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Modeling of the binodal curve of ionic liquid/salt aqueous systems

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A B S T R A C T

Ionic Liquid-based Aqueous Two Phase Systems (ILATPS) are an innovative technique to separate biomolecules that combines the advantages of liquid–liquid extraction and hydrophilic ionic liquids. Most ILATPS are based on ionic liquids and conventional inorganic salts, and the phase envelope, described by the binodal curve, is usually modeled by empirical equations that are used to determine the phase compositions and assess the ionic liquid recyclability. However, these empirical equations may provide a poor extrapolation ability or low accuracy at the extreme regions of the binodal curve or suffer from problems of convergence. Therefore, the aim of this work is the analysis of the binodal curve equations, comparing the models reported in the literature to describe ILATPS and proposing alternative equations to improve accuracy or to reduce the mathematical complexity. For this purpose, a database compiling binodal experimental data of 100 ILATPS has been built, so that the analysis could make it possible to obtain representative conclusions for all these systems. Several models were developed, and different statistical criteria were used to assess the advantages and disadvantages of each one of these models for the binodal curve. The results show that, when accuracy is critical, a proposed model with just an additional parameter reduced more than 25% the residual mean squared error (RMSE) with respect to the commonly used equation, without losing the statistical significance of the parameters. For complex problems where an explicit equation in both the concentration of ionic liquid and of salt is needed, the use of an explicit model developed with 3 adjusted parameters that kept high accuracy ($R^2 > 0.996$ and RMSE < 0.66) is proposed. Finally, the analysis also revealed that a fitting method based on the minimization of relative errors is recommended to increase the accuracy of the binodal curve at high salt concentrations, which is the crucial region for assessing the recyclability of the ionic liquid.

1. Introduction

The separation and purification of biomolecules usually represents about 60–90% of the cost of the final product(s), so downstream processing determines the efficiency and viability of the biotechnological processes [1]. Among the multiple alternatives to separate biomolecules, Ionic Liquid-based Aqueous Two-Phase Systems (ILATPS) stand out for being an innovative technique that combines the advantages of liquid–liquid extraction and ionic liquids [2,3]. ILATPS are powerful alternatives extracting biomolecules and have been widely used in the separation, concentration, and purification of proteins, amino-acids, antibiotics, antioxidants, alkaloids [4–6], among others [2]. They are based on ionic liquids and salts, which form two aqueous phases: an ionic liquid-rich and a salt-rich phase. Many works can be found in literature in which these systems are characterized in terms of the binodal curve, which also makes it possible to compare the various systems with each other to derive information about the mechanisms responsible for the phase separation and the design of novel ATPS. Moreover, an accurate binodal curve is essential to experimentally determine the tie lines by means of the gravimetric method and, in this way, the composition of the two liquid phases [7–9].

However, rigorous models of the binodal curve for ILATPS with a theoretical support are not available. In this way, the binodal curve of ILATPS is usually described by means of the empirical equation proposed by Merchuk and collaborators [2,10,11]:

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$$[IL] = A\exp\left(B[S]^{0.5} - C[S]^3\right) \quad (1)$$

where [IL] and [S] are the mass fractions of ionic liquid and salt expressed as percentage, respectively, and A, B and C are adjusted parameters. It should be noted that Merchuk's equation was originally proposed to describe conventional aqueous two-phase systems based on polymers and salts. However, this equation also provides relatively high values of the R^2 when modeling ILATPS, but it requires 5 parameters (2 fixed and 3 adjusted) to fit the experimental data and some limitations have been detected for this model. In this sense, a higher accuracy may be required for describing the extreme regions of the binodal curve (at very high ionic liquid or salt concentrations) [7,12]. The region of very high salt mass fractions is essential to assess the ionic liquid recyclability to the process, so the accuracy of the binodal curve in this region is particularly important [13]. In addition, Equation (1) may cause problems of convergence when it is used in the resolution of more complex problems (recyclability experimental schemes, for example) due to the fact that it is clearly non-linear and implicit in salt concentration [14]. Therefore, the development of alternative models of the binodal curve that overcome these drawbacks is particularly interesting. In the literature, other empirical expressions have been proposed as alternative models to enhance the accuracy [15–17]:

$$[IL] = \exp\left(a + b[S]^{0.5} + c[S] + d[S]^2\right) \quad (2)$$

$$[IL] = a_1\exp\left(-[S]/b_1\right) + a_2\exp\left(-[S]/b_2\right) + c \quad (3)$$

