

OPEN ABSORPTION-BASED AIR CONDITIONING SYSTEMS

**ESTIMATING LIQUID DESICCANT CONCENTRATION
FROM THE
SPECIFIC ELECTRICAL CONDUCTIVITY**

Calculation Methods for Aqueous LiCl

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Zurich, January 2012**

Introduction

One of the most important advantages of the use of liquid desiccants in sorption-based air conditioning devices, in relation to other systems, e.g. solid desiccant based systems, is the possibility of storing energy as concentrated desiccant. This is particularly important when driving the system with an intermittent energy source e. g. solar thermal energy. Such an energy storage is practically lossless, and has a significantly higher energy density than a thermal storage, as would be necessary in the case of a solid desiccant based system. On the other hand, the flexibility provided by an accurate control of the concentration of the solution supplied to the conditioner (absorber) is more effective than the variation of flow rates, for example. To control, requires the measurement of the desiccant concentration variation in the process, and of the useful effects of this variation upon the desired conditions of the air.

The concentration of a liquid desiccant (aqueous solution) in a process cannot be directly measured as such. It has to be obtained through the measurement of some other, easier to measure, characteristic. Any measurable property having a dependence from concentration is, theoretically, interesting. In practice this measurement needs to be simple, provide a good enough resolution, be reliable and not expensive.

Traditionally, the concentration of an aqueous solution is determined by measuring its density at a given temperature. This may be done by accurate weighing of a well defined volume, with an accurately calibrated areometer, or with a pycnometer. All these methods can only be used statically, since they require sampling, that means they are not suitable for inline measurements as required in dynamic control processes. Some modern mass flow meters, based on the Coriolis force, also provide for density measurement. They are certainly helpful in the laboratory and during development work, but generally not to be found in a commercial air conditioning product. The relationships between density and measures of concentration, salt mass fraction and water load in salt, are depicted in the graphs of Fig.s 1 and 2, respectively.

As may be observed the relationship $\xi - \rho$ is practically linear over the range of interest (approx. $0.32 \div 0.42$) of the salt mass fraction.

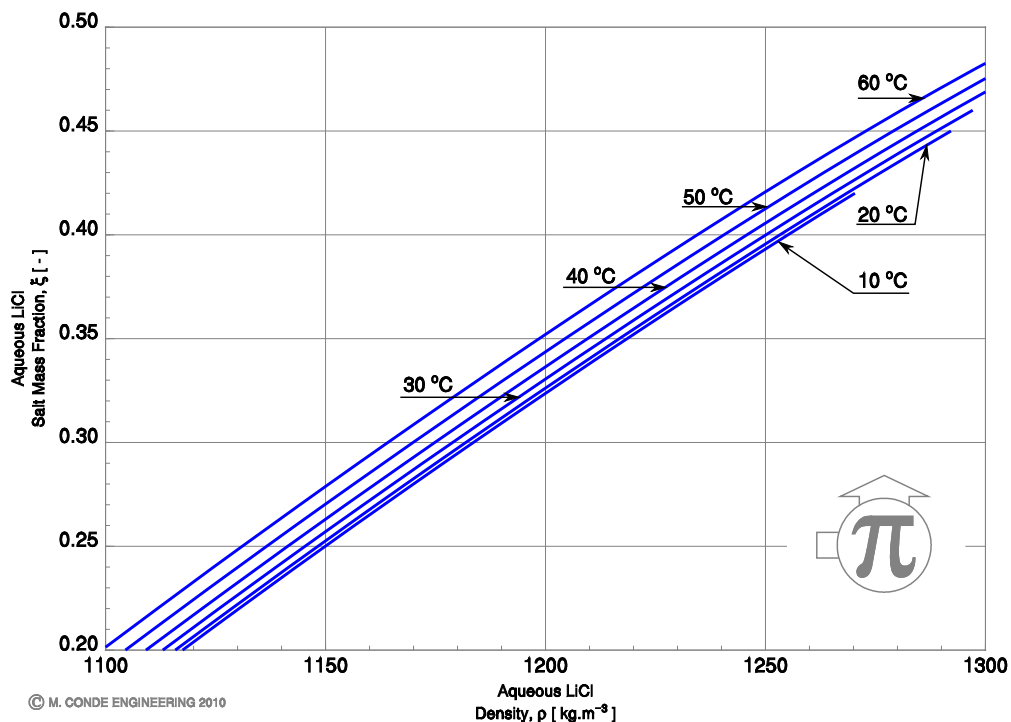


Fig. 1 - Graphical representation of the relationship salt mass fraction (ξ) vs density (ρ) at various temperatures.

