

## LOW HUMIDITY CHARACTERISTICS OF POLYMER-BASED CAPACITIVE HUMIDITY SENSORS

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### Abstract

Polymer-based capacitive humidity sensors emerged around 40 years ago; nevertheless, they currently constitute large part of sensors' market within a range of medium (climatic and industrial) humidity 20–80%RH due to their linearity, stability and cost-effectiveness. However, for low humidity values (0–20%RH) that type of sensor exhibits increasingly nonlinear characteristics with decreasing of humidity values. This paper presents the results of some experimental trials of CMOS polymer-based capacitive humidity sensors, as well as of modelling the behaviour of that type of sensor. A logarithmic functional relationship between the relative humidity and the change of sensor output value at low humidity is suggested.

Keywords: polymer-based capacitive humidity sensors, low humidity measurement, humidity sensors modelling.

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### 1. Introduction

The modern humidity measurements in science and industry emerged around two centuries after the development of early instruments for temperature measurement. De Saussure (1783) built the first hair-tension hygrometer, based on the interaction of water molecules with keratin of a grease-free hair which has a polymeric structure. During the 19th century, a psychrometer was invented in 1825 (August) and later enhanced into an aspiration psychrometer (by Assmann, 1887, for high altitude balloons). Simultaneously, dew-point hygrometers were introduced (Daniell, 1820; Lambrecht, 1881) [1]. In the 20th century a lithium chloride-heated resistive sensor was proposed by Dunmore in 1938 (and patented in 1942) [2]. This sensor output an electrical signal and offered a shorter response time than former hygrometers; moreover, it was feasible to use it in constructing remote indication systems like radiosondes for meteorology.

In 1973, the world's first miniaturised thin-film polymer-based capacitive humidity sensor, trade-marked HUMICAP<sup>®</sup>, was introduced by Vaisala Oy company in two types: for radiosondes, and for general purpose use (*e.g.* in hygrometers, control systems) [3]. So, starting with humidity-dependent mechanical properties of the polymeric keratin structure of hair, hygrometry turned full circle back to polymeric humidity-sensing materials, due to their dielectric properties. The main competitor of the polymer-based design among humidity sensors is the aluminium oxide sensor [4]; also a thin-film porous structure, but prone to calibration drift and a low response rate, more expensive and more delicate than polymer-based sensors. The Al<sub>2</sub>O<sub>3</sub>-based sensors' response signal is proportional to the absolute rather than relative humidity.

A thin (*ca.* 1 μm) polymer film is advantageous, because the capacitance of a parallel-plate capacitor increases inversely proportionally to the film thickness. A thinner film could have

a less homogeneous structure. Even more important is the reduced response time of thin-film sensors for step changes of relative humidity (of the order of seconds).

Since the sensor is a kind of capacitor, the thin film of polymer is sandwiched between two or three metallic electrodes, usually planar (devices with cylindrical geometry are tested as beneficial to obtain a shorter response time). The trouble with a two-electrode sandwich is that the upper electrode must be porous enough to allow water molecules to penetrate freely into the polymer layer, and at the same time the electrical continuity and imperviousness to non-water molecules must be secured. So, the optimum thickness for used metals (gold, chromium, nickel) is ca. 10 nm [5]. Connection of such an ultra-thin metal layer to an electric tap is a difficult technological operation. To avoid this, in many arrangements the upper porous thin electrode is not connected, since as a zero-potential one it ensures parallel running of the electric field lines through the polymer. The two electrically contacted, interdigitated bottom electrodes are placed on a thick and stiff glass substrate.

In some devices, the upper electrode is thick but comb-shaped, to allow better, rapid penetration of water molecules into polymer, although then the active surface of capacitor is reduced by half. In another design only two bottom interdigitated electrodes are applied without the upper porous electrode, and the polymer film is deposited in the last stage of fabrication process; however, the lines of electric field are curved and not parallel.

Many polymeric materials have been tested as humidity sensitive layers, the main feature of which is the presence of a so called free volume, estimated at around 30% of the total volume of the layer. The free volume is a network composed of pores, micro-voids (cavities) and micro-channels, interconnected and characterised by statistical distributions. The polymers for humidity capacitive sensors should be thermally stable and chemically resistive, and the polymer relative permittivity should be low (within a range from 3 to 10 [6]). The detailed composition of a polymer is usually a top secret of its manufacturer.

