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CORRELATION OF THREE-LIQUID-PHASE EQUILIBRIA INVOLVING IONIC LIQUIDS

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ABSTRACT

The difficulty of achieving a good thermodynamic description of phase equilibria is finding a model that can be extended to a large variety of chemical families and conditions. This problem gets worse in the case of systems containing more than two phases or involving complex compounds such as ionic liquids. However, there are interesting applications that involve multiphasic systems, and the promising features of ionic liquids suggest that they will play an important role in many future processes. In this work, for the first time, the simultaneous correlation of liquid-liquid and liquid-liquid-liquid equilibrium data for ternary systems involving ionic liquids has been carried out. To that end, the phase diagram for the system water + [P_{6,6,14}][DCA] + hexane has been determined at 298.15 K and 323.15 K and atmospheric pressure. The importance of this system lies in the possibility of using the surface active ionic liquid to improve surfactant enhanced oil recovery methods. With those and previous measurements, thirteen sets of equilibrium data of ternary systems water + ionic liquid + oil have been correlated. The isoactivity equilibrium condition, using the NRTL model, and some pivotal strategies are proposed to correlate these complex systems. Good agreement has been found between experimental and calculated data in all the regions (one triphasic and two biphasic) of the diagrams. The geometric aspects related to the Gibbs energy of mixing function obtained with the model, together with the minor common tangent plane equilibrium condition, are valuable tools to check the consistency of the obtained correlation results.

Keywords: Multiphase; Ionic Liquid; NRTL; Correlation; LLE

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1. Introduction

Systems exhibiting multiple liquid phases are found in many separation and reaction units. Most of the processes where three liquid phases appear involve microemulsions. In optimal conditions, the addition of a surfactant (or a surfactant ionic liquid) to an oil/water mixture can produce a three-liquid-phase system (water, oil and a middle microemulsion) classified as Winsor type III. This balanced state of interactions is associated with an ultralow interfacial tension that is the basis of surfactant or microemulsion enhanced oil recovery methods [1,2]. Such triphasic organized systems also exhibit important advantages in catalytic reactions, as the compartmentalization of reactants and products reduces the incidence of side reactions. Thus, balanced catalytic surfactants have been successfully used in several reactions, like oxidations [3,4].

The integration of the traditional biphasic system (an aqueous and an organic phase) with a biphasic aqueous system (aqueous solutions of two polymers, a polymer and a salt, or a salt and an ionic liquid) also gives way to three-liquid-phase systems. This process allows the recovery or separation of several compounds simultaneously, being proved as useful for metal recovery, extraction of natural products and waste water treatment [5,6]. There is also the possibility of using these systems as reaction medium, for instance in enzymatic reactions [7]. Another example of multiphase systems is liquid-liquid-liquid phase transfer catalysis. The reaction basically occurs in a middle, catalyst-rich phase, with aqueous and organic reactants transferring from either side to that phase. Ionic liquids are frequently used as phase transfer catalysts. The advantages are the reduction of secondary reactions, the straightforward separation of the products, and the easy recovery of the catalyst for its re-use. Among the tested reactions are alkylations, isomerizations, halogenations, etc. [8]. Moreover, multiphase catalyst systems are also possible when ionic liquids partially miscible with water and oil are used as medium to dissolve the catalyst, being reactants and products distributed between aqueous and oily phases [9].

Phase equilibria involved in these systems are complex. The number of the phases formed and the distribution of the compounds among them depend on the type of components involved, temperature, pressure, and also the presence and concentration of salts drastically affect the phase behavior. For that reason, in spite of the interest of these systems and the need of the knowledge of the equilibria to design/optimize the

corresponding separation processes, the number of studies is very limited. Experimental data on liquid-liquid-liquid equilibria (LLLE) are scarce and many of them do not present a reliable model of correlation or prediction, a key engineering tool in process design. Furthermore, these studies are even scarcer when ionic liquids are present in the multiphasic systems.

Regarding systems involving surfactants, Buraeur *et al.* [10] determined Gibbs phase triangles of the system water-dodecane- C_4E_1 . The authors suggest, analyzing the behavior of different alkyl polyglycol ethers (C_iE_j), that the monomeric solubility of the surfactant in oil and water might be the key to describe the main features of those microemulsion systems. Several works can be found in literature where compositions of tie-line ends and tie-triangles are determined for ternary systems water-oil- C_iE_j [11-16]. Chen *et al.* [11-14] used the UNIQUAC model to correlate only the three-liquid-phase coexisting data. Data of the two-liquid-phase-coexisting regions were not used in the correlation. With the interaction parameters obtained, these biphasic data were predicted with good results in some cases [11,12] and very poor results in other cases [13,14]. Contrarily, Negahban *et al.* [15] and Brandani *et al.* [16] were able to successfully simultaneously correlate biphasic and triphasic data with the NRTL and UNIQUAC models by using specific algorithms. Chen *et al.* [17-19] also presented data for multiphasic systems water-oil-propylene glycol propyl ether and correlations only of the tie-triangles. Stateva *et al.* [20] developed a method to correlate compositions of tie-triangles at different temperatures.

