Properties of Mixtures of Zinc Chloride and *N*-Methylpyridinium Chloride in the Molten State. 3. Solubility of Hydrogen Chloride under Atmospheric Pressure and Comparison with Zinc Chloride–*N*-Ethylpyridinium Bromide Mixtures

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The solubility of hydrogen chloride in *N*-ethylpyridinium bromide/zinc chloride mixtures and in *N*-methylpyridinium chloride/zinc chloride mixtures was investigated as a function of the mole fraction of zinc chloride respectively at 393 and 443 K. The solubility of hydrogen chloride reaches values as high as 6.25 and 7.5 mol/L respectively in pure molten *N*-ethylpyridinium bromide and in pure *N*-methylpyridinium chloride. The solubilities decrease as linear functions of the mole fraction of zinc chloride down to a value of about 0.25 mol/L for a mole fraction of zinc chloride of 0.33. The dissolution of hydrogen chloride is interpreted by the complexation of hydrogen chloride molecules by halide ions yielding bihalide ions ($HClBr^-$ and HCl_2^-).

Introduction

In the preceding papers in this series (*1*, *2*), thermodynamic (heats of mixing and phase diagram), volumetric, and transport (electrical conductivity and viscosity) properties of zinc chloride/*N*-methylpyridinium chloride mixtures were described. In this work, the solubility of hydrogen chloride under a pressure of 1 atm was investigated as a function of the composition of the melt. It seemed interesting to consider also another system very similar to the first one: mixtures of zinc chloride and *N*-ethylpyridinium bromide. The behavior of this last mixture is somewhat more difficult to understand since two different halide ions are present in the melt, but it offers the advantage of having lower melting points than the first one; for some compositions, it is possible to work at temperatures as low as 343 K. The available temperature range is thus larger and some instrumental measurements are more easily carried out.

Experimental Section

1. ***Chemicals***. The synthesis of *N*-methylpyridinium chloride and the origin of the zinc chloride were earlier described (*1*). *N*-Ethylpyridinium bromide was synthesized from 99.6% purity pyridine supplied by Carlo Erba and from 99% purity (P.A. grade) ethyl bromide from U.C.B. Pyridine and ethyl bromide were refluxed respectively over potassium hydroxide and over phosphorus pentoxide. The two compounds were distilled, mixed, and allowed to rest for 24 h.

The precipitated salt was filtered under a nitrogen atmosphere and washed four times with dry ether in order to remove any trace of the reactants. The removal of pyridine being more difficult than that of ethyl bromide, an excess of 10% of the last reactant was allowed in the mixture.

The residual ether was eliminated with a stream of dry nitrogen and the salt was stored under vacuum. The product is a white crystalline solid which is perfectly colorless in the liquid state. The measured melting point is 387 K in agreement with the observations of Vedel and Tremillon (*3*).

The mixtures were obtained as previously described (*3*). Purum grade hydrogen chloride from Fluka was used. In some cases, hydrogen chloride was prepared by reaction between sulfuric acid (96% H_2SO_4 from Carlo Erba, RPE grade) and sodium chloride. The reaction product was then bubbled through sulfuric acid.

2. ***Measurement of the Solubility of Hydrogen Chloride at 1 atm***. A weighed amount of the salt mixture was introduced in a cylindrical cell provided with a bubbler and a gas outlet and dipped into a thermostating bath. After melting of the sample, hydrogen chloride was allowed to bubble in the melt for 3 h. It has been determined that this time was more than long enough in order to reach saturation of the liquid. The saturation sample was quenched, quantitatively dissolved in distilled water and transferred into a 250-mL volumetric flask. An excess of potassium iodide and potassium iodate was added to the solution in order to produce an equivalent amount of iodine according to reaction I.

$$6H_3O^+ + IO_3^- + 5I^- \rightarrow 9H_2O + 3I_2 \qquad \text{(I)}$$

The volume was adjusted to 250 mL and the solution was allowed to rest in the dark for 1 h. Finally, iodine was titrated with a standard solution of sodium thiosulfate. A simple acid–base titration could not be carried out in this case because of the presence of large amounts of zinc compounds in the solution.

3. ***NMR Measurements***. The NMR determinations were carried out with a Model XL100 Varian spectrometer.

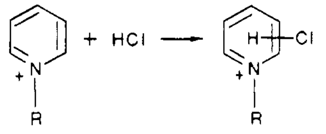
Results and Discussion

The concentration dependence of the solubility of hydrogen chloride in the $EtPyBr/ZnCl_2$ system at 393 K and in the $MePyCl/ZnCl_2$ system at 443 K was investigated for mole fractions of zinc chloride extending from 0.0 to about 0.7 (Table I). The tabulated density values refer to the pure solvents.

