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Enthalpy Measurements on $LiAlCl_4$ and $SnAl_2Cl_8$

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Drop calorimetry measurements between 273 and 950 K on $LiAlCl_4$ and $SnAl_2Cl_8$ are reported. The enthalpies of melting were respectively found to be 18.5 ± 0.5 and 37.6 ± 1.7 kJ mol^{-1}.

This note follows previous work on calorimetric measurements on alkali chloroaluminates (*1*). The lack of available enthalpy and heat capacity for $LiAlCl_4$ and $SnAl_2Cl_8$ led us to carry out a new set of calorimetric measurements. Both compounds are designed for high-efficiency inorganic batteries and catalytic syntheses.

Experimental Section

The measurements are carried out in an ice calorimeter by the drop method. The main features have been described in a previous paper. The crucible is made with platinum–rhodium 10%, which is not corroded by the samples.

Samples were prepared from $AlCl_3$, LiCl, and $SnCl_2$. $AlCl_3$ (Prolabo) was purified in Pyrex ampules under vacuum. $SnCl_2$ (Prolabo) was prepared in sealed ampules. LiCl was heated at 400 °C through a cycle of HCl gas–argon–vacuum. $LiAlCl_4$ and $SnAl_2Cl_8$ were prepared from weighed stoichiometric amounts of LiCl, $SnCl_2$, and $AlCl_3$. They were purified by thermoelectrolysis.

Results

All the experimental data are reported in Table I and were smoothed as polynomials, the coefficients of which were determined by the least-squares method and are rounded off in order to obtain calculated enthalpy values within assumed error. We have also defined an estimation of the variance of smoothed values σ^2 as such as in ref *1*:

$$\sigma^2 = \frac{\sum(H_{\text{est}} - H_{\text{obsd}})^2}{n(n-m)}$$

We give here the standard deviation σ.

The assessment of accuracy and precision on ΔH and C_p (noted here $\Delta H/H$ and $\Delta C_p/C_p$) has been previously reported (*1*, *2*).

Also the heat capacities were determined by differentiating the respective enthalpy–temperature equation with respect to temperature. The least-squares method was also used to determine the melting, as in ref *1*.

***$LiAlCl_4$*.** Measurements were performed on 12.460 g of salt with a crucible weighing 52.780 g. In the solid phase (σ = 124 J)

$$H_T - H_{273} = -40561 + 148.35T \text{ J mol}^{-1} \ (\Delta H/H = 2\%)$$

$$C_p = 148 \pm 13 \text{ J mol}^{-1}\text{ K}^{-1}$$

In the liquid phase (σ = 45 J)

$$H_T - H_{273} = 37295 + 184.67T \text{ J mol}^{-1} \ (\Delta H/H = 0.25\%)$$

$$C_p = 184.7 \pm 0.9 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$T_m = 418 \text{ K}$$

$$\Delta H_m = 18.448 \pm 0.5 \text{ kJ mol}^{-1}$$

Table I

T, K	ΔH_{obsd},[a] J mol^{-1}	Δ,[b] %	C_p, J mol^{-1} K^{-1}
	$SnAl_2Cl_8$		
273.2			231.6
301.9	7 730	−5.9	249.7
326.7	13 862	−1.30	265.4
383.3	29 746	−0.09	301.2
425.1	42 319	+1.27	327.7
470.5	58 681	−0.49	356.4
483.2	75 513		
486.7	87 219		
492.6	104 008	+0.13	388.7
516.6	113 599	−0.11	388.7
559.7	130 491	−0.21	388.7
610.8	149 691	+0.26	388.7
687.8	180 141	−0.07	388.7
	$LiAlCl_4$		
273.2			148.3
348.7	11 239	−0.65	148.3
352.8	11 376	+3.38	148.3
359.6	13 037	−1.99	148.3
391.3	17 522	−0.20	148.3
412.9	23 037		
416.6	24 338		
419.8	31 102		
429.7	41 969	+1.92	184.7
454.5	46 406	+0.48	184.7
466.2	48 881	−0.18	184.7
523.9	59 359	+0.18	184.7
538.4	62 226	−0.16	184.7
602.2	74 011	−0.14	184.7
620.5	77 427	−0.16	184.7
682.2	88 738	−0.04	184.7
753.9	102 035	−0.09	184.7
845.3	118 917	−0.09	184.7
940.9	136 206	+0.18	184.7

[a] $\Delta H_{\text{obsd}} = H_T - H_{273}$, experimental data. [b] $\Delta = 100(\Delta H_{\text{est}} - \Delta H_{\text{obsd}})/\Delta H_{\text{est}}$, with $\Delta H_{\text{est}} = H_T - H_{273}$ from the least-squares fit.