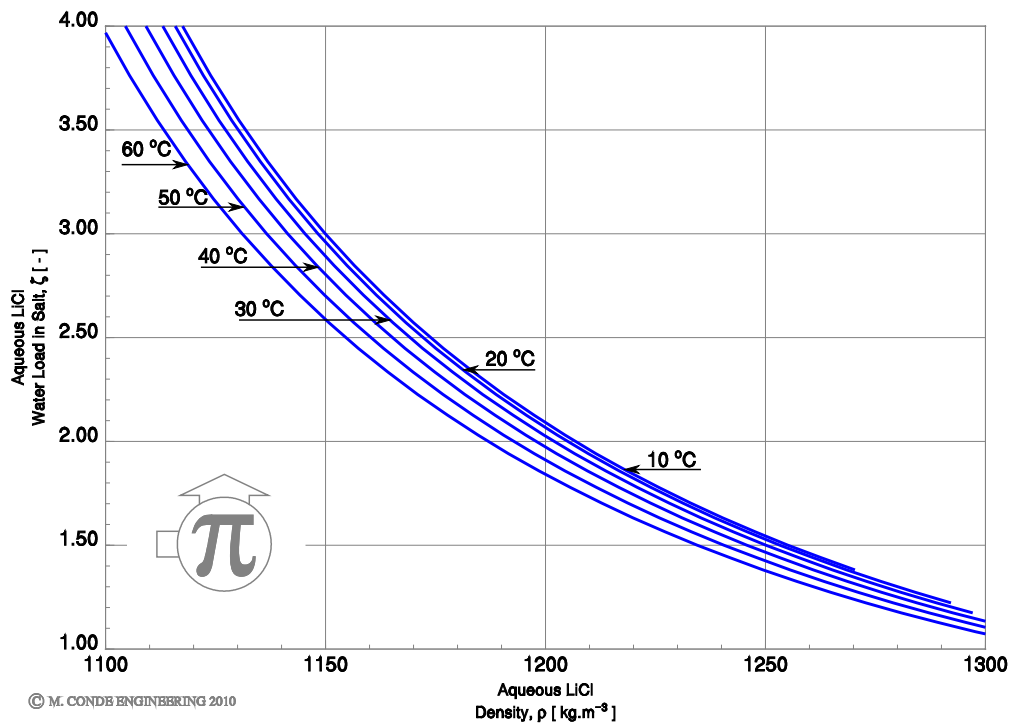


Fig. 2 - Graphical representation of the relationship between the density (ρ) and the water load in salt (ζ) at various temperatures.

A linear approximation of the relationship $\zeta - \rho$, at constant temperature, is only acceptable in very short ranges. The conversion between ζ and ρ might be more practical than a direct conversion to ζ from ρ .

Methods

A practicable method of dynamically measuring the solution concentration, as a control variable in air conditioning equipment, shall not require sampling. For the application in the field, a method based upon the measurement of the electrical conductivity of the desiccant solution may offer an easily feasible alternative for the measurement of concentration. For electrolyte solutions, such as aqueous LiCl, this is certainly applicable, provided that the measurement probes have no metallic parts exposed, which excludes direct resistance measurement. A method due to Relis¹ has been used by several sensor manufacturers to develop sensors able measure the specific electrical conductivity of aqueous electrolyte solutions. To avoid the direct contact of metallic probes with highly corrosive liquids, and the effects of polarization, the method of Relis relies on the use of two similar probes, one generating a magnetic field and the other sensing the intensity of the electric current induced in the electrolyte. This current intensity is a function of the electrical conductivity of the electrolyte, which can, thus, be measured. The utilization of this method requires the knowledge of accurate relationships between the electrical conductivity and the concentration, or some measure of it. The establishment of such relationships, based on literature data, shall be described in the following.

Literature

Most of the literature covers solutions much too dilute to be of any use in the air dehydration process. Measurements undertaken in the low concentration regions were of great interest to theories describing phenomena where the ions are neither constrained by the ion interactions nor by the viscosity of the solution. Typical for this end, are the works of Nickels and Allmand², Scatchard and Prentiss³ and Shedlovsky⁴.

