



Experimental study and modeling of the salting-out effect of KCl on the liquid–liquid equilibria of the ternary system (water + propionic acid + dichloromethane) at 296.65 K

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ABSTRACT

The effect of potassium chloride on the liquid–liquid phase equilibria of the ternary system water–propionic acid–dichloromethane was considered experimentally at 296.65 K, at different salt mass fractions of 5%, 10% and 15%, in the quaternary mixture. The binodal and tie line data were determined by cloud point measurements method and the results showed that the addition of the salt has effectively affected LLE of water–propionic acid–dichloromethane, with a salting out of the propionic acid from the aqueous solution to the dichloromethane phase, particularly at high salt concentrations. The experimental data were correlated considering a modified version of the NRTL model and the deviations between experimental and calculated compositions in both phases for the ternary system using this model were less than 1%. The obtained results confirmed the ability of the NRTL model for the correlation of liquid–liquid equilibrium data for the considered quaternary system water (1)–propionic acid (2)–dichloromethane (3)–potassium chloride (4).

Keywords: Salt effect; Solubility; LLE; NRTL model; Potassium chloride; Propionic acid

1. Introduction

Generally the addition of a salt does influence the solubility of the solute and its distribution between two partially miscible or totally immiscible liquid phases in equilibrium, either increasing or decreasing the solute distribution coefficient which is defined as the ratio of the composition of the solute in the solvent-rich phase to that in the diluent (water) rich phase. These phenomena are known as salting out or salting in, respectively and can be exploited to improve the extraction of the considered solutes.

Propionic acid is one of the most widely used carboxylic acids, which has many applications in chemical and bio-chemical industries [1,2]. The distillation processes are

usually adopted in a great number of separation applications but from technical and economical aspects point of view, a good separation of propionic acid from aqueous solutions can rather be achieved by means of liquid–liquid extraction which can be regarded as one of the most important operation unit used in chemical engineering. In fact many research works [3,4] have considered many organic solvents in order to extract the propionic acid from aqueous solution. However the binodal or equilibrium curve and the tie line data of ternary systems containing (water–propionic acid–organic solvents) [5,6] are needed to design the liquid–liquid contactor and find the optimized operating conditions [7,8].

The effect of lithium chloride, sodium chloride and potassium chloride on the distribution of propionic acid

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between benzene and water at 298.15 K has been investigated by Edwin and Joffe [4]. The method of Hand [9], originally developed for ternary systems, was used to correlate the distribution data for quaternary systems containing salt. The order of decreasing salting-out, on a weight basis was $\text{LiCl} > \text{NaCl} > \text{KCl}$ for the system studied.

Vakili-Nezhaad et al. [10] determined experimental data for the salting-out effect of NaCl and KCl on the ternary LLE data for the two quaternary systems (water + propionic acid + isopropyl methyl ketone and water + propionic acid + isobutyl methyl ketone).

The present paper is part of a research project concerning the study of quaternary systems such as water–propionic acid–dichloromethane–inorganic salt at 296.65 K under atmospheric pressure. In all these systems, the solute was propionic acid and it has a great affinity for water. Therefore in the present study the effect of KCl (the salt), on its distribution between the organic and the aqueous phases was considered, at three different mass percentages of 5%, 10% and 15%.

Generally LLE experimental data are not available or difficult to measure, hence the need for their modeling and prediction, particularly with presence of electrolyte species such as salts. In the literature, various electrolyte theories used for the modeling and the prediction of the salt influence on liquid–liquid equilibria are reported for systems involving water, organic solvents, salts, amino acids, etc. As recent examples one can cite a modeling approach based on the interactions between anions and cations that showed to be more precise at higher concentrations than the original one based on the electrolyte perturbed chain (ePC)-statistical associating fluid theory (SAFT), and also more adequate for the direct modeling of weak electrolyte solutions excluding the need to account for ion-pair formation [11].

In further studies, two ion-specific models, ePC-SAFT and an extended version of COSMO-RS for electrolytes have been used for binary and ternary systems such as MIBK/water and salt/MIBK/water, respectively. The COSMO-RS based approach led to reasonable predictions of the salt influence on LLE whereas ePC-SAFT correlated experimental data quantitatively [12].

Also the influence of salts on the LLE for a binary system such as water/1-butanol was successfully modeled using the ePC-SAFT where with no fitting parameters to LLE data, the salt influence on the 5-hydroxymethylfurfural (HMF) partition was predicted with a good agreement in comparison with experimental data [13].

However in the present study, a data correlation was performed using Tan's modified NRTL activity coefficient model [14], which was selected for its simplicity and its ability to predict reasonably well phase equilibria data involving solvents–salt systems. The determined model interaction parameters and the deviations between the calculated LLE results and the corresponding experimental values are reported.

However in the present work, the activity coefficient model used was proposed in [14] and consisted of splitting the activity coefficient in two parts: the first one γ_{i0} is the activity coefficient in the absence of salt and the second one is τ_{is} the salt–solvent interaction parameter. Therefore the charge interactions are taken into account implicitly by

τ_{is} . The advantage of this model is mainly its mathematical simplicity compared with other complex models dealing with electrolytes, and it does involve the presence and the absence of the salt.

