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ELECTRICAL CONDUCTIVITY OF "JP-8 + 100" ADDITIVES IN HYDROCARBONS AND FUELS

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13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking Royal Military College of Science as follows: The main objective of the proposed work is to examine candidate HITTs additives that have an ability to increase the electrical conductivity of hydrocarbons. In particular, the main emphasis will be on factors that adversely interfere with the conduction process and depress the conductivity response. The research program will aim to: A) establish baseline electrical conductivity for BP and Ethyl additives in a model hydrocarbon (dodecane); B) examine the influence of the factors considered in (A) for JP-8 fuel; C) comparisons of model and real fuel behavior and consideration of the implications for in field behavior. To achieve this, measurements will be made to examine factors, which determine the magnitude of the conductivity response in the model hydrocarbon: 1. The effects of concentration of HITTs additives, 2. The effects of other fuel components on the behavior of HITTs additives. This will include naturally-occurring and refinery introduced components and certain coadditives, 3. The effects of certain physical properties of the bulk hydrocarbon and especially viscosity, on HITTs additive behavior, 4. Additive batch-to-batch variation, 5. Incidences of conductivity dependence on time, 6. Influence of temperature, on conductivity for the working temperature range over which these additives will be used. Especially it is important to examine the temperature dependence of the most important observed effects, 7. There is evidence that certain HITTs additives may cause the formation of microemulsions of water in fuel. The effects on electrical conductivity will be examined.

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1. INTRODUCTION

Most hydrocarbon liquid fuels are known to have low electrical conductivity; as a result, any process involving their movement - such as pipeline flow, filling of tanks and passage through microfilters, may cause a considerable charge build-up with a possibility of causing fires and explosions if a discharge of the static build-up occurs. To avoid such a risk, the static dissipator additive r-Stadis 450 is used to meet the electrical conductivity requirement for aviation fuels. Another commonly experienced problem resulting from the ever increasing high performance demands for aircraft is due to thermal oxidation reactions which give rise to harmful deposits due to the use of fuel as coolant for both engine and airframe. These deposits reduce the overall performance and effectiveness of the engine system, and as a consequence, the cost and frequency of routine maintenance are increased.

The JP-8+100 Programme "directly" addresses the latter of the two above-mentioned problems. The main aim of the JP-8+100 is to increase the thermal stability of JP-8 fuel by the use of additives, and to reduce the tendency for deposit formation. Several of the promising HITTS (**Hi**gh **T**emperature **T**hermal **S**tability) additives which were submitted by manufacturers were found also to increase the electrical conductivity of the fuel.

2. AIMS AND OBJECTIVES

The main aim of this work is to measure the extent to which certain HITTS additives are able to increase the electrical conductivity of fuels, to examine factors which influence this and to consider the possible use of HITTS additives as conductivity improvers.

The current specification for the electrical conductivity of JP-8[1a], lower limit 150 pSm^{-1},upper limit 450 pSm^{-1} at ambient temperature or 29.4°C which ever is the lower, is met by the use of static dissipator additive r-Stadis 450 which is supplied by Octel America. For JP8+100 fuel these limits are $150pSm^{-1}$ and $700pSm^{-1}$. For the similar fuel, NATO F-35, the limits are $50pSm^{-1}$ and $450pSm^{-1}$[1b]. The fact that certain HITTS additives impart enhanced conductivity[2] to fuel suggests the possibility that HITTS additive may perform the dual function of static dissipator as well as thermal stability improver - which can reduce certain obvious costs as well as offer other possible useful technical benefits.

The electrical conductivity response of a fuel to a given concentration of static dissipator is known to be dependent on the chemical constitution of the fuel. Other factors are also known to affect the electrical conductivity of fuel, and detailed studies have been reported by L. Gardner and F. G. Moon[3,4], C. P. Henry[5,6] and B. Dacre *et al.*[7,8]. In contrast, only recently has any similar work been started on one HITTS additive - BETZ 8Q405 and derived packages[2]. This work, therefore, aims to fully characterise the electrical conductivity behaviour of a number of candidate HITTS additives, and also to look at factors which may adversely affect the conduction process (e.g. the presence of co-additives). Another important aspect which is examined is the effect of temperature (and temperature cycle in some cases) on the observed conductivity response of HITTS additives - in the range 0°C to 50°C. The time dependence of solution conductivity is briefly examined.

3. EXPERIMENTAL

3.1 Materials

The materials were obtained from the following sources; HITTS additive BETZ SPEC AID 8Q405(A), had been supplied previously by Wright Patterson AFB, additives 96POSF3256(B), 98POSF3558(C), 99POSF3598(D) and 99POSF3724#144071(E) were supplied by Pratt and Whitney, and these, for ease of reference, will be labelled A, B, C, D and E as indicated, antioxidant Ionol K-65 by British Petroleum, Diethylene glycol monomethyl ether(FSII), N,N-disalicylidene-1,2-propylenediamine (MDA)by Pfaltz & Bauer Inc. and Phenol - loose crystals (99+% A.C.S. Reagent) by Aldrich.

Octel America supplied the reformulated version of the antistatic additive Stadis 450, designated here as r-Stadis Two main fuels were used - these were, dodecane which was supplied by BDH Chemicals/Merk and purified by percolation through a mixed oxide filled column[7], and an additive-free Merox base fuel (fuel F-2) which was supplied by BP Oil Technology Centre. A small number of preliminary experiments used a second additive-free Merox (fuel F-1).

3.2 Stock Solution Preparation

For consistency and reproducibility, the various fixed volume micropipettes (5, 10, 20 and 50μl) which are available for use were calibrated to check their performance specification. Gravimetric testing according to DIN 12650 was the chosen calibration technique, i.e. a method whereby the pipette volume is determined from the mass of the test liquid that was taken up in the pipette via the equation:

$$\text{Volume} = \text{Mass} \div \text{Density}$$

The 50μl micropipette gave the most consistent mass reading of the test liquid used; hence, stock solutions for each additive were prepared such that the addition of 50μl aliquot to 60ml of fuel in the conductivity cell will give exactly a predetermined concentration with which the stock solutions were labelled. For example, if the addition of 50μl (0.05ml) of stock solution to 60ml of fuel is to result in a final concentration of 100mg per litre, i.e.

$$\frac{x \text{ mg of additive}}{60.05} \times 1000 = 100\text{mg per litre.}$$

Then $x = 6.005$, i.e. 6.005mg of additive would have been required in 50μl (0.05ml) of stock solution, i.e. 1ml of stock solution would have contained 120.1mg of additive.

3.3 Conductivity Measurements

Most of the relevant experimental details and purification methods used for this work are as previously described[7]. Conductivity measurements in the range 0°C to 50°C were made using the free standing cell[7], and attendant polarisation effects were eliminated by extrapolation of the conductivity-time data to give the zero time conductivity. Low temperature effects were investigated via two methods, firstly, by allowing the solution (fuel + additive) to cool to about -5°C (or about 5°C below the temperature of interest) in a refrigeration cabinet and monitoring the conductivity at regular temperature intervals as it was allowed to return to ambient temperature. The second method involved repeated cooling of the solution, after the addition of each aliquot of the additive to a cooled fuel before each measurement is made; in this way the solution is kept at a relatively constant temperature of 0°C. In both series of experiments, the temperature of interest was determined by gently stirring the solution with a glass thermometer and noting the relatively stable temperature just before each measurement. Ideally, experimentation in a thermostatically controlled freezing chamber could perhaps have yielded better results.
During and after the completion of each series of conductivity measurements, the resulting solutions were retained; they were left in the experimentation chamber (Faraday Cage) at the initial experimentation temperature for about two to three days to monitor any time dependent changes. If a solution was found to have undergone some change then the experiment was replicated to allow for a more accurate monitoring of the change.

Co-additive conductivity measurements were also carried out on all four HITTS additives(B, C, D and E). Most of the possible combinations and permutations were investigated; their individual interaction with 2mg/l r-Stadis in Merox was also examined. Care was taken to allow conductivity due to the first additive to stabilise before the addition of a second additive, which was also monitored for any instability with time.