Another approach commonly used, with excess Gibbs energy models, is the estimation (prediction) of the triphasic equilibria with parameters obtained from the correlation of the binary systems (LLE or VLE). This modeling has been considered by de Loos *et al.* [21] for the ternary system water-oil- C_7E_5 ; by Schmelzer *et al.* [22-25] for ternary systems water-oil-phenols [22,23] and systems containing aniline or cyclohexylamine [24,25]; and by Revellame *et al.* [26] who investigated the possibility of using solvent extraction to recover lipids from microbial sources for renewable fuel applications. Most of the predictions of three-phase equilibria with interaction parameters obtained from binary systems do not adequately represent all the regions of the phase diagrams.

More evidence of the difficulty in simultaneously correlating LLE and LLLE data is that DECHEMA Chemistry Data Series, Liquid–Liquid Equilibrium Data Collection [27], does not report any result for the correlation of Type III ternary systems. Additionally, as far as we know, packages for regression of thermophysical properties included in the most popular chemical process simulation software, such as Aspen Plus® and ChemCAD®, do not allow this kind of regression. The reasons for this could be the limitations of the models (i.e. classical equations for the activity coefficient) to simultaneously reproduce the different equilibrium regions, and the necessity to implement a specific and robust algorithm for the correlation of these types of systems. The model must be able to give a Gibbs energy of mixing surface (G^M/RT) consistent with the topology required to satisfy the necessary and sufficient Gibbs tangent plane criteria. Therefore, the G^M/RT surface must have pairs of conjugated points with common tangent planes for all the experimental LLE data in all the regions and, at the same time, there must be one common tangent plane to the three liquid compositions corresponding to the LLLE experimental data. Obviously, these requirements are quite demanding for the model to provide acceptable results in many cases. The development of specific algorithms has allowed these correlations to be carried out in a very limited number of cases [15,16,28–32]. Some outstanding works in this area are those of de Loos *et al.* [29] simultaneously correlating LLE and LLLE for water-ethanol-benzene-ammonium sulfate and water-heptanone-caprolactam-ammonium sulfate using the e-NRTL model; and Negahban *et al.* [31] who correlated the equilibrium data of ternary systems water-alcohol-nitromethane with the UNIQUAC model. These same systems were also correlated by Marcilla *et al.* [32] who developed a robust algorithm based on the topology of the Gibbs energy of mixing required by the minor common tangent plane equilibrium condition. The development of that algorithm was motivated by the impossibility of achieving acceptable results using the isoactivity condition along with classical algorithms for LLE data correlation due to convergence problems, regardless of the capacity of the model used for the G^M/RT function. The most important conclusion of that previous paper was the adequate behavior of the correlation algorithm, but the poor correlation results obtained with the NRTL equation for such systems. Later, Revellame *et al.* [28] used a similar procedure based on the topology of the G^M/RT function to correlate LLE and LLLE data simultaneously for the ternary system decane-water-triacetin achieving successful results with the NRTL

model. Focusing on the use of ionic liquids as possible surface active agents able to improve surfactant and microemulsion enhanced oil recovery methods, we have previously determined liquid-liquid-liquid phase equilibria for ternary systems water-ionic liquid-dodecane [33-38]. Due to the above mentioned difficulties, we were not able to correlate the data obtained. Only in the case of the water- $[\text{C}_n\text{mim}][\text{NTf}_2]$ -dodecane, was the PC-SAFT model used to successfully correlate and predict the phase diagrams. The physical background of NRTL and other energy models is poor, especially if they are being applied to systems with ionic liquids. However, their great acceptance in design and optimization processes indicates that they can be a powerful engineering tool to facilitate process design. As NRTL has been widely accepted in the correlation of LLE of biphasic systems involving ionic liquids, the objective of this work is to analyze the possibility of simultaneously correlating LLE and LLLE ternary data for systems with ionic liquids. To that end, the phase diagram for water + trihexyltetradecylphosphoniumdicyanamide, $[\text{P}_{66614}][\text{DCA}]$, + hexane is determined at 298.15 K and 323.15 K. These data and those previously determined for multiphasic systems with ionic liquids [33-38] are correlated using the NRTL model. The correlations are carried out by simultaneously fitting the binary and ternary LLE data together with the LLLE tie-triangle of the systems. This requires the use of the isoactivity equilibrium condition, implemented in a fairly simple algorithm, together with some pivotal strategies that are briefly described below.

