A NEW METHOD FOR DETERMINING SORET COEFFICIENTS IN MOLTEN SALTS, EMPLOYING FIBRE-OPTIC SPECTROSCOPY

Trevor R. Griffiths and Nicolas J. Phillips
School of Chemistry, The University of Leeds, Leeds, LS2 9JT England

ABSTRACT

Soret coefficients are conventionally determined electrochemically from concentration measurements at two positions in a column of liquid exhibiting a thermal gradient. These concentration changes with temperature have not previously been recorded using absorption spectroscopy measurements and Beer's Law. Such measurements can be achieved with a fibre optic spectrophotometer and an accurately calibrated thermal gradient furnace, and many readings were taken, yielding statistically significant Soret coefficient values for Fe(III), Cr(III), and Ni(II) in molten LiCl-KCl eutectic and for Ni(II) in molten Li₂SO₄-Na₂SO₄-K₂SO₄ eutectic. The results were comparable to those obtained in aqueous systems. The necessary precautions are assessed and described. The high temperature systems chosen are probably the most severe test possible for this new technique for determining Soret coefficients.

INTRODUCTION

The Soret effect, the coupling of heat and material transport, is observed as diffusion. The presence of a temperature gradient within a solution gives rise to thermal diffusion processes such that the concentration becomes non-uniform with temperature, with usually the cooler regions becoming the more concentrated. This separation develops until it is exactly balanced by the thermal diffusion process and the system reaches a steady state, referred to as Soret Steady State: thermal diffusion is thus exactly balanced by ordinary diffusion. The Soret coefficient, \( \sigma \), may be defined as

\[
\sigma = \frac{1}{m} \frac{dm}{dT}
\]

where \( m \) is the molality of the ionic complex, to overcome the effect of concentration change with increase in volume, and \( T \) is the temperature (K). Upon integrating we have

\[
\sigma = \frac{1}{m} \int dm - \int dm = \frac{1}{m} \int dm
\]

where \( m \) is the molality of the ionic complex, to overcome the effect of concentration change with increase in volume, and \( T \) is the temperature (K). Upon integrating we have

\[
\sigma = \frac{1}{m} \int dm = \frac{1}{m} \int \frac{dm}{dT} = \frac{1}{m} \int dT
\]
Thus a plot of $\ln m$ against temperature will give a straight line of gradient $\sigma$, the Soret coefficient.

The Soret coefficient of a species in solution can be determined, in principle, by analysis of the concentration of the species in regions of known temperature. Sampling may disturb the system, and so the change in concentration is often monitored by following some physical property until the Soret Steady State is reached. Such properties include change in thermoelectric power, refraction indices or, most commonly, electrochemical measurements. Also, because the temperature must be known accurately the general practice is to have two containers, carefully thermostatted, with the two solutions therein directly linked. The Soret coefficient is therefore usually determined from repetitive measurements, but only between two fixed temperatures.

Since concentration is directly related to absorbance by the well-known Beer-Lambert Law it occurred to us that a vertical column of liquid, under an applied thermal gradient, could be sampled at many temperatures, using a spectrophotometer, to give more statistically significant Soret coefficients. Moreover, the measurements would be simple and applicable to a wide range of ionic species.

We were interested in obtaining the Soret coefficients of transition metal ions in sulphate and chloride melts as part of a study on the hot corrosion of stainless steels, and therefore our choice of conditions for developing and establishing a new technique for measuring Soret coefficients is probably the most testing and severe possible.

An extensive literature survey revealed that Soret coefficients had not previously been determined by spectrochemical techniques and the application of the Beer-Lambert law. Also almost all previous determinations were made between ambient temperatures and 100°C at most, the majority employing electrochemical measurements. There were no determinations using temperatures below ambient and only two at elevated temperatures. Backlund et al (1), using a conventional electrochemical cell, measured thermal diffusion in molten binary mixtures of silver nitrate with alkali nitrates, obtaining Soret coefficient values ranging from $2 \times 10^{-3}$ to $5.5 \times 10^{-3}$ K$^{-1}$. More recently Williams and Philbrook (2) used a vertical column held at a known linear temperature gradient until a steady state for the distribution had been achieved. The melt was then rapidly quenched, and chemically sampled at intervals along its length. Using this approach Soret coefficients at three silver concentrations were found to range from a minimum of $0.08 \times 10^{-3}$ to $1.03 \times 10^{-3}$ K$^{-1}$, but with an estimated error of up to 50% and were obtained for Ag-Te solutions previously held molten in the range

$$\sigma T = -\ln m$$  \hspace{1cm} (2)
899 to 1239 K. The only comprehensive survey of methods employed for the determination of Soret coefficients is still that of Tyrell, published in 1961 (3).

