

# **The Electrical Conductivity of $\text{SmCl}_3$ Aqueous Solutions in The Sub and The Supercritical State**

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## **Abstract**

The electrical conductances of  $\text{SmCl}_3$  aqueous solutions were measured in the temperature range 373 K- 673 K at pressures up to 37.27 MPa, using a flow type electrical conductance cell. By using the measured electrical conductance values, the specific conductance,  $\sigma$ , and the equivalent conductance,  $\Lambda$ , were calculated. The maximum electrical conductance was obtained in the sub critical region at about 548 K. The effect of concentration on both of the specific and equivalent electrical conductance was studied in the concentration range 0.001- 0.009 M. The equivalent conductance was found to increase with the decrease in the concentration. The equivalent conductance at infinite dilution and the association constants were calculated.

**Keywords:** Electric conductance;  $\text{SmCl}_3$ ; Supercritical water; Subcritical water.

## Introduction

Electrical conductance measurements can be used to determine the extent of ionic behavior versus association of a dissolved aqueous electrolyte on the basis of the conductance theories. The concentration of the associated species can be obtained from the measured conductance if the conductance behavior of the completely ionized electrolyte under the same conditions of temperature and pressure can be calculated or estimated. If the conductance measurements were carried out at the sub or the supercritical state, they provide us with accurate information about the degree of association of electrolyte solutions, which have the tendency to associate at high temperature.<sup>1</sup> Besides, such measurements can provide complementary information required for various thermodynamic studies such as volatility,<sup>2</sup> isopiestic<sup>3</sup> and calorimetric<sup>4</sup> measurements. Moreover, they are of great importance for studies such as corrosion, diffusion and deposition processes in hydrothermal processes.

Noyes et al were the first to realize these phenomena when they developed their apparatus to measure the electrical conductance of several electrolytes up to 579 K at saturated water vapor pressure. They managed to study the conductance and the ionization behavior of several common electrolytes. Their work was extended to the calculation of water ion-product from the conductance measurements of ammonium acetate.<sup>5</sup>

An extensive work was focused on measurements of the conductance of alkali metal halide solutions at elevated temperature and pressure by Fogo et al,<sup>6</sup> E. Frank,<sup>7,8</sup> A. Quist, and W. Marshall.<sup>9,10</sup> On contrary, the rare earth salts did not attract many researchers to study the electrical conductance of their solutions. Some investigations were reported by F. Spedding and his co-workers, who studied the electrical conductance of some rare earth salts solutions at 298 K and 0.1 Mpa.<sup>11-15</sup> The first attempt to study the electrical conductance of some rare earth halide solutions at elevated temperature and pressures were reported in 2003.<sup>16,17</sup> Unfortunately, these two studies did not measure the concentration effect . Recently, supercritical water has been suggested as a medium for several reactions. There is a research project to study different complexation reactions of rare earth elements and actinide elements supported by the Japan Society for Promotion of Science. One of the best ways to measure the concentration of these elements during the reactions at the supercritical state is to measure their electrical conductance and to compare it with predetermined values at the same conditions.

Therefore, in this work, it is aimed to explore the concentration effect on the electrical conductance of  $\text{SmCl}_3$ , as an example of the rare earth chloride, and to calculate both of the equivalent conductance at infinite dilution,  $\Lambda_0$ , and the association constant,  $K_a$ .

## Experimental

The essential features of the cell used are shown in Fig. 1, while Fig. 2 shows a schematic representation of the whole apparatus used for the measurements. The detailed descriptions of the cell and the apparatus as well as the measurement procedure are exactly similar to that one described before.<sup>16,17</sup>