4. RESULTS AND DISCUSSION

4.1 Conductivity Behaviour of HITTS Additive Packages

Data on the concentration and temperature dependence of conductivity for each of the HITTS additives and r-Stadis 450 are given in graphical form in figure 9

In a previous report[9] similar results were presented on the conductivity behaviour of Betz SpecAid 8Q405 in an additive-free Merox over a range of temperatures and concentrations (figures 1 to 5 of that report); the same series of experiments have also been carried out in a model fuel - dodecane. The results are presented here as figures 1, 2 and 3 and are used to illustrate the way in which the data have been treated. Arrhenius type behaviour was observed for the change in conductivity with temperature - figure 2 (figure 3 in the previous report[9]). However, a plot of ln{conductivity} versus inverse temperature (1/T) for two 8Q405 concentrations (100 and 300mg/l) in dodecane (figure 3) shows an abrupt change of slope, though this was not as pronounced as that observed for 8Q405 in Merox - figure 5 in the previous report[9]. Also, the measured conductivity in dodecane was ≈ 35% less than an equivalent concentration in Merox.

4.1.1 Data Analysis - 8Q405 in Merox and 8Q405 in Dodecane

As indicated these systems are used to illustrate the way in which the data has been treated.

Some basic statistical analysis of the conductivity data for 8Q405 in Merox and in dodecane confirm the existence of the above-mentioned similarities and differences. It was shown in the previous report[9] that the response of conductivity to temperature, at each 8Q405 concentration, approximated to Arrhenius type behaviour, and so was modelled by the equation:

$$k = A \exp. (-E_a/RT), \qquad \text{Equ. (1)}$$

where:

k = conductivity,
A = constant or pre-exponential factor,
E_a = Arrhenius activation energy
R = molar gas constant
T = Temperature (K).

Alternatively write:

$$\ln k = \ln A - Z/T \qquad \text{Equ. (2)}$$

where $-Z = -E_a/R$ which is calculated from a plot of ln{conductivity} against 1/T. Application of an Exponential Regression or Linear Regression (and Linest Function) expressions to the conductivity data in either the exponential form or the linear form (Equ. (1) or Equ. (2) respectively) allows a quantitative estimate of the "goodness of fit" for each set of data using the resulting R-squared value and the standard deviation.

A combination of Linear Regression and Linest Function was applied to the data from figure 2 above and from figure 4 in the previous report[9] in order to produce the "best fit" lines shown on figures 4 and 5 for 8Q405 in dodecane and in Merox respectively. Table 1 shows the results of statistical calculations on the data from figure 2 and lists the standard error in the slope, the standard error in the intercept, the standard error in the y estimate and the standard deviation of error associated with the "regressed" data. Table 2. shows similar descriptive statistics for data from figure 4 of the previous report[9]. We note,figures 4 and 5, that the data point(s) with the largest deviation from the linear regression line is/are in the neighbourhood of 3.5 to 3.4 x 10^{-3} K^{-1}, i.e. between 285 and 295K. The deviation seems greater with Merox as the test fuel (cf. Figures 4 and 5), as indicated by the "R-squared value" It is also interesting to note that at lower 8Q405 concentrations the deviation is positive (Figure 4 – 100mg/l). Whether or not this is a real phenomenon (or an experimental artefact) is not yet known; however, this initial result suggests a dependence on 8Q405 concentration of the observable deviation from linearity in the neighbourhood 285 and 295K when dodecane is the test fuel.

4.1.2 Conductivity of pure Dodecane and Additive-free Merox

In the absence of additives the electrical conductivities of dodecane and merox fuel used in this work are usually ~1 pSm^{-1} for the former and ~10 pSm^{-1} for the latter.These values are attributable to small amounts of impurities. Though the work of Forster[10], on hydrocarbons, has shown that it is possible to achieve very much lower values than these, by reducing the impurity concentration, this was not necessary for our work due to the fact that most of the solutions examined had considerably higher conductivities. For this reason no corrections for solvent conductivity have been made in the reported values.

In early experiments, initial conductivities, measured following addition of dodecane to a cell i.e before addition of additive, showed much variation. This was attributed to carry over of additive, due to adsorption, between experiments. Adoption of a stricter procedure for cell cleaning, viz three times rinsing with purified dodecane(about 30ml) followed by filling for a two-day period also using pure dodecane and then a final rinse again with dodecane, reduced the spread of values.

4.1.3 Conductivity Response of 8Q405 and Temperature Dependence

Two temperature change regimes were used during preliminary experimentation with 8Q405. In the first the change in conductivity was measured of one prepared solution, at a specified concentration (100mg/l) of 8Q405 in dodecane, as the temperature was cycled through the range; in the second the conductivity of separate solutions, all at the same concentration (also 100mg/l), was measured at fixed temperatures covering the same range of temperatures. Results are summarised in Figure 8. The conductivity was monitored from 0°C through to 60°C and then the solution was allowed to cool to room temperature (25°C) before cooling to 0°C – first cycle. This procedure was repeated to obtain the second cycle. Subjection of a solution of 8Q405 to a thermal cycle (first cycle) was found to increase the subsequent low temperature conductivity value. Moreover, there are indications that if the second cycle was taken to an even higher temperature (>60°C) then the subsequent low temperature conductivity response of the 8Q405 solution is even greater.

Experiments at constant temperature(second method) using 20, 40 and 60°C were also carried out and included above as the non-cycle data. We note the considerable difference in magnitude of these data compared to that of the first cycle data. The reason for the observed difference seems to be due to the difference in time duration over which the two sets of data were collected since this would provide an opportunity for possible reaction of the additive, with solution impurities or cell wall components – particularly at the higher temperatures i.e. the slow increase in temperature (≈2 hours) associated with the "first cycle" data could have promoted such reaction. There was insufficient time to further examine this effect, but since such exposure is not likely to occur in practice we subsequently obtained results via the non-cycle method in which measurements were made within ≈2 minutes of the addition of the additive.

4.1.4 Remarks on the Magnitude of the Conductivity Response due to HITTS Additive

For each additive the concentration range was chosen to cover the treat rate in fuel, as recommended by the manufacturer.

Figure 9 shows the concentration dependence of the conductivity for the HITTS additives B, C, D, E and r-Stadis 450 at 25°C. Although the conductivity increases with concentration there are indications that the plots are not quite linear and that the slope decreases with concentration.

This was also indicated for Betz 8Q405 and r-Stadis 450 in this and in some of our earlier work[2,8,11]. The curvature becomes more evident at higher temperatures. Conductivities at the treat rate concentration have been interpolated from such graphs and are listed, for 25°C, in table 3.

The effectiveness of r-Stadis 450 on a weight–for-weight basis is demonstrated by comparing the responses based on the conductivity increase per 100mgl^{-1} for all the additives studied. This is shown in column 4 of table 3. The behaviour in fuel F-2 is similar to that in dodecane except that the conductivities are generally larger in the fuel by up to ~30% depending on the additive type.

4.2 Magnitude of Conductivity Response in Solutions Containing Binary Combinations of r-Stadis 450/HITTS Additives and Binary Combinations of HITTS Additives in Fuel

The data are presented as the ratio $\kappa_{obs} / \kappa_{pred}$ plotted against concentration of a second additive, where the concentration of additive 1 is fixed and that of additive 2 is varied. κ_{obs} is the observed conductivity of the mixture, whereas, κ_{pred} is that predicted from measurements on the additives individually. Additive combinations are compared below.

4.2.1 Data for r-Stadis / HITTS Combinations

The results for which r-Stadis is constant at $2mgl^{-1}$, are shown in figure 10 for fuel. In all cases the second additive causes an increase in conductivity. The uncertainty in the points in figure 10 is estimated to be ± 5%.

For both C and D the total conductivities are close to the predicted values, indicating that there is no antagonistic interaction between r-Stadis and either additive.

