# A Liquid Thermistor

**A liquid thermistor consisting of a salt-triethylamine-water solution shows a resistance increase of 100% per degree centigrade over a range of 8°C. Outside this specific temperature range, the resistance changes slowly. The altered resistance results from the phase change at the critical solution temperature. While devices of this type can show major hysteresis and are restricted to specific temperatures, their response is faster than a millisecond.**

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## SCOPE

This paper investigates a solution whose electrical resistance changes radically with temperature. Such a solution can be used as a liquid thermistor or a liquid fuse. Since this work has been concerned with large changes in specific conductance, it has been part of the studies in these laboratories aimed at making mass transfer fast and selective.

The change in the observed resistance results from a phase change forming an emulsion near the lower critical solution temperature of an electrolyte solution. This change depends on the composition of the continuous phase of the emulsion. While electrical resistance is frequently used to discriminate between water-in-oil and oil-in-water emulsions (Adamson, 1960), the results here represent, to my knowledge, the first effort to utilize this large effect. Thermistors or fuses based on such a solution are in considerable contrast with other efforts concentrating on liquid metals, which have much lower resistivities (Cohen and Lucovsky, 1972). They also differ from the sharp resistance changes in organic solids, which show much higher resistivities (for example, Kadoi et al., 1972).

## CONCLUSIONS AND SIGNIFICANCE

A liquid thermistor based on a solution of sodium chloride-triethylamine-water shows a large change in resistance with temperature. If triethylamine is present in excess, the resistance increases about 100% per degree centigrade from 18 to 26°C. Outside this specific temperature range, the change is the modest amount expected, a decrease of about 5% per degree. If water rather than triethylamine is present in excess, the resistance decreases about 15% per degree from 18 to 22°C.

For the case of excess triethylamine, the large increase in resistance results because the sodium chloride is concentrated in the water-rich droplets of an emulsion in a triethylamine-rich continuum. For the case of excess water in the solution, the decreased resistance results from the decreased formation of ion pairs in a water-rich continuum.

The response of these devices is rapid—faster than $10^{-3}$ sec. Their response is limited only by the time necessary to form ion pairs and emulsion droplets. However, they can show very large hysteresis if the emulsion separates into two layers. Hysteresis is removed by stirring the solution or by using a surfactant like sodium dodecyl sulfate as the electrolyte and adding the solution to a porous glass frit. Thermistors prepared in this way are stable for at least several months.

While liquid thermistors of this type are more easily adapted to a specific temperature range than pure materials, they are obviously restricted to temperatures where liquid solutions exist. The advantage of their rapid response is compromised by the possibility of hysteresis. If these devices are to find even specialized application, they must be developed further to be smaller than their solid state counterparts and more reversible with temperature.

### EXPERIMENT

Reagent grade chemicals were used without further purification in all experiments. As a result, the solutions were somewhat impure and showed slightly different critical solution temperatures than those in the literature (Campbell and Kartzmark, 1967). Solutions were prepared by weight. Their resistances were measured either by inserting electrodes into a solution stirred at 150 rev./min. or by clamping electrodes on opposite sides of a glass frit with $10^{-5}$ m pores. Resistances were measured with a Shedlovsky or an Industrial Instruments model 2B bridge. The response of the system was measured using an Eigen-Meyer temperature jump apparatus.

### RESULTS AND DISCUSSION

The change in resistivity of a triethylamine-water solution containing 0.1 wt. % sodium chloride is shown in Figure 1. For solutions containing excess water, the resistivity decreases slightly. At 10 wt. % triethylamine, the decreased resistivity is about that expected in a typical electrolyte solution. At 30 wt. % triethylamine, the resistivity decreases more abruptly, but this decrease is still only about 50% from 18° to 22°C.

However, for solutions containing more than 50 wt. % triethylamine, the resistivity increases sharply starting at a temperature of 18°C. Above 26°C, the resistivity again