2. Experimental

2.1. Chemicals

Propionic acid and dichloromethane with stated purities of 99% and 98%, respectively, were supplied by Biochim, Algeria. They were used without any further purification. Distilled water was prepared locally using a GFL 2001/4 distillation unit. Potassium chloride was supplied by Prolabo (MERCK Eurolab, France) and was dried at 200°C in a Heraeus oven. The refractive indices of pure components were measured at 293.15 K and atmospheric pressure, using a digital refractometer Euromex RD 645 with an accuracy of ($\pm 10^{-4}$) which can be considered as very reliable. This was confirmed by the comparison shown in Table 1 and concerning the refractive indices obtained from measurements at 293.15 K with values reported in the literature [15] at the same temperature which was controlled to within 0.01 K using a thermostatic bath.

2.2. Experimental procedure

The binodal curves were determined at 296.65 K using the cloud point method described in detail by Letcher and Siswana [16]. Binary aqueous solvent mixtures of propionic acid and water with different concentrations were prepared in absence and in presence of the salt. Then the solvent (dichloromethane) was progressively added to the binary mixture using a micro-burette. All the weightings were made using an analytical balance Precisa 180 A (UK) accurate to 10^{-4} g. Every mixture was placed inside an equilibrium cell, where it was agitated in order to allow an intimate contact between the components. The cloud point was determined by observing the transition from an homogeneous to an heterogeneous mixture as indicated by the mixture turbidity.

The experimental results of the tie line were determined by preparing ternary and quaternary aqueous solvent mixtures of water–propionic acid–dichloromethane and water–propionic acid–dichloromethane–salt, respectively. Every mixture was placed inside an equilibrium cell, where it was vigorously agitated with a mechanic stirrer (J.P. SELECTA, SA, Spain) for 120 min, and the thermodynamic equilibrium was finally reached, letting the mixture rest for 24 h. The complete process was carried out at constant temperature, by means of a thermostatic bath. The mixture was split into two clear and transparent liquid phases with a well-defined

Table 1
Refractive index at $T = 293.15$ K and $P = 1$ atm of pure component

Component	$n_{\text{Dexp}} (\pm 10^{-4})$	$n_{\text{D}} [11]$	CAS N°
Water	1.3330	1.3329	7732-18-5
Propionic acid	1.3871	1.3874	79-09-4
Dichloromethane	1.4240	1.4242	75-09-2

interface. A sample from each phase was collected and the tie line values were obtained by its titration with a known concentration of sodium hydroxide solution (NaOH) to the phenolphthalein end point. As the acid content of the two phases was analytically determined, the water, salt and dichloromethane contents were found from a material balance.

In fact after the measuring of the concentration of the acid in a phase enables the location of the point which represents it on the binodal curve, hence the concentrations of the other two components in that phase can just be read off. Knowing the weight of the phase enables the calculation of the contents of all other components. The composition of the initial feed mixture enables the calculations of the weight of each component present in the second phase from a material balance.

3. Results and discussion

3.1. Effect of potassium chloride (KCl) on LLE of water–propionic acid–dichloromethane systems

The measured composition of mixtures lying on the binodal curve for the ternary system of (water (1)–propionic acid (2)–dichloromethane (3)) in the absence and in the presence of potassium chloride at different mass percentages and at $T = 296.65$ K are reported in Table 2, with w_i denoting the mass fraction of the component i . The compositions of phases at equilibrium, that is, the tie lines data are given in Table 3, with w_i^I and w_i^II denoting the mass fractions of component I in the aqueous water rich and organic dichloromethane rich phases, respectively.

Fig. 1 shows tie lines of the ternary system water–propionic acid–dichloromethane in the absence of salt. It can be seen that the slopes of these tie lines change. This can be explained by the fact that different feed compositions were considered in a way that the corresponding representing points were inside the two phase's region, ensuring phase splitting. The two equilibrium phases are characterized thermodynamically by the isofugacity criteria and clearly the resulting solute compositions in each phase change depending upon the global composition of the considered ternary mixture; hence the change of the tie lines slopes.

The tie lines slope change may also be explained by possible induced uncertainties of the experimental data or also by a possible three-phase behavior. However in the present study, the experiment runs were repeated to ensure data reproducibility and the three-phase behavior was not encountered.

The effect of addition of potassium chloride on the binodal curves at the different considered salt percentages is clearly seen in Figs. 2–4.

The results show how the salt slightly enlarged the area of the two-phase region, hence slightly increasing the heterogeneity of the system; which is an important consideration in designing a solvent extraction process. Also the figures show how the increase in salt percentage, decreased the mutual solubilities of water and dichloromethane.