For B there are indications of some interaction, though this is not large, and this supports earlier results in dodecane[2].

For E at concentrations $<100mgl^{-1}$ the conductivity is approximately the sum of that for the each individual component, but as the concentration increases, antagonistic effects also increase. The measurements show that at $500mgl^{-1}$ the reduction is ~45%.

4.2.2 Data for HITTS / HITTS Combinations

The data are plotted in figure 11. The uncertainty in the points in figure 11 is estimated to be ±5%.

Results for C+D mixtures show no evidence of interaction, with the observed and the predicted values being close. This also seems to be approximately true for C+B mixtures.

For C+E there are large differences between the observed and the predicted values, similar to those for the Stadis + E mixtures, and these provide clear evidence of antagonistic interactions.

Of the remaining three combinations; D+B, D+E and B+E, the first shows good agreement of the observed and the predicted values, whereas for the other two, departures from the predictions are large and again are similar to those seen in the Stadis+E system.

Experiments in which E is at constant concentration, but the concentration of the second HITTS additive is varied and vice versa, confirm that there is interaction between this additive and the additives C and D.

4.3 Additive Use – Possible Scenarios

It has been well known for many years that the conductivity response of fuels to r-Stadis450 – and also to the discontinued additive ASA-3, show important fuel-to-fuel variation. This was further recently illustrated in an annual survey of AVTUR fuels supplied in the UK in 1997[12]. The conductivity statistics show that in spite of the unquantified influences of several factors, fuel response is extremely variable. In practice the initial doping level of static dissipator could be ~1.0 mgl^{-1} in the hope (!) that this will give a conductivity of ~105-112 pSm^{-1} (r-Stadis450). The 1997 statistics indicate that at this concentration one fuel could register, for example, ~ 80 pSm^{-1} (~0.3%) whereas another might register 400 pSm^{-1} (~2%). The percentages are the percentages of fuel batches showing the recorded conductivity response. The most frequently observed response was 200 pSm^{-1}, seen for ~12% of the fuels.

In the following sections we have considered possible ways in which these additives and their mixtures could be used - with accompanying comments.

4.3.1 Conventional SDA is used and only one of the present JP8+100 additives is approved for use as a HITTS additive.

With the HITTS additive added to the fuel at the aircraft "skin" and the SDA already present, the conductivity of the loaded fuel is due to SDA+HITTS. Control of the SDA doping and a knowledge of the conductivity response is required to ensure that HITTS addition does not exceed the fuel specification upper limit, as indicated in table 3 columns 5 and 6. Compared with C there is less flexibility with D due to its greater contribution to conductivity. Additive E is precluded at its normal treat rate since this alone would cause the upper limit to be exceeded.

For any refuelling operation, into an aircraft already containing some fuel, the conductivity is again determined by both SDA+HITTS and the same considerations apply.

4.3.2 Conventional SDA is used and several JP8+100 additives are approved for use as HITTS additives.

With HITTS additive No.1 added to the fuel at the aircraft "skin" and SDA already present, the conductivity of the loaded fuel is due to both SDA and HITTS No1.

For any refuelling operation, into an aircraft already containing some fuel, a different HITTS additive may be in use. We have to ask how this will influence the conductivity. Can the individual conductivities simply be added or are there interactions which interfere? The data presented in Section 4.2 show that there should be no problems with C, D and B in any combination and that antagonistic effects on conductivities becomes important only with E. However, as already noted, E is precluded.

4.3.3 Conventional SDA is discontinued and several JP8+100 additives are approved for use as multi-task additives.

The additives are chosen not only for their HITTS performance but also for their conductivity properties for which additional proving tests may be required.

For this case, with the current fuel specification, the HITTS additive would need to be added earlier in the handling process, to provide static protection, and this requires the water coalescence problems to have been solved. Also in this case, the present HITTS treat rates may not be sufficient to maintain the required conductivity during fuel handling operations.

Since HITTS compounds are surface active, we expect losses to occur within the pipeline system, so that re-doping may be necessary and re-doping limits would need to be established.

In any instance where re-doping is necessary there is the possibility that a different additive may be used. Continuing with this scenario, it is more likely that mixing of HITTS additives could arise due to refuelling in different places. As discussed earlier, it is only for additive combinations which include E that there is interference with the expected behaviour.

In this scenario it may be necessary to ensure a sufficient HITTS additive concentration, in the fuel entering the aircraft, to achieve HITTS performance. This would present difficulties unless a convenient, simple test is available.

4.3.4 Comment on the Upper Conductivity Limit

The controls and checks required with combinations of Stadis 450 and HITTS additives obviously arise because of the present requirement for an upper conductivity limit in the specification. This is due to problems experienced, at "high" conductivity, with some older fuel gauges still in use in certain older aircraft. It seems that there are no such problems with modern aircraft nor are any expected with future aircraft. Perhaps this limit could be raised or even removed.

4.4 Magnitude of Interference with the Conductivity Response of HITTS Additives -Effects of Antioxidant(Ionol), FSII (DiEGME), MDA and "Impurity"(Phenol).

4.4.1 Antioxidant, MDA, FSII

All the additives, except for r-Stadis and A, contain an antioxidant. We observe that the effect of adding Ionol antioxidant, which is of the hindered phenol type and similar to that already present, has little or no effect on the conductivity of any of the r-Stadis or HITTS additive solutions.

This is also true for MDA and for FSII.

4.4.2Phenol

Previous results, on the influence of m-cresol on the conductivity of Betz SpecAid 8Q460 in an additive-free merox fuel, showed there was little or no adverse effect.

In the present experiments, using unsubstituted phenol, there is very little effect on C and B whereas a modest antagonistic effect is seen for D and E as illustrated in figure 12.

4.5 Magnitude of Conductivity Response: Temperature Dependence of Conductivity in Dodecane

Earlier in 4.1.1 we discussed the treatment of temperature dependence in terms of the Arrhenius equation

It is well known that the influence of temperature on a range of equilibrium and kinetic properties of chemical systems can be represented by a relationship of the type:

$$(d \ln X) / dT = (\text{a characteristic heat or energy quantity}) / RT^2$$

where X is the property, T is absolute temperature and R is the universal gas constant. Integration of this equation can lead, via some approximations, to expressions of the form:

$$R \ln X = A - \Delta H/T$$

of which the Arrhenius equation is one example. The advantage of this equation, to represent temperature dependence, is that the calculated value of ΔH may have a meaning that can be associated with processes occurring within the system. Because of this we have chosen to use this type of equation to represent our results. If we take the property X to be the stable electrical conductivity of a solution then the most important factors which influence its value are ion concentrations and ion mobilities.

A change in temperature may cause changes in the equilibrium constant for the ion producing reactions and so alter the ion concentration.

A change in temperature will also alter the solution viscosity, which in turn alters the ion mobility. If we assume that the ion size is unaffected by temperature, then chemical equilibrium and absolute viscosity are the major factors to consider here. If ΔH_T is the value of ΔH determined from the temperature dependence of conductivity, then we write;

$$\Delta H_T = \Delta H_V + \Delta H_E$$

where ΔH_E is the contribution due to ion equilibria and we equate it to the energy (enthalpy) change which accompanies the ion formation process.

The r-Stadis 450 data are plotted as κ versus temperature, figure 13 and as $\ln(\kappa/\mathrm{pSm}^{-1})$ against 1/T in figure 14 where κ is the conductivity in pSm^{-1}. Again, as for additive 8Q405 discussed in 4.1.1, the plot is not linear and has two fairly distinct parts. Values of ΔH_T for the two linear portions are: (a) 18.7 kJmol^{-1} for the "high" temperature region and (b) 12.6 kJmol^{-1} for the "low" temperature region.