2. Materials and methods

Materials

n-Hexane (99 wt%) was purchased from Sigma-Aldrich. The ionic liquid trihexyltetradecylphosphoniumdicyanamide, $[\text{P}_{66614}][\text{DCA}]$, (CAS no. 701921-71-3), was supplied by IOLITEC with a nominal purity >95 wt%. It was washed with double-distilled water (4 times), passed through a column filled with alumina and active carbon, and finally dried under vacuum (0.5 Pa) and moderate temperature (~343 K) for at least 48 h. Final purity (98%) was confirmed by ^1H NMR and ^{13}C NMR spectroscopy. Water content was measured by Karl-Fischer titration in a Metrohm 737 KF coulometer obtaining values below 500 ppm.

Methods

In order to determine phase diagrams for the ternary system water + [P₆₆₆₁₄][DCA]+ hexane at 298.15 K and 323.15 K and atmospheric pressure, a known composition of the components within the biphasic or triphasic regions was introduced in a jacketed equilibrium cell. The content of the cell was vigorously mixed for two hours by using a magnetic stirrer for systems with two liquid phases, and mechanical stirring for systems with three liquid phases. The temperature was kept constant, with an uncertainty of 0.05 K, by using a Selecta Ultraterm 6000383 thermostatic bath. The cells were then left to settle down between 24 h and 72 h, ensuring that a complete separation of the phases was achieved. Previous tests were carried out applying different stirring rates and settling-down times to ensure the suitability of selected times.

The concentrations of water and n-hexane in the equilibrium phases were analyzed using a Hewlett-Packard HP 6890 Series gas chromatograph, equipped with a thermal conductivity detector and a HP-FFAP capillary column (25 m x 0.2 mm x 0.33 mm). Helium was used as the mobile phase and the injection volume was 1 mL with a split ratio of 50: 1. Temperatures of the detector and injector were set to 503.15 K. The oven temperature program was started at 323.15 K (1.9 minutes), followed by a temperature ramp at 12 K·min⁻¹ up to 373.15 K, a temperature that was kept constant for 0.5 min. An empty column was placed between the injector and the column to protect the analytical column and collect the amount of IL that could not be retained by the liner. Methyl acetate was used as the standard and isopropanol was used as the solvent for sample preparation. For chromatograph calibration, all the weighing was carried out on a Mettler Toledo AE 240 analytic balance with a precision of 10⁻⁴ g. The analysis was carried out for each sample at least four times. If a significant difference (bigger than the corresponding uncertainty) was found, the analysis was repeated. Once water and n-hexane mass fractions were known, the IL composition was obtained by summation to unity.

3. Correlation

The correlation of the systems was carried out using the NRTL model. The optimization of the model parameters was carried out using the GRG (Generalized Reduced Gradient) Nonlinear method with the objective function defined as:

$$O.F._{x,total} = O.F._{x,LL} + O.F._{x,LLL} \quad (1)$$

$$O.F._{x,L_1L_2} = \sum_{j=1}^{NTL} \sum_{i=1}^3 \left(x_{i,j}^{L_1,exp} - x_{i,j}^{L_2,cal} \right)^2 \quad \text{subject to:} \quad \left\{ \sum_{j=1}^{NTL} \sum_{i=1}^3 \left(a_{i,j}^{L_1,cal} - a_{i,j}^{L_2,cal} \right)^2 < \varepsilon \right. \quad (2)$$

$$O.F._{x,L_1L_2L_3} = \sum_{p=1}^2 \sum_{k>j}^3 \sum_{i=1}^3 \left(x_i^{L_p,exp} - x_i^{L_k,cal} \right)^2 \quad \text{subject to:} \quad \left\{ \sum_{p=1}^2 \sum_{k=1}^3 \sum_{i=1}^3 \left(a_i^{L_p,exp} - a_i^{L_k,cal} \right)^2 < \varepsilon \right. \quad (3)$$

where $x_{i,j}$ is the mole fraction of component i in the tie-line j ; $a_{i,j}$ is the activity of component i in the tie-line j ; p, k are indices to define the tie-triangle; L is a liquid phase; NTL is the number of experimental tie-lines; exp and cal are the experimental and calculated equilibrium data; ε is an extremely low tolerance value guaranteeing the fulfilment of the isoactivity in the phases in equilibrium.

Some additional useful strategies were applied to extend the application of the typical isoactivity algorithm for LLE correlation data from the simplest Type I and II to the complex Type III ternary systems that include one tie-triangle.

