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PROPERTIES OF MIXTURES OF ZINC CHLORIDE AND *N*-METHYLPYRIDINIUM CHLORIDE IN THE MOLTEN STATE.
I. PHASE DIAGRAM AND HEATS OF MIXING

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ABSTRACT

The phase diagram of the *N*-methylpyridinium chloride–zinc chloride system was recorded using a visual method consisting of the determination of the temperature at which the melting of a solid sample of a given mixture comes to completion (clear point). Two distectic points were detected at mole fractions of zinc chloride (X_{ZnCl_2}) of 0.33 and 0.50 corresponding to the formation, respectively, of the $ZnCl_4^{2-}$ complex and of a condensed compound. A discontinuity was also observed at $X_{ZnCl_2} = 0.20$, but the experimental data are not accurate enough to discriminate between a congruent and a non-congruent melting point.

A calorimetric technique was used to determine the concentration dependence of the heat of mixing of the system. A very sharp minimum appears at $X_{ZnCl_2} = 0.33$; at this composition, the heat of mixing yields a value of -10.8 ± 0.4 kcal mol^{-1} in agreement with the formation of a very strong complex corresponding to the first distectic point.

INTRODUCTION

Low melting point mixtures of several organic salts with inorganic halides have been widely investigated in recent years. Much attention has been paid to their chemical and electrochemical properties and particularly to their acid–base behavior.

Relatively few papers have been concerned with the physico-chemical properties of these melts which, at first sight, exhibit a more complex behavior than mixtures of simple inorganic salts. In order to make the interpretation of experimental results easier and surer, it seems useful to compare the concentration dependence of several properties over the largest available concentration range. The phase diagram and the heat of mixing of the *N*-methylpyridinium chloride–zinc chloride system form the subject of this first paper. Volumetric properties, transport properties and the solubility of hydrogen chloride in this mixture will be described later on.

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CHEMICALS AND PREPARATION OF THE MIXTURES

N-*Methylpyridinium chloride*

N-Methylpyridinium chloride was synthesized by bubbling methylchloride for 2 h in pyridine thermostated at 80°C. The mixture was then allowed to rest at room temperature for 24 h in order to ensure the crystallization of the reaction product.

The excess of pyridine was eliminated by washing the precipitate three times with ethyl acetate. *N*-Methylpyridinium was further purified by crystallization from a mixture of ethyl acetate and acetonitrile.

The white crystalline product was dried at 120°C under vacuum for 72 h.

The measured melting point was 148°C; the molten salt obtained following this procedure was perfectly colorless. The NMR spectrum of the product is in agreement with literature data [1].

Methyl chloride was a Merck product with a purity of 99.5%.

RPE grade pyridine, supplied by Carlo Erba, was refluxed for 30 min on potassium hydroxide and finally distilled at 115°C.

Methyl acetate and acetonitrile were 99% purity chemicals supplied by Fluka.

Zinc chloride

Anhydrous zinc chloride was an analytical grade UCB product (98% purity) and was stored at 110°C for 24 h before use.

In some cases, the salt was further purified by two successive sublimations under vacuum.

Preparation of the mixtures

Weighed amounts of the two salts were mixed in a pyrex beaker and maintained at 383 K. Once the melting was started the heat evolved made it necessary to cool the mixture by dipping the bottom of the beaker in cold water in order to prevent decomposition of the melt.

The mixtures are generally stable up to temperatures of about 483 K. Above this limit the occurrence of a brownish color and the emission of fumes indicated that the melts decomposed.

PHASE DIAGRAM

Molten mixtures of zinc chloride and *N*-methylpyridinium chloride are characterized by large overcooling phenomena when they are cooled. Therefore, calorimetric techniques were difficult to use and the crystallization temperatures were visually determined as the temperatures at which the solid phase completely disappeared when solid samples were slowly heated.

Experimental

Samples of the investigated molten mixtures were introduced under vacuum in small pyrex tubes, cooled until crystallization occurred and finally sealed. The samples were placed in a thermostating bath which was intensely illuminated, and a cathetometer was used in order to improve the observation.

The temperature was continuously raised until the beginning of fusion of the sample was observed. Thereafter, the temperature was increased by increments of 0.5°C every 30 min up to the point where the sample was completely melted. This clear-point temperature, which is reproducible at ±0.5°C, was taken as the crystallization temperature.