More than 70% of all humidity sensors are the polymer-based capacitive sensors [7], because they offer a very broad range of quasi-linear characteristic of change in output signal versus relative humidity (usually 20–80% RH, and 10–90% RH in improved designs). In a range of 90–100% RH the long-term stability of the sensors becomes poor, hysteresis large, and permanent offset to the sensor can remain. On the side of low humidity: 0–10 (20)% RH, the static characteristic's linearity falls off, and the response time becomes longer; on the other hand, hysteresis is negligible.

In many applications, like generation of pure materials (*e.g.* gases [8]), detection of a trace moisture content in natural gas pipelines, drying of solid materials, in meteorology [9] at high altitudes (climate change studies), or in cosmonautical observations [10, 11], the measurement of low humidity is essential. Some companies meet that need with sensors dedicated to low humidity (*e.g.* HM-1520 Humirel, DRYCAP® DMT 150 Vaisala Oy, K5-W IST AG, HC103M2 E+E Elektronik Ges.m.b.H). For better understanding of different behaviour of the polymer-based capacitive sensors at low and medium humidities, a model of their characteristics at low humidity would be useful.

In this paper, some novel measurement results are presented, and an attempt to suggest possible explanation of the behaviour of the polymer-based capacitive sensors at low humidity is made. Many manufacturers of such sensors often report only a drop in sensor's accuracy in a range of low humidity (the value of maximum error). If a relationship between the low RH values provided by the sensor and the reference values was established, it would help to perform measurements in this range with better accuracy.

## 2. Modelling of polymer-based capacitive humidity sensors

First of all, it should be reminded that no “air saturation with water vapour” takes place. The “saturation” process in a “vacuum – liquid water” system is profoundly the same as in an “air – liquid water” one, and ruled by the Boltzmann’s distribution of energy of water molecules on the surface of liquid phase. The amount of water vapour depends on the number of water molecules that reached the “escape energy” limit at the right tail of distribution, which in turn depends on the absolute temperature. The term “saturation” means here the state of dynamic equilibrium between liquid water and water vapour.

When in 1980’s extensive research on polymer materials for humidity sensors has begun, the question of the theory of polymer-based capacitive humidity sensors operation was posed. If the relative humidity is defined as a ratio of the partial pressure of water vapour  $p_{wv}$  and the partial pressure of the saturated water vapour  $p_s$  at the same temperature, then how can the polymer-based sensors respond to that relative, instead of absolute humidity (as  $Al_2O_3$ -based sensors do respond)?

In 1985, Denton *et al.* [12] suggested that the water molecules follow the Fickian diffusion, and that the molecules inside pores in the polymer layer are in the vapour phase. However, that model did not explain why the number of water molecules should be proportional to the relative humidity. Also, the number density of water molecules in vapour (or specific humidity) is much less than the number density of water molecules in liquid water inside pores.

In 1995 Anderson [13] proposed an alternative model of operation of the polymer-based capacitive sensors. Since water molecules are very small (ca. 0.2 nm) and highly polar, all solid surfaces in contact with air are coated with a layer of physio-sorbed water molecules, attracted mostly by the van der Waals’ forces. There are different polar sites in polymers at which the water molecules can be bound in various ways, *e.g.* between adjacent polymer chains. That means that the inner surfaces of free volume network, interconnected inside a polymer film, should be covered with one or more layers of water molecules. In the Anderson’s model, the first layer adheres closely to the polymer inner surfaces because of hydrogen bonds (relatively strong), whereas next layers – if present – are bound with forces exponentially weaker (mainly the van der Waals’ forces). The volume of voids inside the polymer is filled with water vapour under a partial pressure equal to the partial pressure in the ambient air (see Fig. 1).