General sets of data are provided by the International Critical Tables⁵ and by Lobo and Quaresma⁶. Specific data sets covering the region of interest for the application to both energy storage and air dehydration, are

provided in Lengyel et al.⁷, Molenat⁸, Behret and Schmidhals⁹, Isono^{10,11}. Other sets of data, e. g. Goldsack et al.¹², present unexplained differences to various other sets of data in the higher concentration region, see Fig. 3. Those data sets were not further considered on these grounds.

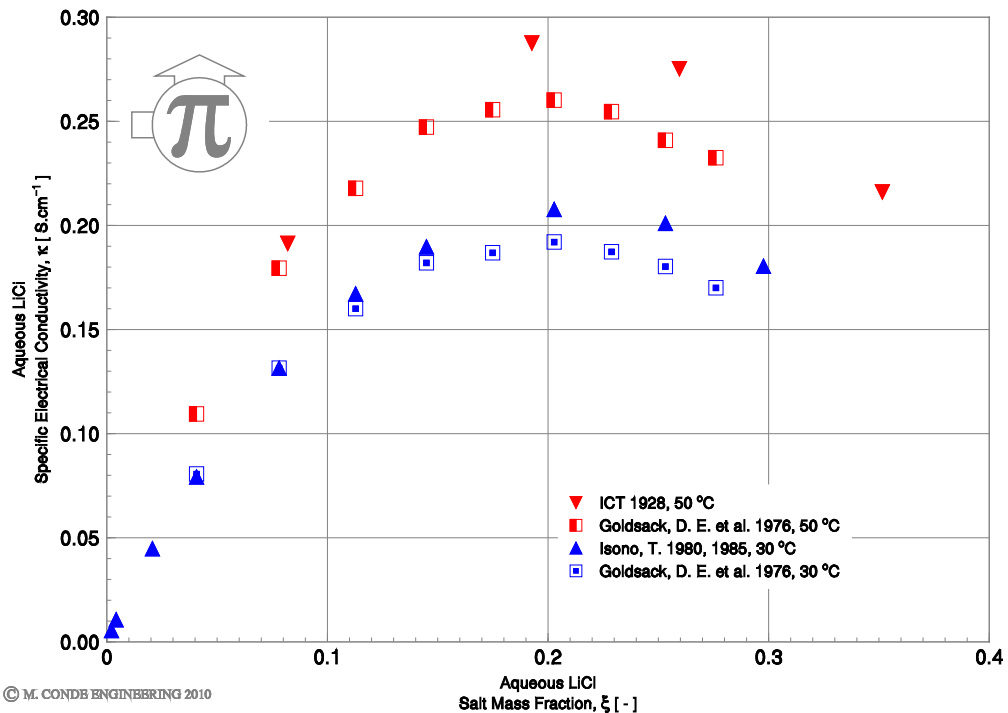


Fig. 3 - Comparison of the data of Goldsack et al., with data from other sources at 30 °C and 50 °C.

Analysis of the Selected Data

The data from the various sources were compiled and plotted for sets reported at the same temperature. Polynomials of the 4th degree on salt mass fraction were adjusted to the data, mostly of various sources, at each of the following temperatures: 15 °C, 20 °C, 25 °C, 30 °C, 35 °C, 40 °C, 45 °C, 50 °C, 55 °C, and 100 °C. The average standard deviation of these polynomials is 0.00127. Figures 4, 5 and 6 show plots of the data and of the adjusted polynomials for the temperatures of 15 °C, 25 °C, and 35 °C, respectively.

Most of the data available correspond to measurements at 25 °C, covering the whole range of concentrations in the liquid phase, Fig. 5. The data show as well that at salt mass fractions past the peak of electrical conductivity, $\xi \approx 0.21$, the scattering increases, which demonstrates the difficulties of measuring accurately as the concentration increases, increasing the viscosity and the interactions among ions. Particularly the data of Lengyel et al.⁷, and Molenat⁸ tend to give lower values of the specific electrical conductivity in this range.

The maximum of the specific electrical conductivity occurs at a salt mass fraction of approximately 0.21 for all data sets considered, with values that increase with the temperature, though not linearly, Fig. 7.