1. In the first step the correlation of the three binary subsystems was carried out independently to obtain a set of the binary parameters of the model. At this point the parameter α_{ij} was assigned the default value of 0.2. Subsequently, the parameters were allowed to change in a specific interval to simultaneously correlate the previous binary LLE data along with the LLLE tie-triangle. When for the best correlation solution found at this point any of the parameter values reached one of the established limits, this limit was extended and the correlation continued until another minimum of the objective function was reached. Finally, the equilibrium data for all the ternary LLE regions were included in the correlation and a similar procedure to limit the changes in the parameters “step by step” was used. In this last step, α_{ij} was considered as an additional correlation parameter to give flexibility to the model. This guided procedure improves the convergence of the correlation algorithm and ensures that the best solution for the model is found. It must be taken into account that the NRTL model has six binary parameters for a ternary system. Consequently, when the three LLE binary subsystems are fitted, the values of all these parameters are already set. Only minimal changes in these interactions parameters, in addition to the variation in the non-randomness parameter, can be admitted to achieve a good representation of the ternary regions without disarranging the binary data.

2. The convergence and robustness of the algorithm was improved not by directly using the mole fractions, but by using additional parameters (which can take any positive or negative value) to optimize the correlation. The relation between the optimization parameters used and the mole fractions are:

$$x_1 = \frac{|P1|}{1 + |P1| + |P2|} \quad (4)$$

$$x_2 = \frac{|P2|}{1 + |P1| + |P2|} \quad (5)$$

$$x_3 = 1 - x_1 - x_2 \quad (6)$$

This procedure guarantees that x_1 , x_2 and x_3 are always positive, lower than 1 and their sum is 1.

3. It is quite common as a correlation method to set the composition of one component in one of the equilibrium phases to its experimental value, with the aim of obtaining the calculated tie-lines or tie-triangle. Compositions calculated in this way are compared with the experimental data. Unlike this usual procedure, our calculations look for the minimization of the deviations between experimental and correlated compositions of the tie-lines and tie-triangle without fixing any calculated equilibrium composition (neither x_1 , x_2 nor x_3) to the corresponding experimental value. This simple strategy avoids some problems of convergence that arise when the values for the model parameters (in some step of the optimization) take values for which no splitting is produced when the composition was fixed to the experimental value.

The solutions obtained using this procedure were checked to guarantee the fulfillment of the Gibbs minor common tangent plane equilibrium condition for ternary systems. Consequently, these results could be considered equivalent to the ones obtained using the previous algorithm [32] based on topological aspects.

4. Results and discussion

Phase diagrams

The phase diagrams for ternary systems water + [P_{6,6,14}][DCA] + hexane at 298.15 K and 323.15 K and atmospheric pressure are shown in Figure 1. Experimental LLE and

LLLE data are presented in Tables S1 and S2 in the Supplementary Material. The objective in carrying out these determinations was to compare the influence of the alkyl chain length of the hydrocarbon on the phase behavior, because we had previously published these phase diagrams with dodecane at 298.15 K and 348.15 K [37]. However, the low boiling point of the hexane limited the maximum experimental temperature of the work to 323.15 K. All these systems are, according to Treybal classification, type III systems because the three binary subsystems are partially miscible. Due to the surface active character of the ionic liquid, the systems could also be classified as Winsor type III with a triphasic region and two biphasic regions around it (the biphasic region at the bottom of the diagram is negligible), as well as a monophasic domain. As in the case of dodecane [37], the three-phase system is composed of two phases that are practically water and hydrocarbon, and a middle phase with a high content of ionic liquid that preferentially solubilizes hydrocarbon. Figure 1 is very similar to diagrams obtained for classical surfactants. However, the three phases appear as a consequence of the immiscibility of the three binaries and the high molecular weight of the ionic liquid implies that, in terms of mass fraction (see Tables S1 and S2), the proportion of the ionic liquid in the middle phase of the triphasic system is very high. This characteristic would disfavor the use of this surfactant in oil recovery. More favorable SAILs are those miscible with water that lead to a Winsor type III system, as is the case of $[P_{4.4.4}][DS]$ [39].

With the temperature, the miscibility of the binary pairs slightly increases, consequently the immiscible region slightly decreases and the apex of the tie-triangle reduces its content of ionic liquid. Water + $[P_{6.6.14}][DCA]$ + hydrocarbon phase diagrams at 298.15 K can be compared for hexane (this work) and dodecane [37]. Solubility of the ionic liquid in both hydrocarbons is negligible. However, there is a bigger solubility of hexane than dodecane in $[P_{6.6.14}][DCA]$. Analyzing the three-phase region formed, both aqueous and organic phases are practically water and hydrocarbon, respectively. The apex of the tie-triangle has a higher content of the ionic liquid and minor content of the hydrocarbon in the case of dodecane.