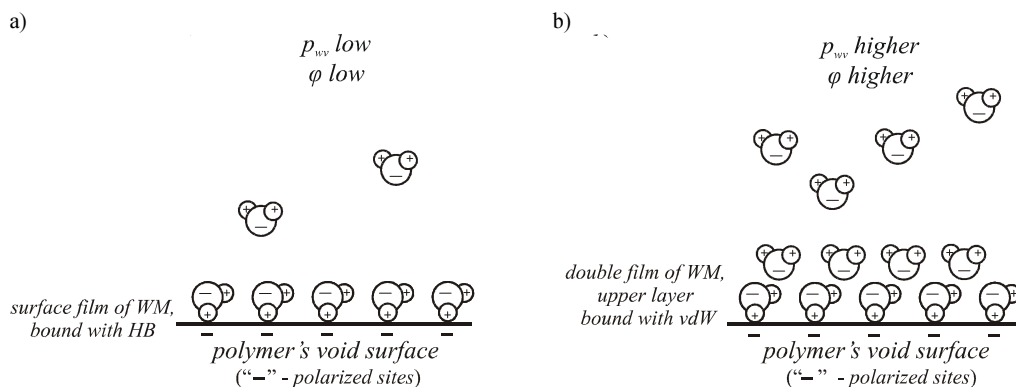


Fig. 1. A schematic illustration of the idea of change in relative humidity  $\phi$  (*i.e.* under the water vapour partial pressure  $p_{wv}$ ) within voids in polymeric materials; a thin *WM* film case (a); a thicker *WM* film case (b) (*HB* – hydrogen bond, *vdW* – the van der Waals’ forces, *WM* – water molecules).

The polymers used for sensing layers in modern capacitive relative humidity sensors are mainly polyimides (although Vaisala Oy used cellulose acetate). Polyimides are heterocyclic polymers which offer some very attractive features when used in capacitive sensors: outstanding thermal-oxidative and chemical stability, high glass transition temperatures, high radiative- and solvent-resistance; they exhibit very good dielectric and mechanical properties with good processability; the dielectric constant relative to water is low [14, 15]. They are also easily integrated into a CMOS type integrating process. The adsorption sites of polyimide chains are mainly oxygen atoms of carboxyl groups  $C=O$ , and to some extent also nitrogen atoms in  $N-C$  groups; some structures of the polyimide family polymers contain also ether groups  $C-O-C$  but their oxygen atoms are only slightly involved in the H-bonding process. Oxygen and nitrogen atoms are strongly electronegative; hence, the adsorption sites on the polyimide backbone attract hydrogen atoms of water molecules and enable adsorption of these molecules based on hydrogen bonding.

In examination of the process of water sorption and uptake in polymers, many sophisticated measurement techniques were applied, mainly gravimetric and vibrational spectrometric ones (*e.g.* NMR, 2D-FTIR, ATR); even experiments with the use of molecules of  $D_2O$  (heavy water) and  $T_2O$  (super-heavy water) were performed. Extensive research of vibrational spectra of humidified polyimide has revealed that on the surface of thin polymer layer water molecules are mostly physio-sorbed by the hydrogen bonding interaction (whereas on the surface of some oxides, *e.g.*  $Al_2O_3$ , they undergo chemisorption which causes dissociation of these molecules and creation of surface hydroxyl groups [16]). Diffusion in polyimides depends on their crystallinity and density, as well as on chain stiffness [17]. In FTIR spectra shifts were observed which can be attributed to carbonyl groups as proton acceptors in dipole-dipole interactions with water molecules, which exhibit a strong intrinsic permanent electric dipole moment [18]; these shifts were fully reversible during the water desorption process. In [19] the activation energy of bonds inside polymer was estimated to be of the order of 1 kJ/mol which is closer to the van der Waals' bonds, and may be attributed to the bonds between water molecules in micropores inside the polyimide layer. That makes some authors formulate a hypothesis of two different water species present inside polyimide: one of single molecules hydrogen-bonded to polymer adsorption sites – which undergo faster sorption – and the other aggregated by the van der Waals' forces in water clusters (or H-bonded in dimers) [18]. In that research, the authors also claim that only one third of all imide interaction sites is available for water molecules; the rest is being involved in intermolecular charge transfer interactions.

In a range of medium and high humidity, in a multilayer shell of water molecules, the physio-sorption based on dipole-dipole or dipole-induced dipole could take place. Intermolecular dispersion forces are unlikely to take part because of strong polar nature of water molecules (no instantaneous dipoles). Ion-dipole interactions are also unlikely to occur because of good dielectric properties of the used polymer layer (no free ions, or only a negligible amount of them). On the other hand, in a range of low humidity, the one-molecule shell of water could cover the polymer surfaces, and H-bonding would dominate. In fact, most sorption measurements start from 10% RH upwards, and the signals of vibrational spectra for lower humidity are too weak.

The water vapour inside pores should be in equilibrium with the upper layer of water molecules' film on the surfaces of free volume network. For example, if the relative humidity outside the sensor increases, more water molecules diffuse into the polymer, and the thickness of the inner water film coating the inner surfaces increases till the increased water vapour pressure over that thicker film reaches a new equilibrium with the ambient partial pressure of water vapour. That Anderson's model accounts also for a weak dependence of the sensor's response on temperature, despite of a strong increase of the saturation partial pressure of water vapour with temperature.

