DENSITY MEASUREMENT FOR CORROSIVE SOLUTIONS AT ELEVATED TEMPERATURES

Kimweri, H.T.H.

Department of Chemical and Process Engineering
University of Dar es Salaam, P.O.Box 35131, Dar es Salaam

SUMMARY

In this work, an apparatus for measuring densities of corrosive solutions at high temperature was developed and used. Densities of dilute aqueous sulphuric acid solutions, containing different amounts of zinc and iron salts were measured at temperatures up to 185° C. In view of the good agreement between consecutive measurements for each solution and the density of water obtained by using this apparatus with that given in literature, for all experiments, the apparatus is recommended to be used for measuring densities of corrosive solutions at high temperatures.

INTRODUCTION

Density means the relationship "mass per unit volume" of a substance. Densities of liquids are important parameters for research and industry. In chemical and process engineering, densities of solutions are used for material balances of processes where stream flows and concentrations are characterized by volume. Density measurement is also used for controlling quality of products and for determining concentration. Density is an important parameter in design and optimization of plants, especially in sizing of equipment.

Anton PAAR Oscillating U-Tube method has become a standard method for density measurement. The Anton PAAR densitometer consists of two parts. One is a sensing unit which contains a U-shaped sample tube connected to a measuring oscillator. The other part is a frequency counter and a digital display component. The hollow U- shaped tube is electromagnetically forced into harmonic oscillation. Periods of oscillation are dependent on the density of the sample in the tube. Thus, by measuring the periods of oscillation, the density or density related properties can be readily evaluated. However, Anton PAAR density meters are very expensive instruments. They are mostly operable at lower temperatures not exceeding 150°C. Those operable at higher temperatures are even more expensive. Hence, it is not justifiable to use such an expensive instrument for measuring densities of ordinary corrosive solutions such as those of dilute aqueous sulphuric acid, at higher temperatures.

However, densities of such solutions are often required for engineering purposes. In pressure leaching, a new hydro-metallurgical process of recovering zinc from zinc sulphide ores, dilute aqueous sulphuric acid solutions containing different amounts of zinc and other metals are used at temperatures up to 185°C. At temperatures above 100°C these solutions are extremely corrosive.

Most of the data for densities of aqueous sulphuric acid-salt solutions are for binary systems only and they are limited to a maximum temperature of 373 K (100°C) (Perry and Green, 1984; Sohnel and Novotny, 1985). Extrapolation of such values cannot be recommended for the evaluation of densities of solutions for the temperature range and most of the compositions used in pressure leaching.

The effect of pressure on the density of a solution was investigated and evaluated (Castellan, 1983). It was found out that the changes in volume of a liquid caused by moderate pressure changes are very small and thus liquids are considered to be incompressible. Therefore, the effect of pressure on the density of liquids can be neglected except at very high pressures. However, a pressure higher than the vapour pressure of the liquid must be applied on the solution to prevent boiling or excessive vaporizing of liquid when measurements of volume are carried out.

EXPERIMENTS

Density measurements were carried out at temperatures ranging from 298 K to 458 K (25 to 185°C). Experiments were conducted for solutions containing sulphuric acid, zinc and iron of the following concentrations (expressed as g/L for the three components respectively): (i) 5,0,0 (ii) 5,110,0 (iii) 5,110,1 (iv) 60,75,0 and (v) 60,75,10. These concentrations of solutions and temperatures were chosen to simulate those solutions and conditions used in pressure leaching of zinc from sulphide ores.

Development of Density Experimental Apparatus

For measuring densities of the solutions at temperatures ranging from 298 and 323 K (25 and 50°C), the Anton PAAR density meter was used. Because of severe corrosiveness of these solutions at higher temperatures and the fact that operation of this instrument was limited to 423 K (150°C), it was necessary to design an equipment that could withstand the corrosiveness involved. Pyrex glass dilatometers were designed. The dilatometers were made of 8 mm (0.008 m) pyrex glass capillary tubes of uniform cross-sectional area. One end of each tube was sealed by glass blowing methods. The open end was then fitted to a ($\frac{1}{8}$-in) stainless steel tubing system for pressurizing, through a ($\frac{3}{8}$ to $\frac{1}{8}$-in) reducing union. Four such dilatometer tubes were constructed. In the design and construction of the dilatometers it was found that pyrex glass was very brittle and slippery (Kimweri, 1990). The glass broke easily when connected with metallic fittings and when the system was pressurized or when nuts were tightened. When nuts were not tightened firmly, the tubes slipped out on pressurizing.