Generally two important parameters, namely the distribution (K_i) and the selectivity (β_{ij}) coefficients are always calculated in any extraction process and are defined as:

Table 2

Binodal curve data for quaternary system water (1)–propionic acid (2)–dichloromethane (3)–salt free basis at $T = 296.65$ K and $P = 1$ atm ($\Delta w_i = \pm 10^{-4}$)

w_1	w_2	w_3
	0% KCl	
0.0245	0	0.9755
0.0379	0.1578	0.8043
0.0692	0.3196	0.6112
0.0921	0.3991	0.5088
0.1063	0.4424	0.4513
0.1639	0.4737	0.3624
0.2923	0.4558	0.2519
0.3788	0.4202	0.2010
0.5223	0.3622	0.1155
0.5442	0.3456	0.1102
0.6260	0.2790	0.0950
0.7918	0.0915	0.1167
0.8497	0	0.1503
	5% KCl	
0.0245	0	0.9755
0.0451	0.1565	0.7984
0.0704	0.1829	0.7467
0.0981	0.4078	0.4941
0.1324	0.4915	0.3761
0.3535	0.4902	0.1563
0.5105	0.3541	0.1354
0.5446	0.3398	0.1156
0.5636	0.3257	0.1107
0.7610	0.1583	0.0807
0.7747	0.1492	0.0761
0.9295	0	0.0705
	10% KCl	
0.0478	0	0.9522
0.0471	0.3272	0.6257
0.0634	0.4117	0.5249
0.1156	0.5011	0.3833
0.3236	0.5048	0.1716
0.4769	0.3967	0.1264
0.4943	0.3855	0.1202
0.5347	0.3707	0.0946
0.8034	0.1567	0.0399
0.9577	0	0.0423
	15% KCl	
0.0245	0	0.9755
0.0593	0.1542	0.7865
0.0619	0.3222	0.6159
0.0779	0.4053	0.5168
0.0957	0.4979	0.4064
0.2414	0.5023	0.2563
0.4768	0.3967	0.1265
0.4997	0.3898	0.1105
0.5347	0.3707	0.0946
0.7733	0.2010	0.0257
0.8142	0.1587	0.0261
0.9577	0	0.0423

$$K_i = \frac{w_i^{\text{II}}}{w_i^{\text{I}}} \tag{1}$$

$$\beta_{ij} = \frac{\left(\frac{w_i^{\text{II}}}{w_i^{\text{I}}}\right)}{\left(\frac{w_j^{\text{II}}}{w_j^{\text{I}}}\right)} = \frac{K_i}{K_j} \tag{2}$$

Applying these equations for the considered system (water (1)–propionic acid (2)–dichloromethane (3)), the distribution coefficients of water and propionic acid are:

$$K_1 = \frac{w_1^{\text{II}}}{w_1^{\text{I}}} \tag{3}$$

$$K_2 = \frac{w_2^{\text{II}}}{w_2^{\text{I}}} \tag{4}$$

And the selectivity of dichloromethane (3) to extract propionic acid (2) from water (1) is:

$$\beta_{21} = \frac{\left(\frac{w_2^{\text{II}}}{w_2^{\text{I}}}\right)}{\left(\frac{w_1^{\text{II}}}{w_1^{\text{I}}}\right)} = \frac{K_2}{K_1} \tag{5}$$

The distribution curves of propionic acid between water and dichloromethane in absence and in presence of salt are shown in Fig. 5.

The corresponding K_1 and K_2 values are also shown in Figs. 1–4 and their variations are more or less regular for the different considered salt percentages, depending on the tie lines slopes. This confirms the salting out effect.

Clearly before the addition of the salt, the distribution curve intersects with the first bisector, indicating a case of solutropy. The distribution curves corresponding to the three considered KCl mass percentages of 5%, 10% and 15% are also shown in the same Fig. 5 where it can be seen that they are all above the first bisector, indicating that the propionic acid mass percentage in the organic phases was

Table 3

Composition of the conjugate phases for the quaternary system water (1)–propionic acid (2)–dichloromethane (3)–salt free basis at $T = 296.65 \text{ K}$ and $P = 1 \text{ atm}$ ($\Delta w_i = \pm 10^{-4}$)

Aqueous phase I			Organic phase II		
w_1^{I}	w_2^{I}	w_3^{I}	w_1^{II}	w_2^{II}	w_3^{II}
0% KCl					
0.8075	0.0666	0.1259	0.0264	0.0104	0.9632
0.7411	0.1501	0.1088	0.0523	0.2377	0.7100
0.6934	0.2045	0.1021	0.0707	0.3165	0.6128
0.5991	0.3020	0.0989	0.1090	0.4366	0.4544
5% KCl					
0.8846	0.0434	0.0720	0.0392	0.0833	0.8775
0.8036	0.1210	0.0754	0.0682	0.2182	0.7136
0.7602	0.1665	0.0733	0.1020	0.3670	0.5310
0.6127	0.2826	0.1047	0.0956	0.3738	0.5306
10% KCl					
0.8824	0.0503	0.0673	0.0537	0.1258	0.8205
0.8684	0.0897	0.0419	0.0536	0.2962	0.6502
0.8116	0.1429	0.0455	0.0626	0.3868	0.5506
0.7642	0.1822	0.0536	0.0876	0.4456	0.4668
15% KCl					
0.9169	0.0451	0.0380	0.0566	0.1867	0.7567
0.8999	0.0751	0.0250	0.0645	0.2953	0.6402
0.8181	0.1532	0.0287	0.0971	0.4659	0.4370