Some samples were prepared with sublimated zinc chloride yielding results which could not be discriminated from those recorded when unpurified zinc chloride was used (see below).

Results

The phase diagram obtained by plotting the clear point as a function of the molar fraction of zinc chloride is shown in Fig. 1. No measurements could be recorded between $X_{ZnCl_2} = 0.6$ and $X_{ZnCl_2} = 0.8$ because the corresponding mixtures yield glasses on cooling.

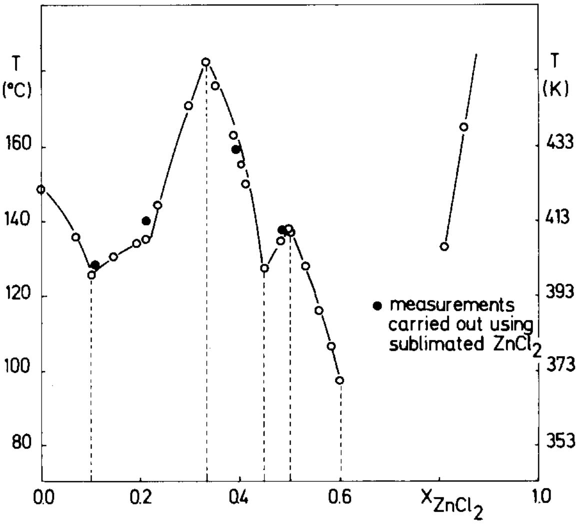

Fig. 1. Phase diagram of the *N*-methylpyridinium chloride–zinc chloride system.

Discussion

The phase diagram clearly shows the occurrence of two distectic points. The first one is observed at a mole fraction of zinc chloride of 0.33 and would indicate the formation of a definite compound with the stoichiometry M_2ZnCl_4 where M^+ represents the *N*-methylpyridinium cation. The second distectic point occurs for a mole fraction of zinc chloride of 0.5 which could be related to the formation of a compound with the general formula $MZnCl_3$.

At $X_{ZnCl_2} = 0.2$, there is a discontinuity in the experimental curve but, in this case, the accuracy of the determinations is insufficient for discrimination between a congruent or a non-congruent melting point characteristic of a M_4ZnCl_6 compound of low stability at the corresponding temperature (399 K).

The tetrachlorozincate ion, $ZnCl_4^{2-}$, has been confirmed by Raman spectroscopy in mixtures of zinc chloride and alkali halides [2,3]. However, the occurrence of the trichlorozincate ion, $ZnCl_3^-$, is questionable and the authors assume the formation of the dimeric ion, $Zn_2Cl_6^{2-}$.

Easteal and Angell [4] determined the phase diagram for the system zinc chloride–pyridinium chloride and characterized three distectic points (for $X_{ZnCl_2} = 0.2$, 0.33 and 0.50) and three eutectic points (for $X_{ZnCl_2} = 0.10$, 0.21 and 0.44) which are in quite good agreement with our determinations. They found one more distectic point at $X_{ZnCl_2} = 0.66$ and two more eutectic points at $X_{ZnCl_2} = 0.58$ and 0.72 which are in a non-available concentration range in this study.

HEATS OF MIXING

As shown by Kleppa and his co-workers, complex formation gives rise to a minimum in graphs where the heat of mixing or the interaction parameters are plotted versus the composition of the system. This minimum occurs for a concentration corresponding to the stoichiometry of the complex species [5,6]. It thus seemed interesting to compare the concentration dependence of the heat of mixing with the phase diagram.

Experimental

Mixtures of *N*-methylpyridinium chloride and of zinc chloride spontaneously decompose at temperatures where pure zinc chloride is liquid (> 556 K). Therefore, solid zinc chloride was added to liquid *N*-methylpyridinium chloride and the calorimetric determinations were carried out using the following technique.