For dodecane the temperature dependence of the absolute viscosity is well documented[13]. In the temperature range corresponding to our conductivity data, a plot of ln(viscosity/Pas) against 1/T is closely linear, from which ΔH_V for viscosity is calculated to be 13.9 $kJmol^{-1}$. This we take to be the viscosity contribution to ΔH_T. In view of the uncertainties in the data, especially in the ΔH_T values (one standard deviation is approximately ± 2$kJmol^{-1}$), we see that: (a) $\Delta H_E \sim 0$ in the "low" temperature region and (b) ΔH_E is slightly positive (~ +5$kJmol^{-1}$) but still small in the "high" temperature region. This suggests that the effect of temperature on the conductivity of r-Stadis 450 in dodecane is dominated by the influence of the viscosity.

The other additives were examined at fewer temperatures, but over the same temperature range. For these we quote only the mean values of ΔH_T which were determined using our data at 300mgl^{-1}. These are; E (ΔH_T =14.6 $kJmol^{-1}$), C (ΔH_T = 9.2 $kJmol^{-1}$), D (ΔH_T = 17.3 $kJmol^{-1}$), B (ΔH_T = 14.5 $kJmol^{-1}$).

We note the similarity with the mean value for r-Stadis 450 and conclude that, for all these packages, viscosity plays an important, if not a dominant role, in the temperature effect.

4.6 Magnitude of Conductivity Response: Temperature Dependence of Conductivity in Fuel F-2

The approach is the same as that described in Section 4.5. Since the temperatures were limited to 0°C, 25°C and 50°C, again we quote only the mean value of ΔH_T obtained for each additive. These were determined from the data at a concentration of 300mgl^{-1} and are as follows: E (ΔH_T =12.2 $kJmol^{-1}$), C (ΔH_T =15.5 $kJmol^{-1}$), D (ΔH_T =19.6 $kJmol^{-1}$), B (ΔH_T =15.7 $kJmol^{-1}$). For r-Stadis 450, in fuel F-1, the range was 20°C to 60°C, which corresponds to the "high" temperature range. The mean value, calculated from the data at 3mgl^{-1}, is ΔH_T =21.6 $kJmol^{-1}$.

Previously, the most extensive data on temperature dependence of conductivity are those obtained by the joint efforts of Henry[14] at Dupont and Gardner and Moon[4] at NRC Canada, for "Old" Stadis 450 in a range of Canadian jet fuels. There seem to be no similar published temperature data on r-Stadis 450. We have compared our data with those from the earlier work.

The Gardner-Moon and Henry data are represented by expressions of the form[4,13]

$$\log_{10} \kappa_1 = n(t_1 - t_2) + \log_{10} \kappa_2$$

where κ_1 and κ_2 are conductivities measured at the temperatures t_1 °C and t_2 °C respectively and n is a "temperature/conductivity" coefficient.

We have calculated values of ΔH_T from their listed values of n and temperature range data. The results, as expected, show fuel to fuel variation, but values fall within fairly narrow limits of approximately 16 to 22kJmol^{-1}.

It is noteworthy that a closer examination of some of their recorded conductivities for the temperature range –34°C to +43°C indicates that the log(conductivity/pSm^{-1})-1/T relationship is not linear, as also seen in our results for r-Stadis in dodecane. There is no viscosity information available for the Canadian fuels but we have obtained an estimate for a "typical" JP-8 fuel using the information provided in the CRC Handbook of Aviation Fuel Properties[15].

The mean value of ΔH_V for the temperature range 0°C to 50°C is 13.0kJmol^{-1}. This is close to the value observed for dodecane. Again it appears that viscosity changes, resulting from temperature changes, have a major effect on conductivity.

4.7 Comments on ΔH Values and Possible Implications

With the exception of additive C in dodecane, all the systems examined in dodecane and in fuel, have ΔH_E values which are near to zero but are generally positive. This reflects the influence of temperature effects on chemical equilibria which gives rise to changes in ion concentrations. With allowances for the uncertainties in the actual values of ΔH_E for the additives studied, clearly they are very small when compared, for example, with ionic dissociations in the gas phase. The latter can be thought of as equilibria in a "solvent" of dielectric constant equal to 1.0 and having no polarity. For example, for the gas phase dissociation of molecular KCl into K^+ and Cl^-, ΔH_E(dissociation) is very high ~ +500kJmol^{-1} and is a major factor prohibiting the dissociation. However, if K^+ and Cl^- ions were produced in the presence of water vapour, then both ions would be stabilised by hydration and the ΔH for production of hydrated ions (neglecting solvation of the molecule KCl) would be reduced to ~ +80kJmol^{-1}. Even so, this is still a fairly high value and it is only in bulk water that KCl is a strong electrolyte ie it is completely dissociated into ions. The precise mechanism via which this system is stabilised is complex, but the behaviour can be described in thermodynamic terms and involves both entropy and enthalpy effects.

Likewise the dissociation of weak electrolytes in water involves enthalpy and entropy effects in which the latter are very important and involve important changes in water structure in the vicinity of ions. Such an effect could be important for Stadis450 and Hitts additives in our solutions.

If we consider the molecules studied in this work to be weak electrolytes, then their behaviour is reminiscent of aspects of the behaviour of weak electrolytes, eg carboxylic acids, in aqueous solution[16]. Examples of these are (i) curvature of plots of $\log K_{dissociation}$ against 1/T (ii) $\Delta H_{dissociation}$ which are small (up to ~ +5kJmol^{-1}) and can be negative. It may seem inappropriate to compare aqueous with non-polar solutions, but the comparison may provide a clue to an explanation of their behaviour.

In earlier work we have speculated on the types of equilibria which may feature as ion producing reactions[7,8] . Simple dissociation of additives to produce ions is energetically extremely unfavourable, as discussed above, and ion stabilising interactions seem to be necessary to generate sufficient ions to provide the observed conductivity. But what are the ion concentrations in these solutions?

4.8 Estimate of Ion Concentrations

To our knowledge there are no reported estimates in the literature. It is both possible and instructive to obtain an estimate of the ion concentrations in these solutions and this has been done as follows:

We base the calculation on a solution containing 100mgl^{-1} of additive in dodecane.

The measured conductivity is in the range 100×10^{-12}Sm^{-1} to 300×10^{-12}Sm^{-1} (i.e.100 to 300pSm^{-1}).

The relationship between conductivity,κ and molar concentration, c, is

$$1000\kappa/c = \Lambda$$

where Λ is the molar conductivity. So

$$c = 1000\kappa/\Lambda$$

Molar conductivities depend on ion size and solvent viscosity and for water at 25°C they range from ~ 20 $\mathrm{Scm^2mol^{-1}}$ for large organic ions such as quaternary ammonium, to ~ 350 $\mathrm{Scm^2mol^{-1}}$ for the hydrated hydrogen ion which has an unusually large value due to an abnormal conducting mechanism[17]. A value of 80 – 100 $\mathrm{Scm^2mol^{-1}}$ seems a more realistic upper limit. We will assume that the ionisation process creates ions having a total molar conductivity of ~100 $\mathrm{Scm^2mol^{-1}}$. If some allowance is made for the change in viscosity from water to dodecane the value is ~ 60 $\mathrm{Scm^2mol^{-1}}$ ($6\times10^{-3}\mathrm{Sm^2mol^{-1}}$).

This gives $c = \sim1.7\times10^{-11}$ mol $\mathrm{l^{-1}}$. Since Λ is unlikely to be in error by a large factor – say by a factor of five, this ion concentration should be a fair indicator of the very low values present.

If we now estimate the molar concentration of additive in solution, then the degree of dissociation can be obtained. For this calculation we require the molecular weight of the additive. If this is taken to be 1000, which may be reasonable for a succinimide type additive, then the molar concentration is 1×10^{-4}mol $\mathrm{l^{-1}}$ and the degree of dissociation is ~ 1.7×10^{-7}. Translated into thermodynamic terms this corresponds to a large and positive value, possibly up to100kJmol^{-1}, for the free energy for ion production ΔG_E. This combined with the small values of ΔH_E implies that the entropy change ΔS_E is large and negative, possibly ~ –300$\mathrm{JK^{-1}mol^{-1}}$, and is the major contributor to the free energy change. This is contrary to expectation for a simple dissociation, for which ΔS would be positive, but is similar to behaviour seen with weak acids in water as mentioned earlier.