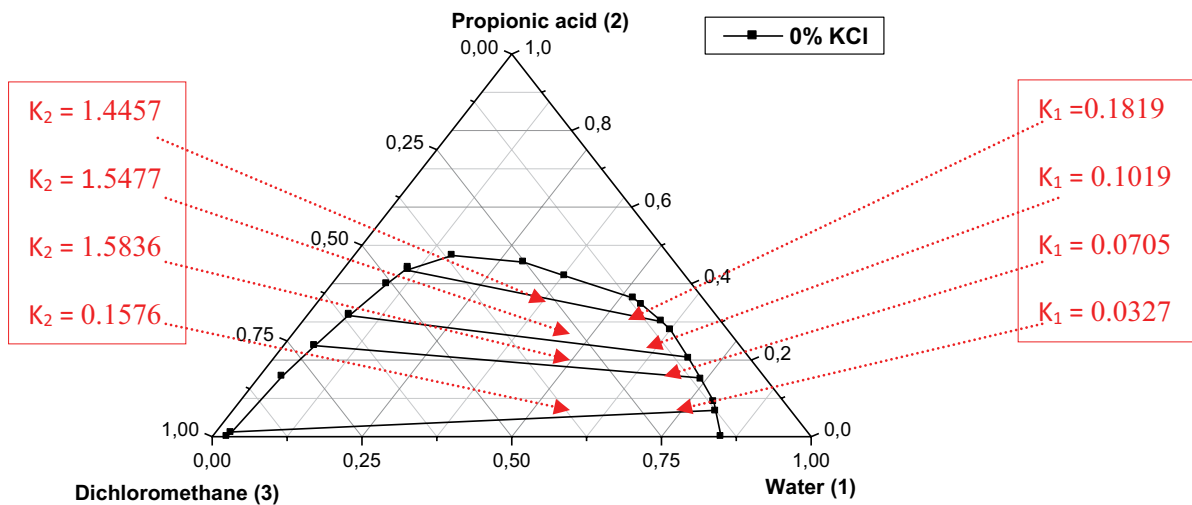


Fig. 1. Binodal curve of ternary system water (1)–propionic acid (2)–dichloromethane (3) in absence of potassium chloride (0% KCl) $T = 296.65 \text{ K}$ and $P = 1 \text{ atm}$.

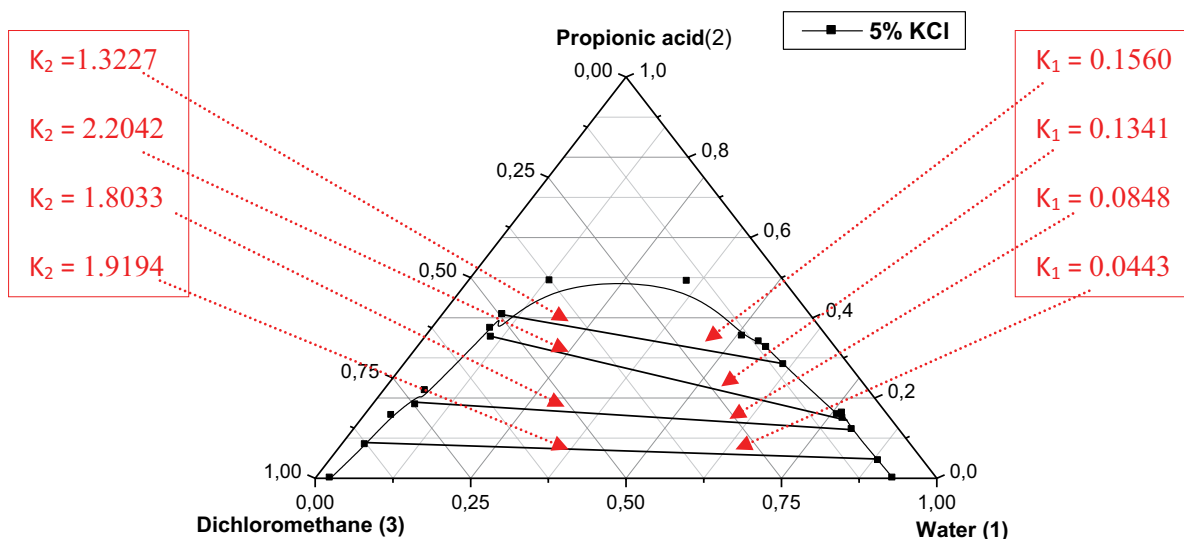


Fig. 2. Binodal curve of quaternary system water (1)–propionic acid (2)–dichloromethane (3)–potassium chloride (4) (5% KCl) at $T = 296.65$ K and $P = 1$ atm.

