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Salting effect of NaCl and KCl on the liquid–liquid equilibria of water + ethyl acetate + ethanol system and interaction parameters estimation using the genetic algorithm

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ABSTRACT

Salting effect of NaCl and KCl on the liquid–liquid equilibria (LLE) of water–ethyl acetate–ethanol system was investigated experimentally at 293.15 K and 1 atm. The salt mass percentages considered were 5 and 10%. The results show that the two electrolytes significantly affected the solubility of the solute in the organic phase, since its distribution coefficient increased with rising amount of electrolyte, causing a salting-out effect which was more pronounced for NaCl than for KCl and could be particularly useful to eliminate solutropy. Interaction parameters for an extended version of the UNIQUAC model were retrieved from the obtained experimental results by means of a combination of the Levenberg-Marquardt and the genetic algorithms.

Keywords: Phase equilibria model; Salting effect; Activity coefficients models; Optimisation

1. Introduction

The great influence of the salting effect on liquid-liquid equilibria may be favourably exploited to act on the distribution of the involved constituents between the present phases. In fact the selection of the solvent extraction as a separation technique depends greatly upon how the solute distributes between the extract and the rafinate phases. Beside the salting effect, various means for altering this distribution in a desirable way are known and one can cite temperature, but the latter has the main advantage of not involving any energy cost.

In fact, the presence of a dissolved salt may influence the phase equilibrium behavior of a liquid mixture significantly. This phenomenon is often referred to as the salting in or salting-out effect [1–4]. The major applications of the salt effect are found in different separation processes such as, for instance, in rectification to shift favourably azeotropic conditions if they may occur, in extraction to alter the miscibility gaps, in absorption and fractional crystallization to alter the distribution coefficients. Consequently, many research programs have been developed to obtain reliable as well as reproducible experimental data for different systems be they liquid-vapour or liquid-liquid, containing various salts. As examples, one can cite [1,2,5–9]. However the present work is dealing with systems involving only liquid–liquid equilibria.

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Generally, the addition of a salt to a liquid–liquid system introduces ionic forces that inevitably affect the phase equilibrium, particularly for partially miscible liquids, inducing changes in the tie lines orientations. This can also be illustrated by certain systems which exhibit a particular behaviour where the tie lines change slopes, indicating variations of the distribution ratio. Salting effect can be very useful for such systems which are termed solutropic by analogy to azeotropic systems in distillation and which may cause similar problems in the design of staged separations.

The salting out is also explained by the fact that when the ions are solvated, some of the water becomes unavailable for the solute which is then salted out from the aqueous phase. This can be exploited to remove organic compounds from water.

The prediction of phase equilibria involved in chemical engineering processes such as solvent extraction, distillation, absorption, reaction engineering, etc; is important since the experimental measurements are not always easy. The modeling of such systems mainly relies on the use of thermodynamics models like the non random two liquids (NRTL), the universal functional activity coefficient (UNIFAC), the universal quasi-chemical activity coefficients (UNIQUAC), etc. The development of the corresponding models relies on a parameter fitting to match the experimental concentrations. This defines the so-called inverse problem which is suitably considered when the mathematical solution to a phase equilibrium model is known, but phenomenological parameters are not.

Generally, a mathematical programming procedure has to be applied to find the best fit of the experimental data. The application of an inverse problem leads to an explicit analytical or approximate solution which is highly sensitive to errors in the experimental data [10].

In this work, the parameter-fitting problem is solved by a genetic algorithm (GA) [11] and the liquid–liquid (LLE) tie lines are predicted by using the Levenberg–Marquardt algorithm technique. This approach is based on a global search method which has proven to be more robust than many current search techniques [12].

In the present study, liquid–liquid equilibrium data were obtained at 293.15 K and atmospheric pressure for the system water–ethanol–ethyl acetate in the presence of sodium or potassium chlorides at two different mass percentages of 5 and 10.

The binodal curve and the tie lines for the considered system at 293.15 K were determined by the method reported in [13] where an integrated optimisation-modeling algorithm was developed to, inversely, estimate the interaction parameters. These latters are incorporated into the chosen thermodynamic model (UNIQUAC) to calculate the liquid–liquid phase equilibrium for the given multicomponent system.

