Density of Molten NaCl-$TiCl_2$-$TiCl_3$ Mixtures

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Densities of nine molten salt mixtures containing ≤ 0.08 mole fraction $TiCl_2$ and ≤ 0.15 mole fraction $TiCl_3$ in NaCl were measured by the Archimedean suspended-sinker method in the temperature range of 800–950°C. Measurement of the density of NaCl by the same method produced a result duplicating that of Van Artsdalen and Yaffe within 0.2%. The partial molar volumes of $TiCl_2$ and $TiCl_3$ calculated from the density data were 45.5 and 74.9 cm^3/mol^{-1}, respectively, which suggests the presence of substantial proportions of $TiCl_3^-$ and $TiCl_4^-$ complexes.

One phase of the Bureau of Mines program of fundamental research into the physicochemical properties of metal-molten salt systems involves a study of the kinetics of the anodic oxidation of titanium metal in molten NaCl-$TiCl_2$-$TiCl_3$ mixtures. These studies require a knowledge of the density of the molten salt as a function of temperature and of $TiCl_2$ and $TiCl_3$ concentrations. The necessary data on densities are not available in the literature; therefore, initially they were obtained by direct measurement during the experiments. This was a time-consuming, unsatisfactory procedure. The objective of the present study was to develop an equation from which densities could be calculated by utilizing temperature and chemical analysis information from each experiment.

Coefficients of the empirical density equations were determined by mathematical analyses of observed densities. Density measurements were made by the Archimedean suspended-sinker method in the temperature range of 800–950°C on molten salt mixtures containing up to 0.08 mole fraction $TiCl_2$ and up to 0.15 mole fraction $TiCl_3$. Over-all accuracy is estimated to have a standard deviation of ± 0.0086 g/cm^{-3}.

Experimental

The salt mixtures were prepared under a helium atmosphere to minimize contamination. The reagent-grade NaCl used in these experiments was purified by melting the NaCl in a nickel crucible, then immersing a titanium basket containing titanium turnings into the melt to remove any oxygen or metallic impurities. The NaCl-$TiCl_2$-$TiCl_3$ mixtures were prepared by passing $TiCl_4$ vapor through titanium granules beneath the surface of the purified NaCl at 850°C. The concentrations of $TiCl_2$ and $TiCl_3$ were controlled by the amounts of NaCl, titanium, and $TiCl_4$ charged to the nickel reaction vessel. Fast-neutron activation analysis of the resulting salt mixtures showed the oxygen content to be consistently less than 0.02 wt %. Other impurities typically present were 26 ppm of Mo and less than 5 ppm each of Fe, Ni, and Cr. $TiCl_2$ and $TiCl_3$ contents were determined by the method of Cattoir et al. *(2)*, on samples taken from the melt after thorough stirring to ensure homogeneity. These samples were handled under dry helium or argon as much as possible to avoid absorption of oxygen or atmospheric moisture.

Density was determined by use of a quartz-spring balance (having a spring constant of 0.01980 g/mm) to measure the buoyant force exerted by the molten salt on a totally immersed plummet made from arc-melted molybdenum suspended by a 0.005-in. diam platinum wire. The volume of the plummet at room temperature (0.5051 cm^3) was determined by weighing it immersed in toluene. Correction for the thermal expansion of molybdenum was based on the equation for its linear thermal expansion coefficient *(4)*,

$$\alpha = 1 + (5.01\,t + 0.00138\,t^2) \times 10^{-6}$$

Prior to immersing the plummet for density measurements, the salt mixture was thoroughly stirred by repeatedly plunging a molybdenum sampling cup into the melt via a sliding feed-through in the inert gas enclosure. This assured the absence of entrapped gas bubbles as well as assuring thermal homogeneity. Temperature of the melt was measured by an immersed molybdenum-sheathed calibrated Type K thermocouple used with a portable millivolt potentiometer. Direct calibration against the freezing point of LiF verified that temperatures were accurate within ±2°C. Depth of immersion of the plummet was held constant to compensate for the volume of the suspension wire immersed in the melt.

To minimize the condensation of salt vapors on the wire, a slow downward flow of helium was maintained along the wire by introducing the helium at a point above the quartz spring and allowing it to flow out through a bubbler from near the bottom of the molten salt crucible, while each series of measurements was made as promptly as possible. Despite the precautions, occasionally a perceptible mass of $TiCl_3$ condensed on the suspension wire. This condensate was assumed to accumulate at a constant rate; so a correction was applied to the data whereby an amount corresponding to the weight of condensate present at the time of each measurement was subtracted from the observed spring extension. No correction was applied for a possible surface-tension force acting on the wire, because the small diameter of the wire was assumed to make any surface-tension effect small enough to be disregarded.

To confirm the over-all accuracy of the procedure, the density of the purified NaCl was determined. The result was

$$\rho_{\mathrm{NaCl}}\ (g/cm^{-3}) = 1.9798 - 5.262 \times 10^{-4}\,t \quad \pm 0.0023 \tag{1}$$

which at 850°C becomes

$$\rho_{\mathrm{NaCl}}\ (g/cm^{-3}) = 1.5325 \pm 0.0023 \tag{2}$$

(Uncertainty limits correspond to 1 std dev.)

