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Effect of density on the electrical conductance of aqueous sodium chloride solutions

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Concentrated sodium chloride solutions are commonly used in electrochemical machining and a knowledge of their conductance is important. A study was made of the conductivity of a range of concentrations from 0·01 M to 5 M to temperatures >500°C and to pressures of 2000 bar. The conductances were found to go through maxima at 250–300°C after increasing in magnitude by a factor of >4.

1. Introduction

Electrochemical machining, ECM, is a form of accelerated corrosion where the workpiece is made the anode in an electrolytic cell [1] and where highly conducting electrolyte is pumped rapidly between the electrodes to allow for high currents and high rates of metal removal. The pH of the electrolyte is important as it usually governs the dissolution kinetics; subsequently salts rather than acids are frequently preferred and sodium chloride is commonly used.

A number of studies of conductance to high temperatures have been made [2–13], one of which (Reference 9) deals with sodium chloride. However, these authors only studied concentrations up to 0·1 M although their temperature and pressure ranges were greater than those used in the present work.

Electrical conductance is a well-suited technique to study electrolytic solvents. By varying pressure and temperature the dielectric constant can be varied over a wide range and the change of ionic dissociation studied. At the same time the viscosity can be reduced [14] thus producing high ionic mobilities, and the purpose of the present work was to study the magnitude of the increase in mobility with a view to a possible use of high temperature electrolytes in ECM.

The work entailed the study of the electrical conductance of sodium chloride solutions to over 500°C and over 2000 bar. The concentrations studied were 0·01 M, 0·1 M, 0·5 M, 1 M, 3 M and 5 M. The large variation in specific conductivity required the use of a variety of cell constants and a number of cells of two basic designs were used.

2. Experimental

2.1. *Apparatus*

The pressure vessel used is shown diagrammatically in Fig. 1. The body of the cell was made from Nimonic 80A and was fitted with a gold liner of internal diameter 5 mm. The electrode lead was fed in at one end, the vessel body was the counter electrode, and a sheathed thermocouple was fed in at the other end. Thermocouples were also fitted to wells in the vessel body but were found to differ by up to 4°C from the inside couple, thus showing the necessity of a thermocouple immediately adjacent to the conductance path. The middle portion of the vessel was heated by an electric furnace with three independently controlled windings and the vessel ends were cooled by water collars. Electrolyte could be fed through from one end of the vessel to the other and was pressurized via a Teflon separator and hand-operated oil pump. The end fittings and pipes were of stainless steel and all internally gold lined. The internal thermocouple and electrode lead were set in crystallised alumina ('Lucalox', General Electric Co).

The cell area was set at the mid-point of the heated section and the cell designs are shown in

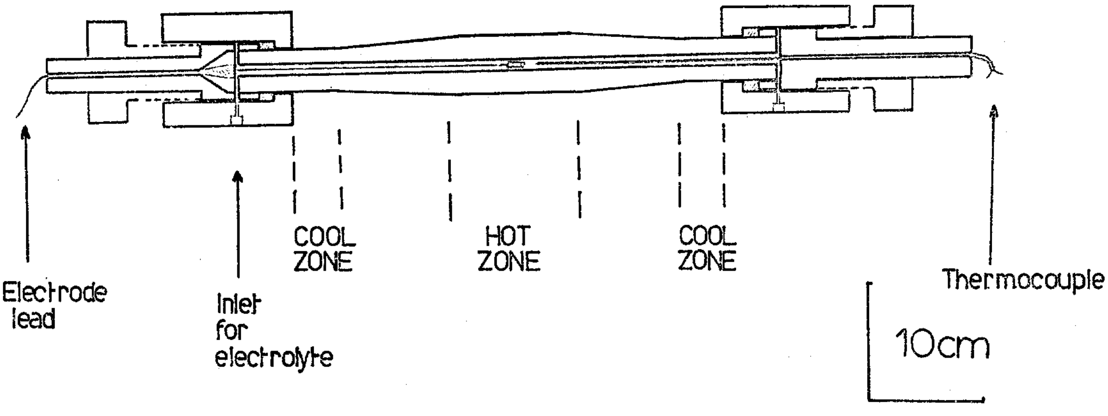

Fig. 1. The pressure vessel.