One explanation is that some of the dissolved water, which in the absence of additive is randomly distributed within the hydrocarbon, becomes, in the presence of the additive, bound to the ions produced. This would lead to considerable loss of entropy which, as a simplification, can be compared to the decrease when water vapour condenses to liquid or possibly to solid.

Such changes are accompanied by entropy decreases of -119 $\mathrm{JK^{-1}mol^{-1}}$and -144 $\mathrm{JK^{-1}mol^{-1}}$ respectively. These are quite consistent with the large change envisaged since it is possible that more than one molecule of water is associated with one ion.

We accept that the above discussion includes several fairly major assumptions. However, its main purpose is to serve as a stimulus to further thinking about the basic science of these systems of which we still know very little.

5. CONCLUSIONS

1. All the studied Hitts additive packages impart conductivity to dodecane and fuel.

2. The conductivities for the three additives B, C and D alone at their recommended treat rates in fuel, all fall within the current fuel specification limits.

3. The conductivity of additive E, at the recommended treat rate in fuel, far exceeds the current fuel specification upper limit.

4. For any binary combinations of the additives r-Stadis450, C and D, the observed conductivity is approximately that for the sum of the individual components and there seem to be no adverse interactions. For B there is evidence of "weak" interaction.

5. For any binary combinations in which one component is additive E, the observed conductivity is less than that for the sum of the individual components and this is indicative of intermolecular interactions.

6. Co-additives and Phenol
   Antioxidant, MDA and FSII have no detrimental effect on the conductivity of Hitts additives. Unsubstituted phenol has a modest antagonistic interaction, but only with D and E.

7. The temperature dependence of the conductivity is mainly due to the temperature dependence of the dodecane or fuel viscosity.

8. The effect of temperature on ion formation equilibrium is small.

9. An estimate of ion concentration has been obtained and provides an indication of how low this is.

10. Tentative arguments suggest that entropy effects have a major controlling influence on ion formation equilibrium constant(s).

6. ACKNOWLEDGEMENTS

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7. DISCLAIMER

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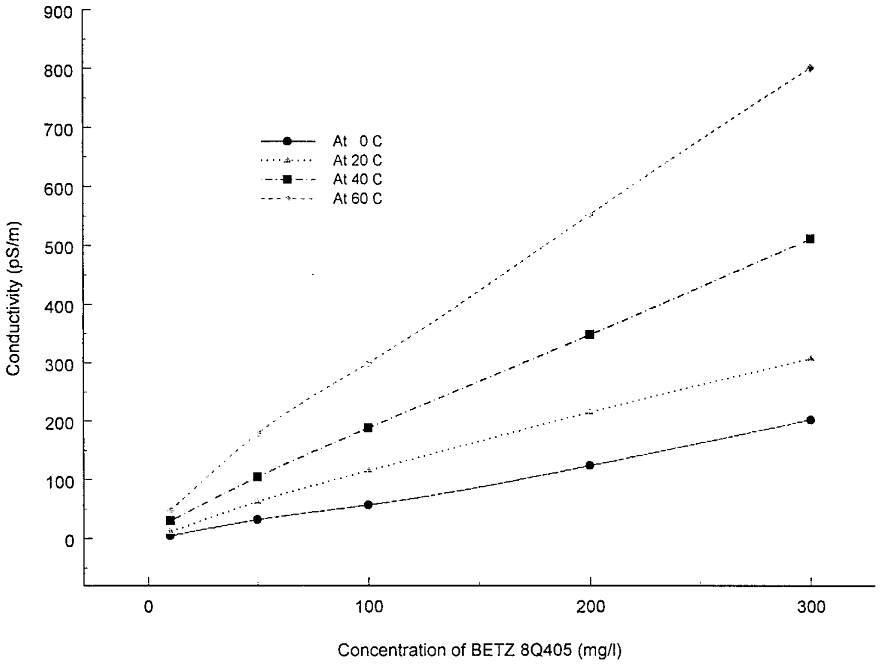

Figure 1 Conductivity vs. 8Q405 concentration at different temperatures in dodecane

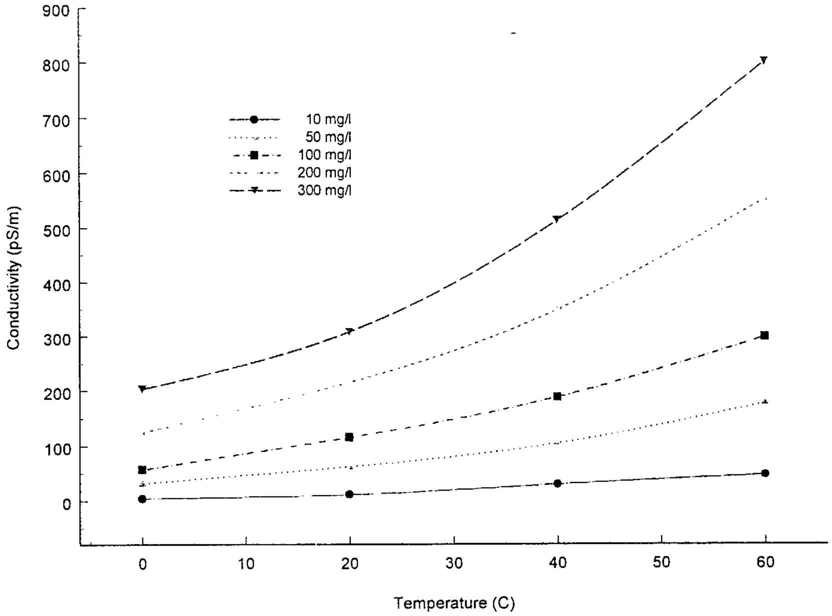

Figure 2 Change in conductivity of dodecane with temperature and 8Q405 concentration

