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Chaotic parameters and their role in quantifying noise in the output signals from UV, TGA and DSC apparatus

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ABSTRACT

Two fractal dimensions and the Liapunov exponent (LE) have been applied to detect noisy output signals from UV spectrophotometer (UV), thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) apparatus of 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid ([emim][$EtSO_4$]). The data collected from these three pieces of equipment were classified before calculating LE, regularization (RD) and box dimensions (BD). The RD and LE are able individually to detect and quantify noisy output signals with a mean error value less than 5% in all cases tested. Given that the LE can be calculated using a really simple method, this chaotic parameter has been selected as the most suitable to detect noise of signals from these apparatus.

1. Introduction

In recent years, ionic liquids (ILs) have continued to attract the interest of researchers. ILs are chemicals composed of an organic cation and an inorganic or organic anion. Due to the nature of ions, ILs exhibit mixed inorganic and organic characters [1]. Recently, due to their unique properties, ILs have attracted increasing attention as replacements for conventional organic solvents in many fields, *viz.* catalysis, extraction processes, electrochemistry, etc. [1,2].

To model and/or control any chemical process, the measurement of IL concentration and the knowledge of their physicochemical properties are required. Due to the lack of knowledge of these topics, softwares which predicts or estimates their properties are being used in the design, modelization and/or control of chemical processes [3–5]. Recently, these measurements have been carried out by the interpolation in physicochemical properties, proton nuclear magnetic resonance (^{1}H NMR) spectroscopy [6], gas chromatograph (GC) [7], UV spectroscopy [4,5], etc. As is known, the presence of noise in this measurement can affect reliable quantification of IL. In relation to the properties of ILs, nearly all physicochemical properties of chemicals are taken from analytical equipment, and these measurements must be carried out with accuracy. As is known, the achievement of this goal depends on the variable measured (melting temperature, heat capacity, composition, etc.), the stability of instrumental response against time, the robustness of its calibration model, etc. All of these can be affected by the presence of noise in the measured property. The measurement process is made difficult and masks the true values of the properties. Given that tiny perturbations might generate an essential change in the state of non-linear systems, when the signal-to-noise ratio (SNR) is low, reliable detection is necessary. Because of this, the models of the processes based on statistical methods such as neural networks [8–10], genetic algorithms [11], fuzzy methods [12], chaotic methods [13], etc. have been applied to check and/or filter noisy signals.

The number of bibliographic references where the chaotic parameters are successfully applied to fault diagnosis is as yet scarce. In the chemistry field, to the best of our knowledge, the application of these parameters to detect noisy output signal without using their specific models is not found in the literature. Because of this, Liapunov exponent and fractal dimension calculated using regularization and box methods have been applied here to detect noisy output signals from UV spectrophotometer (UV), thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC).

2. Materials and methods

Detailed descriptions of the ionic liquid used, UV spectrophotometer, TGA, DSC apparatus and the chaotic parameters used are shown here.

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Table 1
Operating conditions of TGA and DSC experiments.

Operating conditions	TGA	DSC
IL used	[emim][$EtSO_4$]	[emim][$EtSO_4$]
Temperature range (K)	303.15–1173.15	133.15–303.15
Initial weight range of sample (mg)	7–16	9–21
N_2 flow (mL min^{-1})	50	50
Heating rate (K min^{-1})	10	10

2.1. Reagents, solutions and instrumentation

In this work, 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid ([emim][$EtSO_4$], ≥95% purity, from Sigma–Aldrich Chemie GmbH, chloride content <30 ppm) was used. All stock solutions were prepared using an AG 245 Mettler Toledo analytical balance (precision 0.01 mg). A Varian Cary 1E UV–vis spectrophotometer was employed for absorbance measurements using quartz cells with a path length of 1 cm [5].

The weight loss during the sample decomposition was measured by a Mettler Toledo TGA/SDTA851e Thermogravimetric Analyser, using a nitrogen atmosphere. Given the specific chemical to be measured, the TGA experiment mainly depends on its initial weight, temperature, heating rate, and inert gas flow (nitrogen, argon, etc.). Due to the high hygroscopic nature of [emim][$EtSO_4$] IL, all experiments were carried out in a vacuum atmosphere glove box under dry nitrogen. The experimental conditions of every experiment carried out to design, optimize and test the linear models (*vide infra*) are shown in Table 1. The TGA equipment is able to measure the sample weight loss as a function of temperature or heating time with an accuracy of ±1 μg. The sample temperature is measured to an accuracy of ±0.1 K. More details about TGA experiments can be found in the literature [14].