The corresponding solubility isotherms are shown respectively in Figures 1 and 2. A very large solubility (about 7 mol/L) is observed in both cases for the pure *N*-alkyl-substituted pyridinium salt; it decreases according to a linear dependence on the mole fraction of zinc chloride until a value of about 0.25 mol/L is reached for a mole fraction of zinc chloride close to 0.4. At higher $ZnCl_2$ contents, the solubility remains almost constant.

Solubilities of this order of magnitude suggest the occurrence of some chemical interaction between the solute and the solvent. At least three explanations could be provided for the dissolution of hydrogen chloride in the investigated melts.

1. The formation of a complex due to an interaction between the proton of the hydrogen chloride molecule and the π electrons of the aromatic ring (II) as suggested by Goffman and Harrington (*4*) in order to explain the dissolution of hydrogen chloride in molten pyridinium chloride at low temperature, close



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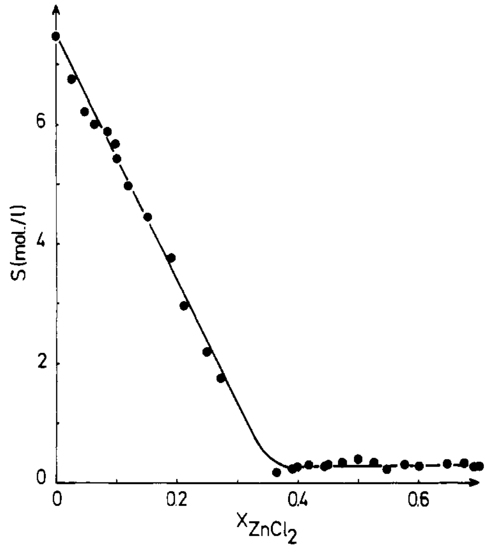

Figure 1. Solubility isotherm of hydrogen chloride in *N*-methylpyridinium chloride/zinc chloride mixtures (T = 443 K).

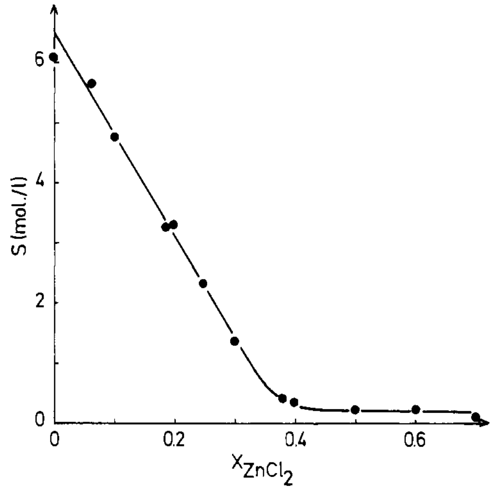

Figure 2. Solubility isotherm of hydrogen chloride in *N*-ethylpyridinium bromide/zinc chloride mixtures (T = 393 K).

to the melting point of the organic salt (323 K).

It must first be recognized that our determinations were carried out at temperatures significantly higher than 323 K. Second, NMR results by Shuppert and Angell (*5*) argue against this explanation. Finally, the reaction II would generate a concentration dependence of the solubility of hydrogen chloride with a shape illustrated in Figure 3 (straight line 1) which disagrees with the experimental results. This explanation must be dismissed.

2. Hydrogen chloride could also react with zinc chloride according to reactions III and IV In this case, the solubility

$$ZnCl_2 + 2HCl \rightarrow ZnCl_4^{2-} + 2H^+ \qquad \text{(III)}$$

$$ZnCl_3^- + HCl + ZnCl_4^{2-} + H^+ \qquad \text{(IV)}$$

of hydrogen chloride is expected to increase with the concentration of zinc chloride in the melt in qualitative agreement with the shape illustrated as curve two in Figure 3. This explanation clearly disagrees with the experimental results.

3. The formation of bihalide ions (HX^{2-}) can also be invoked in order to explain the dissolution of hydrogen chloride (V). If

$$HCl + X^- \rightarrow HClX^- \qquad \text{(V)}$$

$HClX^-$ is a weaker complex than $ZnCl_2X_2^{2-}$ and than the condensed species occurring at $X_{ZnCl_2} > 0.33$ (*6–9*), a linear decrease of the solubility of hydrogen chloride between X_{ZnCl_2} = 0 and X_{ZnCl_2} = 0.33 is expected (straight line three in Figure 3). If HCl competes for X^- ions with the zinc-containing species, a concentration dependence like curve four can be predicted.