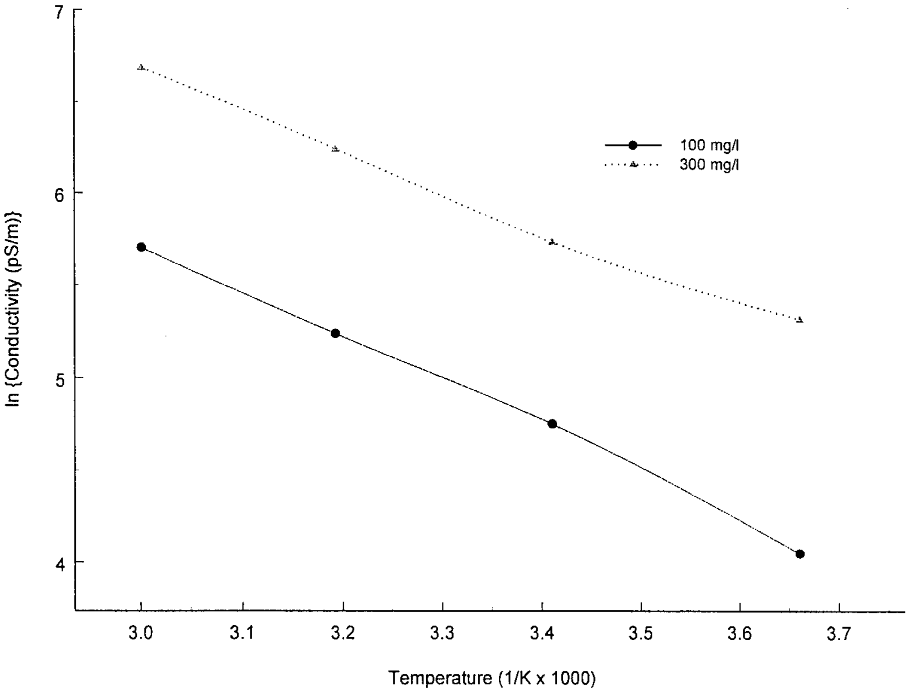

Figure 3 Log conductivity of 8Q405 in dodecane with inverse temperature

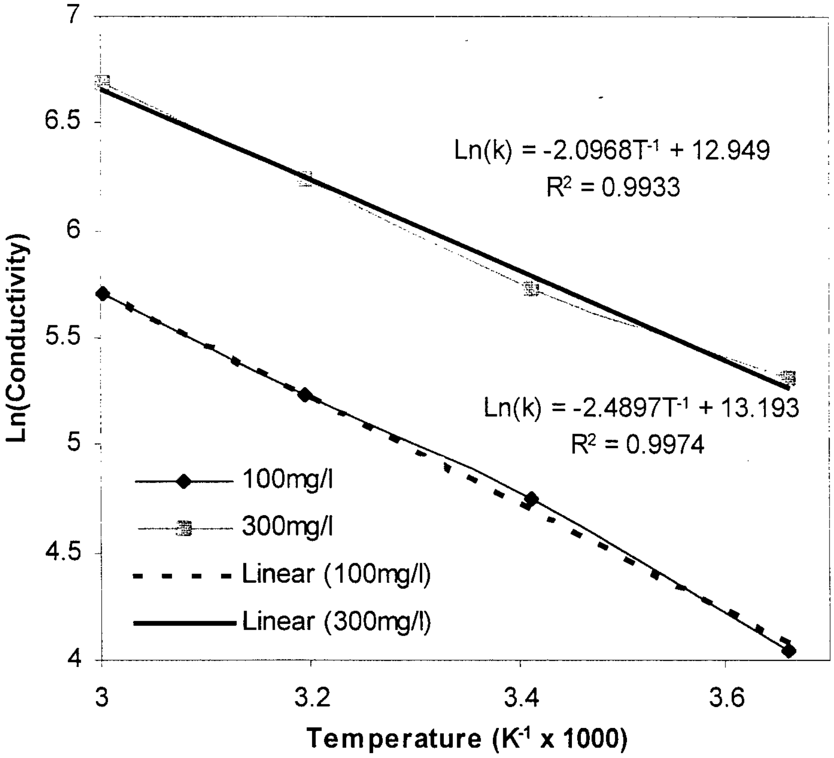

Figure 4 Application of linear regression to data from 8Q405 in dodecane.