2. Experimental

2.1. Chemicals

Ethyl acetate and ethanol were supplied by J. Chemica (Belgium). They were all 99.8 wt % pure. NaCl and KCl were purchased from Labosi (France). Bidistilled water was prepared using GFL 2001/4 distillation unit.

2.2. Analytical methods

A weighed amount of aqueous solution containing a known quantity of solute was mixed with a known quantity of solvent in a stoppered funnel. Quantities of salt were added to make corresponding mixtures of different salt mass percentages of 5 and 10. These mixtures were maintained at constant temperature of 293.15 ± 0.1 K in a thermostatic bath and agitated for an extended period of time until complete dissolution of the salt. The thermodynamic equilibrium was finally achieved by letting the mixture rest for 24 h. After quantitative gravity separation, each phase was weighed. Since both solvents are partially miscible, the analysis procedure consisted of analysing samples from both phases by measuring the respective refractive indexes by means of the digital refractometer Euromex RD 645. Prior to these refractometer measurements, calibration curves giving the change of the refractive index with concentration of the solution have been plotted and used to read off the concentrations of the nonelectrolytes in the organic phase. The concentrations in the aqueous phase solution were obtained from material balance. The amounts of the salt in the aqueous and organic phases were determined by evaporation and material balance, respectively. However this may be imprecise in some cases but remains acceptable as long as the amount of dissolved salt in the organic phase is low.

3. Thermodynamic modeling

3.1. The thermodynamic model

The thermodynamic model used in this work is the extended version of UNIQUAC described in the literature [14]. It is based on the local composition concept [15,16] and is developed from the original UNIQUAC by adding a Debye-Hückel term [17–19]. Thus it consists of three terms: a combinatorial or entropic term, a residual or enthalpic term and an electrostatic term:

$$G^E = G^E_{\text{combinatorial}} + G^R_{\text{residual}} + G^E_{\text{Debye-Huckel}} \tag{1}$$

The combinatorial and the residual terms are identical to those used in the usual UNIQUAC equation. The combinatorial or entropic term is expressed as:

$$\frac{G^{\mathrm{E}}_{\text{combinatorial}}}{RT} = \sum_i^N x_i \ln\frac{\phi_i}{x_i} - \frac{z}{2}\sum_i^N q_i x_i \ln\frac{\phi_i}{\theta_i} \tag{2}$$

z = 10 is the co-ordination number, x, ϕ_i and θ_i are the mole, the volume and the surface fractions of component i, respectively. ϕ_i and θ_i are defined as follows:

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j}; \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \tag{3}$$

r_i and q_i are volume and surface area parameters for component i. The residual, enthalpic term is given as:

$$\frac{G^E_{\text{residual}}}{RT} = -\sum_i^N q_i x_i \ln\left(\sum_j^N \theta_i \tau_{ji}\right) \tag{4}$$

The parameter τ_{ji} is expressed as:

$$\tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right) \tag{5}$$

with the UNIQUAC interaction parameters $\tau_{ji} = \tau_{ij}$.

The combinatorial and the residual terms of the UNIQUAC excess Gibbs energy function are based on the symmetrical activity coefficient convention. The Debye–Hückel electrostatic term is expressed in terms of the symmetrical convention for water and the unsymmetrical convention for ions. The expression for the Debye–Hückel contribution to the excess Gibbs energy is given as follows [20]:

$$\frac{G^E_{\text{Debye-Huckel}}}{RT} = -\frac{4x_n A M_n}{b^3}\left[-b\sqrt{I} + \ln\left(1+\sqrt{I}\right) + \frac{b^2 I}{2}\right] \tag{6}$$

x_n is the mole fraction of solvent, M_n (kg mol^{-1}) is the molar mass of solvent. A is the Debye–Hückel parameter defined as

$$A = \frac{F^3}{4\pi N_A}\left[\frac{d}{2\left(\varepsilon_o \varepsilon_T RT\right)}\right]^{1/2} \tag{7}$$

