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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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Received for review March 3, 1983. Accepted September 21, 1983.

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

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Surface tensions of molten salt hydrates such as $Cd(NO_3)_2\cdot4H_2O$, $Ca(NO_3)_2\cdot4H_2O$, $Cr(NO_3)_3\cdot9H_2O$, $Mn(NO_3)_2\cdot6H_2O$, $Ni(NO_3)_2\cdot6H_2O$, $Zn(NO_3)_2\cdot6H_2O$, and $FeCl_3\cdot6H_2O$ 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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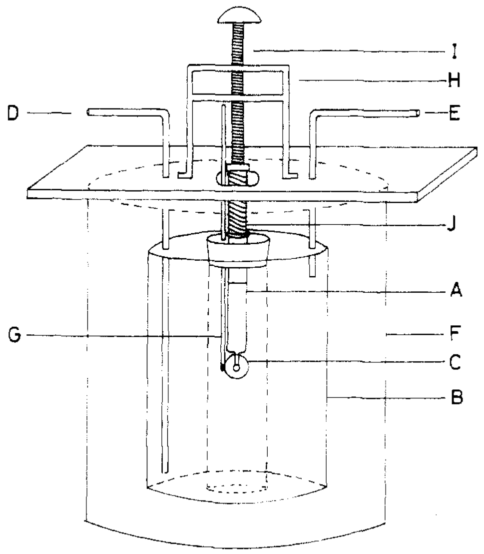

Figure 1. Pendant drop apparatus.

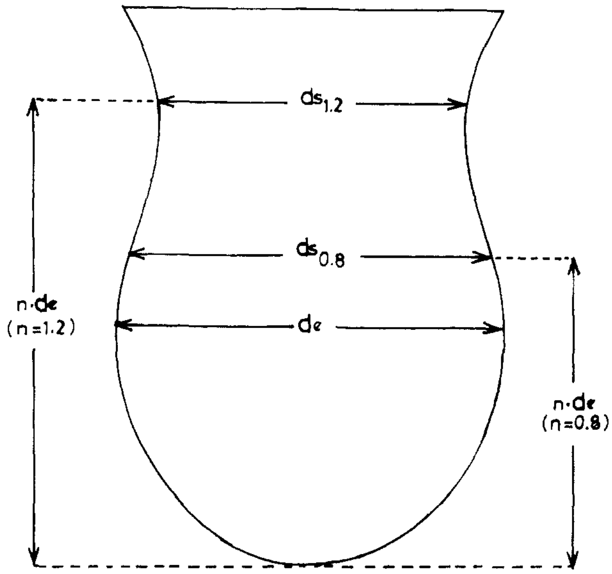

Figure 2. A pendant drop.

Frisch et al. (*12*). The experimental assembly is shown in Figure 1. The drop-forming device was a 5-cm^3 glass syringe (A) with a tip of 2-mm diameter. The diameter of the tip was decided by trial and error so as to get drops of suitable size and shape. The syringe was enclosed in a double-walled glass jacket (B) with an inner diameter of about 4 cm and an outer diameter of 8 cm. The pendant drop could be viewed through a small window (C) of the jacket. Water from a thermostat was continuously passed through the jacket by using the inlet (D) and outlet (E) tubes. The jacket itself was enclosed in a cylindrical electrical furnace (F) of inner diameter 11 cm. The furnace was maintained at the same temperature as the water in the thermostat. The temperature around the drop was measured by using a thermometer (G) and a calibrated chromel–alumel thermocouple (not shown in the diagram) kept close to the drop. With this arrangement, the temperature of the drop could be maintained between ±0.1 °C of the desired value. The stand (H) and screw (I) were used for pushing the piston into the syringe. The spring (J) was used for a smooth upward and downward movement of the piston, for the adjustment of the size and shape of the drops. The whole apparatus was placed on a vibration-free platform.

The pendant drops were photographed by using a 35-mm camera with an objective lens of $f = 4.5$ and 105 mm focal length.