THEORETICAL AND PRACTICAL CONSIDERATIONS

There are some features of our approach which are inherent and others which appertain to spectroscopic measurements at temperatures of around 1000 K.

(a) The Soret coefficient is defined in terms of molality but the Beer-Lambert law employs molarity units: specifically the law states that \( A = \varepsilon c l \), where \( A \) is the measured absorbance, \( \varepsilon \) the molar absorbance, at the wavelength of interest, in \( \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \), \( c \) the concentration in \( \text{mol dm}^{-3} \), and \( l \) is the path length in cm. In principle a correction factor could be applied to absorbance measurements, but if a small temperature range is employed, and we have used around 25°C, then the correction factor is negligible.

(b) Absorbance spectral profiles can change with temperature change, some more than others. Charge transfer to solvent spectra shift and broaden, some quite dramatically over a 25°C range, with a consequent progressive decrease in peak height with temperature increase (4,5): anions such as iodide which exhibit such spectral changes cannot therefore be investigated by our technique. Charge transfer bands arising from intra-electronic transitions between transition metal ions and ligands are much less temperature sensitive, with \( d-d \) transitions even less sensitive, and \( f-f \) transitions probably almost temperature insensitive: we have examined \( d-d \) transitions, recording changes at peak maxima to minimise any broadening contritbutions, and the charge transfer edge of Fe(III). Since this last is a \( d^8 \) species, and since its \( d-d \) transitions are now all Laporte and spin-forbidden, they are thus of low intensity and scarcely discernable on the charge transfer absorption edge.

(c) Normally electronic absorption spectra are recorded through cross-sectional areas around 8 x 10 mm. If solutions are to be held in standard 1 cm silica cells, themselves in a temperature gradient, then a mask must be placed in the light beam in front of the cell. With our instrumentation the light beam could be reduced from 10 mm to 1mm high and still allow sufficient light throughput so that the spectrophotometer could perform within an acceptable response range.

(d) The temperature profile within the solution must be accurately known. A common problem for spectrophotometric measurements, particularly at high temperatures, is the need for two relatively large opposing light ports in the hot zone of a furnace, and hence problems with uniform temperature control. Using thermal gradient furnaces, with
separate heating elements above and below the molten salt sample, does not produce a linear (with distance) temperature gradient in the sample. The sample must first have its temperature profile accurately mapped with a calibrated and preferably miniature, thermocouple.

Other problems and precautions were more specific to the apparatus used and the systems examined and will be included in the next section, but it may be here concluded that absorbance can replace molality in the Soret coefficient eqn. (2) and we can investigate the relationship

$$\ln A = -\sigma T$$  \hspace{1cm} (3)

**EXPERIMENTAL**

**Preparation and handling of materials.** Chemicals were stored, weighed and handled in a drybox maintained at ca. 2 ppm moisture. The eutectic LiCl-KCl, mole cation %, Li, 58.5; K, 41.5. (Unichem Ltd) was used directly from ampoules. The Li$_2$SO$_4$-Na$_2$SO$_4$-K$_2$SO$_4$ eutectic (78, 13.5, 8.5 mole cation % respectively) was prepared by weighing the pre-dried sulphates. The chlorides of iron(III), chromium(III) and nickel(II), and NiSO$_4$, were prepared and dried by standard methods.

Aliquots of these eutectic mixtures, corresponding to a final melt volume of 4.5 cm$^3$ were weighed into a standard 1 cm silica optical cell to which a neck had been attached (so that it would protrude outside the furnace). The cell was sealed before removal from the drybox, and subsequently connected to the dried gas supply. The iron, chromium and nickel salts were either weighed out into sealed vials for later transfer into the molten eutectics, or added with the eutectic mixture in the optical cell.