F is Faradays constant (C mol^{-1}), N_A (mol^{-1}) Avogadro's number, ε_0 the vacuum permittivity (C^{2}J^{-1}m^{-1}), R the gas constant (J mol^{-1} K^{-1}), T is the temperature in Kelvin, d is the density (kg m^{-3}) and ε_r the relative permittivity (dielectric constant) of the solution, d and ε_T are both functions of temperature. Based on tabulated values of the density d and the relative permittivity ε_r of pure solvent, the Debye–Hückel parameter A can be approximated in the temperature range 273.15–383.15 K by the following expression:

$$\begin{aligned} A &= 1.131 + 1.335\times10^{-3}\,(T-273.15) \\ &\quad + 1.164\times10^{-5}\,(T-273.15)^2 \end{aligned} \tag{8}$$

b is considered constant and equal to 1.50 (kg mol^{-1})^{½}. I is the ionic strength defined as

$$I = \frac{1}{2}\sum_t m_i z_i^2 \tag{9}$$

where m_i is the molality of ion i and z_i its charge.

By partial molal differentiation of the combinatorial and the residual UNIQUAC terms, the corresponding contributions to the symmetrical activity coefficients are obtained as:

$$\ln\gamma_i^C = \ln\left(\frac{\phi_i}{x_i}\right) + 1 - \frac{\phi_i}{x_i} - \frac{z}{2}q_i\left[\ln\left(\frac{\phi_i}{\theta_i}\right) + 1 - \frac{\phi_i}{\theta_i}\right] \tag{10}$$

$$\ln\gamma_i^R = q_i\left[1 - \ln\left(\sum_k \theta_k \tau_{ki}\right) - \sum_k \frac{\theta_k \tau_{ik}}{\sum_l \theta_l \tau_{lk}}\right] \tag{11}$$

The infinite dilution terms are obtained by setting x_w= 1 in Eq. (10).

$$\ln\gamma_i^{\infty,C} = \ln\left(\frac{r_i}{r_n}\right) + 1 - \frac{r_i}{r_n} - \frac{z}{2}\left[\ln\left(\frac{r_i q_n}{r_n q_i}\right) + 1 - \frac{r_i q_n}{r_n q_i}\right] \tag{12}$$

$$\ln\gamma_i^{\infty,R} = q_i\left[1 - \ln\left(\tau_{ni}\right) - \tau_{in}\right] \tag{13}$$

By partial molal differentiation of the Debye–Hückel excess Gibbs energy term 6, one obtains for solvent:

$$\ln\gamma_n^{D-H} = \frac{AM_n}{b^3}\left[1 + b\sqrt{I} - \frac{1}{1+b\sqrt{I}} - 2\ln\left(1+\sqrt{I}\right)\right] \tag{14}$$

and for the ions:

$$\ln\gamma_i^{*,D-H} = -z_i^2\,\frac{AI^{1/2}}{1+bI^{1/2}} \tag{15}$$

The activity coefficient for solvent is calculated by adding the three terms:

$$\ln\gamma_n = \ln\gamma_n^C + \ln\gamma_n^R + \ln\gamma_n^{D-H} \tag{16}$$

and the unsymmetrical activity coefficient for ion i is obtained as:

$$\ln\gamma_i^* = \ln\gamma_i^C - \ln\gamma_i^{\infty,C} + \ln\gamma_i^R - \ln\gamma_i^{\infty,R} + \ln\gamma_i^{*,D-H} \tag{17}$$

3.2. Parameter estimation procedure

The calculations of LLE were carried using the UNIQUAC model as given in the thermodynamic section. Binary interaction parameters are usually obtained from experimental LLE data by minimizing a suitably chosen objective function where the most common one is the sum of squared differences between the experimental and calculated composition of all the components over the entire set of tie-lines.

The tie lines calculation are performed by solving isoactivity criteria along with the equations derived from the summation rules and overall mass balances, by means of the Levenberg-Marquardt optimization process [21].

The interaction parameters were estimated by combining the GA method [11] and Levenberg–Marquardt algorithm technique to solve the inverse problem of the phase equilibrium liquid–liquid thermodynamic model, which consists of minimizing an objective function which takes into account all the components and is expressed in weight units as follows:

$$\min .F = \sum_{k=1}^{N_t}\sum_{j=1}^{N_p}\sum_{i=1}^{N} w_{ik}^{jl}\left(x_{ik}^{jl} - x'^{jl}_{ik}\right)^2 \tag{18}$$

with N_t denoting the number of measured tie lines for the salt percentages considered (0, 5 and 10% in this work), N_p the number of phases at equilibrium and N the number of constituents.