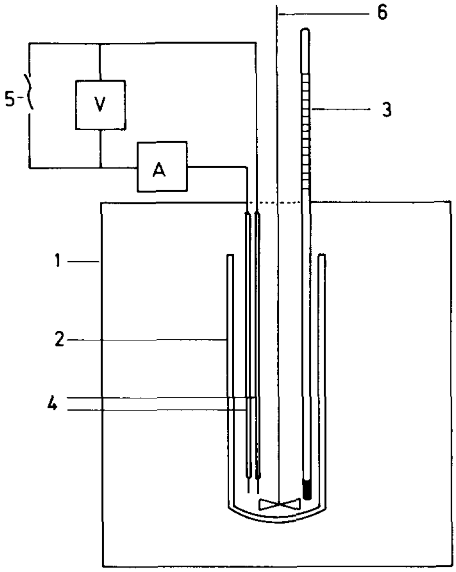

Fig. 2. Calorimetric device. (1) Heat-box; (2) Dewar flask; (3) thermometer; (4) platinum electrodes; (5) autotransformer; (6) stirrer.

The calorimeter is shown in Fig. 2. A Dewar flask is placed in a heat-box thermostated at the working temperature (443 K). A thermometer, a stirrer and two platinum electrodes are introduced into the Dewar through the cover of the heat-box. The platinum electrodes are connected to an autotransformer.

A known amount of *N*-methylpyridinium chloride is introduced into the Dewar flask, melted and thermostated. A weighed quantity of solid zinc chloride which was stored in the heat-box for at least 2 h was then added to the molten organic chloride under stirring and the time dependence of the temperature was recorded. An experimental curve is shown in Fig. 3.

The heat evolved during dissolution of the zinc chloride is proportional to the area delimited by the curve and by the horizontal line at 443 K. In order to evaluate this energy, a temperature–time curve was simulated by releasing heat by the Joule effect; the intensity of the alternative current between the platinum electrodes was regulated by adjusting the potential difference delivered by the autotransformer. This operation is repeated in order to improve the agreement between the experimental and simulated curves, the potential difference and the intensity of the current flowing through the melt being recorded as a function of time. The maximum margin allowed between the area delimited by the experimental and the simulated curves was 5%. The energy (E) delivered to the melt during the simulation is given by

$$E = \sum_i U_i I_i \Delta t_i$$

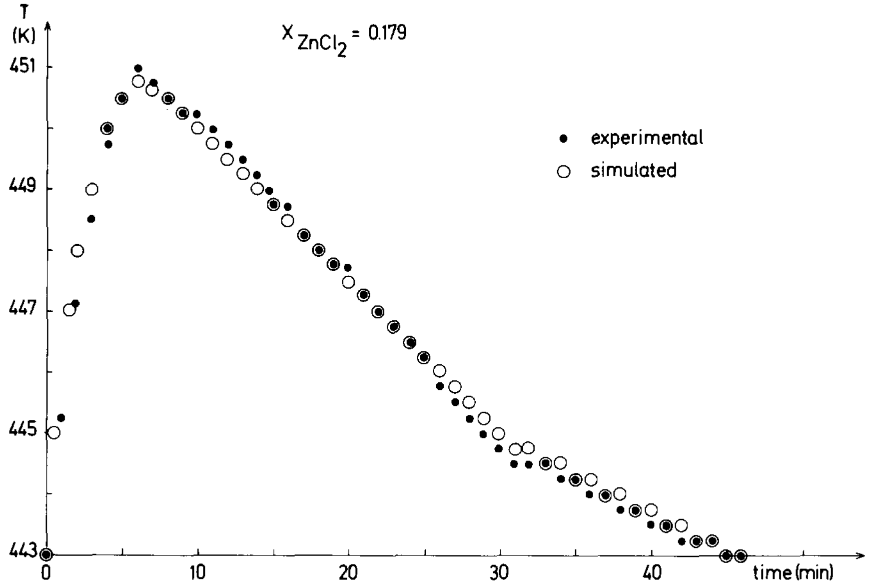

Fig. 3. Experimental and simulated curves for the time dependence of temperature.

where U_i and I_i are, respectively, the potential difference and the current intensity measured during the time interval Δt_i.

For some molar fractions of zinc chloride the heat evolved during the dissolution was large enough to partially decompose the melt. In those cases, the investigated mole fraction was reached by adding successive small fractions of solid zinc chloride and by summing the corresponding heat effects. This procedure can be used starting from pure *N*-methylpyridinium chloride or from mixtures of known composition.