The measurements of the heat flow associated with material transitions as a function of temperature were carried out on a Mettler Toledo DSC821^e. The differential scanning calorimeter equipment was calibrated according to the temperature range used and the manufacturer's instructions [15]. The temperature measurements were carried out with an accuracy of ±0.1 K. The experimental conditions of every experiment carried out to design, optimize and test the linear models are shown in Table 1. In every experiment, stainless steel pans with a volume of 120 μL and a purge flow of 50 mL min^{-1} of dry nitrogen were used. The temperature range is between 133.15 and 303.15 K, whereas the heating/cooling rate is fixed at 10 K min^{-1} [14].

2.2. Chaotic parameters used

Fractal dimension, in general, is a number that quantitatively describes how an object fills its space. In plane geometry, objects are solid and continuous and given that they have no holes, they have integer dimensions. Fractals are rough and often discontinuous, and so, they present non-integer dimensions. From a fractal geometry point of view, the fractal dimension is a measure of complexity that is used to describe the irregular nature of lines, curves, planes or volumes. In this work, the regularization dimension (RD) and the box dimension (BD) using a plain box method have been computed by Fraclab version 2.0 (Toolbox of Matlab version 7.01.24704, R14) [16]. Considering the original signal as fractal, its graph will have an infinite length. Taking into account RD and that all regularized versions have a finite length, the RD measures the speed at which this convergence to the infinite takes place [16]. To calculate BD, the software works exactly in the same way as when computing the regularization dimension except that in this case different box sizes are tested. In almost all cases, on numerical samples, the estimation of fractal dimension by the box method is less accurate than the calculation by the regularization method. All necessary parameters values to calculate RD and BD were selected by default configuration settings of the software used [16].

Table 2
Quantity of [emim][$EtSO_4$] in design and validation processes.

Operating conditions	TGA (mg)	DSC (mg)	UV (ppm)
Design process	7.3142	9.7000	608
First validation process	7.3142	9.7000	608
Second validation process	15.7741	20.8120	10

Liapunov exponents (LEs) characterize the dynamics of a complex process and quantify the average growth of infinitesimally small errors in initial points. LE values characterize the rate of separation of infinitesimally close trajectories. This can be used to measure the sensitivity of a system's behavior to initial conditions [17]. The LE parameter has been calculated following Eq. (1).

$$\mathrm{LE} = \frac{1}{\Delta t_m} \sum_{k=1}^{m} \log_2 \frac{L(t_k)}{L(t_{k-1})} \quad (1)$$

where Δt_m and $L(t_k)$ are the prediction time interval and the distance between the developed points in the phase space, respectively. This parameter is one of the most sensitive to determine chaotic dynamic. Depending on the sign of the maximal LE (MLE), different types of attractors (dynamical systems evolve after a long time) can be found. MLE < 0 represent stable fixed, MLE = 0 or MLE = ∞ imply stable limit cycle or noise respectively and 0 < MLE < ∞ implies chaos which mean that neighboring points of trajectories in the phase space diverge [18–20].

3. Results and discussion

The diagnosis of output signals from UV, TGA and DSC apparatus have been tested here. The test procedure applied consists of five stages: (i) from each piece of equipment, at least ten different profiles have been measured (absorbance, weight loss and rate of heat flow to simple profiles); (ii) ten percentages between 0.10 and 5.41% of a random noise is added to the output signal previously measured; (iii) using these noisy profiles, the LE, BD and RD parameters are calculated; (iv) linear models have been defined; (v) statistical tools are applied to verify the linear models by two types of validation samples. Given that a high correlation coefficient value does not guarantee that any linear regression fits well the data, in every case correlation coefficient and standard deviation have been calculated [21].

3.1. Noisy signals

Taking into account that the noise test of every piece of equipment has been successfully carried out, every output signal is free of noise. The experimental conditions and the sample weight are shown in Tables 1 and 2. Once the output signals of the apparatus have been measured, in order to reach a low signal-to-noise ratio, random data between −1 and 1 have been added to them. To tune the SNR, ten different percentages (0.1, 0.69, 1.28, 1.87, 2.46, 3.05, 3.64, 4.23, 4.82 and 5.41%) of random data have been added to the original signal (free of noise). The total profile and a detail of an enlargement area of the output signal of the TGA, DSC and UV apparatus with 0.1% of noise is shown in Fig. 1. As can be seen the 0.1% noise added is hardly detectable.