where a, a_1, a_2, b, b_1, b_2, c and d are adjusted parameters. Both Equations (2) and (3) contain a higher number of adjusted parameters (4 and 5, respectively) than Merchuk's equation. Another approach reported in previous works [15,17–19] implies a binodal curve model based on statistical geometry methods, developed by Guan et al. [20] for aqueous polymer–polymer systems. This binodal equation has a theoretical support by means of the concept of effective excluded volume (EEV) and contains only two adjusted parameters:

$$\ln\left(V^*_{213}\frac{[S]}{M_S} + f_{213}\right) + V^*_{213}\frac{[IL]}{M_{IL}} = 0 \quad (4)$$

where V^*_{213} is the scaled EEV of salt; f_{213} is the volume fraction of unfilled effective available volume after tight packing of the salt molecules into the ionic liquid molecules network in ionic liquid aqueous solutions; and M_S and M_{IL} are the molecular masses of the salt and the ionic liquid, respectively. It should be highlighted that only this binodal curve model has some theoretical foundation, in contrast with the remaining models, which are purely empirical. Few studies have carried out a comparison among models for the binodal curve [15,17,21]. Nevertheless, these analyses have been done using a reduced number of systems (lower than 10 in all the cases) and very simple statistical criteria, such as the standard deviation and/or the R^2 coefficient. As a result, the conclusions derived from these works with respect to the selection of the binodal curve model cannot be easily extrapolated to the hundreds of ILATPS described in literature.

In this way, the aim of this work is the analysis of the binodal curve equation to describe ILATPS based on ionic liquids and salts, comparing the previous models and proposing either alternative equations which may improve its accuracy or simpler mathematical models that keep successful performances. For this purpose, a database with the binodal data of 100 ILATPS was built and subsequently analyzed so that the conclusions obtained are representative for all these systems. Furthermore, different statistical criteria have been used in order to discuss in detail the advantages and disadvantages of each binodal equation.

2. Methods

2.1. Methodology

The methodology followed in this study is graphically summarized in Fig. 1.

Binodal data from 100 ILATPS systems were compiled from the literature [7,22–30] in order to assure that the conclusions derived from the study are representative of these types of systems. The database created included 100 ILATPS systems, which involved 30 different ILs and 9 different (inorganic and organic) salts. The binodal curves of these ILATPS were determined at room temperature, as liquid–liquid extraction with these systems is usually carried out at this temperature. In addition, it is expected that the conclusions derived in this work from the analysis of the binodal curve of ILATPS at room temperature can also be applied to other temperatures, as the linear dependency of the adjusted parameters of Merchuk's equation with respect to temperature suggests. With respect to the influence of the temperature on ILATPS, the biphasic region decreases with the increase in this variable, which implies that the higher the temperature, the higher the salt and ionic liquid concentrations required for phase separation. However, the intensity of the temperature effect on the phase diagrams depends on the inorganic salt employed [2]. The complete dataset is included in Table S1 as Supplementary Material. For each ILATPS, the binodal data were fitted to each model that was considered in the study, obtaining the values of the adjusted parameters and the statistical criteria that will be described in Section 2.2. Finally, for the discrimination and selection of the models, the means of the statistical criteria were calculated, and these means, for the 100 ILATPS, are the values that will be reported in Section 3 "Results and discussion".

2.2. Statistical criteria for the discrimination and model selection

The discrimination and selection of the binodal curve models has been carried out by means of different statistical criteria that consider the accuracy, the significance of the parameters or the number of adjusted parameters [31]:

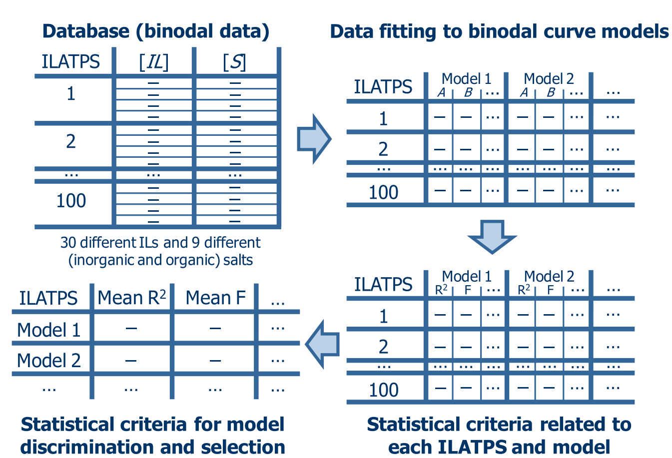

Fig. 1. Scheme of the methodology followed in this work.