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Solubility of Hydrogen Chloride in Zinc Chloride + Sodium Chloride Melts

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Measurement of the solubility of HCl gas in $ZnCl_2$ + NaCl binary molten mixtures has been carried out by an elution technique. The solubility data were found to exhibit trends characteristic of a chemical dissolution process, implying the formation of a complex species. It is suggested that as the melt basicity is increased the predominant species changes from a coordinated zinc species to HCl_2^-, with the more basic melts tending toward behavior exhibited by HCl in pure molten alkali-metal chlorides.

Introduction

Several studies of the solubility of hydrogen chloride gas in molten chloride media have been carried out, the reports of which may be found in the existing literature: in alkali-metal chlorides (*1–3*), alkaline-earth chlorides (*4*), LiCl + KCl eutectic (*5, 6*), NaCl + KCl mixtures (*7*), and $SbCl_3$ (*8*). Those carried out with melts containing zinc chloride are limited to $ZnCl_2$ + KCl (*9*) (45 and 70 mol % $ZnCl_2$), LiCl + KCl + $ZnCl_2$ (*10*) ($0 \leq$ mol % $ZnCl_2 \leq 17.4$), and *N*-ethylpyridinium bromide (*N*-EtPyBr) + $ZnCl_2$ and *N*-methylpyridinium chloride (*N*-MePyCl) + $ZnCl_2$ (*11*).

The first two studies (*9, 10*) found solute behavior characteristic of chemical dissolution processes: the solubility of HCl decreased with an increase in the melt temperature and with a decrease in the mole fraction of $ZnCl_2$ in the molten mixtures. However, the solubilities determined by Prasolov (*9*) were 2 orders of magnitude greater than those determined by Minh and Welch (*10*). The latter researchers employed an elution method of solubility determination, but the method of Prasolov is not described in the translation of the original paper, making it difficult to reconcile the discrepancy. Both groups have, on the basis of their results, postulated the existence of a complex species formed between the HCl and $ZnCl_2$ molecules without giving structural details. However, the results of the solubility measurements in the organic-based melts (*11*) were interpreted in terms of the formation of bihalide ions (HCl_2^-), as in the alkali-metal chlorides, rather than any complexation of the HCl with the aromatic ring or the $ZnCl_2$.

This paper details results obtained from the measurement of the solubility of HCl in $ZnCl_2$ + NaCl melts, which was carried out both to ascertain the nature of the dissolution process and to complement data obtained in a subsequent voltammetric investigation of the system (*20*).

Experimental Section

The solubility of HCl in $ZnCl_2$ + NaCl melts of varying compositions was determined by a simple elution method, known volumes of melts being saturated with HCl gas at atmospheric pressure which was subsequently sparged by passage of argon. Dissolution of the HCl in distilled water followed by titration of the acidic solution against standard NaOH solution provided a quantitative measure of the gas solubility.

The melts were held in a glass beaker inside a flanged glass outer container. The beaker was large enough to take around 250 g of melt, the quantity used for each solubility determination. Fittings in the lid allowed the introduction of a glass thermocouple sheath, gas bubbler, and gas outlet tube. All glass components were made of Pyrex. Before coming into contact with the melts all glassware was degreased, soaked in a 1:1 mixture of concentrated sulfuric and nitric acids, washed, and dried at 150 °C.

Purification of the melt components followed standard procedures (*12*). The $ZnCl_2$ (BDH AnalaR grade) underwent vacuum drying up to temperatures just below melting, removal of oxy/hydroxy/aquo impurities by saturation of the molten form with dry HCl, preelectrolysis, and vacuum filtration. The NaCl (BDH AnalaR grade) was prepared by vacuum drying up to 400 °C. The pure salts were stored in an argon-filled drybox and mixed in the required proportions before use.

The solubility of HCl was measured for melts made up of 80, 65, and 50 mol % $ZnCl_2$ + NaCl at melt temperatures ranging from just above the melting point to around 450 °C. At higher temperatures the volatility of $ZnCl_2$ became appreciable. HCl gas was passed through the melts for 4 h to allow equilibrium to be reached. The bubbler was then lifted from the melt, and a fast stream of argon swept through the system to remove all gaseous HCl. Argon was passed through the melts, displacing the dissolved HCl, the effluent gas being passed through distilled water to remove the HCl from the argon carrier gas. That complete dissolution of HCl was achieved was confirmed by using a series of water-containing Dreschel bottles for the dissolution, with no HCl being detected afterward. The resultant acidic solution was titrated against NaOH solution. This procedure was carried out three times at each temperature, the average value of the solubility being taken each time.

