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Electrical percolation of AOT-based microemulsions with *n*-alcohols

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ABSTRACT

Percolative behaviour of w/o AOT/iC_8/H_2O microemulsions added with different *n*-alkanols is reported. 1-*n*-alcohols and 2-*n*-alkanols presented dissimilarities affecting percolation. Smaller alcohols ease percolation, especially at low concentrations. Greater molecules implied a reinforcement of the surfactant film that delayed the percolation threshold. Also, a neural network based simulation model of the phenomenon has been developed. This single model has only five input variables and can estimate percolation temperature of microemulsions added with the two types of alcohols studied, with an RMSE of 0.98 °C and $R^2 = 0.9740$ (validation dataset values). This is considered a successful prediction rate, following previous developments with other families of additives, that confirms neural networks as reliable tools for percolative behaviour modelling.

1. Introduction

The internal dynamics of water in oil (w/o) microemulsion has been mainly investigated around electrical percolation, a phenomenon involving conductance of these microheterogeneous, self-organizing, dynamic systems [1–4]. A w/o microemulsion is basically formed with three components, the main, non-polar solvent, the other polar solvent, commonly water, and the surfactant that stabilizes the whole system. Everything is self-arranged in microdroplets of the polar solvent dispersed into the non-polar solvent which conforms a continuous phase, being the two domains separated by a thin surfactant film. While microemulsions have regularly low conductivity, it is indeed a significant one when compared with the conductivity of the non-polar solvent alone. Increasing the temperature of the microemulsion firstly produces a gentle increase in its conductivity, but once a certain point is reached, suddenly it sharply rises in virtue of the electrical percolation [5]. This point is known as the percolation threshold, and besides temperature changes, it can be reached modifying the molar fraction of water at constant temperature.

Electrical percolation is strongly dependent on the stiffness of the surfactant film, based on the way single molecules of surfactant fit with one another. In this manner, the presence of other substances may modify rigidity either increasing or diminishing it, depending on the solubility domain of the system where the additive is allocated [6–10]. The effects of several kinds of additives on electrical percolation and other properties of AOT/iC_8/H_2O microemulsions have been extensively studied by our research groups [11–18].

Percolative behaviour has been modelled from effective medium theory approaches [19–24]. Nevertheless, those models do not consider the effect of additives on percolation. As a counterpart, statistical and empirical models have been developed [25–26]. Taking into account that percolation phenomenon depends on so many factors; simulation tools for complex systems might be applied. Recent works of our research group are focused on employing artificial neural network modelling in changes of the percolation threshold of AOT microemulsions [27–30]. In this line, the purpose of this manuscript is to report the percolation threshold changes of AOT/iC_8/H_2O microemulsions when 1-*n*-alcohols and 2-*n*-alcohols are added to the system. Also, models based on neural networks have been developed and contrasted with previous works.

2. Materials and methods

2.1. Reactants

Aldrich provided isooctane and AOT at the highest commercially available purity. Fluka supplied additives, also at the highest purity. Microemulsions were prepared by weight with bidistilled water (conductance ranging from 0.10 to 0.15 μS cm^{-1}), keeping $W = [H_2O]$ /

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[AOT] = 22.2 and [AOT] = 0.5 M (referred to the total volume of the microemulsion) constant.

2.2. Percolation threshold determination

A Crison GPL 32 conductivimeter was employed for conductance measurements. The percolation threshold was detected through percolation temperature determination, following the method described in literature [16–17] in terms of the Sigmoidal Boltzmann Equation (SBE) [31] of Eq. (1), where κ represents conductance, T stands for temperature, and ΔT is a constant range of temperatures, and i, f and p are initial state, final state and the percolation threshold respectively. This method is compatible with the proposal of Kim et al. [32], as depicted in Fig. 1.

$$log\kappa = log\kappa_i \left[1 + \left(\frac{log\kappa_i - log\kappa_f}{log\kappa_f}\right)\left\{1 + \frac{e^{(T-T_p)}}{\Delta T}\right\}^{-1}\right]. \quad (1)$$

2.3. Geometry of additives

Geometrical parameters of *n*-alkanols were determined by MM2 with CS Chem Bats 3D Pro 4.0 by Cambridge Soft Corporation, based on QCPE 395 [33–34], and collected in Table 1.

2.4. Neural modelling

Artificial neural networks are computational tools with learning features, designed by mimicking the way biological neurons process information. As the name suggests itself they are made of several nodes interconnected, commonly referred to as artificial neurons, or just neurons or neurodes. Neurons are functions, and networks are combinations of neurons connected with different weights. Artificial neural networks, exposed to datasets of cases of study, can find and learn inner patterns of the dataset, and so recognize those patterns on new datasets through generalization. This feature has been applied to several problems involving variable prediction [35–36], classification tasks [37] and control systems [38], since they can map non-linear relationships in complex systems [39].