The idea of that model was generally respected (*e.g.* [20]), although its accuracy was rather rough, and in the Anderson's equations both the polymer and water permittivity are not explicitly included. For that reason, many researchers applied the equations based on the modified Clausius-Mossotti equation [21] defined as:

$$\frac{\Delta N\alpha}{3\varepsilon_0} = \frac{\varepsilon_r(\varphi)-1}{\varepsilon_r(\varphi)+2} - \frac{\varepsilon_r(0)-1}{\varepsilon_r(0)+2}, \quad (1)$$

where:  $\Delta N$  is an increase in the number of dipoles (water molecules) per unit volume in the polymer film (a number density, in  $1/\text{m}^3$ ) due to the increase in relative humidity from 0 to  $\varphi$ ;  $\alpha$  is a molecular polarizability (in  $\text{Cm}^2/\text{V}$ );  $\varepsilon_0$  is the vacuum permittivity (in  $\text{F/m}$ );  $\varepsilon_r(\varphi)$  is a relative permittivity of the polymer film at a given relative humidity  $\varphi$ ; and  $\varepsilon_r(0)$  is a relative permittivity of the dry film. Practically, if  $\varepsilon_r(0) = 3$ , then at  $\varphi = 100\% \text{RH}$ ,  $\varepsilon_r(\varphi) = 3.9$ ; the change in relative permittivity  $\Delta\varepsilon_r = \varepsilon_r(\varphi) - \varepsilon_r(0)$  caused by uptake of water molecules is usually small, although the relative permittivity of (highly polarised) water is around 80.

When the influence of temperature on the relative permittivity is taken into account, the modified Debye equation [22, 23] is applied:

$$\frac{\varepsilon_r(\varphi)-1}{\varepsilon_r(\varphi)+2} = \frac{N}{3\varepsilon_0} \left( \alpha + \frac{\mu^2}{kT} \right), \quad (2)$$

where:  $\mu$  is a dipole moment of one water molecule (in SI units:  $\text{C}\cdot\text{m}$ );  $k$  is the Boltzmann's constant, and  $T$  is the absolute temperature (in  $\text{K}$ ).

Even more precise is the modified Kirkwood's equation [24] for a binary system of dielectric materials, when the number density of polymer is practically independent of the humidity:

$$\frac{(\varepsilon_r(\varphi)-1)(2\varepsilon_r(\varphi)+1)}{9\varepsilon_r(\varphi)} = \frac{(\varepsilon_r(0)-1)(2\varepsilon_r(0)+1)}{9\varepsilon_r(0)} + \frac{4N}{3\varepsilon_0} \left( \alpha + g \frac{\mu^2}{3kT} \right), \quad (3)$$

where  $g$  is the Kirkwood correlation factor, a measure of local ordering of the dipoles: if fixing a position of one dipole does not disturb the remaining positions of the neighbouring dipoles, then  $g = 1$ . Generally,  $g$  can be a function of water molecules' uptake. Another feature is that water in confined systems behaves differently from bulk liquid water; the relative permittivity depends on the average size of volume where water is confined [25, 26].

Instead of the theoretically derived formulae containing  $\varepsilon_r(\varphi)$ , some researchers base on the empirical equation by Looyenga for a mixture of two dielectric materials [27]:

$$\varepsilon_r(\varphi) = \left[ \gamma \left( \sqrt[3]{\varepsilon_w} - \sqrt[3]{\varepsilon_r(0)} \right) + \sqrt[3]{\varepsilon_r(0)} \right]^3, \quad (4)$$

where  $\gamma$  is a volume fraction of water absorbed in the polymer, and  $\varepsilon_w$  is a relative permittivity of water, which can be calculated from the following formula [28]:

$$\varepsilon_w = 78.54 \cdot \left[ 1 - 4.6e^{-4}(T - T_0) + 8.8e^{-6}(T - T_0)^2 \right], \quad (5)$$

where  $T_0 = 298 \text{ K}$ .

In the above mentioned research, the aim was to evaluate dynamic changes in time within the sensor polymer's volume by simulation. For that purpose, the water concentration was calculated from the Fickian diffusion equation, and the relative humidity could be obtained using the Henry's law. However, in these formulae the relative humidity  $p_w/p_s$  is not explicitly included. There is a need for a mathematical model taking into account both relative humidity and dielectric constants, also for the low humidity range; that model would be helpful

in estimation of metrological properties of polymer-based capacitive sensors applied to measurements of low humidity values.