**The gas supply.** The ingress of atmospheric moisture to the molten eutectics was prevented by the slow passage of a dried gas over the melt: the velocity of the gas was insufficient to cool or otherwise affect the melt. For the chloride melts argon was used, which had been dried over self-indicating silica gel and 4Å molecular sieve columns, and a synthetic flue gas mixture was used for the sulphate melt. This gas was similarly dried and its composition was, by volume, 16% CO$_2$, 3% O$_2$, 4000 ppm SO$_2$, balance N$_2$. Some of the SO$_2$ was oxidised to SO$_3$ by passage over a platinised Kaowool catalyst at 400°C, and an average concentration of 50 ppm SO$_3$ was obtained. The SO$_3$ was required to prevent the decomposition of the sulphate melt, which otherwise occurs above 600°C.

**Furnaces.** Two types of furnaces were used, one was an isothermal furnace and the other a thermal gradient furnace, with separately controlled heating elements above and below the optical ports, to create
the desired temperature gradient in the melts. The former was used in the conventional way to record the spectra of the iron, chromium and nickel complexes as a function of temperature, to determine the temperature range over which any band broadening was insignificant. Both types of furnace have been described elsewhere (6,7).

Temperature profile. Our approach demands an accurate knowledge of the temperature at all points over which spectra are to be measured. The thermal gradient furnace was therefore carefully calibrated. A cell containing molten salt was secured in place in the furnace, and the furnace in the light beam of the spectrophotometer. A mask with an 8 x 1 mm aperture was located in the middle of the beam and close to the front surface of the cell. The furnace could be raised and lowered precisely, via a 1 mm pitch screw thread. A thermocouple was fixed so that its tip was in line with the aperture and in contact with the side of the cell. A second thermocouple, which had previously been accurately calibrated, was placed in a thin silica protective sheath and then in the melt so that its tip was in the centre of the light beam. The dried gas was also passed slowly over the melt to replicate as far as possible the experimental conditions. When thermal equilibrium had been attained, and the temperature readings had been constant for at least one hour the readings of both thermocouples were recorded, and the furnace position raised 3 mm and the process repeated. It was established that raising and lowering the furnace to a previous position reproduced the previous readings. A calibration plot is shown in Fig. 1.

The calibrated thermocouple was also located at both ends of the aperture and nearer and further from the mask and the above procedure repeated: there was no lateral thermal gradient within experimental error. Spectral determinations of concentration changes could now be made. No change in the temperature profile occurred during these measurements and this was confirmed since the reading from the thermo- couple adjacent to the cell was still the same as that at the same furnace positions during the calibration.

Spectroscopic measurements. A key-board controlled fibre optic spectrophotometer was employed (Guided Wave Analyser, Model 200). The fibre optic probes were set up either side of the furnace and on an optical bench. The single fibres, 0.5 mm diameter, terminated in stainless steel sheaths and against a collimating lens, which produced an only slightly diverging beam. The masked beam therefore entered the cell 1.13 mm high and was 1.30 mm high on exiting. The probes were placed as close to the hot sample as possible without allowing the tip to be overheated, (and thus degrade the fibre coating). The optimum alignment was achieved using a supplied computer program which indicated the light level received by the detector.

Spectra take around 30 sec to collect, and when thermal equilibrium
had been attained five spectra were taken and averaged. Reference spectra were first recorded at selected positions in the thermal gradient, before addition of the transition metal salt. A total of eight baseline spectra were always taken, at 3 mm vertical intervals, and from 400 to 1200 nm at 0.5 nm sampling intervals. Normally this attention to detail is not generally required but it does eliminate any unforeseen errors, including possible minor imperfections in the optical faces of the cell.

Addition of solute. Normally in molten salt spectroscopy, after the baseline spectra have been recorded, the transition metal solute is tipped carefully into the cell and the cell contents stirred or rocked gently until the solute has dissolved. In this work the cell could not be moved as the same thermal gradient would not be obtained again, since some of the melt would be withdrawn on the stirring rod or left higher up on the walls of the cell. Two methods of adding the solute were investigated.