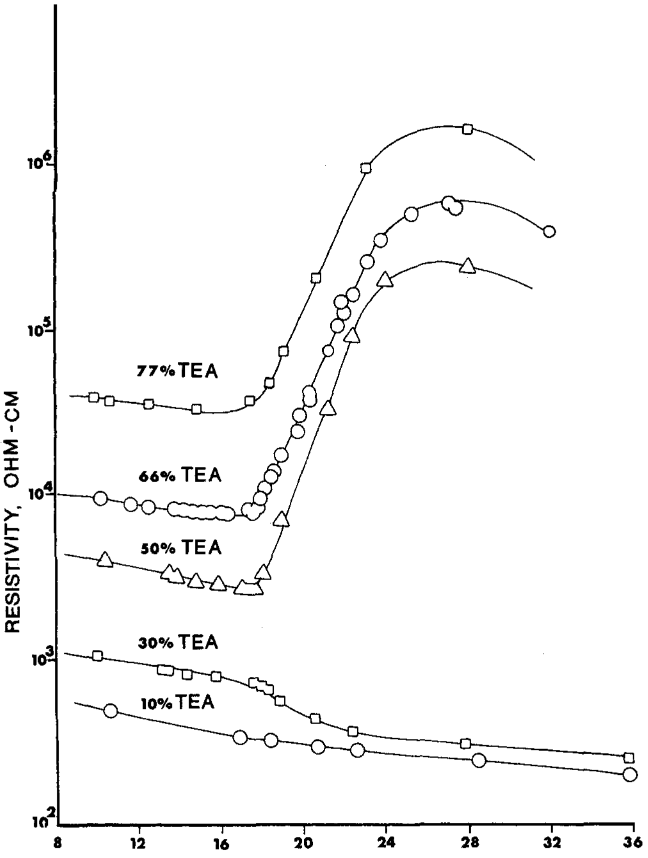

Fig. 1. Variation of resistivity with temperature for 0.1% sodium chloride-triethylammine-water.

reaches a more constant value, about two orders of magnitude above the resistance at 18°C. Over this eight-degree range, the logarithm of the resistivity is approximately proportional to the temperature.

The physical origin of these effects becomes clearer when one looks away from the resistance bridge at the actual mixture of NaCl-triethylamine-water. Below about 18°C, this mixture is a true solution, clear and without any turbidity. Above this critical solution temperature, the system separates into a two phase emulsion. The water-rich phase will contain most of the salt in an ionized form. The triethylamine-rich phase will contain much less salt.

When the water-rich phase is present in excess, it will be the continuous phase in the emulsion. As the temperature increases, the water-rich phase will contain more and more water, and hence more and more salt. As a result, the resistivity will decrease with increasing temperature. This decrease has been shown to result both from increased ionic mobility and from decreased ion pair formation. However, while this small effect could be increased by using a weak electrolyte, it is not investigated further.

### The Case of Excess Triethylamine

When the triethylamine is present in excess, then the triethylamine-rich phase will be the continuous one. As the temperature increases, this phase will contain less and less water and hence less and less salt. The resistivity will then increase with temperature.

This effect can be understood more completely by considering the specific resistance $r$ of a suspension of spheres (Maxwell, 1873):

$$\frac{r}{r_C} = \frac{2r_D + r_C + \phi_D(r_D - r_C)}{2r_D + r_C - 2\phi_D(r_D - r_C)} \tag{1}$$

where $r_C$ and $r_D$ are the specific resistances of the continuous and discontinuous phases, respectively. While this equation is an approximation, more exact expressions (Newby et al., 1973) introduce complexities which obscure the physical significance here. For the continuous phase, the specific resistance is (Robinson and Stokes, 1959)

$$r_C = [(\lambda_+ + \lambda_-)\,C_+]^{-1} \tag{2}$$

where the $\lambda$'s are the ionic conductances and $C_+$ is the cation concentration, all in the continuous phase. When the triethylamine-rich phase is continuous, $r_C >> r_D$ so Equations (1 to 2) become

$$r = \left[\frac{1 + 2\phi_{H_2O}}{\phi_{TEA}}\,(\lambda_+ + \lambda_-)\,C_+\right]^{-1} \tag{3}$$

The solubility of salt in pure triethylamine is much less than the solubility in pure water so that the amount of water in the triethylamine-rich phase dominates $C_+$. As the temperature increases, this amount decreases sharply so that $C_+$ in turn decreases. The resistance then increases.

Thus the dramatic differences for excess triethylamine and excess water shown in Figure 1 result from the fact that the salt is concentrated in the discontinuous and the continuous phases, respectively. One accidental experiment illustrates this dramatically. We first observed a sharp resistance increase with temperature for 47 wt. % triethylamine, but then the resistance suddenly dropped almost instantaneously to substantially less than the initial value. The explanation was that the emulsion had inverted. The triethylamine-rich phase was originally the continuous one in the emulsion; then it became the discontinuous