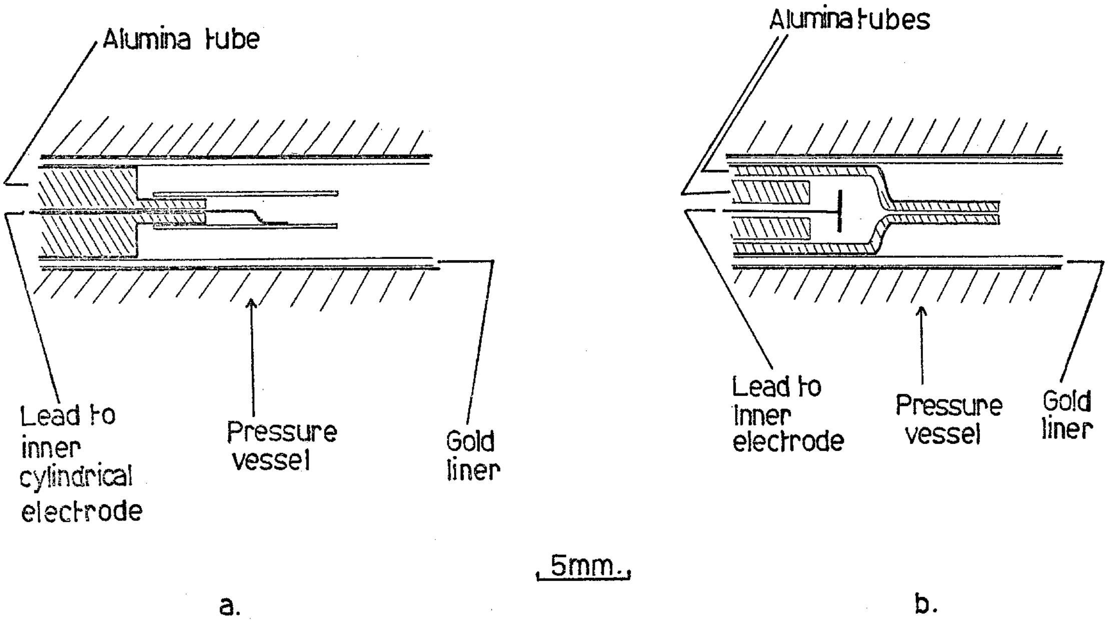

Fig. 2. The conductance cells.

Fig. 2. The low cell-constant type (a) was used for the dilute solutions and type (b) for the concentrated solutions. A variety of cell constants were obtained by varying the size of the electrode in type (a) or by varying the length of the capillary in (b). The platinum electrodes were platinized and displayed a negligible frequency dispersion over the temperature range studied.

A Wayne-Kerr B211 bridge with external generator and null detector were used and extrapolations of conductance to infinite frequency were found to vary by less than 0·1% from those at 10 kHz. Hence this frequency was used for the determinations.

Doubly distilled water and vacuum dried A.R. NaCl were used to make the solutions.

Pressures were measured with Bourdon gauges.

2.2. *Errors*

The design of the cells was such that the effect of temperature and pressure on the cell constant was found to be negligible. A source of error was that of the solvent background conductance, and it was found necessary to correct the conductances of the dilute solutions for the conductance of the water + impurities. After pressure- and temperature-cycling the water the background correction amounted to 1% for the 0·01 M solutions and was negligible for solutions more concentrated than 0·1 M. However, for the more concentrated solutions the lead resistances became important and corrections were made for those (< 1·5%).

The measured pressures were thought to be accurate to 2% and the temperatures to better than 0·5%.

Table 1. Specific conductance of NaCl solutions at 25°C [15]

Molarity	$\kappa.10^3\ \Omega^{-1}\ cm^{-1}$
0·01	1·1853
0·1	10·674
0·5	46·81
1	85·76
3	197·71
5	247·30