The problem of slipping of dilatometer tubes was solved by slightly expanding the open ends of the capillary tubes. Tubes of slightly smaller size than the fittings were intentionally chosen for this purpose. The expansions were made such that the expanded end of the tube just fitted inside a union fitting. Breakage was minimized by using specially made teflon ferrule, instead of stainless steel ones, to provide necessary seal. Expansion of the tube ends made it possible to get firm connection by just tightening the fittings

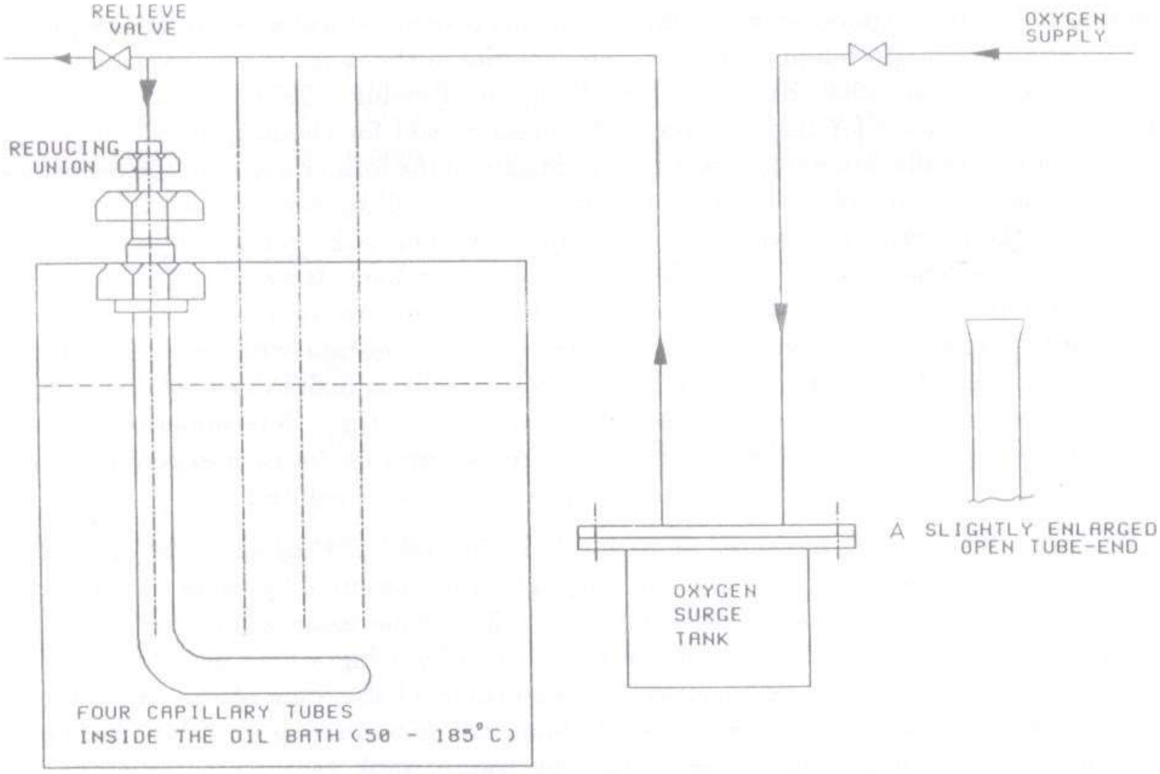

Figure 1: Dilatometer Tubes Density Apparatus

lightly. Also, fixing of fittings to the pressurizing system was done in a way that contact of metallic fittings with hot oil was avoided and hence reduce the thermal expansion which was another cause of loosening fittings. Eventually, the capillary tubes could be pressurized (to 12 atm) without breaking or slipping out of the fittings. A flow diagram of the assembled Dilatometer Density Apparatus is presented in Figure 1.

To obtain sufficiently measurable dilations of solutions, it was important to make the capillary tubes as long as possible. Because of limited depth of the constant temperature bath (about 0.25 m), the capillary tubes were bent to form 90^o angle. In this way, it was possible to construct capillary tubes with exposed (transparent) lengths of 0.531, 0.540, 0.547 and 0.571 m. The solutions inside capillary tubes were heated in a high temperature oil bath. The bath was a TMV 45DD visibility bath obtained from Neslab Instruments. Temperature controller for the bath maintained temperatures to within 0.1 K. For the sake of economy, safety and convenience, the bath oil was an edible peanut oil. The oil could be used continuously at high temperature for up to one month before decomposition occurred. After this period the oil became viscous and visibility was reduced and thus was replaced with fresh oil. For safety reasons the high temperature density apparatus was mounted in a fume hood.