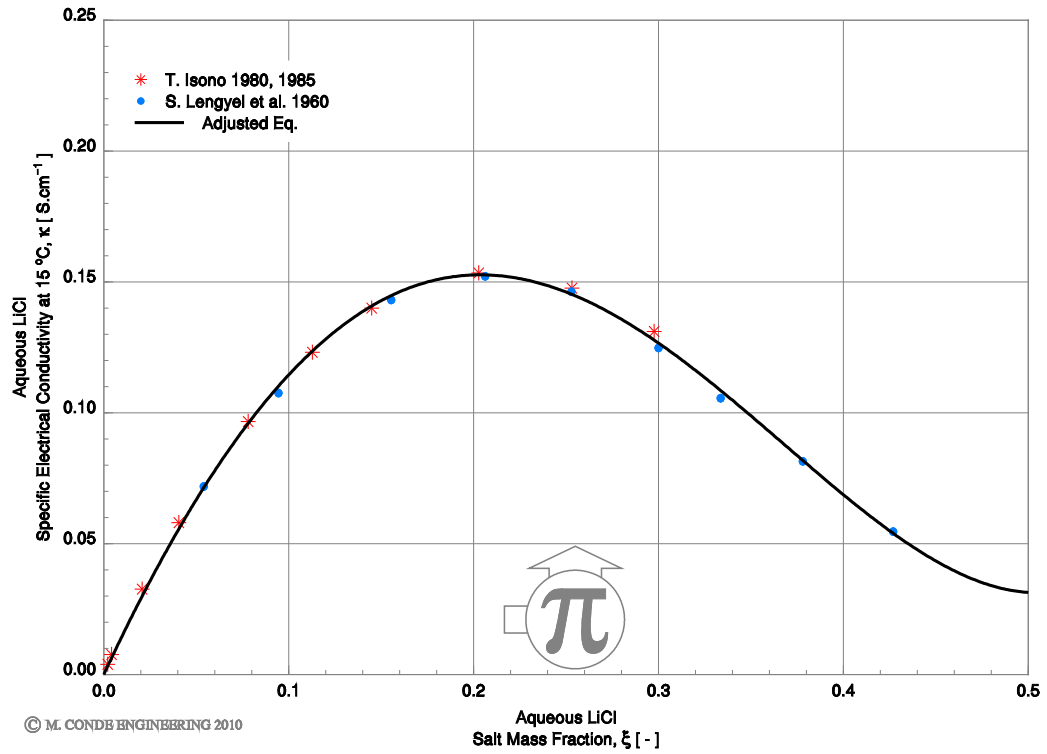


Fig. 4 - Specific electrical conductivity of aqueous LiCl at 15 °C: Data from Isono and from Lengyel et al.

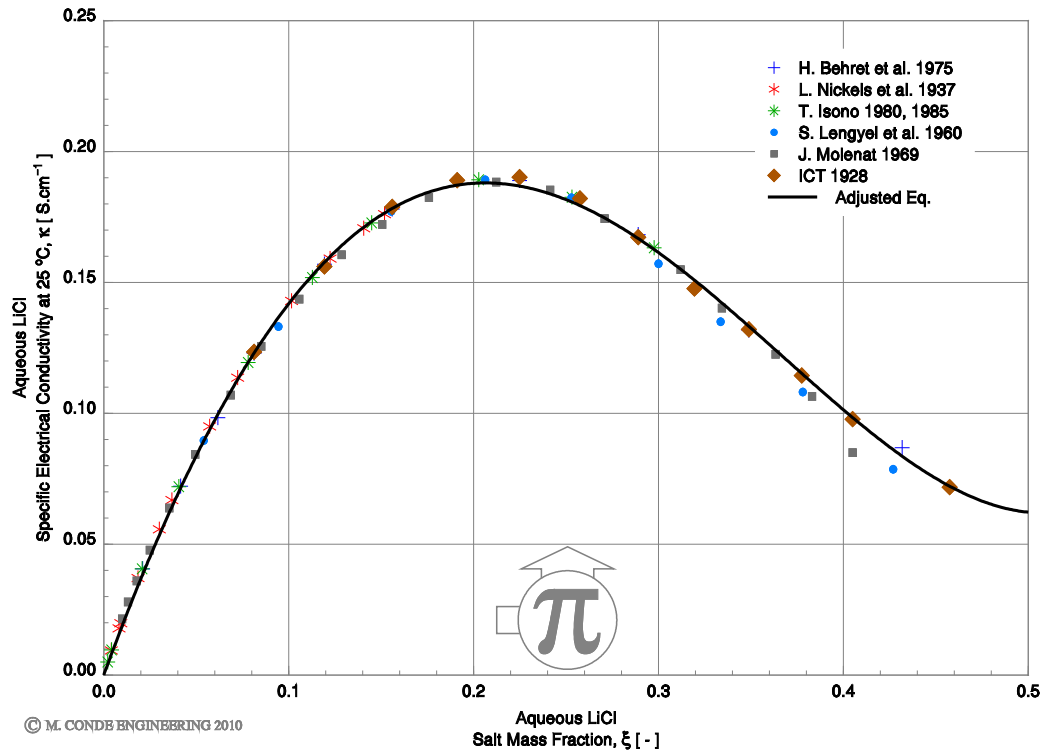


Fig. 5 - Specific electrical conductivity of aqueous LiCl at 25 °C.