## Results and Discussion

The electrical conductances of 0.003, 0.006 and 0.009 M SmCl<sub>3</sub> in aqueous solutions were measured in the temperature range 373 K- 673 K and at pressures up to 37.27 MPa. The specific conductance,  $\sigma$ , was calculated according to:

$$\sigma = k S \quad (1)$$

where  $k$  is the cell constant and  $S$  is the conductivity meter measurement. There was no need for any correction for the solvent contribution to the measured electrical conductance values as the conductivity of H<sub>2</sub>O used as solvent was four orders of magnitude less than the measured values of the prepared solutions at 298 K and 0.1 MPa. Besides, Quist and Marshall had shown that at 100 MPa and 298-773 K, the water conductance is still very

small, on the order of  $1-5 \times 10^{-5} \text{ S. cm}^{-1}$ ,<sup>18</sup> which is still two orders of magnitude less than the measured values of the prepared solutions. Regarding corrosion effect, there was no need for any correction for the corrosion contribution to the measured electrical conductance values as all cell parts in contact with solutions are made of highly pure Pt-Ir alloy of which corrosion is expected to be minimum. Moreover, the corrosion products contribution was minimized by measuring the conductance while the solutions flow at a rate of 0.1-0.2 ml / min. Therefore, the contribution of the solvent and the corrosion products to the electrical conductance was ignored.

Tables 1-3 show the specific conductance of 0.003, 0.006 and 0.009 M  $\text{SmCl}_3$  solutions in aqueous solutions in the temperature range 373 K- 673 K and the pressure range 4.9 MPa – 37.27 MPa, respectively. The error of these data is less than 5% except in the case of solutions of very low density ( $\rho < 300 \text{ Kg m}^{-3}$ ), where it was found to be 6-10 %. These specific conductance data were used to calculate the equivalent conductance according to:

$$\Lambda = 1000 \sigma / z M \rho \quad (2)$$

where  $M$  is the solution molality,  $\rho$  is the solution density and  $z$  is the valency. As all the solutions studied were very diluted, it is possible to assume that the solution density is equal to  $\text{H}_2\text{O}$  density at the same temperature and pressure. The different values of  $\text{H}_2\text{O}$  density at different

temperatures and pressures were obtained from the steam tables.<sup>19</sup> The calculated values of the equivalent conductance,  $\Lambda$ , are given in tables 4-6. Fig. 3 shows the effect of increasing the concentration of  $\text{SmCl}_3$  solution on the equivalent conductance in the concentration range 0.001-0.009 M at 37.27 MPa and different temperatures. It can be noted from Fig. 3 that, the increase in concentration decreases the equivalent conductance, which is the common trend known for all electrolytes. This can be due to the increase of the associated species with the increase in concentration.

In the temperature range, 373 K ~ 525 K, the increase in temperature increases the equivalent conductance. The increase of temperature, in that region, leads to the decrease in the viscosity of the solutions, which increases the ion mobility, which in turn increases the conductance. On the other hand, increasing the temperature decreases the density of the solutions,<sup>20</sup> i.e. reduces the charge carriers per unit volume, which in turn reduces the conductance. It is clear that in all concentrations, the effect of viscosity reduction is the predominant factor in that temperature region.

At temperatures higher than around 525 K, the increase in the conductance with the increase in temperature is much smaller and finally diminished at 550 K. This might be due to the fact that the viscosity does not sharply decrease with the increase in temperature in that region. Therefore, the ionic mobility does not increase rapidly with the increase in temperature compared with the lower temperature region discussed

previously. Besides, in this temperature region, the density continues to decrease with the increase in temperature. The increase of temperature and the decrease of density highly reduce the dielectric constant and enhance ion association. As a result, the charge carriers per unit volume are reduced, which in turn acts to reduce the specific conductance. The effect of the high ionic mobility due to the viscosity reduction seems to be balanced with the decrease of the charge carriers per unit volume for the same solution due to density decrease effect and the ion association effect at about 550 K and the equivalent conductance reaches a maximum.

By increasing the temperature above 550 K approaching the critical point of the solutions, the reduction of the charge carriers per unit volume due to density decrease effect and the ion association effect is predominant and the equivalent conductance starts to decrease with the increase in temperature. Above the critical point, the density decreases much more sharply while the viscosity keeps decreasing at about the same low rate. Consequently, the dielectric constant of the solvent is highly decreased, the ion association is highly increased and the charge carriers per unit volume are highly reduced resulting in faster reduction in the specific conductance. The rate by which the conductance of 0.001 M solution increases in the first temperature range, 373 K ~ 525 K, and the rate by which it decreases in the second temperature range, above 550 K, is much higher compared with the other 3 more concentrated solutions. This also can be attributed to

the ion association effect, which increases with the increase in concentration. The response of the system to the changes in medium density and viscosity in case of concentrated solutions is smaller compared with the less concentrated one.