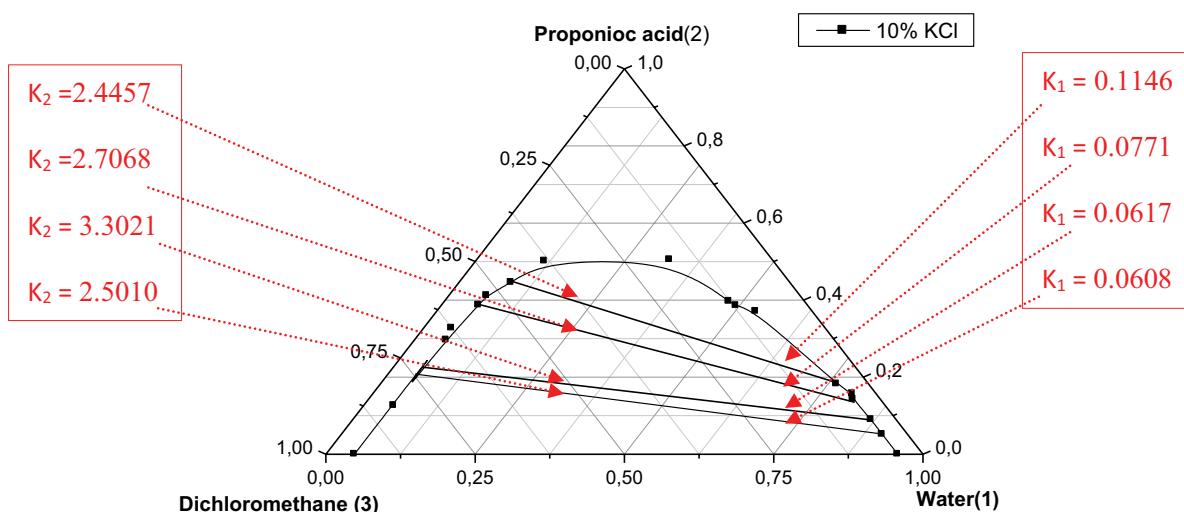


Fig. 3. Binodal curve of quaternary system water (1)–propionic acid (2)–dichloromethane (3)–potassium chloride (4) (10% KCl) at $T = 296.65$ K and $P = 1$ atm.

greater than that in the aqueous phases and confirming that a salting out of propionic acid did occur and increased with the increase of the salt mass percentage, in favor of its extraction. For instance in the absence of the salt and at 296.65 K, an organic phase containing 1% propionic acid is in equilibrium with an aqueous phase containing 7% propionic acid, whereas the addition of 15% potassium chloride reduced the equilibrium aqueous phase propionic acid mass percentage to 4% and increased that in the organic phase to 18%. This effect can be quantitatively verified through the mean distribution coefficient of the propionic acid shown in Table 4.

The results show that the addition of potassium chloride increased significantly the capacity to extract the propionic acid from the aqueous phase, with distribution coefficients all greater than unity. Also the three curves corresponding

to the three different salt mass percentages do not intersect with the first bisector, showing how the addition of the salt had removed the solutropy exhibited for the case of no salt, hence the importance of the salting effect. In fact this, solutropy phenomenon is exhibited by many liquid–liquid systems and as a consequence the solute has a greater affinity for one phase at low concentrations and for the other at higher concentrations. Geometrically this can be seen by the change of the tie lines slope from one direction to another passing through an intermediate horizontal tie line, corresponding to the case where the distribution curve intersects with the first bisector. The addition of the salt is one way to remove this solutropy.

Also as the salt mass percentage increased, K_1 decreased and K_2 increased. This can be explained by the fact that the more salt is present, the more water is retained in the