3.2. Chaotic parameters

Given that all Liapunov exponents are non-integer and positive, Table 3, these describe some different strange attractors; whose

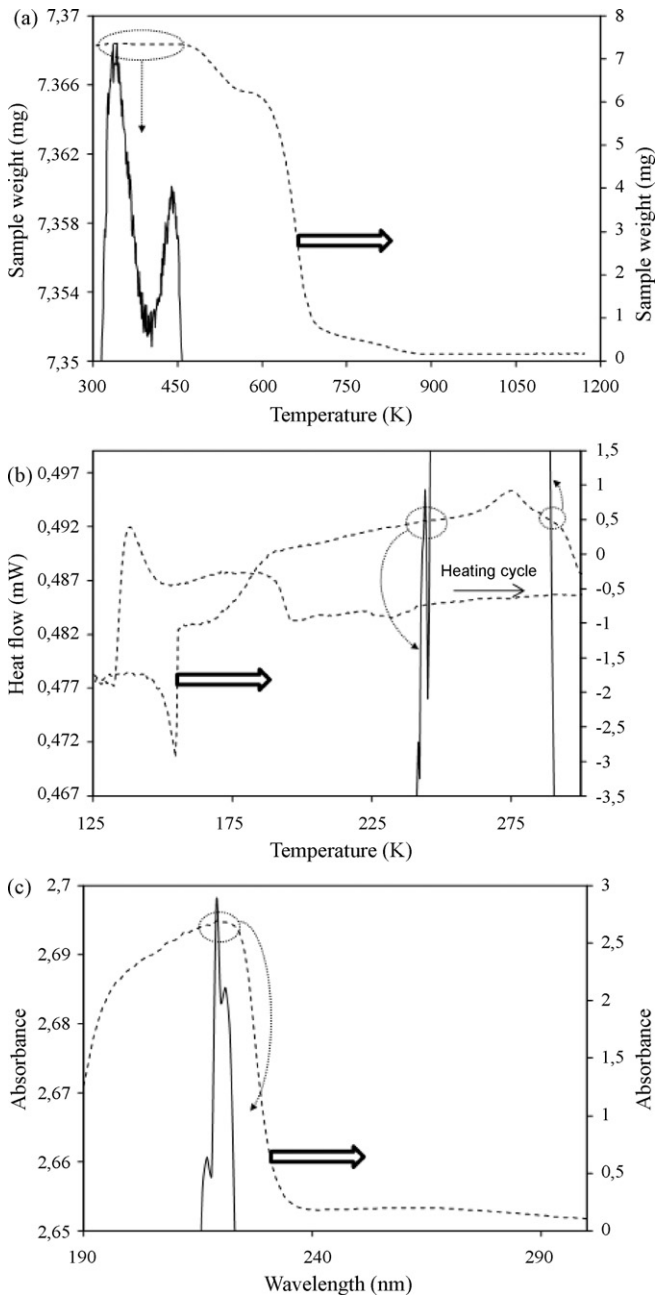

Fig. 1. Output signals with 0.1% of noise: (a) TGA; (b) DSC; (c) UV spectrophotometer (— total profile; ⬭ area of profile enlarged; — enlarged of ⬭).

trajectories appear to skip around randomly. This is probably due to the addition of random noise to the output signals. The LE values calculated using the output signals from the UV spectrophotometer are closer to zero than those from the other apparatus and therefore the trajectories can be explained using other type of attractor. In all cases, LE values are close to 0 and slightly decrease linearly (correlation coefficient, $R^2 > 0.980$) with the added noise percentage except in the DSC case. In this case, the final LE values are a consequence of two different trends, i.e. the variation of LE values with the added noise is made of a slightly increase and decrease depending on the cooling and the heating cycles of the DSC measurements, respectively (see Fig. 1b). And as consequence of this, the final LE values shown a really slightly increase with the added noise. In Table 4 are shown the linear models and their statistical results. In addition, the LE range of values is less than 8×10^{-3} per percentage unit of noise.

Given that RD and BD parameters define the output signals tortuosity and taking into account that the RD and BD values of the added random data (to make the noisy signals) are respectively 2.26 and 1.77, their values increase linearly ($R^2 > 0.973$ and $R^2 > 0.936$, respectively) with the percentage of noise added, Table 3. Their lineal models and statistical results are shown in Table 4.

3.3. Validation processes

Two validation processes have been used. In the first, another sample using the same quantity of [emim][$EtSO_4$] and similar experimental conditions as those used in the linear models design have been used. And finally, in the second, other quantities of [emim][$EtSO_4$] and the aforementioned experimental conditions have been used to calculate new profiles.

In the first validation process, once the profiles of all apparatus have been measured following the experimental conditions shown in Tables 1 and 2, five percentages (1, 2, 3, 4 and 5%) of noise have been added to the output signal of the equipment studied. Then, the chaotic parameters have been calculated. And finally, interpolating these LE, RD and BD values in the models shown in Table 4, every noise percentage added initially has been estimated, Table 5. In the light of these results, a linear relationship between LE and RD parameters and the noise added can be assumed. In this sense, although the relationship between RB and the noise is apparently linear, this statement is not clear enough in all tested cases. Probably due to the fact that if the box method is used to calculate the fractal dimension, the prediction is less accuracy (*vide supra*).