This function is forced to a minimum value by varying the interaction parameters to ultimately fit the calculated tie line compositions to the experimental values by means of Levenberg–Marquardt algorithm technique.

The goodness fit is usually measured by the root mean square deviation (rmsd) defined as

$$rmsd = \left(\frac{-F}{N_p N_t N}\right)^{1/2} \tag{19}$$

In the present work two salt percentages were considered, two liquid equilibrium phases were obtained (extract and rafinate), eight tie lines for both salt percentages and six constituents (water, ethyl acetate, ethanol, Na^+ or K^+ and Cl^-) were involved, leading to the numerical values of 2, 15 and 6 for N_p, N_t and N, respectively.

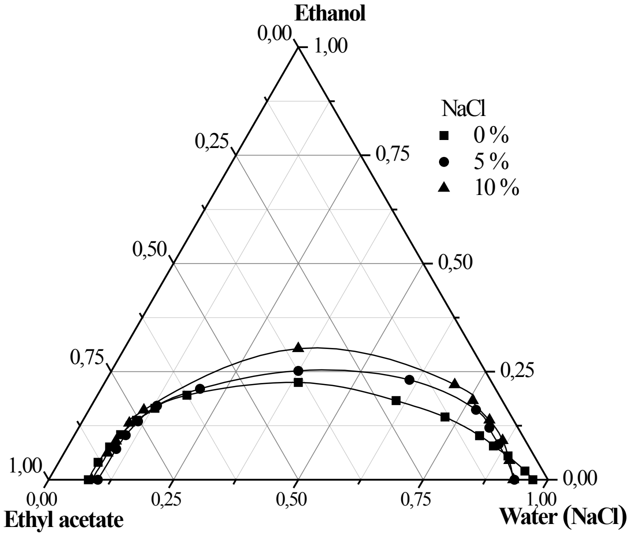

Fig. 1. Binodal curves for different salt weight percentages for the system water (A)–ethyl acetate (B)–ethanol (C)–NaCl (salt-free basis).

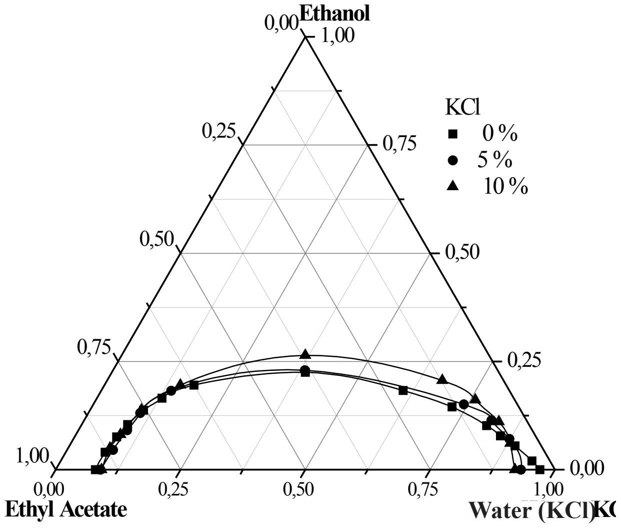

Fig. 2. Binodal curves for different salt weight percentages for the system water (A)–ethyl acetate (B)–ethanol (C)–KCl (salt-free basis).

4. Results and discussion

4.1. The miscibility curves

The experimentally determined binodales curves for the different cases (0%, 5% and 10% NaCl or KCl) are shown in Figs. 1 and 2, for both salts.

From these diagrams it can be noticed that the region of heterogeneity (i.e. the two phase region) increases on adding these salts and this is generally the case. However Fig. 2 shows that the miscibility curve corresponding to 5% KCl remained close to that at 0% KCl. This indicates that the salting effect is more pronounced with NaCl than KCl.