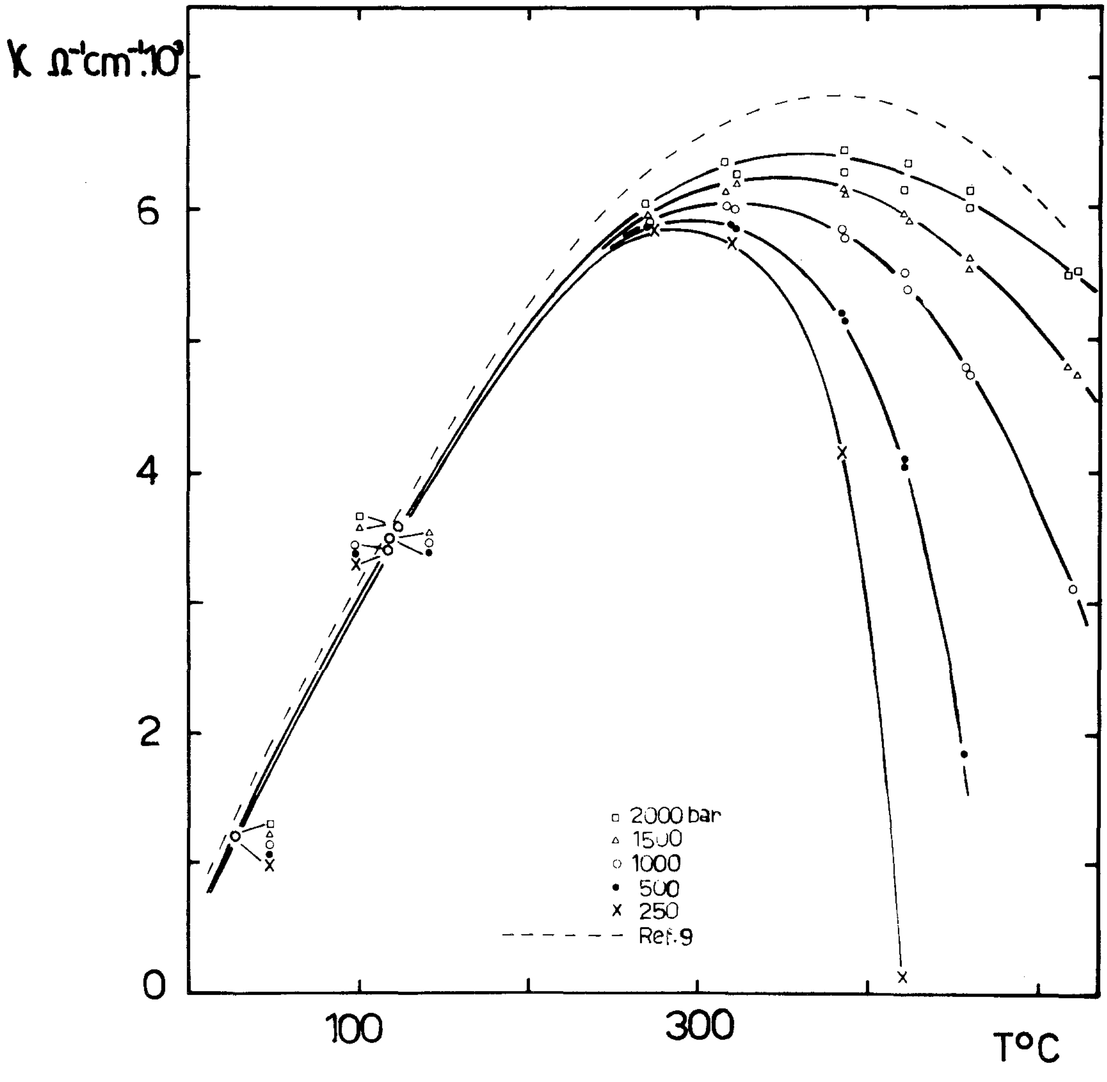

Fig. 3. Isobaric variation of specific conductance with temperature for 0·01 M NaCl solution.

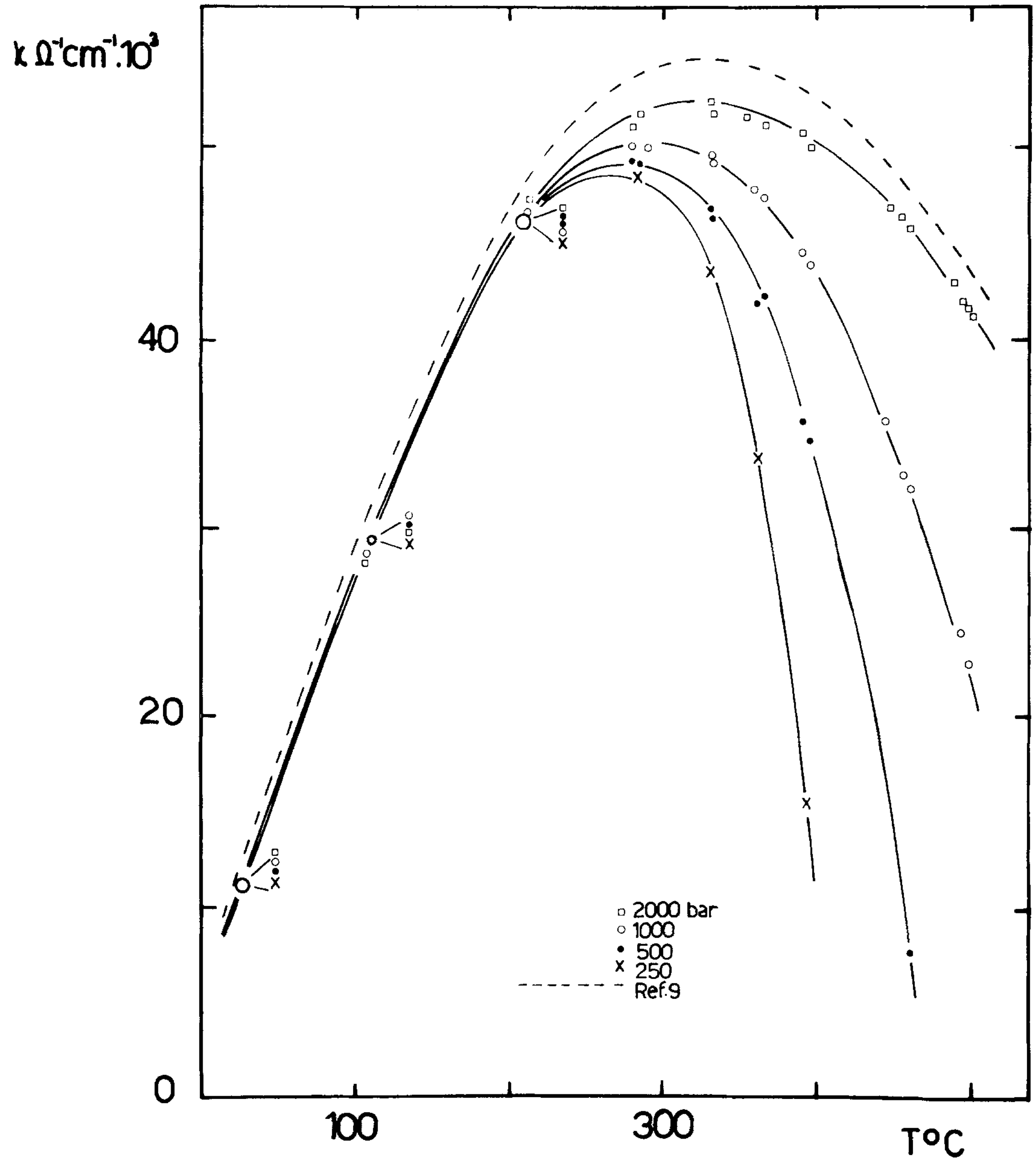

Fig. 4. Isobars for 0·1 M NaCl solution.

