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Surface Tension of NaCl-AlCl₃ Melts

Ernest W. Dewling

Research and Development Centre of the Aluminum Company of Canada, P.O. Box 8400, Kingston, Ontario, Canada K7L 4Z4

Surface tensions have been measured in the range of mole fractions $0.5 < N_{\text{AlCl}_3} < 0.6$ and temperatures $412 < T < 667$ K. The results can be expressed by $\gamma/(\text{mN m}^{-1}) = 212.7 - 0.03947T - 451N_{\text{AlCl}_3} + 306(N_{\text{AlCl}_3})^2$ with a root mean square deviation of ± 0.74 mN m⁻¹.

There are no measurements of the surface tension of NaCl-AlCl₃ melts reported in the literature. Of the methods available, the maximum bubble-pressure method was chosen as requiring a very simple apparatus and not needing an accurate knowledge of the contact angle. Capillary rise measurements were found to be unreproducible, apparently because the contact angle against glass is very variable.

The pressure (p) required to blow a hemispherical bubble on the end of a capillary tube immersed to a depth d below the surface of a liquid is

$$p = 2\gamma/r + \rho g d \quad (1)$$

where γ is the surface tension, r is the radius of the bubble, and ρ is the density of the liquid. The maximum pressure observed just before the bubble detaches comes when r is equal to the radius of the tube; if the contact angle is less than 90°, as it is in this case, the internal radius is taken, and, if the contact angle is greater than 90°, the external radius of the tube is used. Apart from this, knowledge of the contact angle does not enter into the calculation. By making measurements at two different values of d , one can determine both γ and ρ .

Equation 1 is not quite exact since, in practice, the bubble formed is not exactly hemispherical. Correction tables are given by Adam (1), together with a discussion of the method in general.

Experimental Section

The apparatus is shown in Figure 1. A Chromel "A" heater was wound directly on a 25-mm o.d. Pyrex tube, with two strips of asbestos tape down the sides to prevent it from slipping. It was then put inside a 35-mm tube which served as heat insulation. The melt was stirred by bubbling dried argon through it, and its temperature was measured with a platinum-platinum-10% rhodium thermocouple. Temperature control was manual by means of a Varlac.

Capillary tubes were drawn and selected to have a diameter of ~ 0.7 mm; the exact diameter was measured on a metallographic microscope. A slow stream of argon (10-20 bubbles/min) was dried with magnesium perchlorate and passed through. It was found essential not to have any rubber tubing

Table I. Surface Tension and Density Measurements

N_{AlCl_3}	T , K	density, kg m ⁻³	surface tension, mN m ⁻¹
0.520	486	1635	42.6
(0.520)	446	1694	43.7
(0.519)	526	1608	41.3
(0.518)	568	1592	39.5
(0.515)	616	1550	37.7
0.515	437	1695	44.7
0.511	677	1504	35.9
0.506	477	1663	44.9
0.505	577	1590	40.6
(0.505)	520	1635	43.0
(0.503)	652	1548	37.9
0.500	473	1675	44.9
(0.500)	544	1618	42.3
(0.499)	603	1551	38.1
(0.498)	676	1529	36.9
0.499	474	1679	45.2
(0.498)	647	1551	38.1
(0.600)	412	1720	35.9
0.596	475	1634	33.0
0.534	481	1653	38.9
(0.534)	429	1684	41.2
0.533	537	1614	37.8
(0.529)	615	1557	36.0
(0.527)	528	1620	39.0
(0.526)	458	1678	41.6
0.526	431	1690	42.5
(0.578)	412	1689	38.7
0.575	436	1673	37.2
0.603	419	1673	36.3

after the drying agent or the capillary became blocked with a gelatinous deposit (presumably Al₂O₃). The pressure was measured on a dibutyl phthalate manometer; a 1-L ballast flask connected to the system made the pressure oscillation slower and less extreme. With an interval of 5-10 s between bubbles,

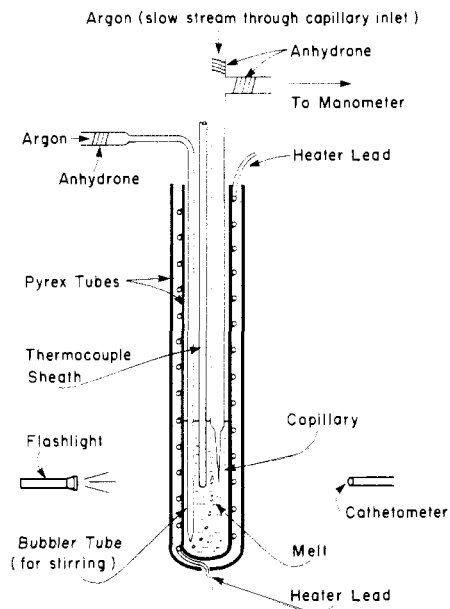


Figure 1. Apparatus for measuring maximum bubble pressure.

lag in response of the manometer was negligible.

The depth of immersion of the capillary and the heights of the manometer limbs were both measured with a Wild cathetometer accurate to 0.01 mm.

Melts were made from reagent-grade sodium chloride and aluminum chloride distilled from another melt to which aluminum powder had been added to remove volatile impurities (notably hydrogen chloride and ferric chloride). They were stirred with a supplementary stream of argon and were analyzed in situ by an electrometric method (2) as required. This involved inserting a thin-walled Pyrex tube containing a NaCl-AlCl₃ melt saturated with NaCl, and measuring the emf between Al wire electrodes in the two melts. Calibration curves of emf vs. composition had been determined previously.

At the start of a measurement, the level of the capillary tip was first determined and then the flow of stirring argon was stopped. The levels of the surface of the melt and the liquid in the manometer were read as rapidly as possible, and then

the stirring was restarted. The depth of immersion was changed, the temperature readjusted if necessary, and the sequence repeated.

The oscillation of the liquid in the manometer as the bubbles formed was very clearly visible; the maximum excursion of the liquid was taken in all cases.

Results

The density of the dibutyl phthalate in the manometer was found by direct comparison with a freshly prepared water manometer. A mean value of $1044.3 \pm 0.3 \text{ kg m}^{-3}$ was found at 298 K; the literature value (3) is 1045 kg m^{-3} at 293 K.

Two capillaries were used: the first was slightly elliptical with axes 0.0615 and 0.0630 cm; the second was round with diameter 0.0705 cm.

Table I shows the results. A horizontal line implies a deliberate change in melt composition. The melt was analyzed at intervals, and it can be seen that a slow drift in composition was occurring because of evaporation losses; the compositions in parentheses are estimated. The uncertainty thereby introduced is a few tenths of 1 mol % AlCl₃. The values of surface tension have been corrected for nonhemisphericity of the bubbles as indicated earlier—the magnitude of the correction was 1–2%.

The densities may be compared with the precise measurements of Fannin et al. (4); they are, on the average, 10 kg m^{-3} ($\sim 0.5\%$) lower.

The surface tensions have been fitted to eq 2 with a root

$$\gamma = 212.7 - 0.0394T - 451N_{\text{AlCl}_3} + 306(N_{\text{AlCl}_3})^2 \quad (2)$$

mean square deviation of $\pm 0.74 \text{ mN m}^{-1}$. A term in TN_{AlCl_3} was not statistically significant, implying that the temperature coefficient is independent of composition.

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