Analytical Models for the Interactions between a Gas Mixture and Quartz Micro Balance Sensor Array Based on Polymers

Abdelaziz Abbas

Department of characterisation and Instrumentation**,** Welding and NDT research Center , route de Dely-Brahim , BP 64 ,311704 Chéraga , Alger, Algérie

E-mail:abbasabdelaziz@yahoo.de

Abstract. The aim of this work is to develop analytical models for the thermodynamic equilibrium at the interfaces (gas mixture / Quarz Micro Balance sensor arrays based on conducting polymers). Differential equations, which describe the change in the partial sensitivities of the sensor array elements depending on the gas mixture components concentrations, and the sensor array parameters, have been developed. Moreover, the responses of the sensor array as a function of the concentrations of the gas mixture components have been modeled.

1.Introduction

Acoustic sensors behave as a mass transducer, namely the response of the sensor to a vapor is proportional to the mass of the analyte. Because of the lack of perfect selectivity, sensor arrays are often implemented for analyse of gas mixture. Many scientific papers concerning the evaluation of acoustic wave sensor array data by using of pattern recognition techniques have been written [1]. However, to our best knowledge, no study has explored the physicochemical behavior at the interfaces gas mixture/ sensor array. Except the empirical formula of Clifford [2] , there is no model that describes the physicochemical behavior of sensor array / gas mixture multi- systems. Further improvement of the sensor array properties requires a better understanding of the processes that occur at the surfaces of the sensor array elements. Therefore, it is important to develop models for the sensor array responses. In previous work, we presented models of the interactions between a mixture of vapors and a sensor arrays consisted of chemical sensors [3] and Metal oxide sensors [4]. In the present report, we extend the application of the developed models to the interaction between **Q**uarz **M**icro **B**alance (QMB) sensor array and a mixture of vapors.

2. Theoretical Aspects

2.1 Interaction between a single QMB- sensor and a gas

If we consider the interaction between a QMB-sensor and a gas , a perturbation of the mass, Δm, on the surface of the sensor causes shifts in the oscillator frequency Δf, according to the equation of Sauerbrey [5-6]

$$\Delta f = f - f^{\text{air}} = -\frac{2(f^{\text{air}})^2}{\sqrt{\mu_Q \rho_Q}} \frac{\Delta m}{A} = K m^{\text{ads}} \tag{1}$$

where Δf in Hertz is the resonant frequency shift due to the added mass; f stands for the measured frequency in the presence of a gas ; f^{air} symbolizes the fundamental resonant frequency of the unloaded device is typically 5 or 10MHz; Δm (or m^{ads}) in g is the added mass (or the mass of adsorbed gas); A in cm^2 is the piezo-electrically active area (area of electrode surface); μ_Q in g cm^{-2} is the shear modulus of quartz ; ρ_Q in g cm^{-3} is the density of quartz. For a given sensor, the parameters fair, A, μ_Q , ρ_Q are constant , therefore they are summarized together with f^{air} in one constant K.

2.2 Interaction between a single QMB- sensor and a mixture of vapors

If we consider the interactions between a single QMB- sensor and a mixture of q-vapors; the frequency of the sensor can be expressed as follows

$$f^* = f^{air} + (K\sum_{j=1}^{q} m_j^{ads}) = f^{air} + (K\sum_{j=1}^{q}(M_j \, n_j^{ads})) \tag{2}$$

where f^* is the frequency of the single sensor , when it interacts with the gas mixture ; m_j^{ads} stands for the adsorbed mass of the jth vapor; n_j^{ads} in mole is the number of adsorption sites that have been occupied by the jth component ; M_j in g mole^{-1} is the molar mass of the jth component of the gas mixture. Most QMB- sensors use polymers (or conducting polymers) as sensitive layer. One of defining features of polymer surfaces and coatings is the chemical regularity of the surface. While many materials can be irregular mixtures of different components, the polymer surfaces tend to be chemically uniform; because of this, adsorption of molecules onto polymer surfaces can be easily modeled by the Langmuir isotherm. If we make the assumptions that there is only one type of active and immobile site, for which all molecules actively compete (competitive adsorption) and that the concentrations of the gas mixture components are small, the number of occupied adsorption sites of the gas mixture component j may be described by the well-known multi-components Langmuir- isotherm [7-8]; by using this model for all gas mixture components , we get