2.3. *Procedure*

The vessel was flushed through and temperature- and pressure-cycled several times for each solution studied, to ensure a constant and reproducible conductance at any temperature and pressure. Prior to their initial use the alumina parts were leached in water and sodium chloride solution for several days. The pressure was cycled stepwise at a constant temperature and conductance measurements made after allowing 2–3 min for equilibrium to be reached.

3. Results

The specific conductance for the six concentrations studied are presented as isobars in Figs. 3–8.

The recorded cell conductances were converted

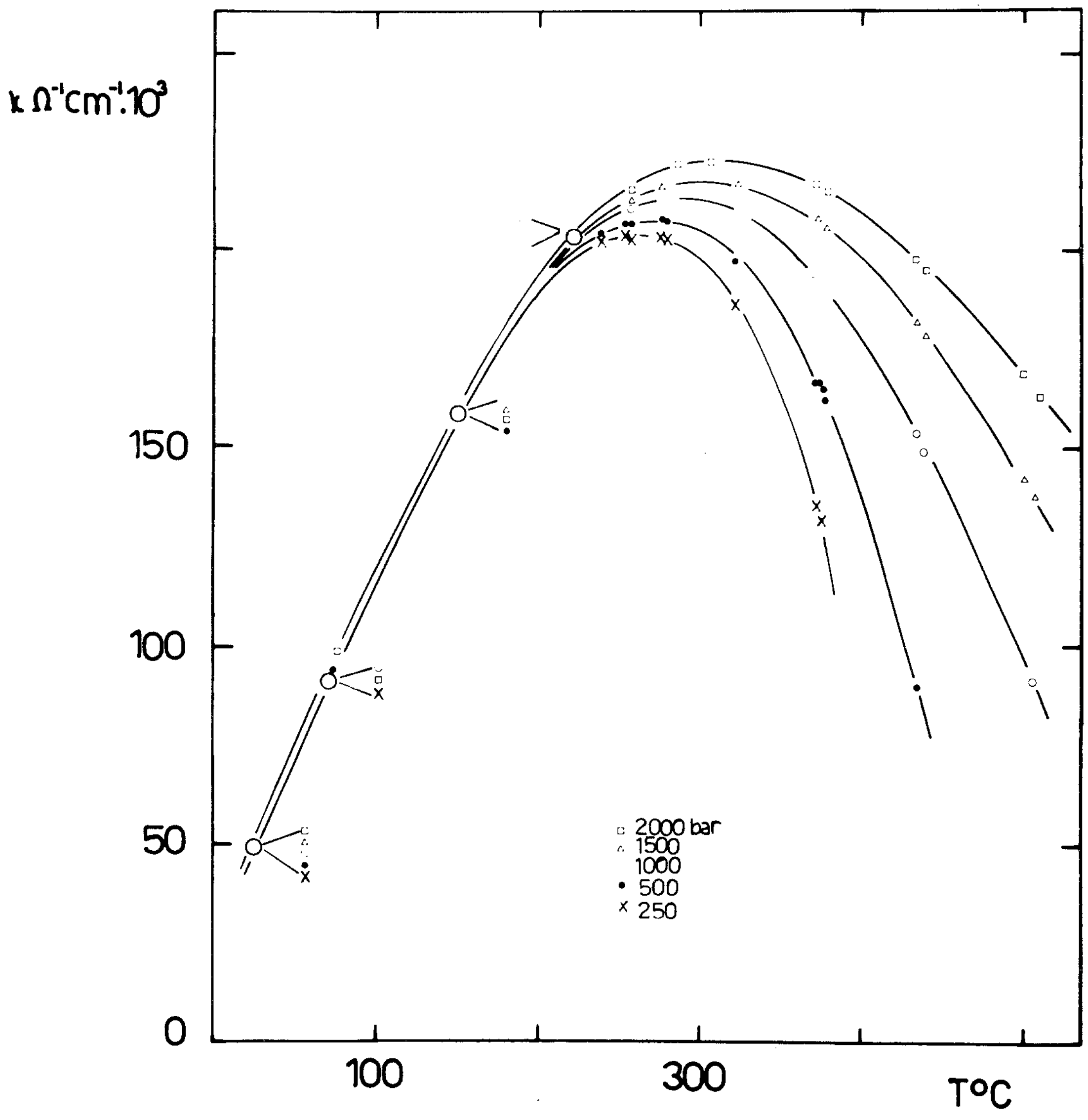

Fig. 5. Isobars for 0·5 M NaCl solution.

to specific conductances using the 25°C data in Table 1 extracted from Robinson and Stokes [15]. The 25°C cell conductance was taken as the lowest of the cluster of isobars; the pressure effect at this temperature was very small and it was felt that the error introduced in this way was negligible. A variety of cell constants were employed ranging from 0·329 for the 0·01 M solution to over 60 for the concentrated solutions.