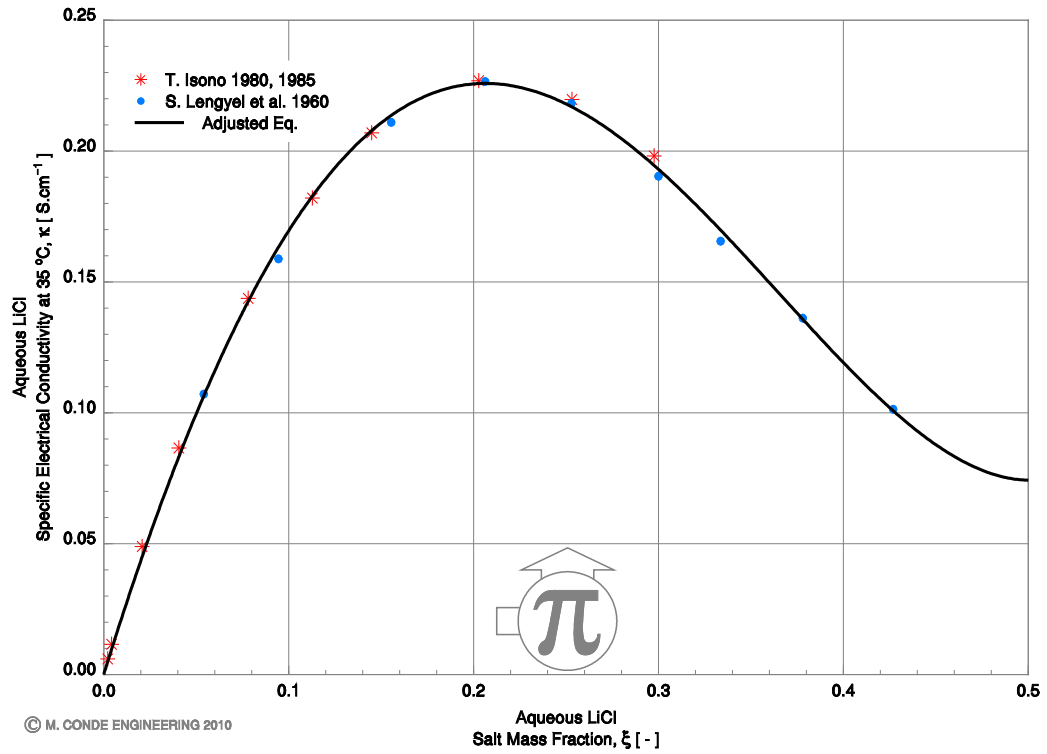


Fig. 6 - Specific electrical conductivity of aqueous LiCl at 35 °C.