Table I. Experimental Values of Solubilities

X_{ZnCl_2}	ρ, g/cm^3	C_{HCl}, mol/L
N-Ethylpyridinium Bromide/Zinc Chloride (393 K)		
0.00	1.378	6.10
0.061	1.410	5.63
0.100	1.433	4.77
0.187	1.470	3.25
0.200	1.489	3.29
0.249	1.520	2.32
0.300	1.556	1.37
0.380	1.600	0.39
0.400	1.624	0.34
0.500	1.681	0.22
0.600	1.790	0.21
0.700	1.915	0.09
N-Methylpyridinium Chloride/Zinc Chloride (443 K)		
0.000	1.100	7.47 ± 0.28
0.025	1.115	6.75 ± 0.25
0.050	1.138	6.22 ± 0.23
0.067	1.153	6.01 ± 0.23
0.086	1.167	5.90 ± 0.22
0.100	1.177	5.68 ± 0.21
0.101	1.178	5.38 ± 0.20
0.121	1.196	4.96 ± 0.19
0.152	1.218	4.46 ± 0.17
0.192	1.257	3.76 ± 0.14
0.212	1.266	2.95 ± 0.11
0.250	1.296	2.18 ± 0.082
0.273	1.314	1.78 ± 0.067
0.367	1.388	0.17 ± 0.08
0.392	1.405	0.24 ± 0.08
0.401	1.411	0.28 ± 0.08
0.419	1.428	0.32 ± 0.08
0.445	1.448	0.29 ± 0.08
0.448	1.452	0.30 ± 0.08
0.475	1.473	0.35 ± 0.08
0.501	1.491	0.40 ± 0.08
0.526	1.517	0.33 ± 0.08
0.548	1.537	0.22 ± 0.08
0.579	1.572	0.32 ± 0.08
0.601	1.597	0.29 ± 0.08
0.649	1.670	0.32 ± 0.08
0.677	1.703	0.34 ± 0.08
0.693	1.717	0.29 ± 0.08
0.703	1.742	0.28 ± 0.08

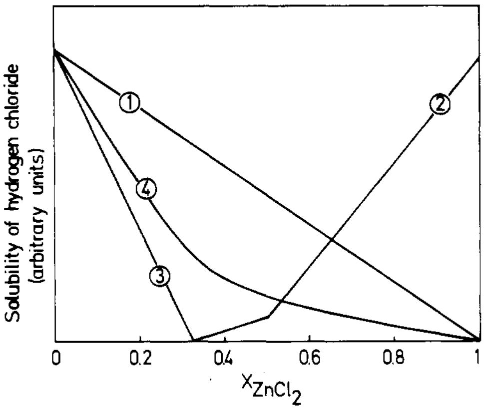

Figure 3. Predicted dependence of the solubility of hydrogen chloride for various dissolution mechanisms.

Clearly, the agreement between the straight line three and the experimental results points to the occurrence of bihalide ions in the melt.

Furthermore, the NMR spectrum of a saturated solution of hydrogen chloride in molten *N*-ethylpyridinium bromide at 388 K shows a singlet with a shift of −10.6 ppm referenced to

Me_4Si. A very similar signal was observed by Shuppert and Angell (*5*) in the case of mixtures of hydrogen chloride and pyridinium chloride and was attributed to the HCl_2^- ions. The authors report that this sharp line disappears at high temperature (>338 K) because a rapid exchange occurs in this case between $N-H^+$ and HCl_2^- protons. In our case, the *N*-substitution of the pyridinium ion allows thus the observation of HCl_2^- ions at higher temperature.

Figures 1 and 2 show that some other process occurs for the dissolution of hydrogen chloride since a solubility of about 0.25 mol/L was measured for $X_{ZnCl_2} \geqslant 0.33$. Our experimental results do not allow any interpretation of this extra solubility. Assuming that this extra solubility remains constant in all the concentration range and particularly for the pure *N*-alkylpyridinium salt, it can be found that the solubility is somewhat lower than the analytical concentration of the *N*-alkylpyridinium halide. In the case of *N*-ethylpyridinium bromide, the solubility of HCl through HX_2^- formation is 6.25 mol/L when the analytical concentration of bromide ions is 7.34 mol/L. For *N*-methylpyridinium chloride, the solubility as HCl_2^- is 7.5 mol/L, the analytical concentration of chloride ions yielding 8.31 mol/L. The complexation reaction of hydrogen chloride by halide ions is thus not quite quantitative and a competition exists between *N*-alkylpyridinium cations and hydrogen chloride for the halide ions.