In any case, systems with water, hydrocarbon (hexane or dodecane) and $[P_{6.6.14}][DCA]$ form a triphasic region stable with temperature, a feature that makes these systems of great interest from the point of view of multiphasic systems applications.

Correlation

The NRTL interaction parameters obtained for the correlation of the system water + [P_{6 6 14}][DCA] + *n*-hexane at 298.15 K and 323.15 K are presented in Table 1. This table also includes the objective function values (Eq. 1-3) and the mean deviation between calculated and experimental concentrations in mole percentage. Figure 1 shows, in triangular diagrams, a comparison between experimental and correlated equilibrium data. A visual inspection of this figure confirms what deviations presented in Table 1 indicate, the NRTL model can be successfully used to perform a simultaneous correlation of experimental LLE and LLLE data for this ternary system.

To check the consistency of the interaction parameters obtained it is very important to avoid possible metastable solutions to the equilibrium condition. We consider that the analysis of the topology of the G^M/RT function is a very valuable tool for that purpose. Consequently, the validation of the parameters presented in Table 1 was performed by combining the use of the G^M/RT surface by means of 3D-representations (which have been rotated and visualized in the entire composition space) and the representation of intersection planes in the directions of all the conjugated compositions calculated by the model. This is required to ensure the fulfilment of the Gibbs minor common tangent equilibrium criterion, which is the unique necessary and sufficient phase equilibrium condition. Figure 2 shows a specific view of the G^M/RT surface versus the composition (mole fraction) obtained as a result of the NRTL correlation for the ternary system water + [P_{6 6 14}][DCA] + *n*-hexane at 298.15K. In this figure, the experimental and calculated tie-lines and tie-triangle are also drawn on the surface, to show its consistency with the behavior of the system according to the Gibbs minor common tangent criteria. Figure 3 shows the G^M/RT curves for the three binary subsystems, and also some curves of intersection of several planes with the G^M/RT surface, those corresponding to the calculated LLLE tie-triangle and two calculated LLE tie-lines chosen as examples. All the calculated tie-lines have been validated using a similar procedure. The minor common tangent equilibrium condition is satisfied in all of the cases, with no presence of metastable solutions which could satisfy the necessary but not sufficient isoactivity equilibrium condition. A similar procedure was carried out to validate the model parameters obtained for this ternary system at 323.15K.

With the aim of confirming the quality of the NRTL model to simultaneously correlate LLE and LLLE data for systems with ionic liquids, we have extended the correlation to other previously determined three-liquid-phase systems involving ionic liquids [33-38]. The selected systems are water + ionic liquid + *n*-dodecane, and measurements were carried out at 298.15K and 348.15K. All of them are Type III ternary systems, including one LLLE tie-triangle, but there are important differences among them. The names of the systems and the corresponding references are presented in Table 2. Table 3 presents interaction parameters obtained with the NRTL model along with the objective function values (Eq. 1-3) and the mean deviation between calculated and experimental concentrations in mol percentage. In Figure S1 (Supplementary Material) two types of figures are presented to show the quality of the results of the correlation for all the ternary systems. These figures show the comparison between the experimental and calculated equilibrium data in triangular diagrams, and the G^M/RT surface calculated with the correlation parameters in triangular prisms. The results of the correlation obtained using the NRTL model are quite good in almost all cases, with the exception of systems with references 4b and 6b. In the 4b system there is a certain deviation between the experimental and calculated tie-lines in the splitting region rich in component 1 as well as in the LLLE tie-triangle. For the 6b system, the correlation parameters obtained provide a very good fitting of the experimental tie-triangle but a poor correlation of the rich-1 component splitting region. The reason is that the experimental data presents an “S-shaped” binodal curve, supposedly very difficult to be fitted with almost any model. As expected, the model gives a good correlation for binary subsystem 1-2 but it extends smoothly to the tie-triangle. A more precise representation of these two systems, especially the 6b system, would require some modification of the classical activity coefficient models with the aim of increasing its flexibility, e.g adding some ternary terms.

Conclusions

The phase diagram for water, hexane and $[P_{6,6,14}][DCA]$ ionic liquid shows a liquid-liquid-liquid region consisting of an upper phase that is practically hexane, a lower phase that is practically water and a middle phase where the ionic liquid solubilizes water and hexane. This triphasic system remains stable with temperature. Therefore, this ionic liquid can be used in applications that require a three-phase system with a structured middle phase. Moreover, the same behavior is obtained by increasing the

alkyl chain length of the hydrocarbon (dodecane) which enlarges the range of possible applications. However, it has to be indicated that the content of the ionic liquid in this middle phase is high, which limits some specific applications such as its use in enhanced oil recovery.