### 3. Experimental setup for measurement of low humidity characteristics

In order to establish the nonlinearity of polymer-based capacitive humidity sensors in the low humidity region, an experimental setup shown in Fig. 2 was used.

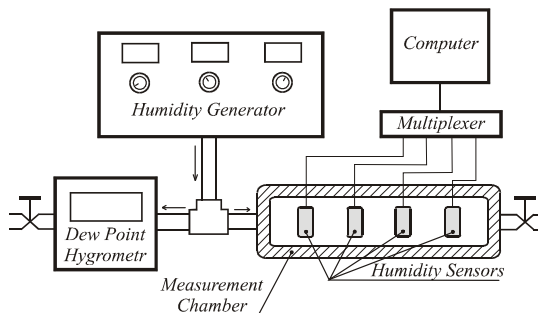


Fig. 2. A schematic of the experimental stand for measuring low humidity characteristics of humidity sensors.

The source of low humidity was a specialized trace humidity generator DG-4 (Michell Instruments/UK). An adjusted low humidity value was obtained by mixing dry air with minute amounts of humid air at a controlled flow rate. The reference instrument, a dew/frost point hygrometer GE Optica 1311 XR (General Eastern Sensing/USA) can measure trace humidity down to  $-80^{\circ}\text{C}$  frost point; its accuracy was confirmed with an NPL-traceable certificate of calibration. A set of four humidity sensors SHT 21 (Sensirion/Switzerland) was placed in a special thick-walled (for temperature equalizing) measurement chamber made of stainless steel with small orifices for mounting the sensors. The humidity generator was connected with both the dew point hygrometer and the measurement chamber by stainless steel tubing, with electro-polished inner surfaces for reducing the risk of condensation. The air flow with a precisely adjusted low humidity level was supplied from the trace humidity generator and divided in a T-shape fitting with a gas flow flux of ca. 200 l/h. In this experiment, the frost point temperature values were set within an interval from  $-40^{\circ}\text{C}$  (0.45% RH) to  $-10^{\circ}\text{C}$  (9.25% RH), stepwise with a step of approximately 5 K. The ambient temperature and pressure were controlled during the experiment. The temperature during measurements was  $(24.0 \pm 0.2)^{\circ}\text{C}$ ; the research lab was air-conditioned.

The sensors under test were SHT-series sensors manufactured by the market-leading Swiss company Sensirion [29]. This choice was motivated by the fact that the SHT sensors are made in CMOS technology which enables to ensure high accuracy (within a 20 to 80% RH range, 3% RH for SHT-71 and 2% RH for SHT-21, and 1.8% RH for SHT-75 within a 10–90% RHT range). These sensors are highly integrated devices; each sensor is individually calibrated and tested, and an electronic identification code is stored on the sensor chip. Each chip contains also a band-gap temperature sensor, an amplifier, an A/D converter, a programmable memory, and a digital interface. For data logging, the manufacturer offers also an evaluation kit EK-H4 (multiplexing device) with hardware and software to interface the sensors with a computer. In the reported sensor trial measurements four SHT-21 sensors, four SHT-71 sensors, and one SHT-75 sensor were tested. Every measurement point was determined after at least 1 hour of keeping a constant humidity level to assure the equilibration of water vapour concentration in the whole system.

#### 4. Results and discussion

As a result of the experimental trials, three sets of low-humidity sensor characteristics were obtained. In Fig. 3 plots of the differences  $\Delta\varphi$  between the relative humidity value  $\varphi_i$  provided by  $i$ -th SHT-21 sensor and the reference value  $\varphi_R$  measured with the dew/frost point hygrometer are shown. For each sensor, six measurement points were determined, starting from the  $-40^\circ\text{C}$  frost point temperature.

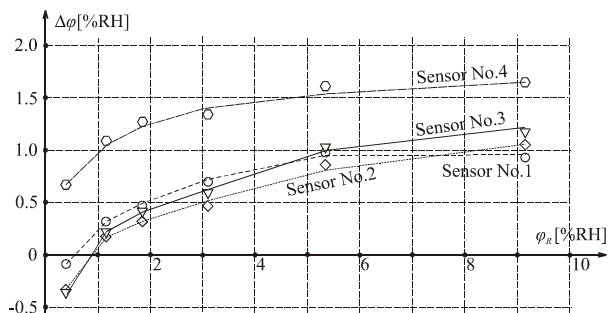


Fig. 3. Plots of the differences  $\Delta\varphi$  between the relative humidity value  $\varphi_i$  provided by  $i$ -th SHT-21 sensor and the reference value  $\varphi_R$ .