First, the solute was dropped, in the form of a lightly compressed pellet, directly on to the surface of the melt. Second, the cell containing eutectic only, after the baseline spectra had been taken, was removed from the furnace, the melt tipped out, and after cleaning and drying, was refilled in the drybox. The anhydrous transition metal salt was first weighed into the cell and the same weight of eutectic used for the baseline spectra was added. The cell was then sealed and transferred to the furnace as before.

The first method is in principle the better but in practice the rate of dissolution was too slow, in excess of 48 h, and by the end of the experiment the cell windows would be etched, due to the temperatures involved. The second method was therefore used. It also has the advantage that because the transition metal salt is largely at the bottom of the cell initially it diffuses upwards upon dissolving in the eutectic melt, and therefore it was possible to monitor this diffusion process spectroscopically. For this study it enabled the time when equilibrium had been reached to be determined. The method was to record spectra at a fixed position some distance above the base of the cell. The upward diffusion was seen as a continual increase in the recorded absorbance spectra: when the spectra did not increase further in absorbance the system was considered at equilibrium. The time taken to attain equilibrium was now 10 - 15 h, and thus spectra could be recorded for Soret coefficient determinations before any detrimental effects on the silica windows occurred.

Problems encountered. When salts melt they often contain initially small gas bubbles, from the air trapped between the powder particles. These generally rise very slowly to the surface, but may need encouraging by applying a little vibration to the cell. Thus before finally locating the cell (containing molten salt) precisely in the thermal gradient it was inspected...
for absence of bubbles.

When chromium(III) chloride was added to the LiCl-KCl eutectic under dried argon the spectrum at first was not stable, and after 20 minutes had changed from that of the octahedral \( \text{CrCl}_6^{3-} \) species to that of the tetrahedral species \( \text{CrCl}_4^{2-} \). Further, a comparison of published Cr(III) spectra in molten chlorides showed considerable variation (and the investigation this engendered will be published elsewhere). This reduction is well known in aqueous and alcoholic solutions when a catalytic amount of Cr(II) is present. The source of the reductant here must be water in CrCl\(_3\) or in the argon gas. The CrCl\(_3\) was analysed and found to contain 11 ppm moisture, which would produce sufficient HCl to bring about complete reduction of the Cr(III). A fresh, dried sample of CrCl\(_3\) gave a stable spectrum, with no evidence of CrCl\(_4^{2-}\) formation after two hours.

However, the bands then began to decrease in height, and after ten hours the spectrum of Cr(III) had disappeared: a green precipitate was observed at the bottom of the cell, and this was later confirmed by X-ray diffraction as Cr\(_2\)O\(_3\). Oxide ions arising from decomposition of the silica cell is not feasible thermodynamically, even at the temperatures of 870-1070 K involved.

Attention was therefore focussed on the oxygen content of the argon, reported as 4-10 vpm by the supplier, but calculations showed this insufficient to precipitate all the chromium, over a ten hour period, at the flow-rate employed. However it is now considered that oxygen had permeated through the plastic tubing used.

The problem was finally eliminated by connecting a vacuum pump to this cell, and pumping continually during the melting of the eutectic: this also rapidly and effectively removed gas bubbles in the melt. After two hours the cell was sealed, and a constant check performed during the experimental run to ensure that the vacuum was constant. Melts so prepared were completely stable for one week and more.

RESULTS

Effect of temperature on spectral profiles. An isothermal furnace was employed to record the spectra of Fe(III), Cr(III) and Ni(II) in the LiCl-KCl eutectic, and Ni(II) in the \( \text{Li}_2\text{SO}_4\)-\( \text{Na}_2\text{SO}_4\)-\( \text{K}_2\text{SO}_4 \) eutectic as a function of temperature. Spectra were recorded at regular temperature intervals and compared with one another by superimposition and by difference. Small variations could be seen between spectra taken around 100°C apart, generally some slight band broadening with temperature increase, as expected. Careful examination showed that the minimum absorbance decrease was around peak maxima, and that over a 25°C range the
absorbance change is negligible. This range was therefore chosen as the maximum for the Soret coefficient determinations. However, for the Fe(III) containing solutions, as indicated earlier, the spectral profile consists essentially of a charge transfer absorption edge containing very weak spin-forbidden bands. This edge was slightly temperature dependent over a 25°C range, and therefore Soret coefficient determinations were made at two wavelengths. The wavelengths chosen were ones at which spin-forbidden peak maxima had been previously identified by fourth derivative analysis (8).