The simultaneous correlation of liquid-liquid and liquid-liquid-liquid equilibrium data for three-phase systems containing ionic liquids is possible using the NRTL model. Thirteen sets of data were successfully correlated using the isoactivity equilibrium condition with some strategies used to improve the convergence of the optimization algorithm to the solution. Besides, the correlation results obtained have been checked for consistency to avoid false or metastable solutions to the isoactivity criterion. The geometric aspects related to the Gibbs energy of mixing function obtained, along with the minor common tangent plane equilibrium condition, have proved to be very valuable tools for such validation. Deviations obtained between experimental and correlated data are low, except in the case of two data sets, one of them with an “S-shaped” binodal curve.

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References

- [1] J.J. Sheng. Modern chemical enhanced oil recovery. Theory and practice. Elsevier, Amsterdam, 2011.
- [2] J.L. Salager, A.M. Forgiarini, J. Bullón. *J. Surfact. Deterg.* 16 (2013) 449-472.
- [3] V. Nardello-Rataj, L. Caron, C. Borde, J.M. Aubry. *J. Am. Chem. Soc.* 130 (2008) 14914-14915.
- [4] M. Fressancourt-Collinet, B. Hong, L. Leclercq, P.L. Alsters, J.M. Aubry, V. Nardello-Rataj. *Adv. Synth. Catal.* 355 (2013) 409-420.

- [5] D. Chen, X. Yang, W. Cao, Y. Guo, Y. Sun, Z. Xiu. *Food Bioprod. Process.* 96 (2015) 99-105.
- [6] C. Zhang, K. Huang, P. Yu, H. Liu. *Sep. Purif. Technol.* 108 (2013) 166–173.
- [7] Z. Li, H. Chen, W. Wang, M. Qu, Q. Tang, B. Yang, Y. Wang. *Chem. Commun.* 51 (2015) 12943-12946.
- [8] G.D. Yadav, O.V. Badure. *Ind. Eng. Chem. Res.* 38 (1999) 2245-2253.
- [9] A.J. Carmichael, M.J. Earle, J.D. Holbrey, P.B. McCormac, K.R. Seddon. *Org. Lett.* 1 (1999) 997-1000.
- [10] S. Burauer, T. Sachert, T. Sottmann, R. Strey. *Phys. Chem. Chem. Phys.* 1 (1999) 4299-4306.
- [11] H. Hu, C.-D. Chiu, L.-J. Chen. *Fluid Phase Equilibr.* 164 (1999) 187–194.
- [12] H. Hu, L.-J. Chen. *J. Chem. Eng. Data* 45 (2000) 304-307.
- [13] B.-J. Lin, L.-J. Chen. *J. Chem. Eng. Data* 47 (2002) 992-996.
- [14] Bo-Jiun Lin, Li-Jen Chen. *Fluid Phase Equilibr.* 216 (2004) 13–20.
- [15] S. Negahban, G.P. Willhite, S.M. Walas, M.J. Michnick. *Fluid Phase Equilibr.* 32 (1986) 49-61.
- [16] S. Brandani, V. Brandani, G. Del Re, G. Di Giacomo. *Fluid Phase Equilibr.* 94 (1994) 313-320.
- [17] C.-H. Su, L.-J. Chen. *J. Chem. Eng. Data* 56 (2011) 589-594.
- [18] C.-H. Su, L.-J. Chen. *J. Chem. Eng. Data* 56 (2011) 2976–2979.
- [19] C.-H. Su, S.-Y. Lin, L.-J. Chen. *J. Chem. Thermodyn.* 47 (2012) 358-361.
- [20] R.P. Stateva, G.St. Cholakov, A.A. Galushko, W.A. Wakeham. *Chem. Eng. Sci.* 55 (2000) 2121-2129.
- [21] C.L. Sassen, A. Gonzalez Casielles, Th.W. de Loos, J. de Swaan Arons *Fluid Phase Equilibr.* 72 (1992) 173-187.
- [22] A. Martin, M. Klauck, K. Taubert, A. Precht, R. Meinhardt, J. Schmelzer. *J. Chem. Eng. Data* 56 (2011), 56, 733–740.
- [23] A. Martin, M. Klauck, A. Grenner, R. Meinhardt, D. Martin, J. Schmelzer. *J. Chem. Eng. Data* 56 (2011) 741–749.
- [24] M. Klauck, A. Grenner, J. Schmelzer. *J. Chem. Eng. Data* 51 (2006) 1043-1050.
- [25] A. Grenner, M. Klauck, R. Meinhardt, R. Schumann, J. Schmelzer. *J. Chem. Eng. Data* 51 (2006) 1009-1014.
- [26] E.D. Revellame, W.E. Holmes, R. Hernandez, W.T. French, A. Forks, T. Ashe, L.A. Estévez. *J. Chem. Thermodyn.* 95 (2016) 105–110.