***$SnAl_2Cl_8$*.** Measurements were performed on 20.120 g of salt with a crucible weighing 51.660 g. In the solid phase (σ = 204 J)

$$H_T - H_{273} = -39258 + 58.739T + (3.163 \times 10^{-1})T^2 \text{ J mol}^{-1} \ (\Delta H/H = 2.4\%)$$

$$C_p = 58.739 + (6.327 \times 10^{-1})T \text{ J mol}^{-1}\text{ K}^{-1} \ (\Delta C_p/C_p = 3.1\%)$$

In the liquid phase (σ = 134 J)

$$H_T - H_{273} = 87298 + 388.67T \text{ J mol}^{-1} \ (\Delta H/H = 0.4\%)$$

$$C_p = 389 \pm 6 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$T_m = 485 \text{ K}$$

$$\Delta H_m = 37.6 \pm 1.7 \text{ kJ mol}^{-1}$$

We reported here new calorimetric measurements on two chloroaluminates of electrochemical interest. The experimental results indicate that the melting of $LiAlCl_4$ appears to be sharper

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than the melting of $SnAl_2Cl_8$. Few data for comparison with these results could be found in the literature (*3*, *4*).

Glossary

σ	standard deviation, J
H	measured enthalpy, J mol^{-1}
T_m, ΔH_m	temperature and enthalpy of melting, K and kJ mol^{-1}
ΔH_{est}	$H_T - H_{273}$ from the least-squares fit, J mol^{-1}
ΔH_{obsd}	experimental data, J mol^{-1}
C_p	heat capacity, J mol^{-1} K^{-1}
n	number of experiments
$n - m$	degrees of freedom

Registry No. $LiAlCl_4$, 14024-11-4; $SnAl_2Cl_8$, 12428-38-5.

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Surface Tension of Some Molten Salt Hydrates by the Pendant Drop Technique

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Surface tensions of molten salt hydrates such as $Cd(NO_3)_2{\cdot}4H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $Mn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, and $FeCl_3{\cdot}6H_2O$ have been measured by using the pendant drop technique. The experimental values are in agreement with those determined by previous workers, obtained by using the differential capillary rise method. With the pendant drop method, it was possible to obtain some new data at low temperatures in the supercooled region where the molten salt hydrates become highly viscous and the other methods are likely to fail to yield accurate results. In the case of the nitrate hydrate melts, the main contribution to the surface tension of the liquid seems to be due to the salt rather than the coordinated water, while in the case of $FeCl_3.6H_2O$, the surface of the melt seems to be predominantly occupied by the coordinated water.

Introduction

Salt hydrate melts have been considered as a class of molten salts (*1*, *2*). Surface, volumetric, and other physical properties of a number of molten salt hydrates have been measured by Jain and co-workers (*3*-*6*). Surface tension measurements in their works were carried out by using the differential capillary rise method. Although the differential capillary rise method is effective in the case of liquids of low viscosity, it may not be suitable in the case of molten salt hydrates at low temperatures, especially below their melting points. The molten salt hydrates become highly viscous at low temperatures and the establishment of equilibrium may require a long time. Moreover, the melts may not be able to wet the capillary properly and the condition of zero contact angle may not be strictly satisfied.

Among the other methods, the maximum bubble pressure method is the most used one but that method is also not suitable because bubbling a gas through a hydrated melt may cause a change in the composition due to evaporation of some of the water from the melt. The bubbling may also cause stirring and thereby crystallization of the melt, making the measurements in the supercooled region difficult.

Since we desired to measure the surface tension of molten salt hydrates at temperatures as low as possible, the pendant drop method was thought to be suitable because it is effective in the case of highly viscous liquids (*7*). Moreover, it is supposed to be a primary standard method (*8*) and the results are independent of contact angle (*9*).

This method was first used successfully for water and some organic liquids (*10*). It has also been applied in the case of molten polymers (*11*) as well as solutions of polymers (*12*) but not so far in the case of molten salts.

For calculation of surface tension from the profile of a pendant drop, the density of the liquid as well as the data regarding the shape parameter are essential. Both these data are available in the literature for the salts under investigation.

It has been observed that some molten hydrated salts can be supercooled well below their equilibrium freezing points and their physical properties have been found to change in a continuous manner through the transition into the supercooled state (*13*). One of the aims of this work was to see whether the surface tensions of molten hydrated salts also vary linearly well below their equilibrium freezing points. The other aim is to apply the pendant drop method for the measurement of surface tension of some molten salt hydrates and to verify the existing literature data.

Experimental Section

The chemicals used in this work were guaranteed reagents supplied by Wako Pure Chemical Industries and Nakarai Chemicals Ltd. (Japan). Purity of the chemicals was checked from their melting points. It was further confirmed by determining the number of moles of water present in 1 mol of the crystalline hydrated salt. The water contents of calcium nitrate and cadmium nitrate tetrahydrates were determined by completely dehydrating a known quantity of the salts at 120-140 °C. For the other salts, standard analytical methods were used (*14*). The numbers of moles of water present per mole of the hydrated salts were as follows: in the case of nickel, zinc, and manganese nitrates and iron(III) chloride, 6 ± 0.03; calcium nitrate, 4 ± 0.03; cadmium nitrate, 4.14 ± 0.02; and chromium nitrate, 9 ± 0.03.

The apparatus used in the present work was basically similar to the one used in the works of Nakajima (*15*), Wu (*11*), and

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