4. Discussion

4.1. *Comparison with previous work*

In the present work cell conductances were determined which were converted to specific conductances using the literature values in Table 1. Specific conductances so computed differ by about 10% from those reported by Quist and Marshall [9] for

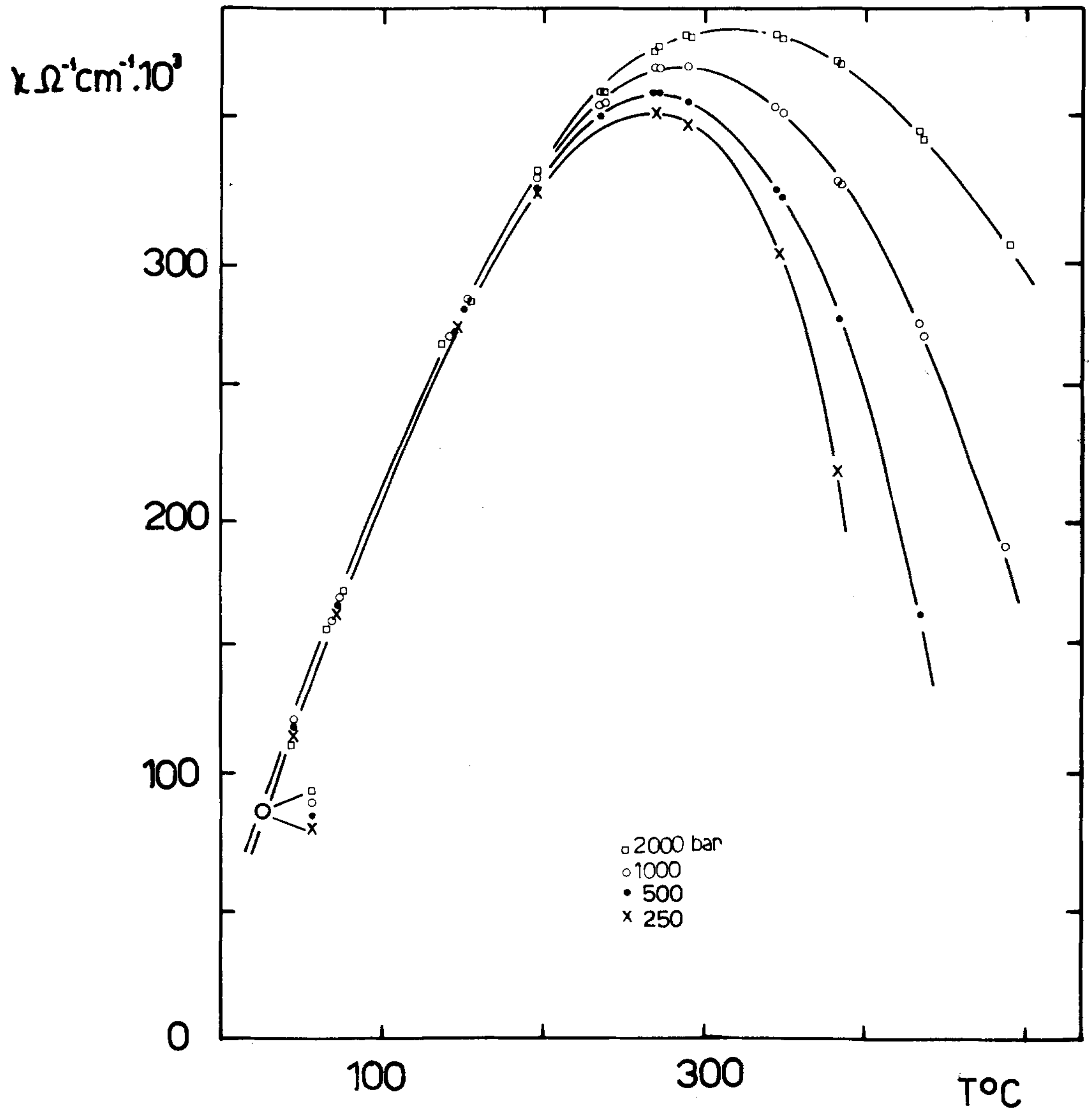

Fig. 6. Isobars for 1 M NaCl solution.

Table 2. Conductance χ $(\Omega^{-1}\,cm^{-1} \times 10^3)$ *at the temperature T(°C) of the peak*

Pressure (bar)	250		500		1000		1500		2000	
Molarity	*κ*	*T*	*κ*	*T*	*κ*	*T*	*κ*	*T*	*κ*	*T*
0·01	5·89	290	5:95	295	6·04	320	6·22	335	6·42	360
0·1	48·9	265	49·4	275	50·4	290	–	–	52·0	325
0·5	205	260	209	270	214	285	218	300	224	320
1	359	260	367	270	378	280	–	–	392	315
3	894	275	908	285	939	305	963	335	993	350
5	1150	290	1170	295	1200	320	–	–	1250	370

the 0·01 M and the 0·1 M solutions. This difference is retained throughout the studied temperature range and is displayed for the 2000 bar isobars as the dashed lines in Figs. 3 and 4. The more