The experimental procedure was as follows. The salt under investigation was melted in an airtight flask and kept at about 65 °C for 1 h for maturing. Some of the melt was sucked into the syringe which had been previously kept in the jacket held at about 70 °C. The syringe was immediately replaced in the jacket. A pendant drop was then formed at the tip of the syringe by using the screw arrangement. The focusing arrangement of the camera was made with a movie light. The temperature of the drop was allowed to remain at a desired value. The drop was made to fall down and a fresh drop was allowed to form, which was subsequently photographed with an electronic flash, at various intervals of time after its formation. Subsequent measurements were made by lowering the temperature in steps until crystallization of the salt commenced.

Measurements of drop diameters were made on magnified photographs, with an accuracy of better than 0.002 cm. The magnification factor was determined by photographing a stainless steel needle of known diameter, before and after each experiment.

The surface tension was calculated by using the relation

$$\gamma = g\Delta\rho d_e^2(1/H)$$

where g = gravitational acceleration; $\Delta\rho$ = difference between densities of the liquid and the surrounding medium; d_e = equatorial (largest) diameter of the drop; $1/H$ = shape factor, which is a function of the ratio, $S_n = d_{sn}/d_e$; d_{sn} is the diameter of the drop at a distance n times d_e, as measured from the apex of the drop. n takes the values 0.8, 0.9, 1.0, 1.1, and 1.2 (see Figure 2). The values of $1/H$ corresponding to various d_{sn} values were obtained with the tables published by Roe (*16*).

The difference between the surface tension values calculated for the same drop but with various S_n values was comparable with the experimental error. This was taken as a criterion for the equilibrium. Each drop was given sufficient time to assume equilibrium shape before it was photographed. During the exposure time of the drops to the atmosphere, the surface tension values did not show any change with time of exposure. This implies that, during this time, there is no change in stoichiometry of the melt due to either absorption of moisture or evaporation of water from the surface of the drops. Long times of exposure were avoided because of the possibility of adsorption of impurities on the surface of the drops. The suitability of the age of drops was determined from the consistency of $1/H$ values corresponding to various values of S_n ratios. At least two drops were photographed at the same temperature and at various time intervals. The performance of the experimental setup was previously verified by measuring the surface tension of water and some organic liquids like glycerol and ethylene glycol. The experimental values of the surface tension of these liquids were in agreement (within 1%) with the literature data.

The error in the experimental results was calculated by using the procedure described by Ambwani and Fort (*9*). The overall maximum error in the measurement of surface tension was estimated to be ±0.3%.

Density data required for the calculation of surface tension were taken from the literature (*3*, *4*, *17*, *18*). Extrapolated values of density were used at low temperatures assuming that the linearity between density and temperature still holds.

Results and Discussion

In the case of the salts studied, the surface tension was found to vary linearly with temperature in the range studied. The surface tension–temperature equations and related data are presented in Table I. Figure 3 shows a comparison of the surface tension values from the present work with the literature data, shown by solid lines. From the agreement between the two sets of data, it can be concluded that the apparatus used