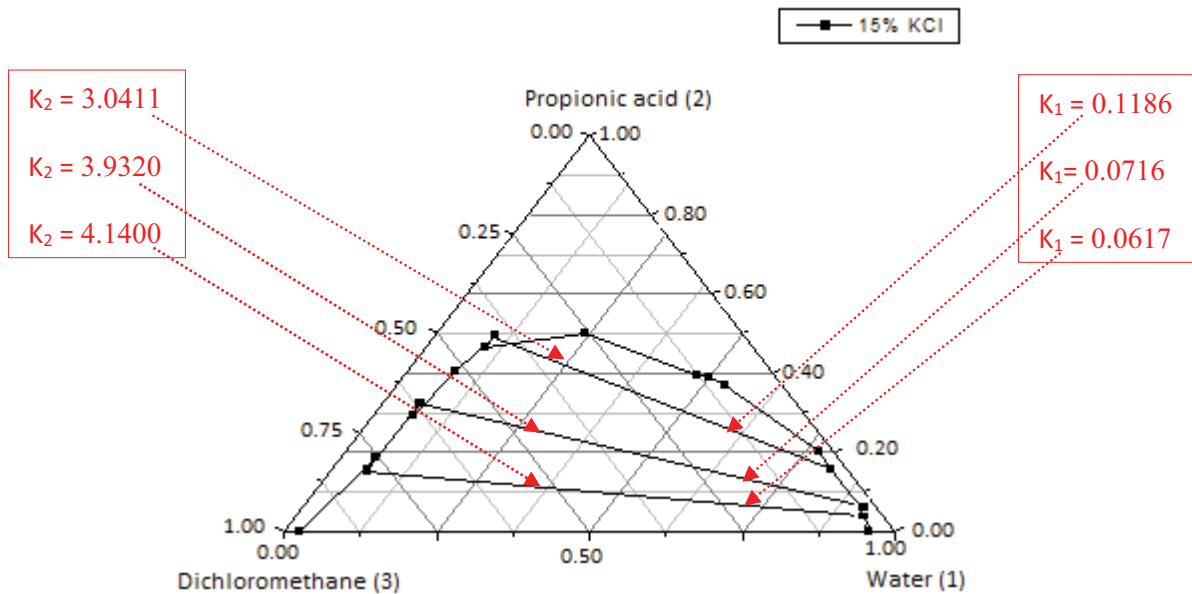


Fig. 4. Binodal curve of quaternary system water (1)–propionic acid (2)–dichloromethane (3)–potassium chloride (4) (15% KCl) at $T = 296.65$ K and $P = 1$ atm.

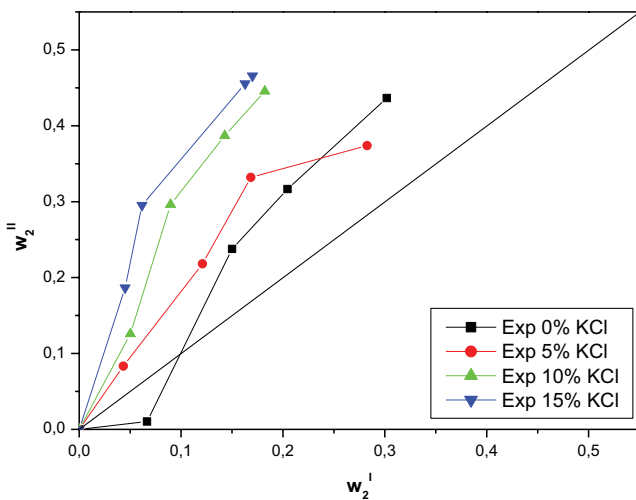


Fig. 5. Comparison of the distribution curve of propionic acid at different concentration of salt for water (1)–propionic acid (2)–dichloromethane–KCl system at $T = 296.65$ K and $P = 1$ atm.

aqueous phase and the more propionic acid is salted out towards the organic phase, hence decreasing K_1 and increasing K_2 , according to Eqs. (1) and (2), respectively.

3.2. Parameter estimation and correlation

The measured experimental liquid–liquid equilibrium data were used for estimation of new liquid–liquid molecular parameters for NRTL model [17]. In this work, a modified version of the NRTL model taking into account the presence of the salt [14] has been used for the correlation of the equilibrium data for the system water–propionic acid–dichloromethane–KCl.

According to the NRTL model, the activity coefficient of component i in the absence of salt, γ_{i0} is expressed as follows:

$$\ln \gamma_{i0} = \left[\frac{\sum_{j=1}^{j=3} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{k=3} G_{ki} x_k} + \sum_{j=1}^{j=3} \frac{x_j G_{ji}}{\sum_{k=1}^{k=3} G_{ki} x_k} \left(\tau_{ij} - \frac{\sum_{m=1}^{m=3} x_m \tau_{mi}}{\sum_{k=1}^{k=3} G_{kj} x_k} \right) \right] \quad (6)$$

where:

$$\tau_{ji} = \frac{(g_{ji} - g_{jj})}{RT} \quad (7)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (8)$$

with g_{ji} the energy of interaction between components j and i , R the universal gas constant, T the temperature and α_{ij} the non-randomness factor assumed to be 0.2 [17].

In a salt–solvent mixture and according to [14], the activity coefficient γ_{is} of the component i is given as follows:

$$\ln \gamma_{is} = \ln \gamma_{i0} + \tau_{is} \quad (9)$$

with τ_{is} the salt–solvent interaction parameter and γ_{i0} the activity coefficient in the absence of salt.

Despite its simplicity, this model has led to reliable results in most cases. However the major inconvenient is the fact that the interaction parameters τ_{is} are dependent on the salt concentrations. For instance for a ternary system and for a given salt percentage it is necessary to estimate six and twelve interaction parameters corresponding to the cases of the absence and presence of the salt, respectively, hence

Table 4

Mean distribution coefficients (K_i) and selectivity (β_{ij}) for water (1)-propionic acid (2) - dichloromethane (3)-KCl at $T = 296.65$ K

System	K_1	K_2	β_{21}
Water–propionic acid–dichloromethane–0% KCl	0.1819	1.5838	8.7128
Water–propionic acid–dichloromethane–5% KCl	0.1560	1.9703	12.6283
Water–propionic acid–dichloromethane–10% KCl	0.1146	3.3010	28.8000
Water–propionic acid–dichloromethane–15% KCl	0.0840	3.7070	44.1310

eighteen interaction parameters in total: $(\tau_{ij})_{i=1,3; j=1,3}$ and $(\tau_{ij})_{i=1,4; j=1,4}$. It should be noted that according to Tan's model the salt is treated as a component and the constituting cations and anions are not considered individually, simplifying this model since there is no need to calculate the charge interactions similar to those between K^+ and Cl^- for the case of KCl. Concerning the salt, only its interactions with the solvent and the solute are taken into account. Reasonable results were obtained in most cases [14,18,19].