The conductance data for  $\text{SmCl}_3$  as a function of temperature, density and concentration allowed the calculation of the limiting equivalent conductance, equivalent conductance at infinite dilution, and a preliminary evaluation of the association equilibrium. Due to the nature of the experiment and the increased uncertainty at low density, the conductance measurements do not give enough information about the exact nature of the remaining charge carriers at such low density. Besides, it is not possible to get information about the associated (neutral) ion pairs. Therefore, following the assumptions of Marshall and co-workers,<sup>9,10,18</sup> and the analysis method given by Goemans and co-workers both of the equivalent conductance at infinite dilution, and the preliminary evaluation of the association equilibrium were calculated.<sup>21</sup> As a first step, the initial estimate of the equivalent conductance at infinite dilution,  $\Lambda_0$ , can be calculated using Onsager equation:

$$\Lambda = \Lambda_0(A + B\Lambda_0)I^2 \quad (3)$$

where  $I$  is the ionic strength and can be calculated from:<sup>21</sup>

$$I = M\rho_w \quad (4)$$



when association is highly expected Shedlovsky equation can be applied:

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_o} + \frac{M\rho_w S(z) f_{\pm}^2 \Lambda}{K_a \Lambda_o^2} \quad (5)$$

where  $f_{\pm}$  is the mean molar activity coefficient of the ions,  $K_a$  is the molar ion-pair association constant and  $S(z)$  is an adjusting parameter which is a function of the molar concentration, the limiting equivalent conductance, and the limiting Onsager slope. The mean molar activity coefficient was calculated according to Marshall and co-workers:

$$f_{\pm} = \text{EXP10}\left(\frac{-0.509 I^{0.5}}{1 + I^{0.5}}\right) \quad (6)$$

Equation 5 can be rearranged to be:

$$\Lambda = \frac{\frac{-S(z)}{\Lambda_o} + \sqrt{\frac{S(z)^2}{\Lambda_o^2} + \frac{4M\rho_w S(z)^2 f_{\pm}^2}{K_a \Lambda_o^2}}}{\frac{2M\rho_w S(z)^2 f_{\pm}^2}{K_a \Lambda_o^2}} \quad (7)$$

Finally values of  $\Lambda_o$  and  $K_a$  and  $S(z)$  were calculated by minimizing the sum of the squares:

$$\sum (\Lambda_{\text{Experimental}} - \Lambda_{\text{Calculated}})^2 \longrightarrow 0 \quad (8)$$

assigning equal weight to all concentrations. The resulted limiting equivalent conductance data as well as the association constants at different temperatures and densities are shown in table 7. The uncertainty in these data is expected to be less than 1%. The values of the negative logarithm of the association constant, pKa, indicates that partial

association takes place between  $\text{Sm}^{3+}$  ions and  $\text{Cl}^-$  ions even at moderate all temperatures and densities. This was not the case of other alkaline salts reported by Goemans and co-workers, where partial association was detected only at  $300^\circ\text{C}$  and density smaller than  $750 \text{ kg/m}^3$ . Such findings suggest that the association of the rare earth salts is much higher compared with alkali salts. Fig. 4 shows the change in the  $\text{p}K_a$  with medium density regardless the system temperature. It can be easily detected that the decrease in density, increases the association constant, which agrees with the findings of Marchall and co-workers,<sup>9,10,18</sup> Goemans and co-workers<sup>21</sup> and Ho and co-workers.<sup>1</sup>

#### 4. Conclusion

The electrical conductances of  $\text{SmCl}_3$  aqueous solutions were measured in the temperature range 373 K- 673 K at pressures up to 37.27 MPa using a flow type electrical conductance cell. The measured electrical conductance values were used to calculate the specific conductance,  $\sigma$ , and the equivalent conductance,  $\Lambda$ . The maximum electrical conductance for all concentrations was obtained in the sub critical region at about 550 K. The equivalent conductance was found to decrease with the increase in the concentration through the entire temperature and pressure range studied. The equivalent conductance at

infinite dilution,  $A_o$ , and the association constants were calculated. The association of the rare earth salts was found to be much higher compared with alkali salts.