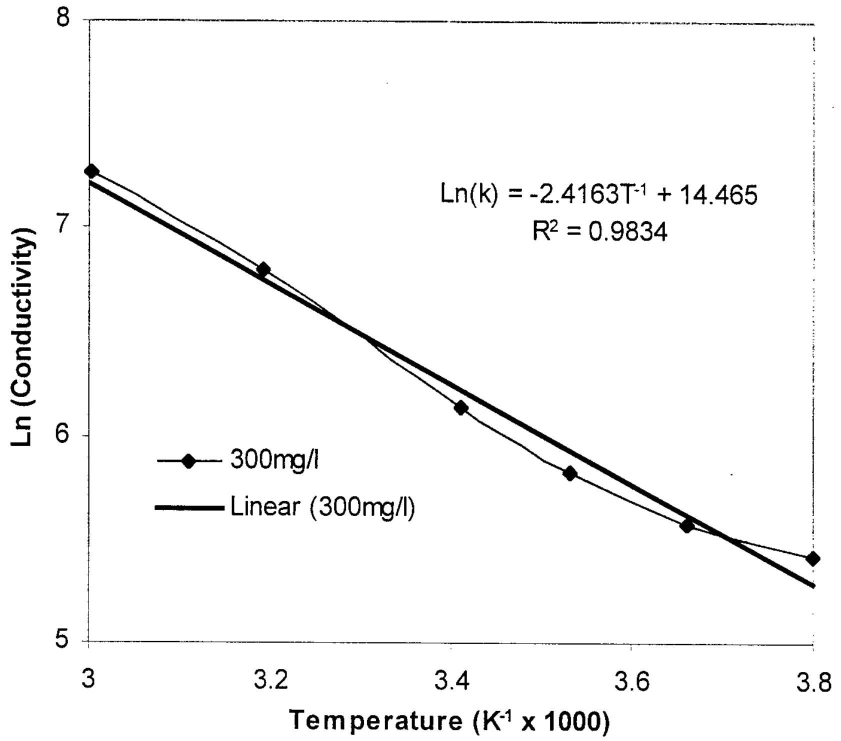

Figure 5 Application of exponential regression to data from 8Q405 in Merox-1

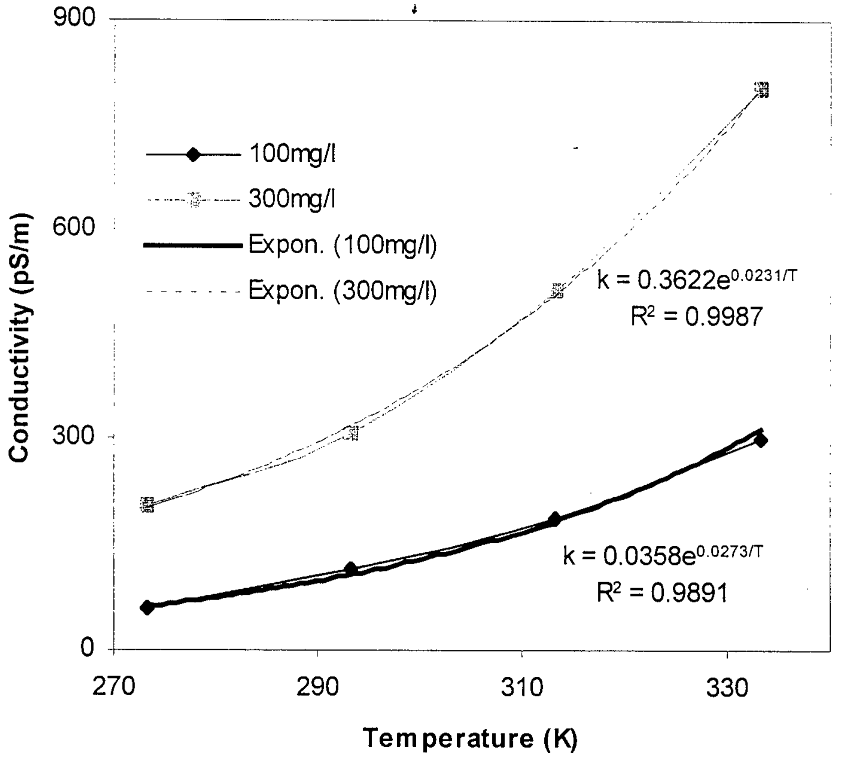

Figure 6 Application of linear regression to data from 8Q405 in dodecane

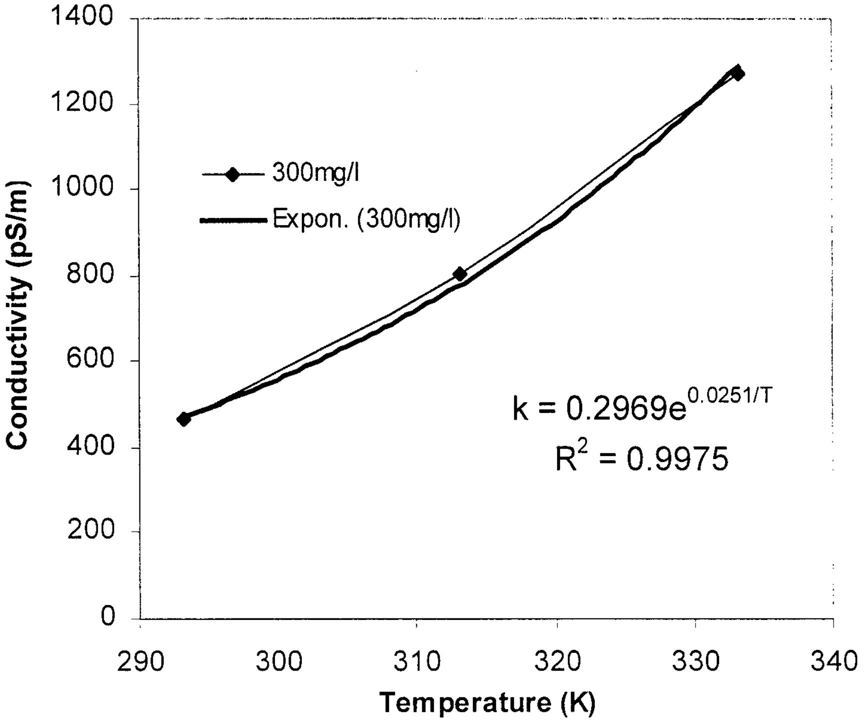

Figure 7 Application of exponential regression data from 8Q405 to Merox-1

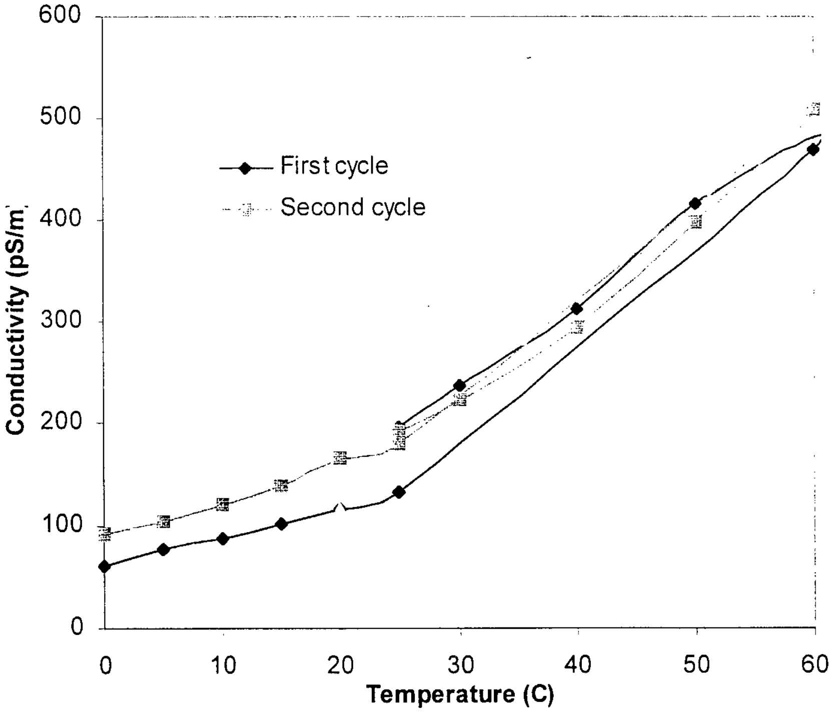

Figure 8 Effect of thermal cycle on the response of 8Q405

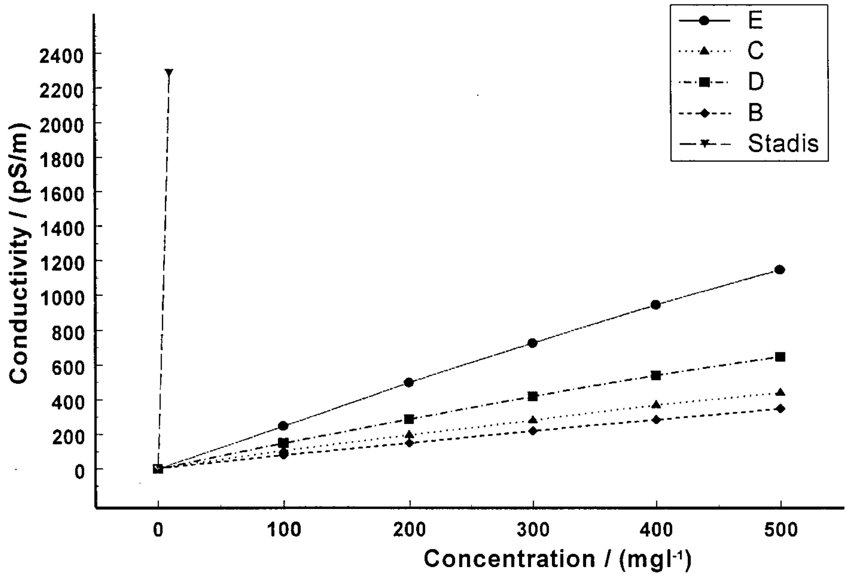

Figure 9 Change in Conductivity with Concentration of r-Stadis 450 and Additives B, C, D and E in Dodecane at 25°C

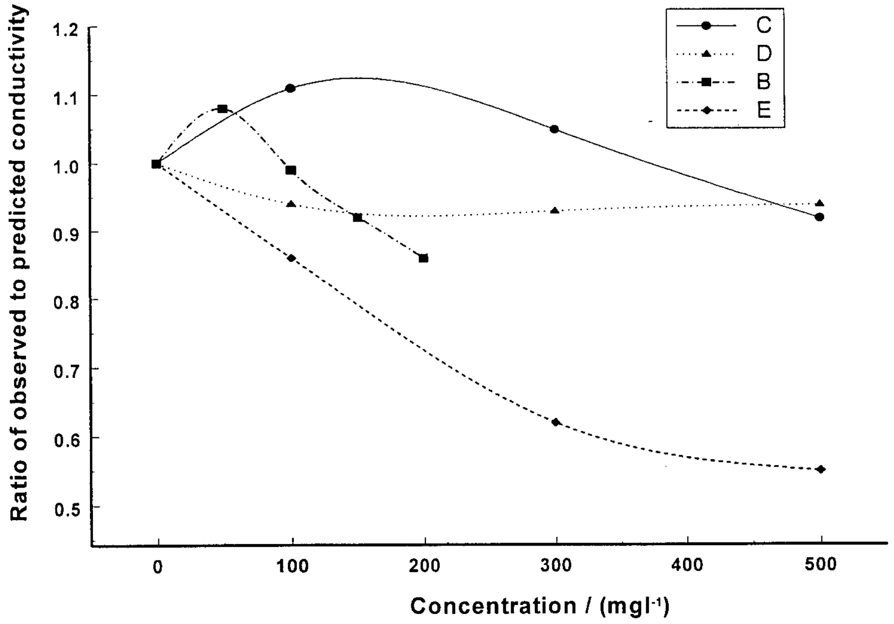

Figure 10 The Conductivity of r-Stadis 450 in Combination with Additives B, C, D and E, for r-Stadis constant at 2mgl^{-1}, in Fuel F-2, at 25°C. Plot of [κ_{observed} / $\kappa_{\text{predicted}}$] vs. concentration of additive.

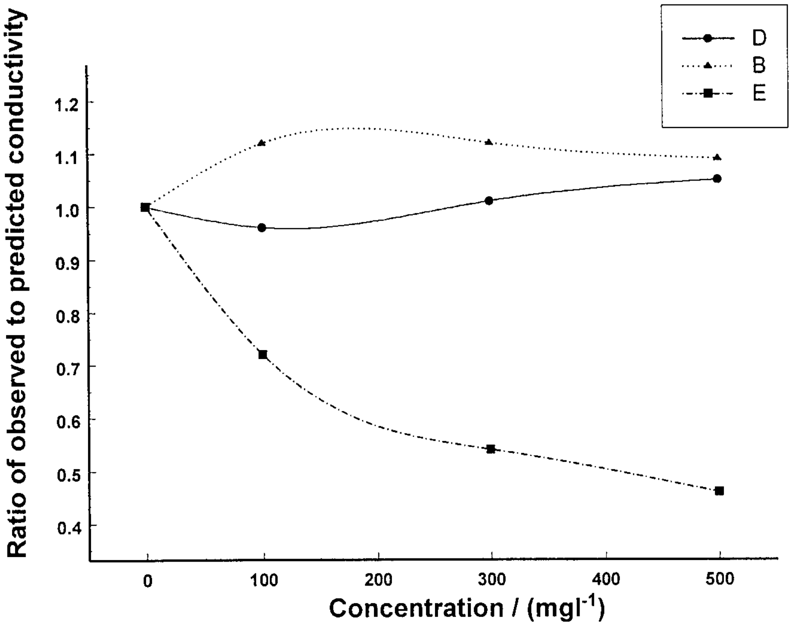

Figure 11 The Conductivity of Additive C in Combination with Additives B, D and E, for C constant at $500 mgl^{-1}$, in fuel F-2 at 25°C.
Plot of $[\kappa_{observed} / \kappa_{predicted}]$ vs. concentration of additive.

