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THERMODYNAMIC MODELING OF PSEUDOTERNARY AQUEOUS TWO PHASES SYSTEMS WITH DEEP EUTECTIC SOLVENTS

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Abstract – Liquid–liquid equilibrium (LLE) data used in this work were previously obtained by our group research. The quaternary systems were composed to cholinium chloride: glucose + poly(propylene)glycol (400 $gmol^{-1}$) + H_2O at 298.15 K. The Non-Random Two-Liquid (NRTL) model has been used to fit the DES-based aqueous two-phase systems. The interaction parameters of the models were estimated. The liquid−liquid equilibrium (LLE) experimental data were well correlated to the activity coefficients of the NRTL model, and the mean deviations were less than 1,1%.

Keywords: Quaternary Systems; Phase equilibria; Extraction; NRTL.

Introduction

Aqueous two-phase systems (ATPS) is a kind of liquid-liquid extraction which are composed by two immiscible aqueous solutions [1, 2]. In general, the ATPSs are composed of aqueous solution of two polymers, two salts or a polymer and a salt [2, 3].

Several compounds have been studied as substitute of the conventional compounds in ABS, such as ionic-liquids, organic solvents and deep eutectic solvents [4-13]. Deep eutectic solvents (DES) are a kind of green solvents formed by the association of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) [9]. Several authors studied the DES-based ABS with the main purpose of extract biomolecules [6, 10-13]. Passos et al. [7] and Farias et al. [8] evaluated the DES stability in ATPS and both works proved that the DES complex (between the HBA and HBD) are disrupted due to the high-water content present at the ATPSs, and consequently these systems are actually quaternary systems. Farias et al. [8] reinforce the necessity to quantify each of the four compounds to characterize the tie-lines composition in this type of ATPS. In the same way, the thermodynamic modeling needs to be done considering all the four compounds e not a pseudo-ternary system. The NRTL model was previously used to correlate the experimental data of DES-based ATPS with a low mean deviation [8]. The same authors also evaluated the liquid-liquid equilibrium of DES-polymer ATPS. However, the thermodynamic modeling applied to DES-based ATPS are low explored.

Considering the lack of results about thermodynamics modeling in the quaternary systems, or DES-based ATPS, in this work, the experimental data published in a previous study [14], were correlated with the NRTL model for the activity coefficient, with estimation of new interaction parameters of quaternary systems.

Thermodynamic Modeling - NRTL model

The NRTL model was proposed by Renon and Prausnitz (1968) [15], and was based on local composition concept and it is applicable to partially miscible as well as totally miscible systems. Especially for partially miscible systems, LLE, it provides a helpful representation.

Usually, mole fractions are used for the calculation of activity coefficients using NRTL, but in ATPS the mass fractions were used, because of the mole fractions of polymers (Poly(propylene)glycol - PPG, for example) are very small quantity due to its large molecular mass.

Therefore, Stragevich and d'Ávila (1997) [16] used mass fractions for the calculation of activity coefficients of a component in polymeric solutions using NRTL model. Using mass fractions, the NRTL model at constant temperature is presented as follows:

$$ln\gamma_i = \frac{\sum_j \frac{\tau_{ji} G_{ji} w_j}{M_j}}{\sum_k \frac{G_{ki} w_k}{M_k}} + \sum_j \left[\frac{w_j G_{ji}}{M_j \sum_k \frac{G_{kj} w_k}{M_k}} \left[\tau_{ij} - \frac{\sum_k \frac{\tau_{kj} G_{kj} w_k}{M_k}}{\sum_k \frac{G_{kj} w_k}{M_k}} \right] \right] \quad (1)$$

$$\tau_{ij} = \frac{A_{0ij} + A_{1ij} T}{T} \quad (2)$$

$$G_{ij} = exp\left(-\alpha_{ij} \tau_{ij}\right) \quad (3)$$

where A_{0ij} and A_{1ij} are the characterisc parameters of energy of the i-j interactions, and parameter α_{ij} is related to the non-randomness of the mixture.