One of the most extended neural models is the multilayer perceptron, because it works as a universal approximator [40]. It is composed of several layers of neurons with different features, as depicted in Fig. 2. The first one is the input layer that collects inputs for the network. The last one is the output layer where values for output variables based on inputs are obtained. Intermediate layers, sometimes referred to as hidden layers act as operators and connectors between layers. The backpropagation algorithm returns part of the information to the network in training, when the network is modelling the dataset. Our

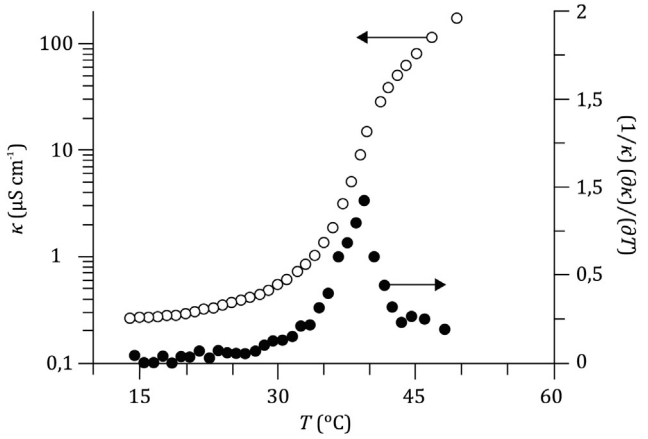

Fig. 1. Determination of T_p of a w/o AOT/iC_8/H_2O microemulsion in the absence of an additive ([AOT] = 0.5 M, W = 22). Black dots stand for the Kim et al. approach, white dots for the Moulik et al. SBE method [15].

Table 1
Percolation temperature for each microemulsion studied and input values for the neural model. Composition in all cases was [AOT] = 0.5 M and W = 22.2, with additive concentration referred to the waterpool volume [45].

Additive	Molecule	No. C	a_0/Å^2	lc/Å	log P	pK_a	[C_n]/M	T_p/°C
1-*n*-alkanols	1-*n*-ethanol	2	1.34	2.16	0.07	14.83	0.05	34.4
							0.10	33.5
							0.25	32.7
							0.50	27.5
	1-*n*-propanol	3		3.48	0.55	14.83	0.05	34.6
							0.10	34.5
							0.25	34.0
							0.50	30.3
	1-*n*-butanol	4		4.84	0.97	14.83	0.05	35.1
							0.10	37.2
							0.25	37.0
							0.50	37.3
	1-*n*-pentanol	5		6.14	1.39	14.83	0.05	36.3
							0.10	38.0
							0.25	39.3
							0.50	39.9
	1-*n*-hexanol	6		7.30	1.80	14.83	0.05	37.3
							0.10	39.3
							0.25	43.4
							0.50	44.1
	1-*n*-heptanol	7		8.70	2.20	14.84	0.05	37.4
							0.10	39.3
							0.25	44.4
							0.50	46.9
	1-*n*-octanol	8		9.40	2.64	14.83	0.05	38.0
							0.10	40.5
							0.25	47.3
							0.50	50.4
	1-*n*-nonanol	9		11.20	3.05	14.83	0.05	38.9
							0.10	42.6
							0.25	47.5
							0.50	50.6
	1-*n*-decanol	10		12.35	3.47	14.83	0.05	39.5
							0.10	42.9
							0.25	49.6
							0.50	54.6
2-*n*-alkanols	2-*n*-propanol	3	1.86	2.16	0.38	14.73	0.05	27.0
							0.10	27.6
							0.25	29.7
							0.50	31.7
	2-*n*-butanol	4		3.48	0.87	14.73	0.05	30.3
							0.10	31.1
							0.25	33.5
							0.50	38.1
	2-*n*-pentanol	5		4.84	1.29	14.73	0.05	33.4
							0.10	34.7
							0.25	37.8
							0.50	43.0
	2-*n*-hexanol	6		6.14	1.70	14.73	0.05	35.7
							0.10	37.8
							0.25	41.1
							0.50	48.7
	2-*n*-heptanol	7		7.30	2.12	14.73	0.05	38.9
							0.10	40.9
							0.25	46.5
							0.50	m/r
	2-*n*-octanol	8		8.70	2.54	14.74	0.05	41.1
							0.10	43.4
							0.25	m/r
							0.50	m/r
	2-*n*-nonanol	9		9.40	2.96	14.74	0.05	42.8
							0.10	45.3
							0.25	m/r
							0.50	m/r
	2-*n*-decanol	10		11.20	3.37	14.73	0.05	45.5
							0.10	48.4
							0.25	m/r
							0.50	m/r