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Table 1 Specific conductance of 0.003 M SmCl<sub>3</sub> in H<sub>2</sub>O (S cm<sup>-1</sup> x 10<sup>-3</sup>)

Pressure (MPa)	Temperature (K)								
	373	473	523	548	573	598	623	648	673
9.81	2.575	4.385	4.573	4.340					
14.71			4.595	4.362	4.029	3.741			
19.61	2.586	4.396	4.607	4.385	4.052	3.785	3.341	2.675	
24.52		4.396	4.640	4.429	4.085	3.818	3.452	2.864	1.798
26.97							3.508	2.953	1.887
29.42	2.586	4.407	4.673	4.462	4.107	3.874	3.574	3.019	2.087
31.87							3.641	3.108	2.187
34.32		4.407	4.706	4.507	4.107	3.918	3.696	3.197	2.375
37.27	2.597	4.407	4.729	4.540	4.107	3.974	3.774	3.241	2.420

Table 2 Specific conductance of 0.006 M SmCl<sub>3</sub> in H<sub>2</sub>O (S cm<sup>-1</sup> x 10<sup>-3</sup>)

Pressure (MPa)	Temperature (K)								
	373	473	523	548	573	598	623	648	673
9.81	3.008	5.839	5.828	6.050					
14.71			5.872	6.005	6.027	5.583			
19.61	3.041	5.883	5.916	6.016	6.038	5.794	5.073	4.151	
24.52		5.905	5.950	6.016	6.083	5.861	5.117	4.373	2.775
26.97							5.184	4.407	3.053
29.42	3.064	5.916	5.994	6.038	6.127	5.850	5.228	4.540	3.197
31.87							5.261	4.573	3.297
34.32		5.939	6.038	6.094	6.205	5.861	5.306	4.684	3.374
37.27	3.097	5.950	6.061	6.116	6.283	5.872	5.395	4.817	3.541

Table 3 Specific conductance of 0.009 M SmCl<sub>3</sub> in H<sub>2</sub>O (S cm<sup>-1</sup> x 10<sup>-3</sup>)

Pressure (MPa)	Temperature (K)								
	373	473	523	548	573	598	623	648	673
9.81	3.130	6.982	7.837	7.992					
14.71			7.903	8.025	6.982	6.360			
19.61	3.141	7.060	7.925	8.059	7.015	6.471	5.717	4.529	
24.52		7.093	7.959	8.059	7.015	6.505	5.883	4.762	3.074
26.97							5.983	4.873	3.119
29.42	3.164	7.137	7.981	8.147	7.015	6.582	6.038	4.928	3.297
31.87							6.094	5.051	3.419
34.32		7.160	8.025	8.292	7.049	6.660	6.161	5.095	3.508
37.27	3.164	7.193	8.025	8.314	7.137	6.749	6.227	5.239	3.630

Table 4 Equivalent conductance of 0.003 M SmCl<sub>3</sub> in H<sub>2</sub>O (S cm<sup>2</sup> eq<sup>-1</sup>)

Pressure (MPa)	Temperature (K)								
	373	473	523	548	573	598	623	648	673
9.81	297.2	559.3	630.4	636.2					
14.71			629.3	632.6	616.9				
19.61	297.0	556.1	626.9	629.7	612.5	636.5	618.5		
24.52		554.0	627.7	630.6	610.6	624.8	613.7	630.7	
26.97							613.9	611.3	
29.42	295.7	553.3	628.6	630.2	607.7	621.0	617.1	601.2	656.4
31.87							621.5	603.3	600.3
34.32		551.3	629.7	631.8	601.9	617.7	623.7	604.4	557.1
37.27	295.9	550.1	630.8	633.8	598.8	621.1	629.5	599.8	535.0

Table 5 Equivalent conductance of 0.006 M SmCl<sub>3</sub> in H<sub>2</sub>O (S cm<sup>2</sup> eq<sup>-1</sup>)