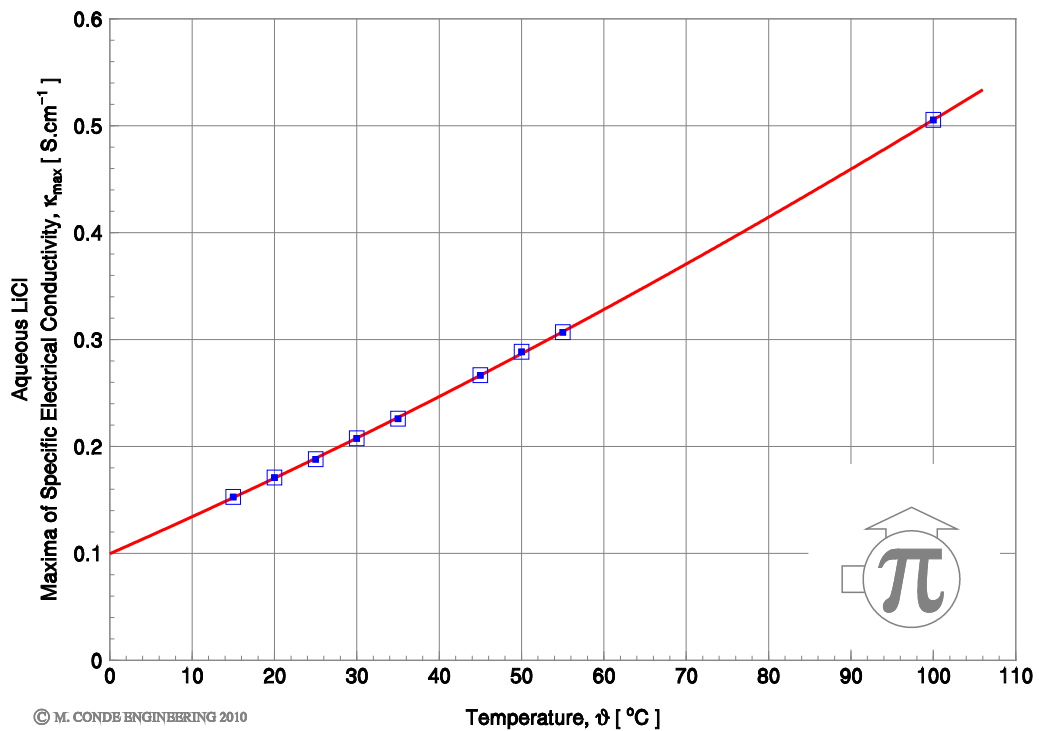


Fig. 7 - Evolution of the maxima of specific electrical conductivity with temperature.

The maxima of the specific electrical conductivity are described as function of the temperature by equation [1] in the range $0\text{ }^{\circ}\text{C} \leq t \leq 100\text{ }^{\circ}\text{C}$:

$$\kappa_{\max}(\tau) = 0.2884 - 2.8822 \tau^{0.8} + 2.69334 \tau^{1.2}$$

$$\tau \equiv \frac{t}{273.15} + 1 \quad [1]$$

A Method for Practical Use to Determine the Salt Mass Fraction from Measurements of the Specific Electrical Conductivity

For applications concerning energy storage or air dehydration, or both, the range of useful salt mass fractions is usually limited to 0.32 to 0.42, that is, well past the maximum of the specific electrical conductivity. I shall now describe a practical model that relates the salt mass fraction (or the water content in salt) to the specific electrical conductivity of the solution, which can be measured. The model consists essentially of an empirical relationship between the relative salt mass fraction and the relative specific electrical conductivity as defined in equation [2]:

$$\xi^* = \frac{\xi}{\xi(\kappa_{\max})}$$

$$\kappa^* = \frac{\kappa}{\kappa_{\max}(\tau)} \quad [2]$$

The empirical relationship is described by equation [3]:

$$\xi^* = f(\kappa^*)$$

$$= 1.0 + 1.59636(\kappa^*)^{-0.15} - 1.59471(\kappa^*)^{0.85} + 0.37891(\kappa^*)^{2.5} - 0.35026(\kappa^*)^{15} \quad [3]$$

$$\kappa^* \leq 1$$

This equation returns values that are always larger than 1.0, as it has been established for salt mass fractions larger than that at the maximum of the specific electrical conductivity. Fig. 8 shows a comparison of this model with literature data.

This same model may as well be used to relate the water load in salt to the specific electrical conductivity, provided the necessary variable transformations are made, Fig. 9.