Results and Discussion

The elution method used in this determination of the solubility of HCl gas in $ZnCl_2$ + NaCl melts employed an apparatus somewhat more basic than that used for previous studies (*13*). Variations include evacuation of the melt chamber following melt saturation with the solute gas (*2*) or isolation of known volumes of the gas-saturated melt from which the dissolved gas could be eluted, thus ruling out the necessity of density data (*1, 7*). The former step is impractical for $ZnCl_2$-rich melts since the high vapor pressure of $ZnCl_2$ would result in a loss of that component. The evacuation step also relies on the solute gas remaining in the melt while evacuation of the system is occurring. The rapid stream of

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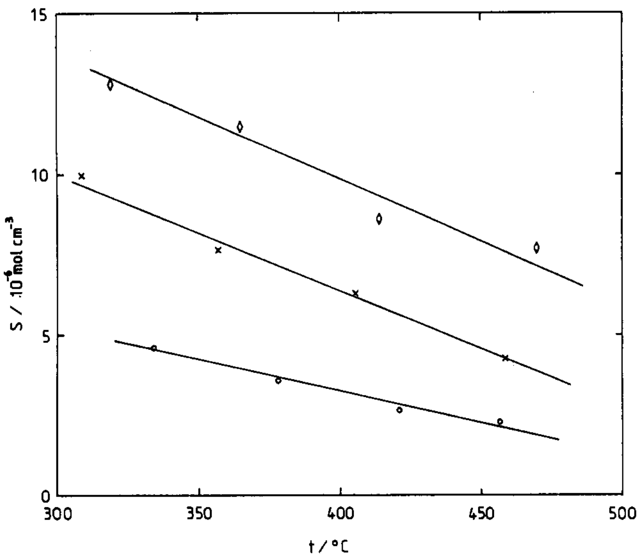

Figure 1. Solubilities of HCl in $ZnCl_2$ + NaCl molten mixtures: ◇, 80 mol % $ZnCl_2$; ×, 65 mol % $ZnCl_2$; ○, 50 mol % $ZnCl_2$.

argon is expected to have replaced the HCl atmosphere with one of argon prior to the elution step. Since the densities of $ZnCl_2$ + NaCl melts have been determined (*14, 15*), the masses of the mixtures were recorded and their corresponding volumes calculated, to give the solubilities (mol cm^{-3}). In the viscous pure molten $ZnCl_2$ the passage of HCl caused the formation of minute bubbles which could not be removed. Consequently, no data were collected for this system.

That the argon purge removed the HCl from the melt was verified by cyclic voltammetry; the details of these measurements are given elsewhere (*20*). The use of an inert gas to purge HCl/Cl_2 during melt purification steps is a standard practice (*12*).

The solubilities of HCl at varying temperatures in molten mixtures of $ZnCl_2$ + NaCl, shown in Figure 1, are seen to decrease with a decrease in the mole fraction of $ZnCl_2$ and with an increase in the melt temperature. The rate of decrease in solubility with rise in melt temperature becomes smaller as the melts are made more basic, implying that in the alkali-metal chloride rich melts the solubility behavior of HCl tends toward that in pure molten alkali-metal chloride. One study has found that the HCl solubility in molten NaCl decreases very slightly with an increase in the temperature (*2*), whereas three others have indicated a slight increase in solubility with temperature (*1, 3, 7*). Two mechanisms of gas dissolution may be considered: those of chemical and physical dissolution. The former involves interactions between the solute and solvent molecules, resulting in the formation of one or more complex ionic species. Solubilities in this case are found to be relatively high and to decrease with increasing solvent temperature. Physical dissolution characteristics are shown by solutes that do not interact with the solvent, leading to lower magnitudes of the solubility values which increase with increasing solvent temperature. Heats of solution for systems exhibiting physical solubility are found to be endothermic.