Pressure (MPa)	Temperature (K)								
	373	473	523	548	573	598	623	648	673
9.81	173.6	372.4	401.6	443.4					
14.71			402.0	435.4	461.4				
19.61	174.7	372.2	402.6	432.1	456.4	487.2	469.6		
24.52		372.1	402.4	428.3	454.6	479.5	454.9	481.6	
26.97							453.7	456.2	
29.42	175.1	371.4	403.2	426.4	453.3	468.9	451.4	452.0	502.8
31.87							449.1	443.8	452.5
34.32		371.5	404.0	427.1	454.7	462.0	447.6	442.8	395.7
37.27	176.4	371.4	404.2	426.9	458.0	458.9	449.9	445.7	391.4

Table 6 Equivalent conductance of 0.009 M SmCl<sub>3</sub> in H<sub>2</sub>O (S cm<sup>2</sup> eq<sup>-1</sup>)

Pressure (MPa)	Temperature (K)								
	373	473	523	548	573	598	623	648	673
9.81	120.4	296.9	360.1	390.5					
14.71			360.7	387.9	356.3				
19.61	120.3	297.7	359.5	385.8	353.5	362.7	352.8		
24.52		298.0	358.9	382.5	349.5	354.8	348.6	349.6	
26.97							349.1	336.3	
29.42	120.6	298.7	357.9	383.6	346.0	351.7	347.5	327.1	345.7
31.87							346.7	326.8	312.9
34.32		298.6	357.9	387.5	344.4	350.0	346.5	321.1	274.2
37.27	120.1	299.3	356.8	386.9	346.9	351.6	346.2	323.2	267.5

Table 7 Limiting equivalent conductance and association constant

Temperature, K	Density, g/cm <sup>3</sup>	$\Lambda_o^*$	$\Lambda_o$	pKa
473	0.871	856.3	867.7	2.86
473	0.878	869.9	881.9	2.86
473	0.882	871.8	883.6	2.86
473	0.885	882.7	894.4	2.87
473	0.888	885.1	896.6	2.87
473	0.890	890.0	901.0	2.87
523	0.806	1229.9	1263.9	3.05
523	0.811	1262.2	1295.0	3.05
523	0.816	1279.8	1311.8	3.06
523	0.821	1296.2	1328.6	3.06
523	0.826	1306.9	1338.2	3.06
523	0.830	1320.0	1350.0	3.06
523	0.833	1333.5	1363.1	3.06
548	0.766	1368.6	1403.8	3.08
548	0.774	1399.4	1434.4	3.09
548	0.780	1414.7	1448.2	3.09
548	0.787	1438.5	1470.6	3.09
548	0.793	1458.7	1487.9	3.08
548	0.796	1460.6	1488.5	3.08
573	0.726	1415.5	1456.9	3.14
573	0.735	1433.1	1474.8	3.14
573	0.743	1457.9	1498.1	3.14
573	0.751	1456.9	1497.2	3.14
573	0.758	1463.6	1503.2	3.14
573	0.762	1470.7	1510.6	3.14
598	0.661	1521.4	1578.2	3.22
598	0.679	1513.0	1572.7	3.21
598	0.693	1504.6	1564.1	3.21
598	0.705	1495.5	1553.9	3.20
598	0.711	1495.9	1552.3	3.19
623	0.600	1531.5	1591.3	3.27
623	0.625	1519.6	1581.6	3.26
623	0.635	1517.7	1580.0	3.26
623	0.644	1506.6	1566.9	3.25
623	0.651	1497.7	1556.0	3.24
623	0.659	1491.4	1549.2	3.23
623	0.666	1485.0	1541.5	3.22

\* From Onsager equation.