- [27] W. Arlt, M.E.A. Macedo, P. Rasmussen, J.M. Sørensen. Liquid-Liquid Equilibrium Data Collection. Chemistry Data Series; Vol. V, DECHEMA: Frankfurt.
- [28] E.D. Revellame, W.E. Holmes, R. Hernandez, W.T. French, L. Lerma, A. Forks, T. Ashe, L.A. Estévez. *J. Chem. Thermodyn.* 67 (2013) 21–27.
- [29] G.H. van Bochove, G.J.P. Krooshof, T.W. de Loos. *Fluid Phase Equilibr.* 194-197 (2002) 1029–1044.
- [30] F. Denes, P. Lang, M. Lang-Lazi. *ICHEME Symp. Series* 152 (2006) 877-890.
- [31] S. Negahban, G.P. Willhite, S.M. Walas. *SPE Reservoir Eng.*, August (1988) 1017-1024.
- [32] A. Marcilla, M.M. Olaya, M.D. Serrano, R. Velasco, J.A. Reyes-Labarta. *Fluid Phase Equilibr.* 281 (2009) 87-95.
- [33] S. Lago, H. Rodríguez, M. Khoshkbarchi, A. Soto and A. Arce. *RSC Adv.* 2 (2012) 9392-9397.
- [34] S. Lago, M. Francisco, A. Arce, and A. Soto. *Energ. Fuel* 27 (2013) 5806-5810.
- [35] S. Lago, B. Rodríguez-Cabo, A. Arce, A. Soto. *J. Chem. Thermodyn.* 75 (2014) 63-68.
- [36] I. Rodríguez-Escontrela, I. Rodríguez-Palmeiro, O. Rodríguez, A. Arce and A. Soto. *Colloid Surface A* 480 (2015) 50-59.
- [37] I. Rodríguez-Escontrela, I. Rodríguez-Palmeiro, O. Rodríguez, A. Arce, A. Soto. *Fluid Phase Equilibr.* 405 (2015) 124-131.
- [38] I. Rodríguez-Palmeiro, O. Rodríguez, A. Soto and C. Held. *Phys. Chem. Chem. Phys.* 17 (2015) 1800-1810.
- [39] I. Rodríguez-Escontrela, I. Rodríguez-Palmeiro, O. Rodríguez, A. Arce and A. Soto. *Fluid Phase Equilibr.* 417 (2016) 87-95.

Table 1. NRTL parameters (J/mol) obtained for the simultaneous correlation of LLE and LLLE data of the ternary system water (1) + [P_{6 6 6 14}][DCA] (2) + hexane (3) at 298.15K and 323.15K. Objective function (O.F.) and mean deviation have also been included.

T (K)	Parameters	NRTL			O.F.*	Mean Dev. (%)**
		Pair 1-2	Pair 1-3	Pair 2-3		
298.15	A _{ij}	17226.8	15940.5	-16720.1	1.7·10 ⁻³	0.11
	A _{ji}	-2123.4	13813.4	38580.1		
	α _{ij} =α _{ji}	0.2289	0.2560	0.0865		
323.15	A _{ij}	11493.1	14847.0	-14313.7	1.3·10 ⁻³	0.27
	A _{ji}	-537.4	13805.9	46391.9		
	α _{ij} =α _{ji}	0.2916	0.2834	0.1205		

* O.F. calculated by Eq 1-3
** Mean dev. between cal. and exp. conc. in mol pct.

Table 2. Ternary systems, with a three-liquid phase region, that are considered in this study.

System	T (K)	Code	Literature ref.
Water + [P _{6 6 6 14}]Cl+ dodecane	298.15	1a	[33]
	348.15	1b	[34]
Water + [P _{6 6 6 14}][NTf ₂] + dodecane	298.15	2a	[35]
	348.15	2b	
Water + [P _{6 6 6 14}][(iOc) ₂ PO ₂]+ dodecane	298.15	3a	[36]
Water + [P _{6 6 6 14}][DCA]+ dodecane	298.15	4a	[37]
	348.15	4b	
Water + [C ₁₀ mim][NTf ₂] + dodecane	298.15	5a	[38]
	348.15	5b	
Water + [C ₁₂ mim][NTf ₂] + dodecane	298.15	6a	[38]
	348.15	6b	

Table 3. NRTL parameters (J/mol) obtained for the simultaneous correlation of LLE and LLLE data of the ternary systems water (1) + ionic liquid (2) + n-dodecane (3) listed in Table 2. Objective function (O.F.) and mean deviation have also been included.