Spectral changes across the thermal gradient. Figs 2-5 show the spectra recorded for the four systems under investigation in the thermal gradient furnace, at 3 mm vertical intervals, after the systems have reached the Soret steady state condition. The spectra were recorded first upon progressively lowering the furnace in the light beam and then raising it, and each pair of spectra were identical within experimental error, confirming no disturbance to the thermal equilibrium.

Soret coefficient determinations. Figs 6-9 show plots of ln(absorbance) against temperature (eqn. 3) for each of the four systems, and a good linear relationship is seen, as now expected. The value of the Soret coefficient is obtained from the slope of these plots, and the results, and their standard derivations are collected in the Table, together with some selected published values. Also as expected the results for the band edge studies of Fe(III) have more scatter than those for Cr(III) and Ni(II), obtained around peak maxima.

DISCUSSION

An examination of the Table shows that the results obtained here are comparable with those found at elevated temperatures, as well as those reported for transition metal ions in aqueous solutions. We have therefore shown that, with due care and attention to detail, Soret coefficients can be obtained from absorption spectra for species around 900 K. This new technique is therefore viable and has great potential. There are however several observations which should be made concerning this study and concerning future applications.

(a) Although each Soret coefficient has been determined from eight data points, instead of the normal two, much more data are in principle available for use. With each spectrum digitised at 0.5 nm intervals there are several hundred data points, and hence wavelengths at which Soret coefficients may be determined, and with greater precision. Computer programs could be written to extract progressively absorbance data from a set of spectra at one wavelength; calculate a least squares fit to ln(absorbance) against temperature; and prepare a plot like Figs. 6-9. A plot of Soret coefficient, with its standard deviation, against wavelength
would then be expected to be linear and independent of wavelength, but
to have the largest, and probably unacceptable standard deviations either
side of peak maxima. Soret coefficients determined this way would thus
be definitive, compared with the more common approach of making
concentration measurements at only two temperatures. It was not
considered appropriate to extend our high temperature data in this way
but, having established this new method for determining Soret
coefficients, that it should next be applied to aqueous systems.

(b) The fibre optic spectrophotometer system has certain advantages over
more conventional spectrophotometers. Normally samples have to be
enclosed in a light-tight housing, but the optical arrangement of a fibre
optic spectrophotometer, together with the light collecting properties of
optical fibres, means that the absorption spectra of samples can be
recorded in daylight, and hence of hot glowing samples. Molten salt
spectroscopists have generally used a reversed beam optical system which
eliminates unwanted light (this is only commercially available on the Cary
14H spectrophotometer). We initially used this instrument in an attempt
to determine Soret coefficients, but the optical system required too high
an aperture in the mask for adequate spectra, and hence the temperature
of the section examined contained too large a temperature gradient for
acceptable Soret coefficients. The investigation did however define the
problems to be overcome, and indicated that Soret coefficients were
potentially available from absorbance measurements and the Beer-
Lambert law.

This present study therefore made use of furnaces with large optical
ports, designed to admit a light beam of standard cross-sectional area for
use with 1 cm cells. As indicated earlier this necessitated detailed
assessment and calibration of the temperature profile in the melt. In
future, furnaces with much smaller optical parts could be used, since
optical fibre probes fitted with collimating lenses are only a few
millimeters in diameter. Thus better thermal gradients will be available,
and if taller cells were used, the maximum usable temperature difference
could be employed over an extended vertical distance, and larger mask
apertures (or possible no masks) could be used, all features that would
make Soret determinations easier and more accurate. In addition, the
fibre optic spectrophotometer manufactured by Guided Wave now has a
photo multiplier detector which records absorbance values to the seventh
decimal place. We have conducted tests which have shown that data are
reliable to the fifth and probably to the sixth decimal place.