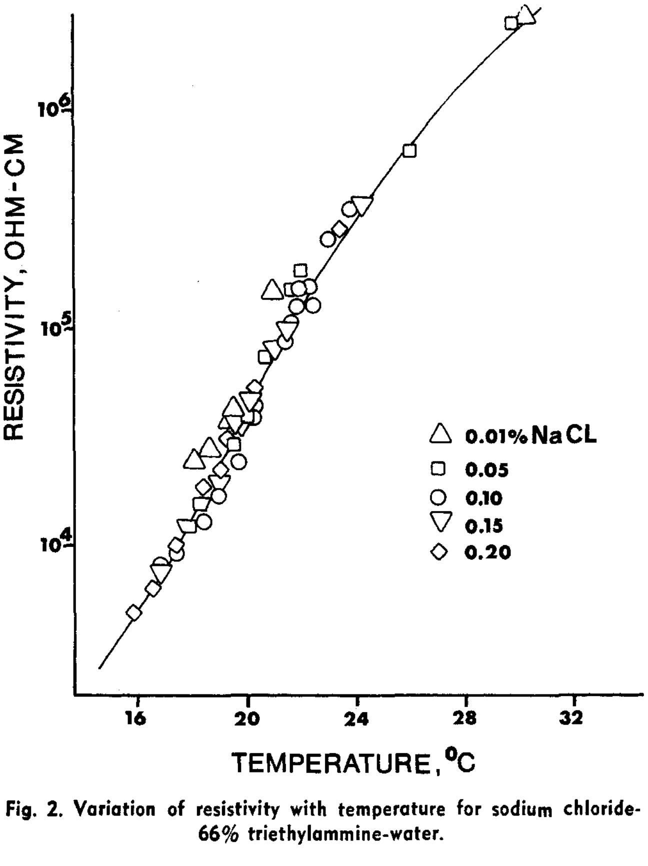

Fig. 2. Variation of resistivity with temperature for sodium chloride-66% triethylammine-water.

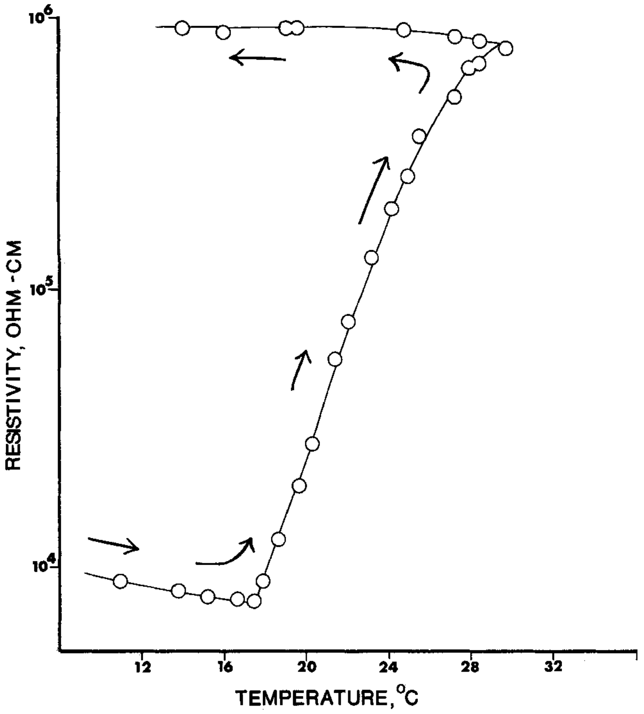

Fig. 3. Hysteresis in an unstirred mixture of 0.1% sodium chloride-66% triethylammine-water. (The arrows indicate the direction of temperature change.)

one, effecting the drop in resistance.

The resistance of the emulsion containing excess triethylamine seems to be independent of salt concentration as shown in Figure 2. I suspect that this represents an accidental cancellation of two factors. The first factor is that adding salt lowers the resistance. The second factor is that adding salt lowers the temperature at which the emulsion first forms; thus at a given temperature, the weight fraction water and hence the salt's solubility in the triethylamine-rich phase are decreased. It is easy to see how these factors could sometimes cancel; I cannot see why they should cancel exactly in all cases.

### Hysteresis

The resistances shown in Figures 1 and 2 were obtained both when the temperature was rising and when it was falling. No systematic difference occurred between the two cases. However, these experiments were made with a stirred solution in which the emulsion was maintained by stirring.

If the emulsion is not stirred, major hysteresis such as that shown in Figure 3 occurs. In this experiment, a cold solution was placed between two horizontal electrodes separated vertically by about 0.015 m. As the temperature was raised at 0.5°C/min., the system separates into two layers. The lower layer is formed as the heavier water-rich droplets fall out of the solution; the upper triethylamine-rich layer has a very high resistivity. While the layers form rapidly because of free convection, they do not diffuse back together at all rapidly when the temperature is lowered at the same rate. Indeed, without stirring, the high resistivities below 17°C shown in Figure 3 would drop back to the initial values only after many months.

We minimized this hysteresis by using 0.2% sodium dodecylsulfate as the electrolyte and by placing the solution in a glass frit with 1-3$\mu$ pores. When the temperature is raised, the solution in the pores still should form two phases, but these phases can not separate large distances. As a result, the separated phases should quickly interdiffuse when the temperature is lowered. Experimentally, we found that hysteresis is still evident at times below 2 sec., but the resistance changes obtained are comparable to those with stirring.