4.2. The tie lines

The experimentally measured tie-line data for the ethyl acetate–ethanol–water system, with and without the presence of salts NaCl and KCl are shown in Tables 1–5.

From the results, one can see that the distribution of the salts is different in the two conjugated phases in equilibrium with concentrations in the aqueous phase always much higher than in the organic phase.

In the literature liquid–liquid equilibrium data were found for the system ethyl acetate–ethanol–water at different temperatures such as 25, 35 and 45°C [22] but not at 20°C as was the case for the present work. However the obtained results shown in Table 1 are qualitatively in agreement with those at 25°C reported in [22].

Figs. 3 and 4 show, at different salt percentages, the position of the distribution curves relative to the first bisector which geometrically represents conjugated organic and aqueous phases with equal solute mass fractions, i.e. $X_{ca} = X_{cb}$, and hence illustrating a solutropy case.

Fig. 3 shows a solutropy for 5% NaCl which is eliminated at 10% whereas for KCl a solutropy takes place at both salt percentages, i.e 5 and 10%.

Table 1
Tie-line data for ethyl acetate–ethanol–water system (weight fraction basis)

Organic phase			Aqueous phase		
Ethanol (C)	Ethyl acetate (B)	Water (A)	Ethanol (C)	Ethyl acetate (B)	Water (A)
0.0400	0.9185	0.0415	0.0600	0.0820	0.8580
7.80	0.8540	0.0680	0.1041	0.0922	0.8037
11.20	0.7950	0.0930	0.1471	0.1160	0.7369
15.20	0.6890	0.1551	0.1760	0.1440	0.6800

Table 2
Tie-line data for ethyl acetate–ethanol–water–sodium chloride system at 20°C and 5% NaCl (weight fraction basis)

Organic phase					Aqueous phase				
Cl^-	Na^+	Ethanol (C)	Ethyl acetate (B)	Water (A)	Cl^-	Na^+	Ethanol (C)	Ethyl acetate (B)	Water (A)
0.0022	0.0014	0.0469	0.8864	0.0631	0.0261	0.0169	0.0460	0.0946	0.8164
0.0022	0.0014	0.0953	0.8392	0.0619	0.0249	0.0161	0.0830	0.0970	0.7790
0.0022	0.0014	0.1419	0.7915	0.0630	0.0236	0.0153	0.1149	0.1057	0.7405
0.0029	0.0019	0.1827	0.7287	0.0838	0.0230	0.0149	0.1439	0.1116	0.7066

Table 3
Tie-line data for ethyl acetate–ethanol–water–sodium chloride system at 20°C and 10% NaCl (weight fraction basis)

Organic phase					Aqueous phase				
Cl^-	Na^+	Ethanol (C)	Ethyl acetate (B)	Water (A)	Cl^-	Na^+	Ethanol (C)	Ethyl acetate (B)	Water (A)
0.0018	0.0012	0.0518	0.8937	0.0515	0.0552	0.0358	0.0373	0.0798	0.7919
0.0018	0.0011	0.1063	0.8460	0.0448	0.0528	0.0342	0.0695	0.0822	0.7613
0.0039	0.0025	0.1590	0.7815	0.0531	0.0497	0.0323	0.0946	0.0855	0.7379
0.0051	0.0033	0.2062	0.7135	0.0719	0.0482	0.0313	0.1151	0.0899	0.7155

Table 4
Tie-line data for ethyl acetate–ethanol–water–sodium chloride system at 20°C and 5% KCl (weight fraction basis)

Organic phase					Aqueous phase				
Cl^-	Na^+	Ethanol (C)	Ethyl acetate (B)	Water (A)	Cl^-	Na^+	Ethanol (C)	Ethyl acetate (B)	Water (A)
0.0015	0.0016	0.0434	0.8962	0.0573	0.0205	0.0226	0.0522	0.0871	0.8176
0.0015	0.0017	0.0848	0.8527	0.0593	0.0197	0.0218	0.0939	0.0918	0.7728
0.0021	0.0023	0.1258	0.7871	0.0827	0.0183	0.0202	0.1290	0.1015	0.7310
0.0044	0.0048	0.1666	0.6808	0.1434	0.0159	0.0176	0.1585	0.1141	0.6939

A useful use can also be made of the first bisector line since the upper region represents phases where the solute mass fraction X_{cb} is greater than X_{ca} whereas the lower region concerns the phases where X_{cb} is less than X_{ca}.