$$f^* = f^{air} + (K\sum_{j=1}^{q}(M_j \, n_j^{max} \, \frac{b_j \gamma_j n_j}{1+(\sum_{j=1}^{q} b_j \gamma_j n_j)})) \tag{3}$$

where n_j^{max} in mole is the maximal number of adsorption sites that can be occupied by the jth gas mixture component; n_j is the initial number of mole of the gas j , γ_j stands for the ratio n_j^{eq} /n_j ; n_j^{eq} stands for the mole number of the free particles of the gas j at thermodynamic equilibrium; b_j is a dimensionless parameter; it describes the thermodynamics at the sensor / gas j interface.

2.3 Interactions between a sensor array and a mixture of vapors

We consider a system with m sensors and q different chemical species. The frequency f of the multi-sensor can be represented by a composite state function; namely, it depends on the frequency values of the individual sensors, which in turn depend on the gas mixture component concentrations and temperature. A small variation df of the frequency of the sensor array may be determined with the chain rule. Furthermore, the response of each chemical sensor must be a state function; this is an essential precondition for the operational and practically useful sensors .Under this condition df_i^* is a total differential; it can be expressed as follows

$$df = \sum_{i=1}^{m} df_i = \sum_{i=1}^{m} \frac{\partial f}{\partial f_i^*} df_i^* = \sum_{i=1}^{m}\sum_{j=1}^{q} \lambda_i \, S^{f_{ij}^*, n_j} \, dn_j \tag{4}$$

where f_i stands for the frequency of ith sensor array element ; f_i^* is the frequency of the single sensor i, when it interacts with the gas mixture; λ_i=df/ df_i^* is a dimensionless coefficient that describes the influence of the sensitivities of the sensor array elements and the influence of the gas mixture composition on the response of the sensor array; f_{ij}^* is the contribution of gas mixture component j in the frequency of the single sensor i; $S^{f_{ij}^*, n_j}$ symbolizes the partial sensitivity of the ith sensor array element, when it interacts with the component j of the gas mixture. We assume and show later that the following relationship is valid

$$S^{f^*_{ij},n_j} = \left(\frac{\partial f^*_i}{\partial n_1}\right)_{n_2,\dots,n_j,\dots,n_q} = \frac{df^*_{ij}}{dn_j} = \frac{f^*_{ij}}{n_j} = \frac{f^*_{ij}+df^*_{ij}}{n_j+dn_j} = \text{constante} \tag{5}$$

The indefinite integral of the relationship (4) by making use of the assumption (5) gives

$$f = \int \sum_{i=1}^{m}\sum_{j=1}^{q}\lambda_i\, S^{f^*_{ij},n_j}\,dn_j = \sum_{i=1}^{m}\sum_{j=1}^{q}\lambda_i S^{f^*_{ij},n_j}\int dn_j = \sum_{i=1}^{m}\sum_{j=1}^{q}\lambda_i S^{f^*_{ij},n_j} n_j \tag{6}$$