### Response

The final aspect of the performance of this device is its response. When its temperature is raised from 16 to 19°C in a microsecond (Caldin, 1964), the solution becomes turbid with a half life faster than one millisecond. This result is independent of salt concentration and instrument dimensions. Since the onset of turbidity coincides with the altered resistance, this implies that the resistance change occurs at a similar speed. While this is considerably faster than the response times of most fuses, the total resistance change is of course much less. Whether this system can find application will require further development on a well-defined practical problem.

### Other Chemical Systems

Similar resistance changes are observed in other chemical systems such as isobutyric acid-water and sodium chloride-methanol-cyclohexane. These cases involve upper critical solution temperatures so the resistance changes are the opposite of those reported here. These effects are smaller.

The location of the temperature range over which these effects occur is not limited to near the critical solution temperature exhibited by the binary solution but can be altered by the addition of another component. If this new component is soluble in both solvents, an upper critical solution temperature will be lowered and a lower critical solution temperature will be raised. If the new component is much more soluble in one solvent than in the other, the opposite effects occur: an upper critical solution temperature is raised and a lower critical solution temperature is lowered (Prigogine and Dufay, 1954). For example, in this work, the lower critical solution temperature, and hence the location temperature range where the resistance changes fast, is decreased about 10°C per mol/l sodium chloride added. In addition, one might be able to minimize hysteresis by using such a solution in a gel or liquid crystal in place of the porous glass frit. Thus in developing a device based on this effect, one need not be constrained by the critical solution temperatures of the binary systems.

## ACKNOWLEDGMENTS

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## NOTATION

$C_+$ = concentration of cation in the continuous phase
$r$ = specific resistance of emulsion
$r_C$, $r_D$ = specific resistances of continuous and discontinuous phases, respectively
$\lambda_i$ = ionic conductance of ion $i$
$\phi_C$, $\phi_D$ = volume fractions of continuous and discontinuous phases, respectively

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# Independent Reactions in the Presence of Isomers

**In reacting systems, the number of independent chemical reactions, the number of components, and the number of chemical species are generally assumed to be so related that the sum of the first two equals the third. Standard methods of obtaining the number of independent reactions (that is, formation equations or rank of the element-by-species matrix) may fail when chemical isomers appear in reactant streams, product streams, or both. The errors encountered with various types of isomers are delineated in this paper along with corrective measures. The element-by-species matrix is judged to be more suitable as a starting point than formation equations when matrix size and number of manipulations are considered.**

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## SCOPE

**Process design requires initial completion of all material and energy balances. The designer must be able to enumerate the numbers of independent material balances, independent reactions, and degrees of freedom. When chemical isomers are present in the reactant and/or product streams, the usual techniques for establishing the quantities may, and frequently will, fail to produce correct results. The objectives of this paper are to provide corrective action to one of the standard techniques so as to eliminate such failures, to incorporate these corrections into a few simple statements which may be added to an existing rank-determining computer program, and to plan the program for use as a subroutine in a more extensive program to calculate the degrees of freedom for any configuration of elements in a process specification.**

## CONCLUSIONS AND SIGNIFICANCE

**When isomers appear in the product and/or reactant streams of a processing unit, the usual methods of relating numbers of species, numbers of components, and numbers of independent reactions may be inapplicable. Two common methods are the establishment of the numbers of independent reactions by the method of formation equations or, alternately, the determination of the number of components as the rank of the element-by-species matrix. In either instance, the total number of chemical species can readily be counted. Then, using the generally accepted relationship that the number of species is equal to the sum of the numbers of components and independent reactions, either method allows the calculation of the missing element in this relationship.**

**When isomers are present neither one of these methods can be counted upon to give correct results. It is therefore impossible either to establish the number of independent material balances which can be drawn around the unit or to calculate the enthalpy change attributable to the reactions. Since these calculations relating quantities in the external streams of the unit must precede all calculations of internals (that is, design considerations), no systematic analysis of material balances, energy balances, or numbers of independent specifications can be established.**

**This paper presents a method and a computer program for obtaining correct numbers of independent material balances and chemical reactions, thereby allowing preliminary design calculations to proceed. It is shown that either the element-by-species matrix or the formation equations matrix may constitute a starting point. The former is chosen and emphasized here since it provides a much smaller matrix and a greatly reduced number of matrix manipulations.**

**Using the computer program developed here, a more extensive program can be written providing the degrees of freedom available to the designer for any processing elements or unit. This latter program, which is the ultimate objective motivating the present work, will be presented at a subsequent date.**

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[*] Supplementary material has been deposited as Document No. 02250 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., N. Y., N. Y. 10017 and may be obtained for $1.50 for microfiche or $2.00 for photocopies.