Still from Figs. 3 and 4, the curve corresponding to 0% salt is below the bisector, whereas for 5% and 10% salt percentages, the curves move above the bisector indicating a more favourable ethanol distribution in the organic phase than in the aqueous one.

Table 5
Tie-line data for ethyl acetate–ethanol–water–sodium chloride system at 20°C and 10% KCl (weight fraction basis)

Organic phase					Aqueous phase				
Cl^-	Na^+	Ethanol (C)	Ethyl acetate (B)	Water (A)	Cl^-	Na^+	Ethanol (C)	Ethyl acetate (B)	Water (A)
0.0035	0.0039	0.0459	0.8825	0.0642	0.0417	0.0460	0.0448	0.0783	0.7892
0.0031	0.0034	0.0946	0.8406	0.0583	0.0399	0.0440	0.0787	0.0821	0.7553
0.0038	0.0042	0.1431	0.7778	0.0711	0.0382	0.0422	0.1076	0.0881	0.7239
0.0058	0.0064	0.1891	0.6914	0.1073	0.0368	0.0406	0.1308	0.0957	0.6961

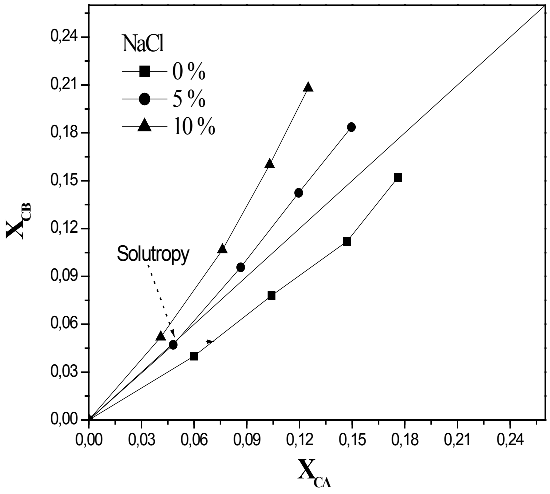

Fig. 3. Effect of NaCl on the equilibrium distributions for different salt weight percentages for the system water (A)–ethyl acetate (B)–ethanol (C) (salt-free basis).

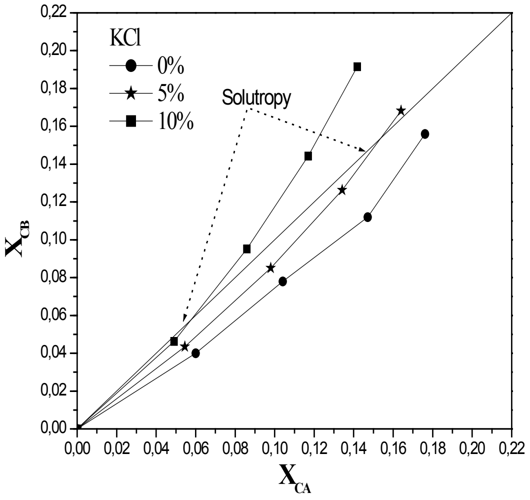

Fig. 4. Effect of KCl on the equilibrium distributions for different salt weight percentages for the system water (A)–ethyl acetate (B)–ethanol (C) (salt-free basis).

As mentioned earlier and from the above figures, one can say that NaCl induces a better "Salting-out". This is in agrement with the results reported in [18–21,23–25] where it has been shown that the number of water molecules 'caging' a sodium ion is greater than the one of potassium. This can be explained by the fact that, although both cations Na^+ and K^+ are monovalent, Na^+ are more hydrated than K^+ since the hydration energies are equal to 407 and 324 kJ/mol, respectively, as reported in [25].