Experimental Procedure

The Anton PAAR densitometer was calibrated by using distilled water and ethylene glycol as calibration fluids. Both liquids have known densities in the range of temperatures used in this work (Gallant, 1968; Keenan, 1968; Wong and Hayduk, 1990). Usually, distilled water and air are used for this purpose. The main reason for choosing ethylene glycol instead of air as a calibration fluid was that the density of the former was near the expected range of densities of the solutions. After calibration the densitometer was used to measure densities of the experimental solutions at 25 and 50°C. On each occasion, a sample was injected into the density meter U-tube by using a plastic syringe. It was then left to attain the desired temperature. In this equipment, the desired temperature is attained when the vibrating frequency reading on the densitometer remains constant with time. This took about 5 minutes. The temperature in the densitometer was maintained by circulating water at constant temperature. For each solution, at least three determinations of the vibrating frequency were made at each temperature. An average for each experiment was recorded and used in calculating the density of each particular solution.

Densities of solutions were measured at 50, 95, 125, 155 and 185°C by using the dilatometers. The total exposed length of each capillary tube was measured by using a measuring rule. The solutions were then charged into a capillary tube using a long syringe. Air bubbles in the solutions inside the tube were removed by using a long flexible and thin copper wire. In order to get measurable magnitudes of dilations of the solutions, a minimum column inside the capillary tube of about 0.35 m was required. Next, the tubes were connected to a pressurizing system. An oxygen surge tank was also connected to the system to stabilize the pressure by increasing the total volume of the gas. Before heating, the whole system was pressurized to a total pressure slightly above the vapour pressure of water at the experimental temperature. This was necessary to prevent the solutions from boiling. The bath temperature was then raised to 50°C (323 K). At this temperature, the initial length of the solution inside the capillary tube was measured and recorded. The lengths were accurately measured by using a cathetometer readable to 0.01 mm. In order to increase visibility inside the oil bath, a light bulb was put on the other side of the bath, i.e. opposite to the side where the cathetometer was placed. Subsequent lengths were taken at 95, 125, 155 and 185°C. Lengths were measured in triplicate.

These lengths were afterwards used to calculate the densities of respective solutions by applying mass balances. As a check on the method, the dilatometers were calibrated using distilled water. The calibration gave small correction factors which accounted for minor effects such as evaporation of the solutions and thermal expansion of the tubes. Dilation of the solutions was clearly observable, in every case being at least 0.7 cm.

Calculation of Density

The densities were calculated in two stages. The first one involved calculations based on the vibrating frequency readings obtained with density meter. Readings of the vibrating frequency are related to density as follows:

$$\rho_E - \rho_W = \kappa(\tau_E^2 - \tau_W^2) \tag{1}$$

Values of calibration constants at 298 and 323 K were found by substituting densities of distilled water and ethylene glycol. By substituting the calibration constants and readings of the vibrating frequency, density of each solution was determined.

The second stage involved calculation of densities based on dilations of solutions obtained by using dilatometers. For this purpose, principles of mass balances were applied. If the loss of water due to evaporation was neglected, the mass of a solution was supposed to be the same at all temperatures:

$$Mass\ at\ 50^{\circ}C = mass\ at\ temperature\ T = constant \tag{2}$$

The mass can also be expressed by an equation in terms of density of a solution, cross-sectional area of the capillary tube and length of a solution inside the tube:

$$Mass\ at\ 50^{\circ}C = (\rho ALe)_{50^{\circ}C} = (\rho ALe)_T \tag{3}$$

The capillary tubes used in taking measurements were of uniform cross- sectional area. Therefore, Equation (3) becomes:

$$\rho_1 Le_1 = \rho_T Le_T \tag{4}$$

By using precise (density meter measured) densities at 323 K, and lengths of solutions measured at this temperature and at higher temperatures, densities were calculated at all conditions. To compensate for both possible liquid evaporation of solutions and expansion of the tubes, the tubes were calibrated using distilled water. Correction factors were calculated as a ratio of density of water taken from literature (Keenan, 1969) to that calculated using equation (4). The equation is:

$$r = \frac{\rho_a}{\rho_{me}} = \frac{mass}{ALe_a}.\frac{ALe_{me}}{mass} \tag{5}$$

Values of correction factor obtained for each tube were used for calculating density of each solution by correcting measured lengths of the solution. Rearrangement of Equation (5) yields:

$$Le_a = \frac{1}{r} Le_{me} \tag{6}$$

RESULTS AND DISCUSSION

Calculated values of densities in kg/m^3 are presented in Table 1. Based on the precision of measurements of dilation, the maximum error for these densities had been estimated to be $\pm 0.2\%$. Densities measured by using the density meter (at 25 and 50°C) had higher accuracies of about $\pm$ 0.05%.