Calculation of the heats of mixing

When the investigated mixture is obtained directly from the pure components, the heat of mixing (ΔH_M) is calculated according to the following formula

$$\Delta H_M = \frac{\sum_i U_i I_i \Delta t_i}{4.184} \frac{S_{exp}}{S_{sim}} \frac{M^A X_A + M^B X_B}{m^A + m^B} - \Delta H_f^B X_B$$

where S_{exp} and S_{sim} are the area delimited, respectively, by the experimental curve and by the simulated curve; M^A and M^B are the molecular masses, respectively, of *N*-methylpyridinium chloride and of zinc chloride; X_A and X_B are the corresponding mole fractions; m^A and m^B are the masses of the components involved in the mixture; ΔH_f^B is the latent heat of fusion of zinc chloride at the temperature of the experiment (443 K).

For mixtures obtained by adding zinc chloride to a previous solution, the heat of mixing is obtained from

$$\Delta H_M = \frac{\frac{\sum_i U_i I_i \Delta t_i}{4.184}\,\frac{S_{exp}}{S_{sim}} + \Delta H_M^0\left(\frac{m^A}{M^A}+\frac{m_0^B}{M^B}\right) - \Delta H_f^B\left(\frac{m^B-m_0^B}{M^B}\right)}{\frac{m^A}{M^A}+\frac{m^B}{M^B}}$$

where ΔH_M^0 is the heat of mixing for the initial mixture, m_0^B and m^B being the total masses of zinc chloride, respectively, in the initial mixture and in the final mixture.

The latent heat of fusion of zinc chloride at 443 K was estimated from the following thermodynamic cycle; the values of the molar heats at constant pressure of solid and liquid zinc chloride were found in the literature [7].

$$\begin{tikzcd}
ZnCl_{2(s)} \arrow[r, "\Delta H_f^B\ (556\ K)", "556\ K"'] & ZnCl_{2(l)} \arrow[d, "-C_p\ (ZnCl_{2(l)})\cdot 113"] \\
ZnCl_{2(s)} \arrow[u, "C_p\ (ZnCl_{2(s)})\cdot 113"'] \arrow[r, "\Delta H_f^B\ (443\ K)"] & ZnCl_{2(l)}
\end{tikzcd}$$

ΔH_f^B (443 K) = 5540 cal mol^{-1} + (24.10 − 16.14) 133 cal mol^{-1} = 4640.5 cal mol^{-1}.

Results

The heats of mixing were determined at 443 K for mole fractions of zinc chloride extending to 0.575. Starting from one pure sample of molten *N*-methylpyridinium chloride, determinations of heats of mixing were obtained for several X_{ZnCl_2}: the first one by mixing the pure components, the other ones by adding known amounts of zinc chloride to previously obtained solutions. Results obtained in one such series are identified by the same letter behind the value of the mole fraction in Table 1.

For $X_{ZnCl_2} = 0.338$, the measurement was carried out at 458 K in order to prevent crystallization of zinc tetrachlorozincate whose melting point is about 456 K. This higher temperature could not be adopted for all the determinations because in these conditions decomposition occurred for several melts at the maximum temperature reached after mixing. This enthalpy of mixing was used without any correction. This procedure is

TABLE 1

Heats of mixing of the system *N*-methylpyridinium chloride–zinc chloride at 443 K (for meanings cf (a)–(f) and *, see text)

X_{ZnCl_2}	ΔH_M (cal mol^{-1})	X_{ZnCl_2}	ΔH_M (cal mol^{-1})
0.000	0.000	0.241	−6800 ± 100
0.041(a)	−463 ± 6.9	0.241(d)	−6700 ± 200
0.042(b) (c)	−670 ± 10	0.270(c) (e)	−7400 ± 250
0.103(a) (f)	−1630 ± 34	0.277(c)	−8000 ± 300
0.113(b)	−2230 ± 47	0.301(c)	−9000 ± 360
0.116(c)	−2400 ± 50	0.338*(e)	−10500 ± 390
0.130(a)	−2740 ± 71	0.403	−7300 ± 150
0.170	−3730 ± 36	0.447(f)	−4350 ± 91
0.179(c) (d)	−4500 ± 121	0.474	−6200 ± 130
0.228(c)	−6200 ± 190	0.575	−3400 ± 51

justified by the observation that the heats of mixing for the systems CsCl–$ZnCl_2$ and AgCl–$ZnCl_2$ vary at most by 4% for a temperature change of 15°C [8]. The corresponding result is identified by an asterisk in Table 1.