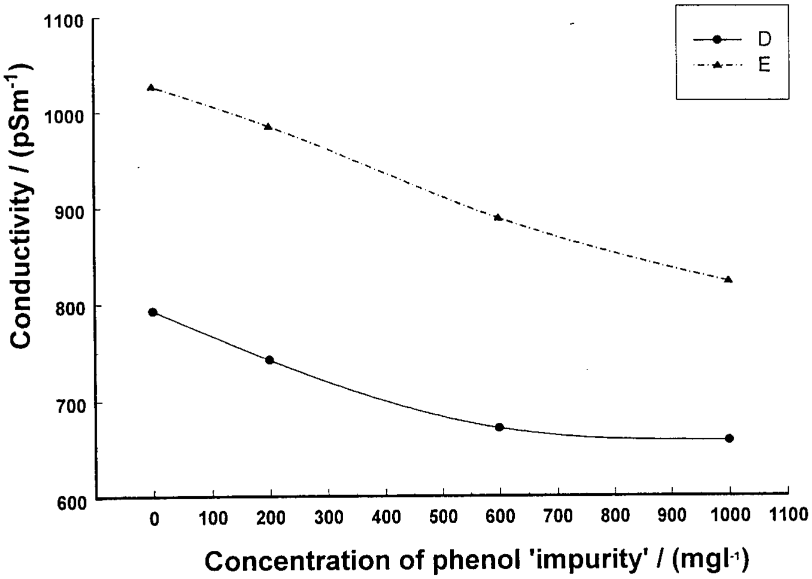

Figure 12 The Effect of Phenol 'Impurity' on the Conductivity of E and D in Fuel F- 2. Concentration of both E and D is $500 mgl^{-1}$.

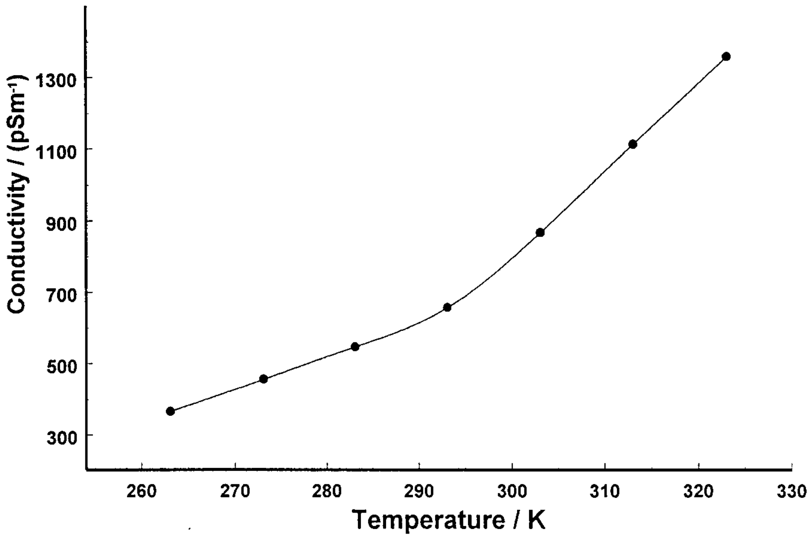

Figure 13 The Effect of Temperature on the Conductivity of r-Stadis 450 in Dodecane. Stadis Concentration is 3 mgl^{-1}.

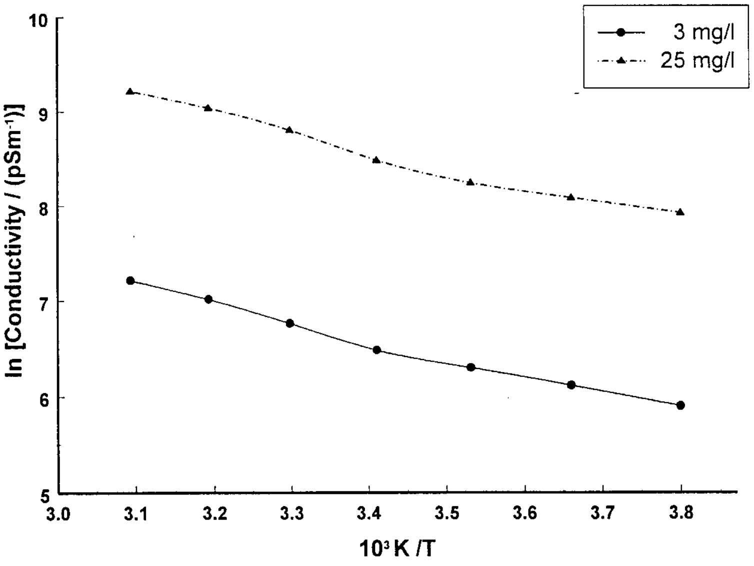

Figure 14 The Effect of Temperature on the Conductivity of r-Stadis 450 in Dodecane. Plot of ln [Conductivity /pSm^{-1}] vs. 1/Temperature

Table 1 Descriptive statistics from 8Q405 in dodecane using linest function.

Temp^{-1} (x 10^3)	100mg/l	300mg/l	Linest output for 100mg/l		Slope	Intercept	Linest output for 300mg/l		Slope	Intercept
3.6608	4.0478	5.3163			-2.4897	13.1933			-2.0968	12.9491
3.4111	4.7518	5.7326			♦0.0896	♠0.2981			♦0.1221	♠0.4062
3.1932	5.2398	6.2410		R^2	0.9974	♥0.0441		R^2	0.9932	♥0.0600
3.0015	5.7029	6.6884	Sta. dev. of error			0.0177	Sta. dev. of error			0.0286

♦= the standard error in the slope, ♠= the standard error in the intercept, ♥= the standard error in the y estimate.

The above slopes correspond to E_a = 20.7 ± 0.7 kJ mol^{-1} and 17.4 ± 1.0 kJ mol^{-1} for 100 and 300mgl^{-1} respectively.

Table 2 Descriptive statistics from 8Q405 in Merox using linest function.

In this case E_a = 20.1 ± 1.3 kJ mol^{-1} (300mgl^{-1})

Temp^{-1} (x 10^3)	300mg/l				
3.7999	5.4216	Linest output for 300mg/l		Slope	Intercept
3.6608	5.5752			-2.4162	14.4653
3.5315	5.8291			♦0.1570	♠0.5409
3.4111	6.1376		R-Squared	0.9833	♥0.1042
3.1932	6.7947		Std. Dev. of error		0.0427
3.0015	7.2623				

Table 3
Conductivity of solutions of SDA and HITTS additives at 25°C

Additive	Hydro-carbon	Conductivity/pSm^{-1}		Upper conductivity limit imposed on SDA contribution /pSm^{-1}	
		At Treat Rate	Per 100 mgl^{-1}	JP8 (450max)	JP8+100 (700max)
r-Stadis450	Dodecane	700	20000		
	Fuel F-1	760			
	Fuel F-2	780			
B (96-POSF-3256)	Dodecane	180	70		
	Fuel F-1	216		234	484
C (98-POSF-3558)	Dodecane	210	95		
	Fuel F-2	175		275	525
D (99-POSF-3598)	Dodecane	320	139		
	Fuel F-2	363		87	337
E (99-POSF-3724)	Dodecane	940	235		
	Fuel F-2	1250		Limit exceeded by E	Limit exceeded by E