Table 1. Densities of Solutions at Experimental Conditions

Solution	Temperature, K					
	298	323	368	398	428	458
Water	997.1	988.0	965.3	939.1	912.3	881.6
5/0/0	1001	991.8	966.7	943.9	918.2	887.9
5/110/0	1256	1245	1217	1186	1155	1118
5/110/1	1261	1247	1220	1189	1159	1121
60/75/0	1206	1193	1164	1134	1107	1073
60/75/10	1236	1224	1194	1165	1139	1104

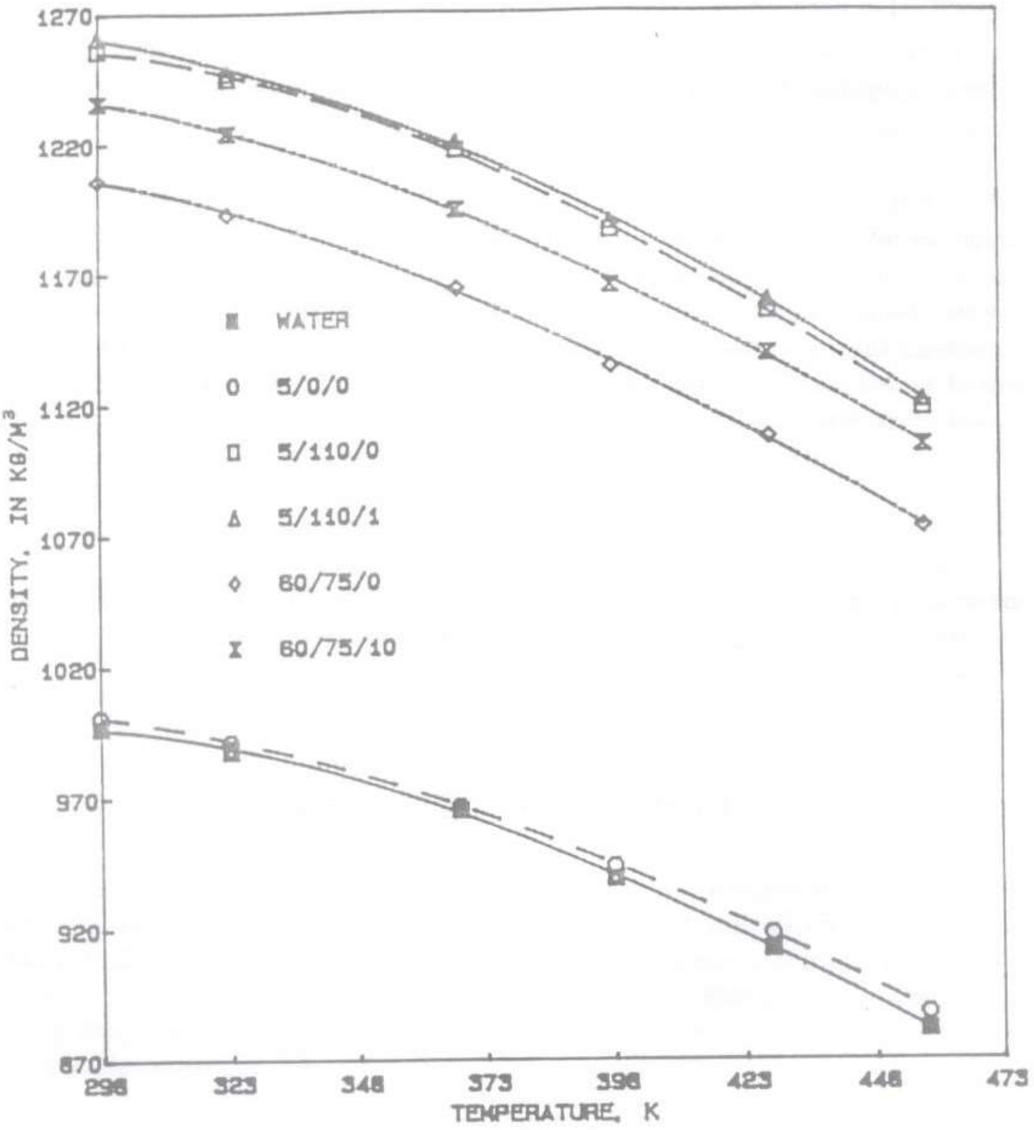

Figure 2: Densities of Acid-Salt Solutions at Experimental Conditions

Except for water, it was not possible to find densities for direct comparison with those of solutions used in this work. During the calibration of the dilatometers a small error for each tube of less than ±1.0% was found because of the expansion of the tubes and a small correction factor for each was required. In view of good agreement between consecutive measurements for water and all other solutions, the dilatometer apparatus is considered to be reliable and the results are considered to be satisfactory. Densities of solutions at experimental temperatures are shown in a graphical form in Figure 2.

It can be observed from Figure 2 that, as expected, densities decrease with increase in temperature. While the decrease is small at lower temperatures it becomes significantly large at higher temperatures. This behaviour can be expected because of the usual increase of volumes of liquids caused by thermal expansion as liquids are heated up. The decrease in densities of the experimental solutions followed the same pattern as that of water.

The effect of concentration of electrolytes on densities is also shown in Figure 2. Densities increase with an increase in salt and/or acid concentration. However, the effect of zinc and iron concentrations seemed to be larger than that for sulphuric acid. For example, for the solution containing 110 g/L zinc, 5 g/L acid and 1 g/L iron, the density was about 27% higher than that of pure water, whereas, the density was only about 21% higher than that of water for the solution containing 60 g/L acid and 75g/L zinc.

Some reddish brown precipitates (probably of a complex iron salt) were produced from the solution containing 110 g/L zinc, 5 g/L acid and 1 g/L iron during the density determination at 428 and 468 K (155 and 185°C). Similar precipitates have been reported in pressure leaching for leach processes conducted under low acidity, where precipitates are caused by formation of plumbojarosite ($PbFe_6(SO_4)_4(OH)_{12}$) (Chalkley and Weir, 1983). However, there was no evidence that the precipitates affected the overall densities of solutions determined by the dilation method, at temperatures where precipitates occurred. The density was higher than that of the corresponding solution which contained no iron and continued to follow the same pattern as for the rest of the solutions inspite of the occurrence of precipitates.