The differentiation of eq.6 using the rules of algebra and the comparison with eq.4, leads to the following differential equation

$$\sum_{i=1}^{m}\sum_{j=1}^{q}\lambda_i\, n_j\, dS^{f^*_{ij},n_j} = 0 \tag{7}$$

The relationship (7) is a Gibbs Duhem like equation ; it connects the change of the partial sensitivities of the sensors with the concentrations of the gas mixture components and the multi-system coefficients λ_i . To find an analytical model for the sensor array response, we consider the total differential in eq.4 and rewrite it by introducing a new dimensionless coefficient β_i , we get

$$df = \sum_{i=1}^{m}df_i = \sum_{i=1}^{m}\lambda_i\, df^*_i = \sum_{i=1}^{m}\sum_{j=1}^{q}\lambda_i\, d(f^{air}_i + f^*_{ij}) = \sum_{i=1}^{m}d(f^*_i)^{\beta_i} \tag{8}$$

where β_i is a dimensionless coefficient. It is given by

$$\beta_i = \frac{f^*_i}{f_i}\lambda_i = \frac{d\ln f_i}{d\ln f^*_i} \tag{9}$$

The indefinite integral of (8) leads to the relationship

$$f = \sum_{i=1}^{m}(f^*_i)^{\beta_i} = \sum_{i=1}^{m}\sum_{j=1}^{q}(f^{air}_i + (S^{f^*_{ij},n_j}n_j))^{\beta_i} = \left(f^{air} + (K\sum_{j=1}^{q}M_j\, n^{max}_j\, \frac{b_j\gamma_j n_j}{1+(\sum_{j=1}^{q}b_j\gamma_j n_j)})\right)^{\beta_i} \tag{10}$$

which represents the frequency of the sensor array as a function of the initial concentrations of the gas mixture components.

3.Results and discussion

The differential equations (7) and the function (10) were developed using the properties of functions of state. Therefore, they apply to all cross-reactive chemical sensors .In this paper, we defined a novel dimensionless coefficient λ_i. This variable has a similar meaning as the fugacity coefficient when we consider the interactions between the particles of real gas. At macroscopic scale, the assumption (5) is not valid, since the ratio df^*_{ij}/dn_j (slope of the tangent of the graph of the function $n_j \xrightarrow{g} f^*_{ij} = g(n_j)$ at the point $(n_j,\ f^*_{ij})$ is unequal f^*_{ij}/n_j (slope of the straight line f^*_{ij} = constant. n_j). The assumption (5) is fulfilled, if we go to small scales over and divide the system (sensor) in small discrete subsystems (sub-sensors). In the integration of f^*_i in eq. 7, one can imagine the sensor divided in an infinite number of discrete sub sensors, and the gas mixture M decomposed into infinitely many equivalent sub mixtures dM. Each sub-sensor interacts independently of the other sub sensors, with a sub mixture, and shows now a constant sensitivity with respect to the components of the sub mixtures. The response of the sensor is then obtained by integrating the responses of the discrete sub-sensors. Although the decomposition of the system in multi-

system and the use of the relationships (5) are virtual and cannot be realized experimentally, these models are necessary and helpful for the development of our differential equations.

4.Conclusion

In this paper, novel differential equations and their solutions are developed. The eq.7 can be useful for checking experimental data for consistency. The function (10) shows that the Clifford model is a special case of a rather general result.

5.References

[1]   Hierlemann A , Weimar U, Kraus G, Schweizer-Berberich M and Goepel W 1995 *Sensors & actuators B.* **26-27** 126

[2]   Althainz P, Goschnick J, Ehrmann S and Ache H J 1996 *Sensors & Actuators*. *B* **33** 72

[3]   Abbas A and Bouabdallah A 2007 *Journal of Mathematical Chemistry*. **42 (4)** 1023

[4]   Abbas A and Bouabdellah A 2010 *Sensors &. Actuator . B* **145** 620

[5]   Araya-Kleinsteuber B and Lowe C R 2007 *Handbook of Biosensors and Biochips* (Weinheim :J. Wiley & Sons , pp 1-21.

[6]   Khot L R, Panigrahi S and Lin D 2011 *Sensors & Actuators. B* **153** 1

[7]   Zhou X, Yi H, Tang X, Deng H and Liu H 2012 *Chemical Engineering Journal.* **200–202** 399

[8]   Denayer J F, Baron G V, Jacobs P A, Martens J A   2000 *Phys. Chem. Chem. Phys.* **2** 1007