This agrees, within less than twice the standard deviation, with results obtained by Van Artsdalen and Yaffe *(5)*, for which

$$\rho_{\mathrm{NaCl}}\ (g/cm^{-3}) = 1.9911 - 5.430 \times 10^{-4}\,t \quad \pm 0.0007 \tag{3}$$

and at 850°C

$$\rho_{\mathrm{NaCl}}\ (g/cm^{-3}) = 1.5296 \pm 0.0007 \tag{4}$$

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Table I. Densities of Individual Salt Mixtures

Ti^{2+}, wt %	Ti^{3+}, wt %	Mole fraction $TiCl_2$	Mole fraction $TiCl_3$	Density[a] (where t is in °C) (g/cm^{-3})	No. of data points for each mixture
0.00	0.00	0.00000	0.00000	$1.9798 - (5.262 \pm 0.155) \times 10^{-4} t \pm 0.002$	16
5.83	1.00	0.78480	0.01345	$2.0232 - (4.777 \pm 0.257) \times 10^{-4} t \pm 0.005$	17
3.43	3.31	0.04700	0.04532	$2.1636 - (6.477 \pm 0.186) \times 10^{-4} t \pm 0.005$	26
2.31	1.03	0.02966	0.01322	$2.0845 - (6.259 \pm 0.205) \times 10^{-4} t \pm 0.003$	23
1.79	3.70	0.02418	0.04996	$2.0718 - (5.640 \pm 0.134) \times 10^{-4} t \pm 0.002$	28
5.39	5.81	0.08062	0.08679	$2.2703 - (6.651 \pm 0.087) \times 10^{-4} t \pm 0.003$	48
0.50	1.57	0.00634	0.01991	$2.0455 - (5.517 \pm 0.172) \times 10^{-4} t \pm 0.005$	42
0.35	10.07	0.00538	0.15472	$2.2167 - (6.530 \pm 0.039) \times 10^{-4} t \pm 0.002$	63
1.79	0.22	0.02245	0.00276	$2.0283 - (5.642 \pm 0.109) \times 10^{-4} t \pm 0.003$	28
4.06	3.02	0.05576	0.04145	$2.2037 - (6.249 \pm 0.050) \times 10^{-4} t \pm 0.002$	52

[a] Error shown for temperature coefficient is 1 std dev. Final error shown for each density equation is estimated standard deviation of precision of calculated density. These equations are valid over temperature range 800–950 °C.

Results and Discussion

Results of density measurements on individual salt mixtures are shown in Table I.

Multiple regression analysis of all the density measurements combined yielded the following results in terms of temperature, Ti^{2+} concentration, and Ti^{3+} concentration:

$$\rho(\mathrm{g/cm^{-3}}) = 2.0372 - (6.009 \pm 0.143) \times 10^{-4} t + (0.0158 \pm 0.0004) \text{ wt \% } Ti^{2+} + (0.0132 \pm 0.0002) \text{ wt \% } Ti^{3+} \quad (5)$$

(where t is in °C), with a standard deviation of ±0.014; and in terms of mole fractions,

$$\rho(\mathrm{g/cm^{-3}}) = 2.0463 - (6.053 \pm 0.131) \times 10^{-4} t + (1.111 \pm 0.024) X_{\mathrm{TiCl_2}} + (0.818 \pm 0.013) X_{\mathrm{TiCl_3}} \quad (6)$$

with a standard deviation of ±0.013.

A somewhat higher precision can be obtained by using an equation having additional terms (but only at the cost of decreased significance of the individual coefficients):

$$\rho(\mathrm{g/cm^{-3}}) = 2.0462 + 1.4515 X_{\mathrm{TiCl_2}} - 2.1976 X_{\mathrm{TiCl_3}} - 19.811 X^2_{\mathrm{TiCl_2}} + 19.793 X^2_{\mathrm{TiCl_3}} + 38.753 X_{\mathrm{TiCl_2}} X_{\mathrm{TiCl_3}} + (-5.8836 - 23.874 X_{\mathrm{TiCl_2}} + 40.863 X_{\mathrm{TiCl_3}} + 415.86 X^2_{\mathrm{TiCl_2}} - 272.96 X^2_{\mathrm{TiCl_3}} - 420.47 X_{\mathrm{TiCl_2}} X_{\mathrm{TiCl_3}}) \times 10^{-4} t \quad (7)$$

with a standard deviation (precision) of ±0.0068; the estimated accuracy (including estimated uncertainties in the underlying data) is ±0.0086.

To determine from our data the partial molar volumes of $TiCl_2$ and $TiCl_3$, it was necessary to assume that the partial molar volume of NaCl in the molten salt mixtures is identical to the known molar volume of pure NaCl. Under this assumption, analysis of the data in terms of molar volume of the salt mixture at 850°C yielded the following result:

$$\tilde{V}_{\mathrm{mix}} (\mathrm{cm^3/mol^{-1}}) = 38.214 X_{\mathrm{NaCl}} + (46.6 \pm 6.2) X_{\mathrm{TiCl_2}} + (75.4 \pm 3.8) X_{\mathrm{TiCl_3}} \quad (8)$$

For comparison with these results, theoretical values of molar volume for pure $TiCl_2$ and $TiCl_3$ were calculated from the known densities of the pure solids *(1, 3)*. These values are 38.8 cm^3/mol^{-1} for $TiCl_2$ and 57.3 cm^3/mol^{-1} for $TiCl_3$. If the difference between these molar volumes—i.e., 18.5 cm^3/mol^{-1}—represents the volume contribution of a single chloride ion bonded to a titanium atom, then comparison with the experimental values of partial molar volumes in the NaCl–$TiCl_2$–$TiCl_3$ molten salt mixture suggests that in the molten salt an additional chloride ion may be coordinated to the titanium halide. The melt thus contains substantial proportions of the anionic complexes $TiCl_3^-$ and $TiCl_4^-$, or other such species of complexity greater than $TiCl_2$ and $TiCl_3$.

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