The interaction parameters are obtained by the minimization of the following objective function described and used in [20]:

$$F = \sum_j \sum_i \left[(\gamma_i x_i)^I - (\gamma_i x_i)^{II} \right]^2 \quad (10)$$

The minimization technique is based on the simplex method version Nelder–Mead as used by Ghizellaoui and Meniai [21].

The obtained values for the binary interaction parameters for the system water–propionic acid–dichloromethane with 0, 5%, 10% and 15% KCl are shown in Table 5.

At this stage, the values of the required interaction parameters are available and can be used to predict the equilibrium data using the modified NRTL model as shown in Fig. 6.

In Fig. 6, X_{cal} and X_{exp} denote the molar fractions of each constituent in all corresponding aqueous and organic equilibrium phases and from the graphs of this figure show the comparisons of the predicted data with the experimental values where it can be seen that nearly all the points are located

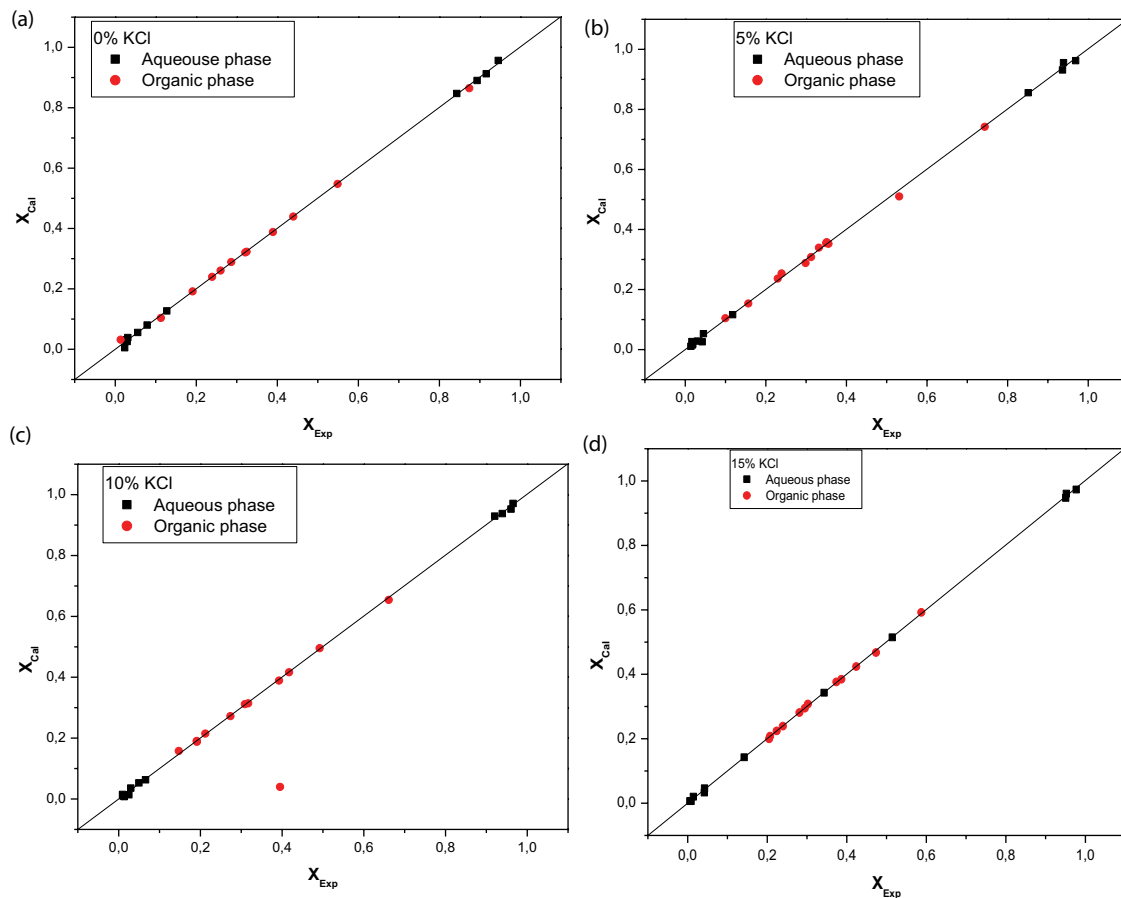


Fig. 6. Correlation of LLE of water (1)-propionic acid (2)-dichloromethane (3) system at 296.65 K (a) 0% KCl, (b) 5% KCl, (c) 10% KCl and (d) 15% KCl.