Experimental

The experimental data used in this work were previously obtained by the group and have already been published by Farias et al. [14]. The systems evaluated were composed to cholinium chloride: glucose + poly(propylene)glycol (400 $gmol^{-1}$) + H_2O at 298 K. Three different molar ration cholinium chloride: glucose, 2:1, 1:1 and 1:2, were evaluated.

Parameter Estimation

The estimation of the model parameters followed the procedure described by Stragevitch and d'Ávila (1997) [16]. The previous procedure consists of the minimization of an objective function (Eq. 11) using the simplex method [17] and several direct calculations of the equilibrium curve.

$$OF = \sum_k^D \sum_j^M \sum_i^{N-1} \left(x_{ijk}^{I.exp} - x_{ijk}^{I.calc} \right)^2 + \left(x_{ijk}^{II.exp} - x_{ijk}^{II.calc} \right)^2 \quad (11)$$

With the set parameters, comparisons between the compositions calculated and experimental of the two phases system were made through the deviation (RMSD - root mean square deviation),

given by Eq. 12:

$$\delta_x = 100.\sqrt{\frac{\sum_i^M \sum_j^N \left(x_{ij}^{I.exp} - x_{ij}^{I.calc}\right)^2 + \left(x_{ij}^{II.exp} - x_{ij}^{II.calc}\right)^2}{2MN}} \quad (12)$$

Results and Discussion

To represent the liquid-liquid equilibrium phase diagrams data published in a previous work [14] the Non-Random Two-Liquid (NRTL) model was applied. Comparisons between the experimental and calculated data were made through mean deviations between the experimental

One can see in Table 1 a satisfactory representation of liquid–liquid equilibrium of quaternary system composed by Cholinium chloride (HBA) + Glucose (HBD) + PPG + H_2O was obtained by all molar ratios of HBA: HDB. The NRTL models were able to represent the phase split over the entire range of compositions analyzed. The mean deviations were found to be < 1,1 %.

In this model, the mean deviation is below the value considered in the literature for adequate agreement (3 %) [18]. Thus, the NRTL model is well-fitted with the experimental data indicating its feasibility for describing the behavior of other equilibrium systems.

TABLE 1 - NRTL FITTED PARAMETERS OF QUATERNARY SYSTEM COMPOSED BY CHOLINIUM CHLORIDE (HBA) + GLUCOSE (HBD) + PPG + WATER AT 298.15 K AND ATMOSPHERIC PRESSURE.

HBA:HBD molar ratio	Parameters (i – j)	$A(0)_{ij}$	$A(0)_{ji}$	$Alfa(0)_{ij\ or\ ji}$	RMSD %
2:1	Cholinium Chloride – Glucose	-8927.6	7949.8	0.2000	1.1
	Cholinium Chloride – PPG	7154.1	575.5	0.2003	
	Cholinium Chloride – Water	-1011.1	-9000.0	0.3425	
	Glucose – PPG	1735.6	-2805.3	0.2517	
	Glucose – Water	-64.1	-5146.7	0.2429	
	PPG - Water	-856.9	2002.7	0.2000	
1:1	Cholinium Chloride – Glucose	-9000.0	7511.2	0.2122	1.1
	Cholinium Chloride – PPG	8730.8	567.2	0.2260	
	Cholinium Chloride – Water	-1100.5	-8973.5	0.4378	
	Glucose – PPG	1983.3	-2582.8	0.2000	
	Glucose – Water	-63.5	-5083.7	0.2947	
	PPG - Water	-858.3	1947.1	0.2123	
1:2	Cholinium Chloride – Glucose	-8192.2	509.0	0.2122	0.9
	Cholinium Chloride – PPG	3491.9	1456.3	0.2260	
	Cholinium Chloride - Water	97.3	-558.9	0.4035	
	Glucose – PPG	1171.8	-6178.5	0.2000	
	Glucose – Water	-1705.8	-2911.4	0.2947	
	PPG - Water	-874.3	1896.7	0.2121	

Conclusion

The NRTL model was used to correlate the equilibrium results for the quaternary system to determine the activity coefficient. A good correlation between the models and the experimental data was observed. The binary interaction parameters obtained in this work can be used in project, simulation and operation of aqueous two-phase extraction processes biochemical industry.

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