CONCLUSIONS AND RECOMMENDATIONS

Although the use of dilatometers to measure density of solutions is cumbersome compared to the use of a density meter, dilatometers can be used effectively in determining densities of corrosive solutions at elevated temperatures. The use of dilatometers for determining densities of solutions at high temperatures is reliable and practical. Except for the cathetometer, the dilatometer tubes can be made locally in Tanzania. Taking into account expenses involved in acquisition of a density meter while such an expensive equipment is limited on operation temperature and can be corroded, the use of dilatometers for determining densities of corrosive solutions at high temperatures is an attractive option.

NOMENCLATURE

A - Cross sectional area of a dilatometer tube; m^2
Le - Length of solution inside dilatometer tube; m
r - Correction factor
T - Temperature; K

Greek Letters

κ - Density calibration constant, $kg/(m^3/s)$
ρ - Density, kg/m^3
τ - Vibrating frequency, s^{-1}

Subscripts

a - Actual value
E - Value for Ethylene glycol
me - Measured value
T - Value at temperature T
W - Value for water
1 - Value at initial conditions

REFERENCES

Castellan G.W., Physical Chemistry, Addison-Wesley, (1983).

Chalkley M.E. and Weir D.R., Miniplant Pressure Leaching of Zinc, Paper Presented at the 13th Annual Hydro-metallurgical Meeting of the CIM Metallurgical Society, Edmonton, Canada, (1983).

Gallant R.W., Physical Properties of Hydrocarbons, Gulf Publishing Co., Houston, Texas, (1968).

Keenan J.H., Steam Tables, (1969).

Kimweri H.T.H., Solubility of Oxygen in Aqueous Sulphuric Acid-Metallic Salt Solutions under Pressure Leaching Conditions, M.A.Sc. Thesis, University of Ottawa, (1990).

Perry R.H. and Green D.W., Perry's Chemical Engineers' Handbook, Sixth Edition, McGraw Hill, (1984).

Sohnel O. and Novotny P., Densities of Aqueous Solutions of Inorganic Substances, Elsevier Science Publishing Company, (1985).

Wong C.F. and Hayduk W., Molecular Diffusivities for Propene in 1-Butanol, Chlorobenzene, Ethylene Glycol, and n-Octane at Elevated Pressures, *J. Chem. Eng. Data*, **35**, 3, (1990).