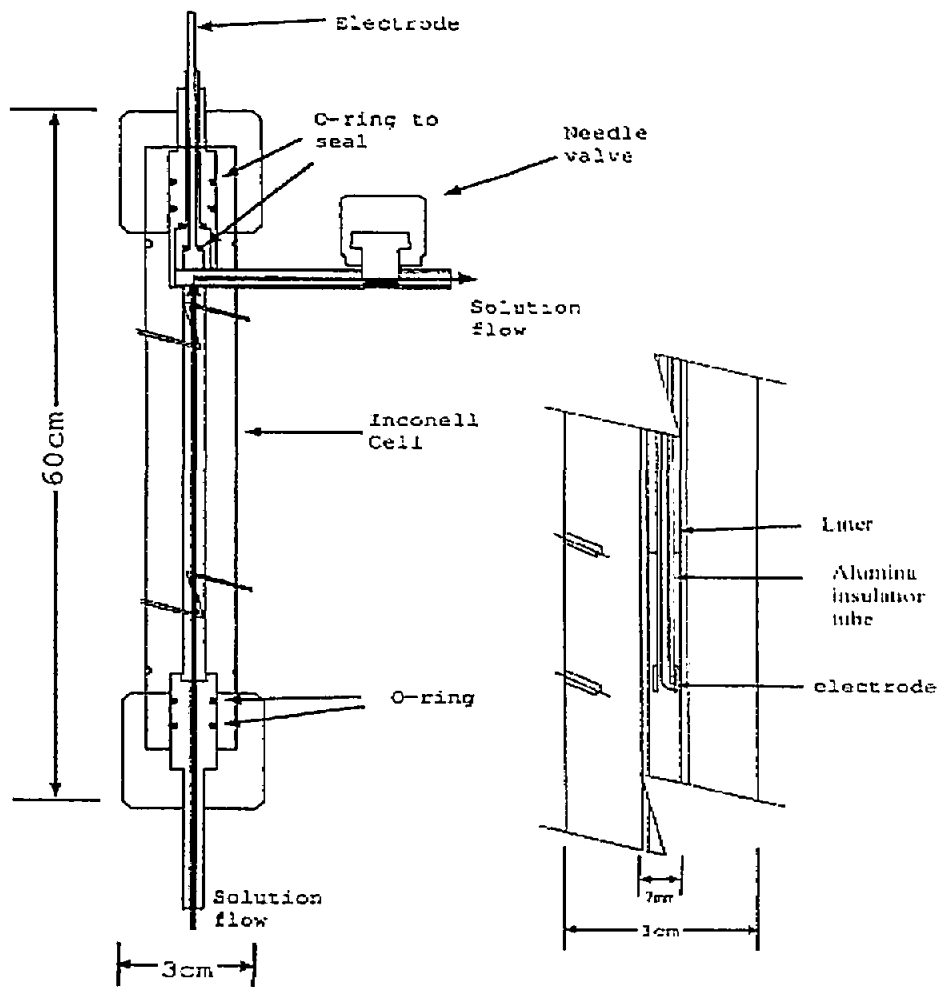


Fig. 1 The flow type conductance cell

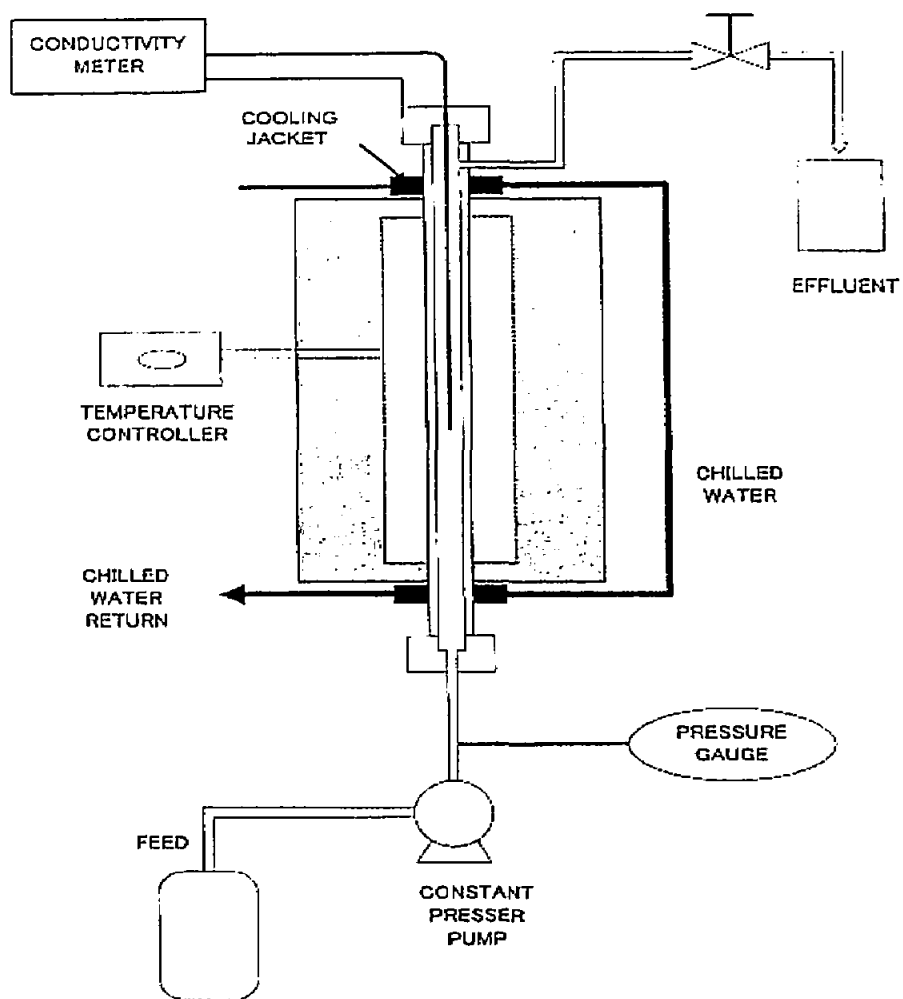


Fig. 2 Schematic representation of the whole apparatus used