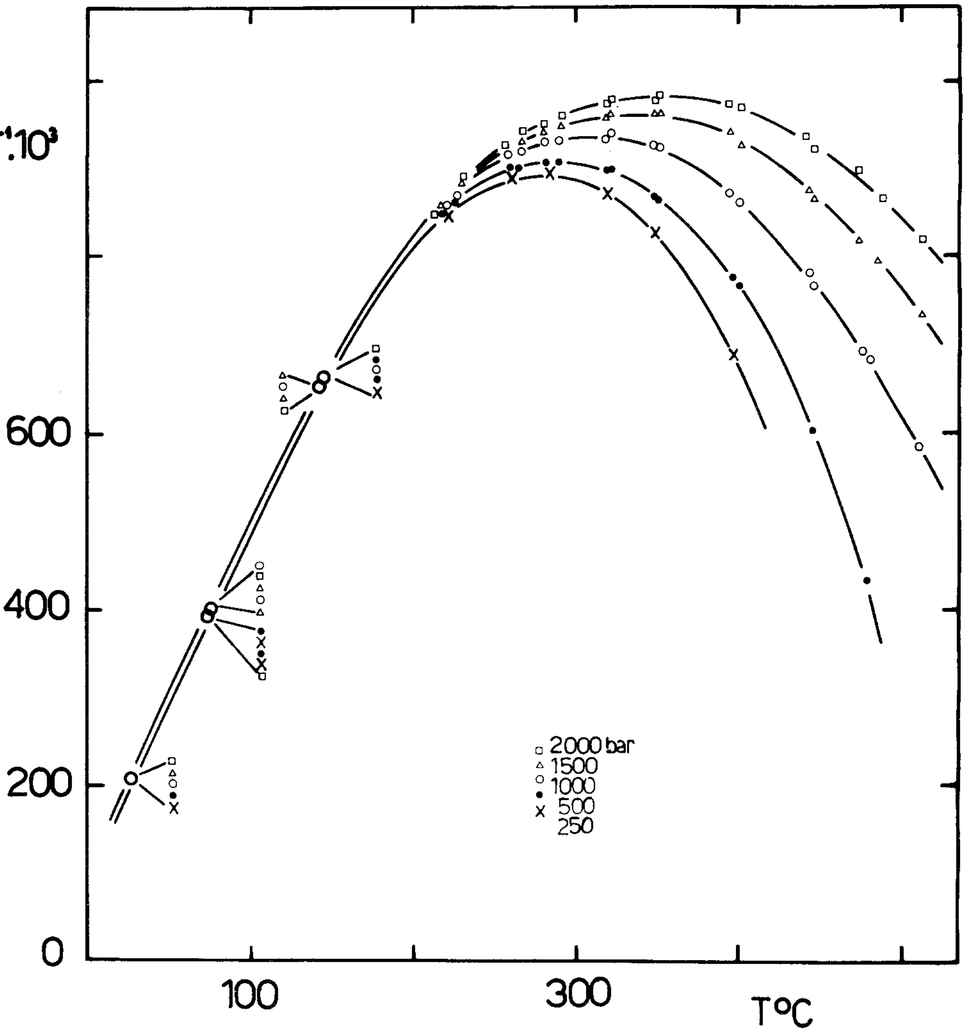

Fig. 7. Isobars for 3 M NaCl solution.

concentrated solutions have not previously been studied.

4.2. *The conductance maximum*

The specific conductance of all the solutions studied rose rapidly over the temperature range to 200°C with only a small effect of pressure. Within the precision of the results no cross over of the isobars could be claimed as recorded by Quist and Marshall [9]. Above 250°C maxima occurred in the isobars as recorded in Table 2 depending upon the applied pressure and upon the solution concentration. Up to the maxima the greatest relative rise in conductance occurred for the dilute solutions (see Table 3) but rises of >450% were still obtained for the more concentrated solutions. This is a considerable rise and should prove significant in ECM. It is seen that both the conductance maximum and the relative increase fall with increase in concentration to a minimum between 0·5 and 1 M, thereafter rising. For each concentration the temperature of the conductance maximum rises with increase in pressure, and the magnitude of the conductance at the maximum increases with concentration.

Two opposing effects occur as a result of increase in temperature. The conductance will tend to increase as a result of thermal agitation and because the structure of the solvent breaks down