Conventional spectrophotometers normally are restricted to the fourth
decimal place. Thus absorbance changes and differences can now be
resolved to an accuracy more than an order of magnitude better than
previously.

For making measurements at high temperatures the necessary
separation between the fibre optic probes (to prevent decomposition of the organic coating on the silica fibres, which is required for total internal reflection within the fibre walls) means that a photomultiplier detector must be used; a silicon detector is not sufficiently sensitive under these conditions. However, developments are expected in fibre optic technology and that in future alternative heat-resisting coatings may become available, and the probes could be located closer to the molten salt solution, and silicon detectors employed.

(c) There are fibre optic spectrophotometers commercially available which use photodiode array detectors. These instruments could also be used for Soret coefficient determinations. They have the advantage that spectral scans are more rapid, generally less than one per second, compared with around 30 seconds which the Guided Wave Analyser needs to record a spectrum. However, speed is not essential when measuring a system at equilibrium. Currently photodiode arrays do not cover the same spectral range as photomultiplier, silicon and germanium detectors, but again developments are expected. Photodiode arrays have inherently less resolution than can be obtained with grating instruments, though this does not significantly reduce the number of wavelengths at which absorbance measurements may be made.

(d) When our results in Table 1 are compared with other published data some interesting conclusions may be drawn. Our extensive literature survey also revealed that Soret coefficients have been determined for atoms, molecules and electrolytes, but not for specific ions. This is largely because of the techniques used which, unlike absorption spectroscopy, do not specifically focus on only one ionic species, for example the emf technique for the thermoelectric power of an electrolytic thermocouple (8). However there are points in common.

Soret coefficients are by definition temperature independent, and our results are certainly not atypical. Our results were not obtained at the highest temperatures employed, which is around 1200 K for molten Ag-Te solutions by Williams and Philbrook (2), but they are for concentration measurements of the system while hot. Soret coefficients are also often reported as appertaining to a particular temperature, but this is the mean of the high and low temperatures employed. Thus our results could be described as applying to around 878 K.

Soret coefficients, according to the standard definition, eqn. 2, are negative, but can be obtained as positive if calculated by other ways. Of course, when electrolytes are not considered but, say, two organic solvents, then one will have a negative Soret coefficient and the other a positive.

We would draw attention to a possible correlation, not remarked
upon previously. When a series of electrolytes is studied, sometimes a trend may be seen. For example, in Table 1 we include the data for a series of chlorides in water, reported by Ikeda and Miyoski (9). These results are for concentrations of $1 \times 10^{-2}$ mol$^{-1}$ dm$^{-3}$ and a mean temperature of 25°C. The datum for LiCl is in brackets because it was used as a reference. The data for the other electrolytes appear to increase with increasing cation size. The quaternary ammonium ions are hydrophobic and hence are not solvated whereas the proton in HCl in these dilute solutions will be solvated and thus effectively much larger than its crystallographic radius. When we look at our data for the transition metal complexes we can detect a similar trend. For example, the octahedral $\text{[Ni(SO}_4\text{)}_3\text{]}^{2-}$ complex ion is larger than the tetrahedral ion $\text{[NiCl}_4\text{]}^{2-}$, which has a more negative Soret coefficient, and the tetrahedral ion $\text{[FeCl}_4\text{]}^{-}$, with the central ion at a higher oxidation state, will therefore be smaller still, and this ion has an even more negative Soret coefficient.

When we examine the molten nitrate data of Backlund et al. (1) reproduced in Table 1 we would point out that these are selected data, and that the proposals for the identity of the species present are ours. The concentration of the alkali ion is the 10 mole per cent value, except for caesium, where the lowest concentration given was 17.5 mole per cent. It is reasonable to suppose that these cations, except lithium, have an approximately octahedral arrangement of six oxygen atoms surrounding them, supplied by three planar nitrate ions in approximately the locations expected if they were acting as bidentate ligands: such an arrangement is well known for transition metal ions in nitrate melts (10). Further, the Soret coefficients are essentially the same at all concentrations of alkali metal ion, around $1.3 \pm 0.3 \times 10^{-3}$ K$^{-1}$, including lithium, except at the 5 and 10 mole per concentrations where they are around $5.5 \times 10^{-3}$ K$^{-1}$. This leads us to speculate that under these conditions the smaller lithium ion has four essentially monodentate nitrate ions about itself, and is therefore larger, and thus has a higher Soret coefficient. At the higher lithium concentrations there is a greater competition for the nitrate ions, the species becomes smaller as the cation is less 'solvated' and so its Soret coefficient in these mixture drops to around $2.2 \times 10^{-3}$ K$^{-1}$.