Registry No. EtPyBr, 1906-79-2; MePyCl, 7680-73-1; $ZnCl_2$, 7646-85-7; HCl, 7647-01-0.

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Received for review March 25, 1986. Accepted September 15, 1986.

Apparent Molar Heat Capacities and Volumes of Aqueous Solutions of $MgCl_2$, $CaCl_2$, and $SrCl_2$ at Elevated Temperatures†

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Heat capacity (C_p) and density (d) data at 0.6 MPa and in the temperature range 298.15–373.15 K are presented for aqueous $MgCl_2$, $CaCl_2$, and $SrCl_2$. Data were obtained over the concentration (m) ranges 0.1–0.53 mol·kg^{-1} for $MgCl_2$, 0.03–0.98 mol·kg^{-1} for $CaCl_2$, and 0.03–2.0 mol·kg^{-1} for $SrCl_2$. The values of C_p and d of a solution relative to that of water were measured with a precision of ±0.1 mJ·K^{-1}·g^{-1} and ±5 μg·cm^{-3}, respectively, at all temperatures. The C_p and d results were used to calculate the apparent molar heat capacities (${}^{\phi}C_p$) and volumes (${}^{\phi}V$), respectively. Our ${}^{\phi}C_p$ results at room temperature are in good agreement with available literature data; however, our ${}^{\phi}C_p$ values at 348.15 and 373.15 K differ considerably from the high-temperature literature data available only for $MgCl_2$, because of the much lower precision (±2 to ±13 mJ·K^{-1}·g^{-1}) of the C_p measurements reported in the literature.

Introduction

The present work is part of a continuing effort from this laboratory to obtain thermodynamic data for aqueous species at elevated temperatures. The importance of this work for modeling applications in the nuclear industry (e.g., waste management and safety) and in nonnuclear areas has been discussed in our earlier papers (*1–4*). We have recently reported apparent molar heat capacities, ${}^{\phi}C_p$, and volumes, ${}^{\phi}V$, up to 373 K for a number of 1:1 aqueous electrolytes (*3*). In this paper, we extend our studies to the 2:1 aqueous electrolytes, $MgCl_2$, $CaCl_2$, and $SrCl_2$.

While ${}^{\phi}C_p$ and ${}^{\phi}V$ data for aqueous 2:1 electrolytes are available at 298.15 K (*5–8*), very few values are available at higher temperatures (*9–12*). This is because both heat capacity, C_p, and density, d, were difficult to measure at elevated temperatures before the recent development of flow microcalorimeters (*1*, *13–15*) and flow densimeters (*1*, *16*, *17*) able to withstand higher operating temperatures and pressures. In this paper, we present measured values of C_p and d along with calculated ${}^{\phi}C_p$ and ${}^{\phi}V$ values for aqueous $MgCl_2$, $CaCl_2$, and $SrCl_2$ (a fission product electrolyte) from 298.15 to 373.15 K, at a constant pressure of 0.6 MPa. In an accompanying paper (*18*), we apply Pitzer's ion-interaction model (*1*, *4*) to our data, combined with some literature data of comparable precision (*5–12*), to obtain partial molar heat capacity, $\bar{C}^0_{p,2}(T)$, and volume, $\bar{V}^0_2(T)$, functions, and to generate temperature-dependent equations for calculating other thermodynamic properties (such as the enthalpy, Gibbs energy, and osmotic coefficient) of these electrolytes at higher temperatures.

Experimental Section

To apply the ion-interaction model (*4*), a large number of high-precision $C_p(T,m)$ and $d(T,m)$ measurements are required over a wide range of T and m. This approach yields reliable temperature-dependent $\bar{C}^0_{p,2}(T)$ and $\bar{V}^0_2(T)$ functions, along with ion-interaction parameters (*4*).

The flow C_p microcalorimeter and flow vibrating-tube densimeter system, and the operating procedure used for all the measurements, were similar to those described in detail elsewhere (*1*). The chemicals used for this study were obtained from Fisher ($MgCl_2$) and Alfa Products, Ventron Division ($CaCl_2$ and $SrCl_2$). Details of sample handling and solution preparation were similar to those described earlier (*1*). Simultaneous

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† Issued as AECL-9036.

0021-9568/87/1732-0072$01.50/0