The experimental results are collected in Table 1 and in Fig. 4. The standard deviations were estimated by attributing the largest error to the surface determinations and by assuming that each determination could be characterized by a standard deviation of 1.5%.

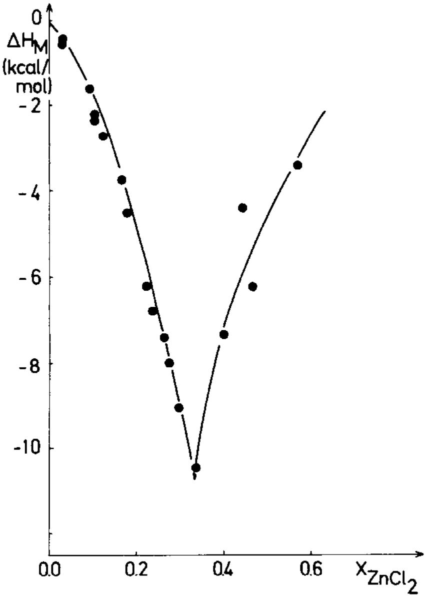

Fig. 4. Concentration dependence of the heat of mixing of the *N*-methylpyridinium chloride–zinc chloride system.

Discussion

A systematic investigation on the heats of mixing of zinc chloride or bromide with the corresponding alkali halides was carried out by Kleppa and Papatheodorou [6,8]. For most of these systems, the interaction parameter, defined as the enthalpy of mixing divided by the product of the mole fractions of the components of the mixture ($\Delta H_M/X_1X_2$) shows a minimum value for $X_{ZnCl_2} = 0.33$. According to the authors this minimum reveals the formation of large amounts of a stable complex at that composition. This assumption is in agreement with spectroscopic investigations which conclude to the occurrence of the tetrahalozincate ion, ZnX_4^{2-} [9–11]. The heats of mixing increase with the radius of the alkali cation, the stability of the complex species thus increases according to the sequence: Li < Na < K < Rb < Cs. In the case of lithium-containing mixtures, no minimum is observed showing the lack of formation of $ZnCl_4^{2-}$.

The concentration dependence of the interaction parameter is shown in Fig. 5 which shows a sharp minimum at $X_{ZnCl_2} = 0.33$ in agreement with the previously cited literature. Papatheodorou and Kleppa have determined a heat of -6.4 kcal mol^{-1} for the mixture of zinc chloride and cesium chloride at 938 K with $X_{ZnCl_2} = 0.33$. In this work a value of $\Delta H_M = -10.7$ kcal mol^{-1} was found for the zinc chloride–*N*-methylpyridinium system with $X_{ZnCl_2} = 0.33$ at 443 K.

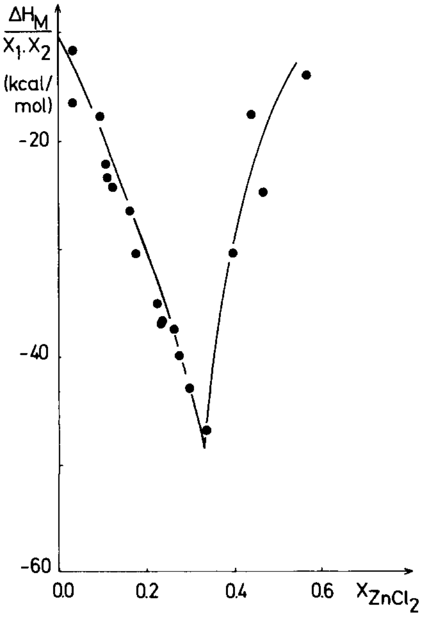

Fig. 5. Concentration dependence of the interaction parameter of the *N*-methylpyridinium chloride–zinc chloride system.

These results are not directly comparable; they were not recorded at the same temperature and the behaviors of a cesium cation and of a *N*-methylpyridinium cation should not be described according to the same model. However, the results obtained in this work agree with the sequence of heats of mixing recorded by Kleppa and Papatheodorou for the mixtures of zinc chloride and alkali chlorides: the largest enthalpy of mixing is measured for the *N*-methylpyridinium salt which also contains the largest cation.

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