We finally note that the only transition metal salt for which a Soret coefficient has been determined is NiCl$_2$ in water at $5 \times 10^{-3}$ mol$^{-1}$ dm$^{-3}$ at 25°C, with values reported of $2.67 \times 10^{-3}$ K$^{-1}$ (11) and $3.20 \times 10^{-3}$ K$^{-1}$ (12). These values apply to octahedral $\text{[Ni(H}_2\text{O)}_6\text{]}^{2+}$ and are numerically very close to our values for NiCl$_4^{2-}$ in molten chloride around 600°C. This gives us further confidence in the validity of our data, and demonstrates further that Soret coefficients for the other transition metal ions can conveniently and accurately be determined in aqueous and other room temperature media by our approach.
CONCLUSION

At this time we content ourselves with pointing out a possible trend with the size of the diffusing ion, and which might not be unexpected.

The majority of the data available was recorded in the 60’s and little has been published recently. If Soret coefficients can be determined with greater precision then the validity or otherwise of this and other trends can be established, and their implications examined. We believe that this new approach, of measuring Soret coefficients from absorbance data, has been shown to work under extreme conditions and now should be applied systematically to, in particular, transition metal ions in aqueous and other room temperature systems. The improved accuracy thereby anticipated to result will permit genuine correlations to emerge.

ACKNOWLEDGEMENTS

NJP thanks the Science and Engineering Research Council and the Central Electricity Generating Board, N.E. Region, for a CASE Award. We also thank Dr H.V. St. Aubyn Hubbard for valued discussions. T.R.G. thanks the Royal Society and the University of Leeds for contributions towards travel expenses.
### Table. A List of Soret Coefficients $\sigma$

| Species | Solvent | Temperature Range/K | Wavelength /nm | Soret Coefficient $/10^3 K_1$ | Correlation Coefficient |
|---------|---------|---------------------|----------------|-------------------------------|-------------------------|
| $[\text{FeCl}_3]$ | (Li,K)Cl | 867-892 | 532 | -5.45 | 0.988 (a) |
|         |         |         | 548 | -4.80 | 0.965 (a) |
| $[\text{CrCl}_6]^3-$ | (Li,K)Cl | 866-890 | 555 | -5.08 | 0.995 (a) |
|         |         |         | 800 | -4.70 | 0.994 (a) |
| $[\text{NiCl}_4]^2-$ | (Li,K)Cl | 866-891 | 627 | -3.15 | 0.999 (a) |
|         |         |         | 703 | -3.91 | 0.989 (a) |
| $[\text{Ni(SO}_4)_3]^4-$ | (Li,Na,K)SO$_4$ | 865-890 | 456 | -2.83 | 0.996 (a) |
|         |         |         | 980 | -3.35 | 0.999 (a) |
|         |         | Low     |      |      |            |
|         |         | High    |      |      |            |
| $[\text{Li(NO}_3)_4]^3-$ | (Li,Ag)NO$_3$ | 496 521 | 5.5±0.7 | 1 |
| $[\text{K(NO}_3)_4]^3-$ | (K,Ag)NO$_3$ | 537 612 | 1.4±0.2 | 1 |
| $[\text{Rb(NO}_3)_4]^3-$ | (Rb,Ag)NO$_3$ | 531 605 | 1.2±0.1 | 1 |
| $[\text{Cs(NO}_3)_4]^3-$ | (Cs,Ag)NO$_3$ | 464 564 | 1.3±0.2 | 1 |