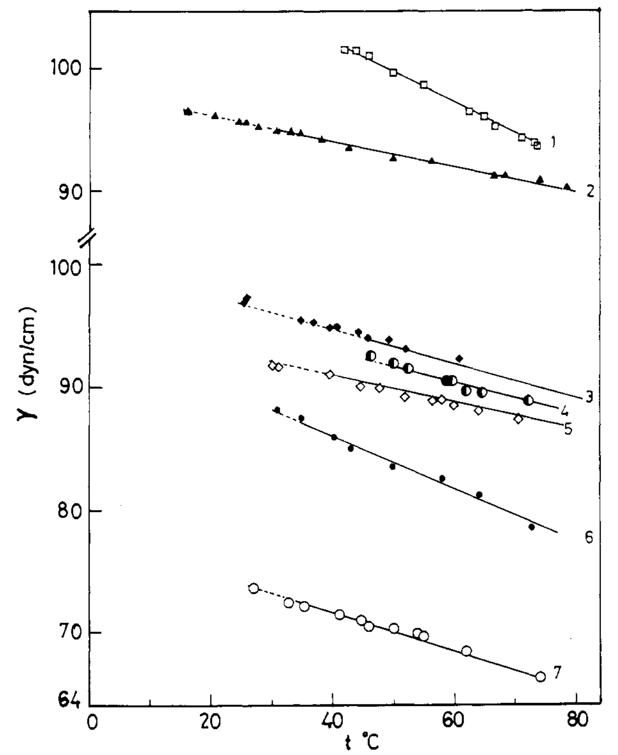

Figure 3. Comparison of surface tension values with the literature data (points, present work; solid lines, literature data from ref *4* and *5*; broken lines, measurements outside the range of the literature data): (1) $Cd(NO_3)_2{\cdot}4H_2O$, (2) $Mn(NO_3)_2{\cdot}6H_2O$, (3) $Ca(NO_3)_2{\cdot}4H_2O$, (4) $Ni(NO_3)_2{\cdot}6H_2O$, (5) $Zn(NO_3)_2{\cdot}6H_2O$, (6) $Cr(NO_3)_3{\cdot}9H_2O$, (7) $FeCl_3{\cdot}6H_2O$.

Table I. Surface Tension-Temperature Equations for the Molten Salt Hydrates

salt	γ (dyn/cm) = a − bt: a	b	SD	temp range, °C	temp range (lit.),[a] °C
$Cd(NO_3)_2{\cdot}4H_2O$	111.84	0.244	0.12	42-73	42-73
$Ca(NO_3)_2{\cdot}4H_2O$	100.47	0.137	0.20	25-61	45-81
$Cr(NO_3)_3{\cdot}9H_2O$	94.84	0.218	0.32	31-79	35-78
$Mn(NO_3)_2{\cdot}6H_2O$	98.17	0.101	0.19	16-80	31-77
$Ni(NO_3)_2{\cdot}6H_2O$	99.18	0.148	0.23	45-72	50-77
$Zn(NO_3)_2{\cdot}6H_2O$	95.24	0.113	0.15	30-71	39-78
$FeCl_3{\cdot}6H_2O$	77.49	0.146	0.21	27-74	34-73

[a] Reference *4*.

in the present work is capable of giving accurate results in the case of molten salt hydrates.

Linearity of surface tension values well below their melting points implies that there may not be any significant change in the structures of the melts in the supercooled region.

The present method is found to be especially useful in getting surface tension data at lower temperatures. In the present work, it was thus possible to obtain some new data at such low temperatures where the other methods may not be able to yield accurate results or may even fail to work. In the case of calcium nitrate tetrahydrate, the surface tension data were available only above 45 °C. With the present method, it was possible to shift the lower temperature limit of measurements down by about 20 °C and in the case of manganese nitrate hexahydrate, by about 15 °C.

It is interesting to note that the surface tension values of the nitrate hydrate melts are quite high, being more than 15 dyn higher than those of water at the same temperature. The surface tension of $FeCl_3{\cdot}6H_2O$, however, is just about 2-3 dyn higher than that of water. Their temperature coefficients are also comparable.

The surface tension of molten anhydrous calcium nitrate (*19*) at 560 °C (i.e., near its melting point) is 101.5 dyn/cm while that of calcium nitrate tetrahydrate at its melting point (42.7 °C) is 94.62 dyn/cm. The surface tension of water at 42.7 °C is, however, about 69 dyn/cm. From this, it appears that the surface tension of the hydrated melts is shared by the salt and its coordinated water in different proportions. In the case of the nitrate hydrate melts, the surfaces may be predominantly occupied by the salt molecules and therefore the surface tension value is closer to that of the anhydrous salt rather than that of water. From the comparison of the temperature coefficients of the surface tensions of $Ca(NO_3)_2.4H_2O$ and water (0.137 and 0.17 dyn/cm °C (*20*)), it can be concluded that the surface tension of molten $Ca(NO_3)_2.4H_2O$ is governed by the calcium nitrate molecules.

On the other hand, the surface tension of $FeCl_3{\cdot}6H_2O$ appears to be governed by its water of crystallization due to predominant presence of water molecules on the surface.

Registry No. $Mn(NO_3)_2{\cdot}6H_2O$, 17141-63-8; $Ca(NO_3)_2{\cdot}4H_2O$, 13477-34-4; $Ni(NO_3)_2{\cdot}6H_2O$, 13478-00-7; $Zn(NO_3)_2{\cdot}6H_2O$, 10196-18-6; $Cr(NO_3)_3{\cdot}9H_2O$, 7789-02-8; $FeCl_3{\cdot}6H_2O$, 10025-77-1.

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Received for review March 14, 1983. Accepted August 23, 1983.