System	Parameters	NRTL			O.F.*	Mean Dev. (%)**
		Pair 1-2	Pair 1-3	Pair 2-3		
1a	A_{ij}	38654.9	12478.6	-3301.6	$2.6 \cdot 10^{-3}$	0.37
	A_{ji}	-9406.3	12731.7	22860.5		
	$\alpha_{ij}=\alpha_{ji}$	0.1904	0.2952	0.2907		
1b	A_{ij}	59762.6	13953.9	-4225.3	$1.8 \cdot 10^{-3}$	0.37
	A_{ji}	-15943.3	13302.3	12385.7		
	$\alpha_{ij}=\alpha_{ji}$	0.1415	0.2446	0.6292		
2a	A_{ij}	27181.1	12589.2	-6398.7	$4.7 \cdot 10^{-4}$	0.14
	A_{ji}	-8483.3	13453.4	23329.1		
	$\alpha_{ij}=\alpha_{ji}$	0.0527	0.2327	0.1785		
2b	A_{ij}	31109.5	17022.3	-7419.0	$3.0 \cdot 10^{-3}$	0.36
	A_{ji}	-10977.6	16086.5	24576.1		
	$\alpha_{ij}=\alpha_{ji}$	0.0608	0.2350	0.2050		
3a	A_{ij}	67904.7	12202.3	-27790.1	$7.7 \cdot 10^{-4}$	0.27
	A_{ji}	-25998.7	2630.0	-8335.0		
	$\alpha_{ij}=\alpha_{ji}$	0.0938	0.1671	0.0181		
4a	A_{ij}	19101.4	35019.0	-3095.1	$3.3 \cdot 10^{-3}$	0.42
	A_{ji}	-3143.5	14949.5	19546.5		
	$\alpha_{ij}=\alpha_{ji}$	0,1970	0,2138	0,1929		
4b	A_{ij}	26023.7	33675.8	-1470.4	$2.1 \cdot 10^{-2}$	0.99
	A_{ji}	-5466.5	18253.8	18169.2		
	$\alpha_{ij}=\alpha_{ji}$	0,1796	0,2309	0,2769		
5a	A_{ij}	28972.7	12986.8	-5037.8	$1.0 \cdot 10^{-3}$	0.23
	A_{ji}	-9532.6	12208.6	22677.0		
	$\alpha_{ij}=\alpha_{ji}$	0.0671	0.1881	0.0805		
5b	A_{ij}	31558.0	15977.5	-4450.9	$1.5 \cdot 10^{-3}$	0.26
	A_{ji}	-9499.3	15546.4	26547.4		
	$\alpha_{ij}=\alpha_{ji}$	0.0980	0.1968	0.1037		
6a	A_{ij}	14343.3	15399.7	-26961.1	$3.9 \cdot 10^{-3}$	0.33
	A_{ji}	5911.8	15260.9	51628.2		
	$\alpha_{ij}=\alpha_{ji}$	0.3625	0.3092	0.0268		
6b	A_{ij}	17086.1	18184.6	-9015.1	$1.4 \cdot 10^{-2}$	0.59
	A_{ji}	5285.7	16382.9	34067.7		
	$\alpha_{ij}=\alpha_{ji}$	0.3574	0.3336	0.0832		

* O.F. calculated by Eq 1-3

** Mean dev. between cal. and exp. conc. in mol pct.

Figure 1. Experimental LLE and LLLE (tie-triangle) data, in mole fractions, and their corresponding correlated data obtained with the NRTL model for the ternary system water (1) + $[P_{66614}][DCA]$ (2) + hexane (3): a) $T=298.15K$ b) $T=323.15K$.

Figure 2. G^M/RT surface obtained from the correlation of the experimental LLE and LLLE (tie-triangle) data (mole fractions) of the ternary system water + [P_{6 6 6 14}][DCA] + hexane at 298.15K using the NRTL model. Tie-lines and tie-triangle are also drawn on the surface.

Figure 3. Curves of intersection of several planes with the G^M/RT surface obtained as result of the correlation with the NRTL model of the ternary system water (1) + [P₆₆₆][DCA] (2) + hexane (3) at 298.15K: a-c) the three binary subsystems, d) calculated LLE tie-triangle, e-f) two calculated LLE tie-lines.