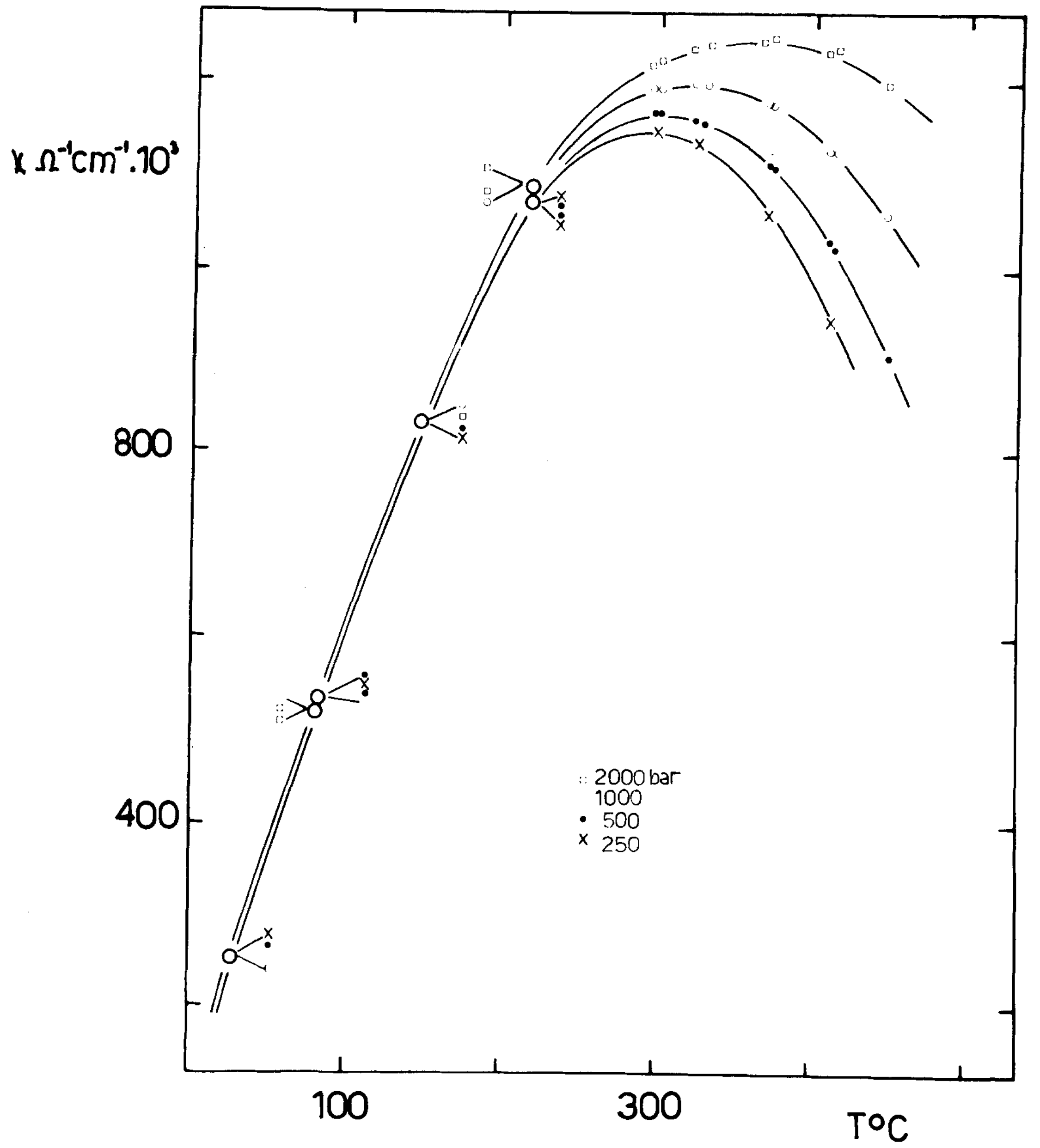

Fig. 8. Isobars for 5 M NaCl solution

(less viscous), but at the same time the number density of conducting species will be lowered as the density of the solvent decreases. These effects become balanced at the conductance maximum. The effect of salt concentration on the conductance maximum is presumably also a balancing of solvent destructuring and electrolyte density.

4.3. *The molar conductance*

A plot of molar conductance against density would be expected to reveal information on the structural changes occurring in the liquid. However, in the present work such plots were not made for two reasons. The first is that for the temperatures and

Table 3. Relative increase in conductance over that at 25 °C

Pressure (bar)	250	500	1000	1500	2000
Molarity					
0·01	4·82	4·88	4·93	5·11	5·26
0·1	4·39	4·44	4·50	–	4·61
0·5	4·19	4·28	4·38	4·47	4·53
1	4·15	4·22	4·28	–	4·35
3	4·32	4·40	4·53	4·65	4·75
5	4·54	4·62	4·74	–	4·94