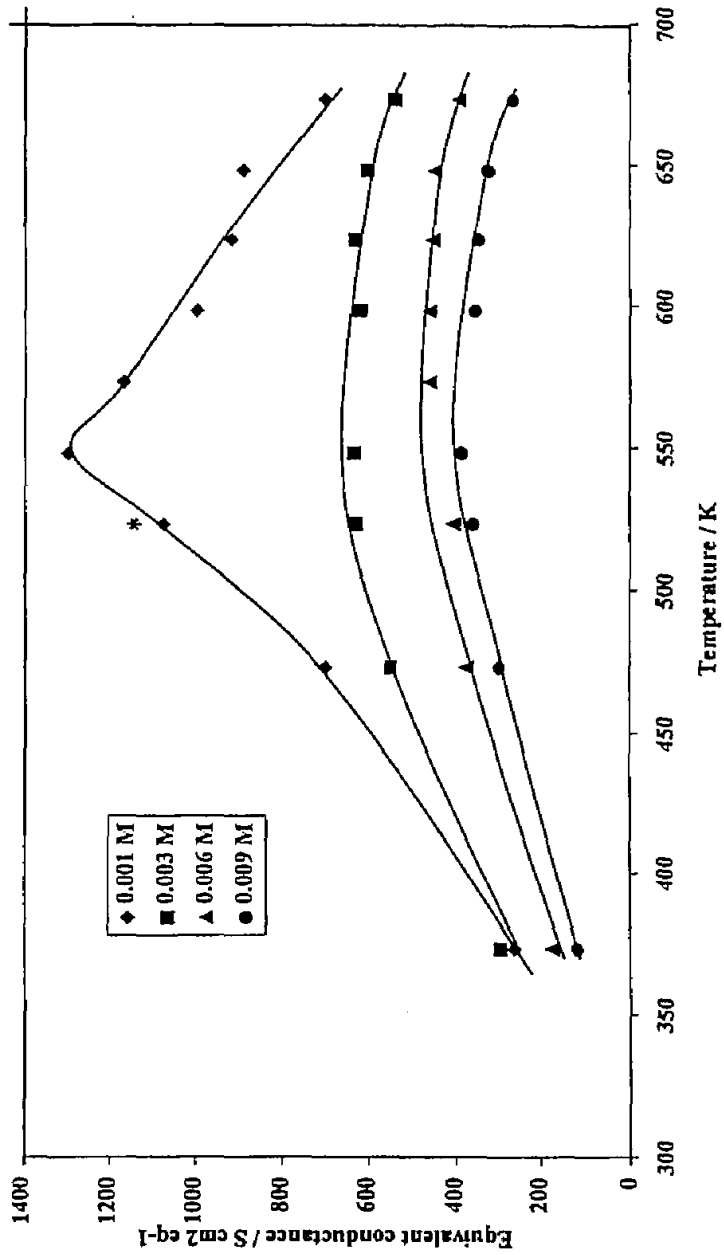


Fig. 3 Effect of concentration on the equivalent conductance of SmCl<sub>3</sub> at different temperatures; \* data from reference 16