HCl dissolved in $ZnCl_2$ + NaCl melts follows trends characteristic of a chemical dissolution process. Earlier work using $ZnCl_2$ + KCl melts (*9*) showed an initial increase in HCl solubility with temperature, which gave way to a decrease above 380 °C, with a decrease in the mole fraction of $ZnCl_2$, also causing a decrease in solubility. However, the solubilities of HCl in the latter melt system were 2 orders of magnitude greater than those determined in $ZnCl_2$ + NaCl melts during this work. The solubilities of HCl in LiCl + KCl + $ZnCl_2$ melts (*10*) are slightly lower than those in $ZnCl_2$ + NaCl, but also exhibit trends characteristic of a chemical dissolution process. Without knowledge of the method used by Prasolov (*9*), it is difficult to account for the large discrepancy between the sets of results. The error in the results obtained in this work is around ±15%. Most researchers give an error of ±5% or greater (*13*).

Table I. Heats of Solution for the Dissolution of HCl Gas in Various Molten Chlorides

solvent	t/°C	ΔH_d/(kJ mol^{-1})	ref
80 mol % $ZnCl_2$ + NaCl	319–470	−13.2 ± 8.4	this work
65 mol % $ZnCl_2$ + NaCl	309–459	−19.2 ± 10.3	this work
50 mol % $ZnCl_2$ + NaCl	334–457	−21.3 ± 4.5	this work
NaCl	820–1020	−0.5 ± 1.6	2, 3
KCl	789–987	−4.0 ± 0.6	3
RbCl	722–972	−9.4 ± 1.6	3
$CaCl_2$	820–1000	28.0 ± 2.9	4
$SrCl_2$	890–1022	38.1 ± 1.2	4
70 mol % $ZnCl_2$ + KCl	310–500	−4.2 ± 6.8	9
45 mol % $ZnCl_2$ + KCl	350–550	−11.6 ± 15.2	9
LiCl + KCl (eutectic)	500–675	14.7 ± 1.5	5

Using the method of Andresen (*16*), estimated values for the heats of solution of HCl in $ZnCl_2$ + NaCl were determined. These are shown in Table I, along with those calculated for other systems. The exothermic heats of solution for the HCl/$ZnCl_2$ + NaCl systems are indicative of chemical dissolution processes. Similarly, the alkali-metal chlorides have exothermic ΔH_d values, whereas HCl in the alkaline-earth chlorides appears to undergo a physical dissolution process. This has been further confirmed by IR spectroscopic studies (*17*), which showed that HCl is present as monomers in molten alkaline-earth chlorides, whereas it is associated into complexes of the type $Cl{-}H{\cdots}Cl^-_{melt}$ in the molten alkali-metal chlorides.

A variety of species and equilibria may be present in solutions of HCl in $ZnCl_2$ + NaCl melts, all dependent on factors such as melt composition and temperature (*18*). However, the two species most popularly invoked are a coordinated zinc species, thought to be responsible for the catalytic activity shown by molten $ZnCl_2$ in hydrocracking processes (*19*), and the bihalide ion HCl_2^-, thought to exist in solutions of HCl in alkali-metal chloride melts (*1–3, 11, 17*). If a coordinated zinc complex is formed, the solute HCl molecules act in the same way as alkali-metal chlorides: enhancing the formation of four-coordinate zinc species, $ZnCl_4^{2-}$, by breaking down the polymeric $ZnCl_2$ melt structure. Trends observed during determination (*21, 22*) of the effects of high-pressure HCl on the transport properties of molten $ZnCl_2$ + KCl (46 mol % KCl) indicate that such a process may occur. In $ZnCl_2$ + KCl melts, the weaker polarizing nature of K^+ ions results in a greater availability of Cl^- ions than in $ZnCl_2$ + NaCl melts. Thus, the formation of protonated chlorozincate species in the former melt system should be lower than in the latter, the HCl molecules having to compete with Cl^- ions for sites around the Zn^{2+} cations.

Conversely, if the bihalide ion is the only species formed, its formation should be enhanced in the more basic melts due to the greater availability of Cl^- ions. The HCl would be in competition with the $ZnCl_2$ for the available Cl^- ions. In this case the HCl solubility would be greater in $ZnCl_2$ + KCl melts than in $ZnCl_2$ + NaCl, as determined experimentally (*9*). However, the increase in HCl solubility with an increase in the mole fraction of $ZnCl_2$ indicates that this could not be the only process occurring.