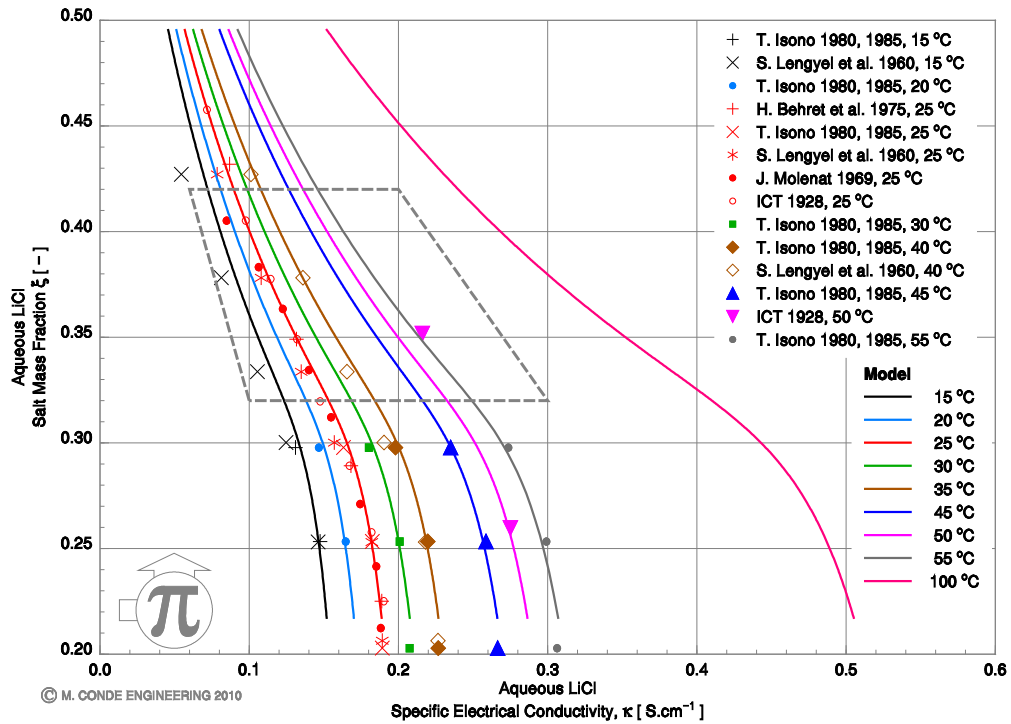


Fig. 8 - Comparison of the practical model with data. The gray polygon defines the range of interest for applications to energy storage and air dehydration.

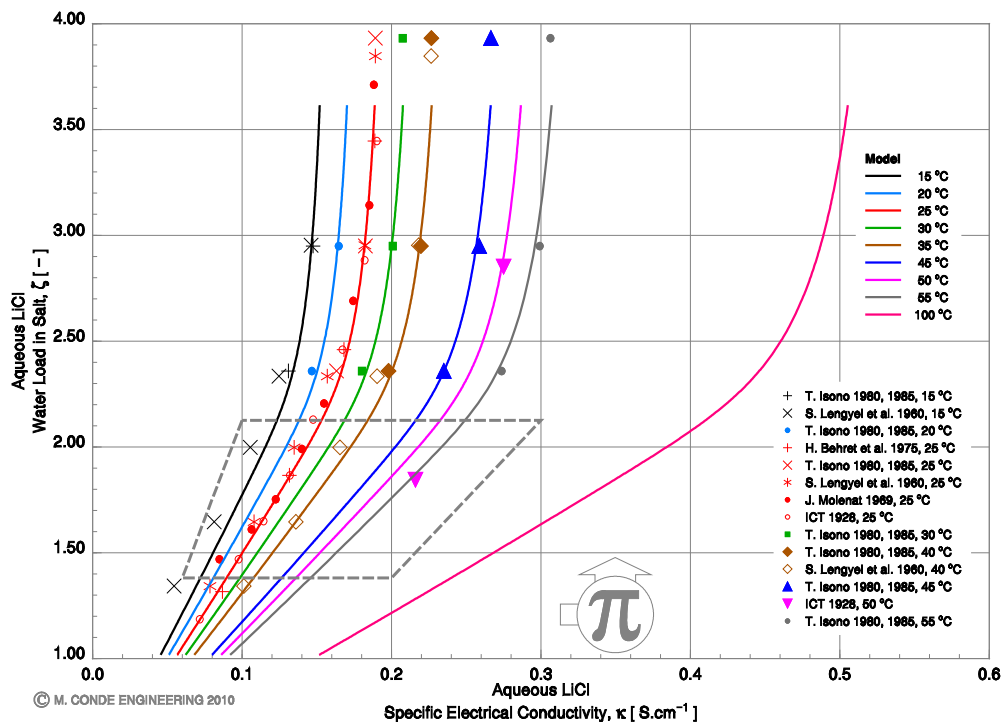
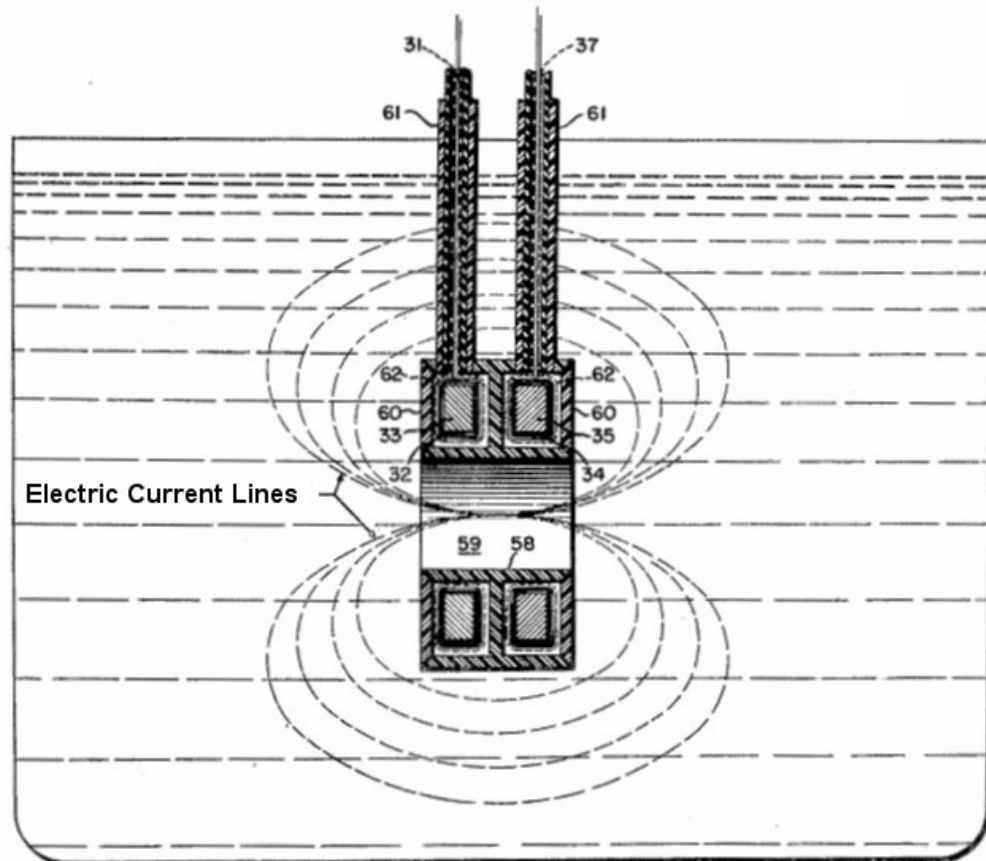


