even visual checking that all solute had dissolved, it is believed that the "solution" was actually a suspension.

Zinc Oxide

The solubilities reported for zinc oxide had relatively high uncertainties attached, because of their low values and the analytical procedures. Since this work was completed, the solubility of zinc oxide has been reported as 0.07 mole % at 450° by melt turbidimetry[12]; having regard to the different methods used in the determinations, and the experimental problems involved, agreement with the present results is considered satisfactory.

Latent Heats of Fusion of Solutes

The literature value of L_f for cobalt[114] was derived from phase diagrams of the systems $CoCl_2/FeCl_2$ and $CoCl_2/PbCl_2$, in the same way as in the present work; having regard to the different systems and the inaccuracies inherent in methods used to determine solubility, agreement was very good. The value of 15.1 kcal/mole obtained here for nickel(II) chloride assuming an ideal solution, must be regarded as in satisfactory agreement with the literature value[5] which was obtained by direct heat capacity measurements.

Values of L_f for the other solutes were not found in the literature, so that the values above are the first reported by any method. They are of the same order of magnitude as values listed[13] for similar compounds: the value of 5.0 kcal/mole for zinc sulphate is comparable with 3.5 kcal/mole for magnesium sulphate and 6.7 for calcium sulphate, while the value of 18.0 kcal/mole for zinc oxide is comparable with 18.5 kcal/mole for magnesium oxide and 12.0 for calcium oxide and the value of 13.6 kcal/mole for chromium(III) chloride with the values for the high-melting rare earth chlorides, which vary from 7.0 kcal/mole ($HoCl_3$) to 13.0 ($LaCl_3$).

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