An explanation that could account for the solubility behavior is as follows. In $ZnCl_2$ + MCl melts containing small amounts of alkali-metal chloride (MCl), the HCl dissolves to form a protonated chlorozincate, such as $H_2^{2+}ZnCl_4^{2-}$. As the melts are made more basic, HCl_2^- becomes the predominant species, the solubility behavior tending toward that seen in pure molten alkali-metal chlorides. The likelihood of a bare proton existing in these melts is low: such a polarizing species is certain to attract negatively charged species to it. This explanation accounts for most of the phenomena observed experimentally: the increase of solubility with the mole fraction of $ZnCl_2$, the lower solubility of HCl in $ZnCl_2$ + NaCl than in $ZnCl_2$ + KCl melts, the exothermic heats of solution, and the decrease in HCl solubility with increasing melt temperature.

Conclusions

The solubility data for HCl in molten $ZnCl_2$ + NaCl binary mixtures were found to exhibit trends characteristic of a chemical dissolution process, implying the formation of a complex species. It has been postulated that as the melt basicity is increased the species predominantly formed changes from a coordinated zinc species to HCl_2^-, with the more basic melts tending toward behavior exhibited by HCl in pure molten alkali-metal chlorides.

Literature Cited

(1) Ukshe, E. A.; Devyatkin, V. N. *Russ. J. Phys. Chem.* **1965**, *39*, 1222.
(2) Novozhilov, A. L.; Devyatkin, V. N.; Gribova, E. I. *Russ. J. Phys. Chem.* **1972**, *46*, 1398.
(3) Novozhilov, A. L.; Devyatkin, V. N.; Gribova, E. I. *Russ. J. Phys. Chem.* **1972**, *46*, 1066.
(4) Novozhilov, A. L.; Gribova, E. I.; Devyatkin, V. N. *Russ. J. Inorg. Chem.* **1972**, *17*, 1345.
(5) Van Norman, J. D.; Tivers, R. J. *J. Electrochem. Soc.* **1971**, *118*, 259.
(6) Minh, N. Q.; Welch, B. J. *Aust. J. Chem.* **1975**, *28*, 965.
(7) Ukshe, E. A.; Devyatkin, V. N. *Russ. J. Phys. Chem.* **1965**, *39*, 1641.
(8) Ryabov, V. G.; Solomonov, A. B. *Zh. Prikl. Khim.* **1981**, *54*, 1821.
(9) Prasolov, Y. G.; Kostin, L. P.; Ketov, A. N. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **1964**, *17*, 162 (AWRE translation).
(10) Minh, N. Q.; Welch, B. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *92*, 179.
(11) Claes, P. F.; Coppe, C. R.; Simonis, L. A.; Glibert, J. E. *J. Chem. Eng. Data* **1987**, *32*, 70.
(12) White, S. H. In *Ionic Liquids*; Inman, D., Lovering, D. G., Eds.; Plenum Press: New York, 1981; Chapter 12.
(13) Field, P. E. In *Advances in Molten Salt Chemistry*, 3rd ed.; Braunstein, J., Mamantov, G., Smith, G. P., Eds.; Plenum Press: New York, 1971; p 89.
(14) Bloom, H.; Weeks, I. A. *Trans. Faraday Soc.* **1971**, *67*, 1410.
(15) Yoko, T.; Crescent, R.; Tsukagoshi, Y.; Ejima, T. *Nippon Kinzoko Gakkaishi* **1978**, *42*, 1179.
(16) Andresen, R. E.; Ostvold, T.; Oye, H. A. In *Proceedings of the International Symposium on Molten Salts*; Braunstein, J., Ed.; The Electrochemical Society: Princeton, NJ, 1976; p 111.
(17) Novozhilov, A. L.; Gribova, E. I.; Devyatkin, V. N. *Russ. J. Inorg. Chem.* **1972**, *17*, 1081.
(18) Hamilton, H. G. Ph.D. Thesis, University of London, 1989.
(19) Struck, R. T.; Zielke, C. W. *Fuel* **1981**, *60*, 795.
(20) Hamilton, H. G.; Inman, D. To be published.
(21) Hubble, B. R. Ph.D. Thesis, Kansas State University, 1971.
(22) Hubble, B. R. *Diss. Abstr. Int., B* **1971**, *32*, 3283.

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