It can be seen that  $\Delta\varphi$  gradually falls off from linearity with decreasing the frost point temperature (and the relative humidity), and that for sensors Nos1–3 the plots practically overlap, whereas for sensor No. 4 the shape of plot is very similar, albeit shifted up by an offset value. The highest correlation coefficients were obtained for fitting these characteristics with a logarithmic approximation function.

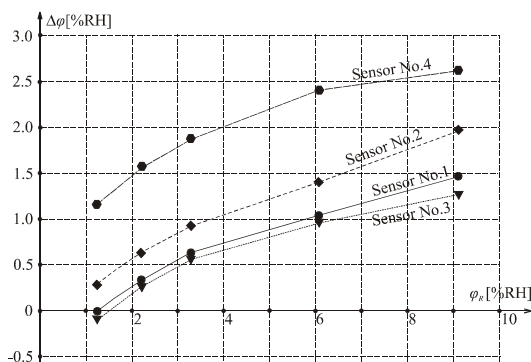


Fig. 4. Plots of the differences  $\Delta\varphi$  between the relative humidity value  $\varphi_i$  provided by  $i$ -th SHT-71 sensor and the reference value  $\varphi_R$ .

In Fig. 4 plots of the differences  $\Delta\varphi$  between the relative humidity value  $\varphi_i$  provided by  $i$ -th SHT-71 sensor and the reference value  $\varphi_R$  measured with the dew/frost point hygrometer are shown. For each sensor, five measurement points were determined, starting from the lowest value  $-30^\circ\text{C}$  of frost point temperature – because it turned out that for humidity below 0.5% RH, the SHT-71 and SHT-75 sensors provided a dummy value of 0.1% RH. Actually, only above 0.5%RH the displayed measurement data were calculated from raw processed integer codes by the sensors' electronics. Despite of the operating range declared in the technical datasheet from



0%RH to 100%RH, the interval 0–0.5% RH is excluded from the sensors' scope. In the SHT-21 sensors (newer than SHT-71) such a limitation was not noticed. The plots are similar to the SHT-21 ones, although look slightly skewer. Also for SHT-71, the highest correlation coefficients were obtained for fitting these characteristics with a logarithmic approximation function.

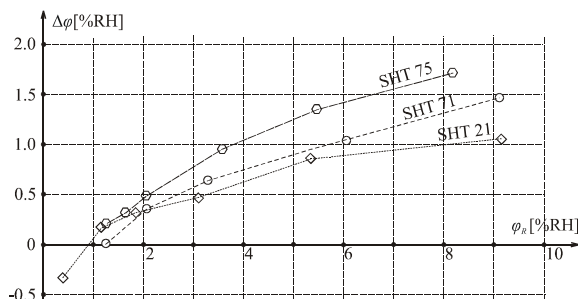


Fig. 5. Comparison of plots of the differences  $\Delta\phi$  between the relative humidity value  $\phi_i$  provided by SHT-21, SHT-71 and SHT-75 sensor items, and the reference value  $\phi_R$ .

The plots of the differences  $\Delta\phi$  between the relative humidity value  $\phi_i$  provided by SHT-21, SHT-71 and SHT-75 sensor items and the reference value  $\phi_R$  are shown in Fig. 5. The characteristic of SHT-75 exhibits similarity to SHT-71 rather than to SHT-21 one. It seems that the better accuracy declared for SHT-75 for medium humidity values has no impact on the accuracy within the low humidity range.

## 5. Conclusions

The tested polymer-based capacitive humidity sensors manufactured in CMOS technology exhibit in a range of low relative humidity 0–10% RH a nonlinearity of characteristics which increases when the humidity decreases towards 0% RH. The shapes of plots of these characteristics are similar, and it seems that a kind of regularity, independent of sensor's chip structure, takes place. The best fit approximation function of this nonlinearity shows a logarithmic dependency. Because some models of polymer sorption equilibrium (*e.g.* Flory-Huggins [24]) contain logarithmic dependencies, it could be possible that some interaction processes in water vapour molecules-polymer chains inside polymeric materials could be described by logarithmic relationships which could not be explicitly observed within a range of medium humidity values, but could only be revealed at low humidity (that might be *e.g.* hydrogen bond interactions of logarithmically distributed strengths.) A model of the behaviour of polymer-based capacitive humidity sensors for low humidity values would be useful to explain that nonlinearity, which suggests a logarithmic relationship between the relative humidity and the output value of the sensor.

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