**Solute**

- HCl: H$_2$O, 290 305, 8.95, 9
- LiCl: H$_2$O, 290 305, (-0.01), 9
- KCl: H$_2$O, 290 305, 1.58, 9
- Me$_4$NCl: H$_2$O, 290 305, 5.17, 9
- Et$_4$NCl: H$_2$O, 290 305, 8.61, 9
- h-Pr$_4$NCl: H$_2$O, 290 305, 10.91, 9
- n-Bu$_4$NCl: H$_2$O, 290 305, 13.27, 9
- NiCl$_2$: H$_2$O(b), 290 305, 2.67, 11
- NiCl$_2$: H$_2$O(b), (c), 3.20, 12

(a), This work. (b), Concentration of NiCl$_2$ was $5 \times 10^{-3}$ mol$^{-1}$ dm$^3$. (c) No temperature range given but Soret coefficient reported at 25°C (298 K). The selected molten nitrate data, ref. (1), is for alkali ion concentrations of 10 mole per cent, except for caesium where it is for 17.5 mole per cent.

251
REFERENCES

1. V. Backlund, J. Dupuy, S. Gustafsson and A. Lundén, Z. Naturforsch., A22, 471 (1967).
2. R.K. Williams and W.O. Philbrook, J. Electrochem. Soc., 138m 1034 (1981).
3. H.J.V. Tyrell, Diffusion and Heat Flux in Liquids, Butterworths. 1961.
4. T.R. Griffiths and R.H. Wijayanayake, Trans. Faraday Soc., 66, 1563 (1970).
5. M.J. Blandamer and M. Fox, Chem. Rev., 70, 59 (1970).
6. T.R. Griffiths and P.J. Potts, Inorg. Chem., 14, 1039 (1975).
7. T.R. Griffiths, K. King and D. Mortimer, Power Ind. Res., 2, 79 (1982).
8. T. Ikeda and H. Kimura, J. Phys. Chem., 69, 41 (1965).
9. T. Ikeda and H. Miyoshi, J. Phys. Chem., 70, 3361 (1966).
10. C.H. Liu, J. Hasson and G.P. Smith, Inorg. Chem., 7, 2244 (1968).
11. T. Ikeda, H. Ohe and S. Kawamura, Bull. Chem. Soc. Jap., 41, 2858 (1968).
12. C.J. Petit, M.-H. Hwang and J.-L. Lin, Int. J. Thermophys., 7, 687 (1986).

Figure 1. Plot of temperature against distance in an optical silica cell containing molten salt in the thermal gradient furnace, showing the thermal profile obtaining therein.
Figure 2. Charge transfer absorption edge for Fe(III) in molten LiCl-KCl eutectic recorded at different positions within the thermal gradient when the system was at the Soret Steady State.

Figure 3. Ligand field spectrum of Cr(III) in molten LiCl-KCl eutectic recorded at different positions within the thermal gradient when the system was at the Soret Steady State.
Figure 4. Ligand field spectrum of Ni(II) in molten LiCl-KCl eutectic recorded at different positions within the thermal gradient when the system was at the Soret Steady State.

Figure 5. Ligand field spectrum of Ni(II) in molten Li$_4$SO$_4$-Na$_2$SO$_4$-K$_2$SO$_4$ eutectic recorded at different positions within the thermal gradient when the system was at the Soret Steady State.
Figure 6. Plot of ln(absorbance) at 539 and 549 nm against temperature from the spectra in Figure 2. Slope of the least square linear fit to the data is the Soret coefficient. The goodness of fit is indicated by the correlation coefficient.

Figure 7. Plot of ln(absorbance) at 555 and 800 nm against temperature from the spectra in Figure 3. Slope of the least squares linear fit to the data is the Soret coefficient. The goodness of fit is indicated by the correlation coefficient.
Figure 8. Plot of In(absorbance) at 627 and 703 nm against temperature from the spectra in Figure 4. Slope of the least squares linear fit to the data is the Soret coefficient. The goodness of fit is indicated by the correlation coefficient.

Figure 9. Plot of ln(absorbance) at 456 and 980 nm against temperature from the spectra in Figure 5. Slope of the least square linear fit to the data in the Soret coefficient. The goodness of fit is indicated by the correlation coefficient.