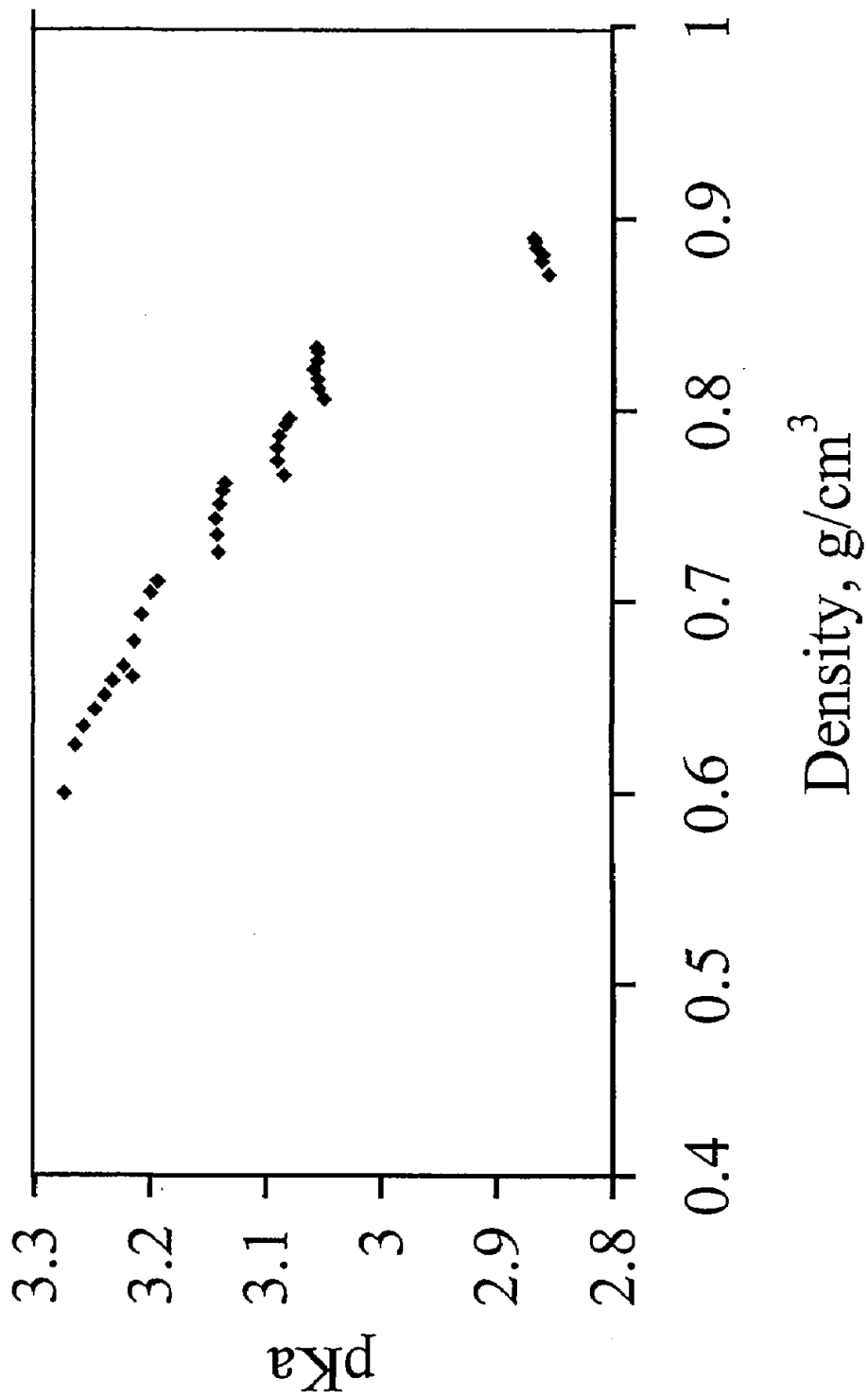


Fig. 4 Effect of medium density on association constant.