In the second validation process, the noise percentage added is similar to first validation process and the quantity of sample is different from the samples used at the design stage, Table 2. As is expected, the statistical results are the worst (in all cases $R^2 < 0.78$

Table 3
Chaotic parameters.

Noise (%)	TGA			DSC			UV		
	LE	RD	BD	LE	RD	BD	LE	RD	BD
0	0.1617	1.0043	0.8848	0.05416	1.3020	0.9251	2.614×10^{-4}	1.6646	0.9964
0.1	0.1613	1.0048	0.8839	0.05417	1.3069	0.9250	2.611×10^{-4}	1.6698	0.9860
0.69	0.1578	1.007	0.8956	0.05418	1.3080	0.9311	2.585×10^{-4}	1.7358	1.0268
1.28	0.1530	1.0097	0.9139	0.05420	1.3104	0.9424	2.554×10^{-4}	1.8181	1.0608
1.87	0.1476	1.0112	0.9287	0.05422	1.3138	0.9554	2.518×10^{-4}	1.8895	1.0984
2.46	0.1422	1.0143	0.9385	0.05423	1.3179	0.9623	2.477×10^{-4}	1.9487	1.1203
3.05	0.1369	1.0162	0.9540	0.05425	1.3226	0.9724	2.431×10^{-4}	1.9974	1.1342
3.64	0.1320	1.0197	0.9637	0.05426	1.3277	0.9777	2.380×10^{-4}	2.0387	1.1457
4.23	0.1275	1.0202	0.9685	0.05427	1.3330	0.9852	2.324×10^{-4}	2.0746	1.1612
4.82	0.1232	1.0226	0.9724	0.05428	1.3385	0.9894	2.263×10^{-4}	2.1057	1.1716
5.41	0.1193	1.0250	0.9772	0.05429	1.3441	0.9945	2.197×10^{-4}	2.134	1.1754
Range	0.0424	0.0207	0.0924	1.3×10^{-4}	0.0420	0.0694	4.170×10^{-5}	0.4694	0.1790

Table 4
Linear models* and statistical results calculated during the design process (correlation coefficient R^2 and standard deviation, σ).

	LE				RD				BD			
	a	*b*	R^2	σ	*a*	*b*	R^2	σ	*a*	*b*	R^2	σ
TGA	−122.7	19.9	0.998	0.07	261.1	−262.3	0.995	0.08	54.0	−47.9	0.965	0.20
DSC	4.2×10^4	2.3×10^3	0.988	0.12	137.2	−178.7	0.980	0.20	73.2	−67.7	0.984	0.16
UV	-1.3×10^5	35.0	0.980	0.16	11.1	−18.7	0.973	0.19	27.9	−28.1	0.936	0.31

*Noise (%) = $a \times$ [chaotic parameter] + b.

Table 5
Estimation values of noise added in the first validation process.

Noise (%)	TGA			DSC			UV		
	LE	RD	BD	LE	RD	BD	LE	RD	BD
1	0.97	0.87	0.80	1.05	1.05	1.05	0.93	0.93	0.70
2	1.99	2.21	1.70	2.11	2.21	2.13	1.82	1.72	1.69
3	3.04	3.23	3.30	3.11	3.23	2.15	2.91	2.71	3.33
4	3.99	4.15	4.21	3.98	4.16	4.24	3.90	4.18	4.25
5	4.98	4.81	4.76	4.91	4.81	4.90	5.14	5.24	4.70

and standard deviation, $\sigma < 3$). This is due to the fact that in all cases tested, the output signals depend on the quantity of IL used, and as the chaotic parameters calculated quantify the main characteristic of their profiles, the linear relation between chaotic parameters and noise has changed. From these results, when the intention is to detect noise using the method described here, the concentration value of the sample must be constant. The presence of noise in an output signal can be easily detected using LE or RD parameters. Given that LE values can be more easily calculated, Eq. (1), this chaotic parameter is the most suitable to detect and quantify the noise in noisy output signals.

4. Conclusions

In this work, the random noise of noisy output signals has been detected and quantified by the application of three chaotic parameters, *viz.* Liapunov exponent, regularization and box dimensions. To make the noisy signals used, random data between −1 and 1 have been added to different percentages on different output signals free of noise from a UV spectrophotometer, a thermogravimetric analyzer and a differential scanning calorimeter. Given that their correlation coefficient values reached in the design and in the first validation process ($R^2 > 0.980$, in most cases), linear relations between the LE or RD parameters and the quantity of random noise added can be assumed. Taking into account as a criterion the simplicity of the mathematical procedure to calculate these parameters, LE is the most suitable parameter for the required purpose.

In the chemistry field, thanks to these novel mathematical relations, detection and quantification of noisy signals can be achieved. In addition, the mathematical method developed and applied is very simple.

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