Fig. 9 - Application of the practical model to relate the water load in salt to the specific electrical conductivity of the solution.

Instruments to Measure the Specific Electrical Conductivity of Liquid Desiccant Solutions

Using the basic principle patented by Relis in 1951, shown schematically in Fig. 10¹, several manufacturers now offer sensors that can be applied to the dynamic measurement of the specific electrical conductivity.



Adapted from Relis, US Pat. 2542057

Fig. 10 - Principle of inductive measurement of the electrical conductivity of electrolytes patented by Relis¹.

The principle proposed by Relis, relies on a sensor with two inductors, one working as emitter and the other as receiver. The receiver inductor senses the intensity of the electric current induced in the electrolyte solution. This intensity is a measure of the availability of ions, and, thus of the solution conductivity. Together with a measurement of the desiccant solution temperature, the method described allows for the determination of the solution concentration as salt mass fraction, or as water load in salt.

Application

The control and regulation of an advanced liquid desiccant-based air conditioning system (ALDACS), including or not chemical energy storage, requires the measurement (as control variable) of the desiccant solution concentration. The concentration, as explained above, can be obtained through simultaneous inline

measurements of the temperature, and either the density or the specific electrical conductivity¹. From this measurement, it is a simple matter to determine either the salt mass fraction in solution, (ξ), or, the water load in salt, (ζ).

This measurement is necessary at at least one point in the liquid desiccant loop, for example, to control a mixing valve feeding the conditioner (absorber) with the adequate desiccant concentration. Accurate mass balances on the air side could, then, permit the calculation of the solution concentration at other points in the loop. Since, however, the measurement of the air humidity is usually not very accurate, thus practically excluding accurate mass balances, measurement of the desiccant concentration at some other point(s) in the loop might be desirable.

Nomenclature

κ	specific electrical conductivity,	[S.cm ⁻¹]
ξ	salt mass fraction in solution,	[-]
ζ	water load in salt,	[-]
ρ	density,	[kg.m ⁻³]
τ	dimensionless temperature,	[-]
t	temperature,	[°C]

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¹ Eventually also any other readily measurable property with a simple, and known, concentration dependency.

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