Table 5
NRTL binary interactions parameters τ_{ij} for the system water (1)–propionic acid (2)–dichloromethane (3) with 0, 5%, 10%, 15% KCl at 296.65 K

<i>i</i>	<i>j</i>	0%		5%		10%		15%	
		$(\tau_{ij})_0$	$(\tau_{ji})_0$	$(\tau_{ij})_s$	$(\tau_{ji})_s$	$(\tau_{ij})_s$	$(\tau_{ji})_s$	$(\tau_{ij})_s$	$(\tau_{ji})_s$
Water	Propionic acid	0.478	0.258	5.586	−1.425	2.295	1.466	1.253	−0.366
Water	Dichloromethane	4.561	2.402	6.016	2.445	5.646	0.920	8.780	1.690
Water	KCl	–	–	0.787	1.811	0.596	0.401	0.949	0.636
Propionic acid	Dichloromethane	10.813	−3.685	5.096	−0.510	−0.135	0.514	−3.027	−2.652
Propionic acid	KCl	–	–	2.036	1.072	1.632	2.168	0.347	1.362
Dichloromethane	KCl	–	–	5.341	3.261	1.713	2.171	0.924	0.692

on the first bisector line, indicating an excellent agreement between the two sets of values, that is, experimental and predicted.

In order to confirm the reliability of the calculated results comparatively with the experimental values, the root mean square deviation (RMSD) was used. It is defined as follows [22]:

$$RMSD = 100 \sum_i \sum_j \sum_k \frac{|w_{ijk}^{Cal} - w_{ijk}^{Exp}|}{(N_p N_t N)} \quad (11)$$

With w^{Exp} and w^{Cal} the experimental and calculated mass fractions, subscripts *i*, *j* and *k* designate the component, phase and tie line, respectively, N_p , N_t , N denote the number of measured tie lines for the considered salt percentages considered (0, 5%, 10% and 15% in this work), the number of phases at equilibrium (two phases: aqueous and organic phases) and *N* the number of constituents (three, excluding the salt).

Therefore Eq. (10) becomes:

$$RMSD = 100 \sum_i \sum_j \sum_k \frac{|w_{ijk}^{Cal} - w_{ijk}^{Exp}|}{(6N_t)} \quad (12)$$

The calculated RMSD values are listed in Table 6 and they also do confirm the excellent agreement between the experimental values and the calculated results.

The experimental liquid–liquid equilibria diagrams and the variation of K_i and β_{ij} vs. the salt concentration are already shown in Figs. 1–4 and Table 4, respectively. Therefore any plots on the same graphs involving these two sets of values would with no doubt be very close.

4. Conclusion

Liquid–liquid equilibrium data for the quaternary system water–propionic acid–dichloromethane–KCl at 296.65 K are experimentally determined by cloud point measurements method. The effect of addition on the original ternary system was observed by the increase of the distribution coefficient of the propionic acid and the increase of the two-phase region.

The addition of potassium chloride improved propionic acid extraction by dichloromethane as the solvent. The importance of this salting effect was also illustrated when

Table 6
Calculated root mean square deviation (RMSD) for water (1)–propionic acid (2)–dichloromethane (3) ternary and quaternary systems at $T = 296.65$ K

System	RMSD (%)
Water–propionic acid–dichloromethane	0.428
Water–propionic acid–dichloromethane–5%KCl	0.679
Water–propionic acid–dichloromethane–10%KCl	0.427
Water–propionic acid–dichloromethane–15%KCl	0.269

a solutropy case was eliminated by acting on the salt mass percentage.

With these experimental data, new binary interaction parameters corresponding to the solvent–solvent interaction for the NRTL model and to the salt–solvent interaction for the NRTL modified model were estimated. The estimated parameters were used to correlate the data by means of the NRTL model. The results were expressed as mean average relative deviation between the experimental and calculated values of the composition of two phases in equilibrium. The results showed the capabilities of the NRTL to predict the equilibrium data in presence and in absence of salts with an excellent precision.

Finally the study of the salt effect on the distribution of a solute between two partially miscible liquid is worth and may have a great potential for various engineering applications.

Symbols

ARD	–	Average relative deviation
<i>K</i>	–	Distribution coefficient
LLE	–	Liquid–liquid equilibrium
NRTL	–	Non-random two liquids
<i>T</i>	–	Temperature
<i>w</i>	–	Mass fraction
<i>x</i>	–	Mole fraction

Greek

α	–	Non randomness parameter in the NRTL model
β	–	Selectivity coefficient
γ	–	Activity coefficient

Subscripts

1	—	Water
2	—	Propionic acid
3	—	Dichloromethane
<i>i</i>	—	Component
<i>j</i>	—	Phase
<i>k</i>	—	Tie line
<i>i</i> 0	—	Component <i>i</i> in absence of salts
<i>i</i> s	—	Component <i>i</i> in presence of salts
<i>ij</i> 0	—	Interaction of <i>i–j</i> pair in absence of salts
<i>ijs</i>	—	Interaction of <i>i–j</i> pair in presence of salts

Superscripts

Exp	—	Experimental
Cal	—	Calculation
I	—	Aqueous phase
II	—	Organic phase

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