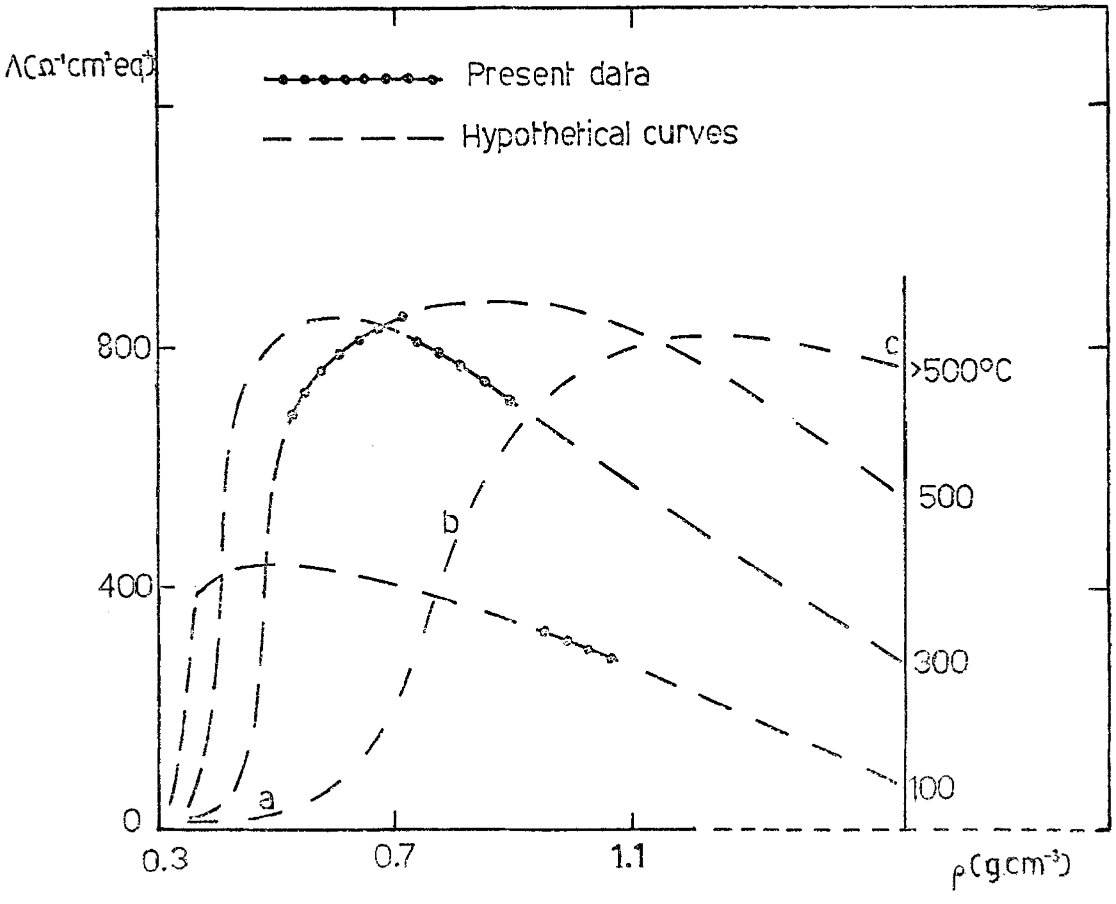

Fig. 9. Equivalent conductance as a function of density for 0·01 M NaCl solution.

pressures studied, the density range proved to be too short. The other reason is that such plots require precise density data for these solutions. For the dilute solutions, use of the data for pure water [16–18] is probably acceptable; for the more concentrated solutions the density variations cannot be assumed to be those of pure water, and the data available [19] are not precise enough for this application. The Λ/ρ plots for the two dilute solutions 0·01 M and 0·1 M were found to be essentially the same as reported [9] and an idealized plot may be constructed as shown in Fig. 9. From this, observations on the anticipated change of structure of the liquid may be compared with liquids of other types. Referring to the >500°C isotherm several different zones may be identified as follows. Zone (a) is a region of low conductivity at the low solution densities; the solvent has a low dielectric constant, there is much association and few migrating species. In zone (b) the conductivity increases as the number of migrating ions is increased. Zone (c) is one of falling conductivity at high pressures as the free volume is squeezed out of the liquid and the ion mobility is restricted. At the limit of high density, when the liquid becomes a glass (assuming crystallization does not interfere), the ionic mobility will become virtually zero. This model assumes the liquid to have a simple structure and departures may be found for solutions of salts other than 1:1 salts, particularly so if protons are involved in the dissociation [6–8]. In this case modes of migration of the Grotthus-chain type may arise as the protons are liberated.

The behaviour of the solutions whereby the low density order of the isotherms is reversed at high densities can be compared with behaviour reported for the molten salts. For example, liquids like mercury (II) iodide [20] which are largely associated and show 'abnormal' temperature dependence of conductance at low pressures, become 'normal' at high pressures and show temperature coefficients of the type shown by fused alkali nitrates and chlorides at the lower pressures [21]. Because of the structural nature of water it is not surprising that sodium chloride solutions behave abnormally. The constant volume activation energy

$$(E_\Lambda)_v = RT^2\left(\frac{\partial \ln \Lambda}{\partial T}\right)_v,$$

derived statistically [21] as

$$-R\left(\frac{\partial \ln \kappa}{\partial \frac{1}{T}}\right)_P + \frac{\alpha_p}{\beta_T}\, RT^2\left(\frac{\partial \ln \kappa}{\partial P}\right)_T,$$

where α and β are the expansivity and compressibility may be interpolated from Fig. 9 as changing from 'abnormal Arrhenius' values at low densities to positive 'normal' values at the higher densities, and this behaviour is probably unique in liquids. At least for HgI_2 there is evidence to suggest that the phenomenon is purely one of density, and at constant density the activation energies would all become positive [22]. Clearly there are structural changes brought about in water solutions by thermal changes even at constant volume. $(E_\Lambda)_v$ is highly volume dependent, and theories have been developed [23, 24] to acknowledge the importance of free volume in addition to $(E_\Lambda)_v$ at low volumes (high densities). Much work on melts and aqueous solutions that form glasses has been carried out in this low temperature region [25, 26]. It seems a liquid exists in a limited density range where the Arrhenius temperature dependence holds. The work on glasses shows that at high densities free volume rather than activation energy becomes important, and the present work shows that at low densities association occurs and activation energies decrease and may become negative. At any particular reference point, such as ambient temperatures, a liquid may be in any one of these regions with a corresponding temperature dependence of the conductance. These may also be closer together in some liquids than in others and the particular region should be pressure dependent because association decreases as pressure increases, and liquids which at atmospheric pressure show abnormal temperature dependence should become normal on the application of pressure. Density data on the concentrated solutions are not yet available, but to take this analysis further a system should be studied which is water soluble over the entire range of dilution to the molten salt [27].

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