Generally for a given system, only few experimental tie lines date are available since their measuring at various salt concentrations is not always easy and can be a tedious process. Therefore empirical correlations can be of a great utility. In the present work, the consistency of the obtained experimental data can be assessed graphically by means of a method based on the following Eisen–Joffe equation [26]:

$$\log\left(X_{CB} / X_{BB}\right) = \left(a + bX_S\right) + \left(c + dX_S\right)\log\left(X_{CA} / X_{AA}\right) \quad (20)$$

where *a*, *b*, *c* and *d* are constants whose magnitude depends on the nature of the system components, the nature of the salt used and the temperature but are independent of salt concentration.

The constants in Eq. (20) were determined graphically using the tie-line data obtained in this work at the three salt concentrations (0, 5 and 10%) and the obtained values for both salts are shown in Table 6:

Table 6
Constants of the Eisen–Joffe equation for NaCl and KCl

Constants in the Eisen–Joffe equation	NaCl	KCl
a	0.01594	–0.00141
b	4.4315	3.9046
c	1.18243	1.17952
d	0.954	1.7032

The results obtained using the corresponding correlations are compared to the experimental values as shown in Figs. 5 and 6 where an excellent agreement is obtained. The standard deviation values are 0.01858 and 0.02208, for NaCl and KCl, respectively.

The values of selectivity which depend directly on the solute concentration in the aqueous solution were calculated for all these cases to examine their variation with the addition of salt. From Figs. 7 and 8 which reproduce the curves representing $X_{CB}/(X_{CB}+X_{AB})$ vs. $X_{CA}/(X_{CA}+X_{AA})$ at different considered salt weight percentages, it can be seen that the presence of dissolved salts had a great influence on the selectivity.

4.3. Interaction parameter values

The obtained optimal sets of interaction parameters are shown in Tables 7 and 8.

To assess the reliability of these parameters, they were used in UNIQUAC model described above to calculate the various activity coefficients for the components in the system and hence the equilibrium compositions. Although usually it is quite difficult to obtain a good correlation of quaternary systems including an inorganic salt, using models as UNIQUAC-electrolyte due to the complex nature of the problem, the agreement with the experimental values was good since the calculated rela-

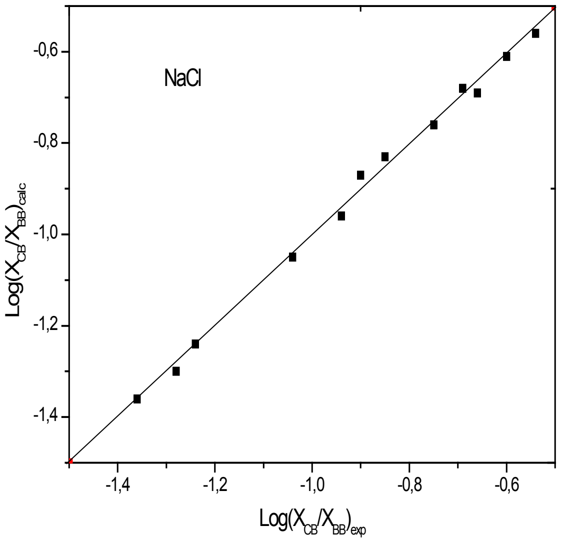

Fig. 5. Assessment of the Eisen–Joffe equation (NaCl).

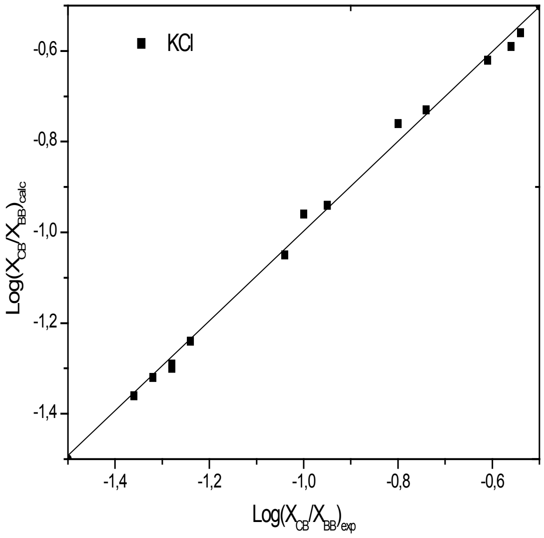

Fig. 6. Assessment of the Eisen–Joffe equation (KCl).

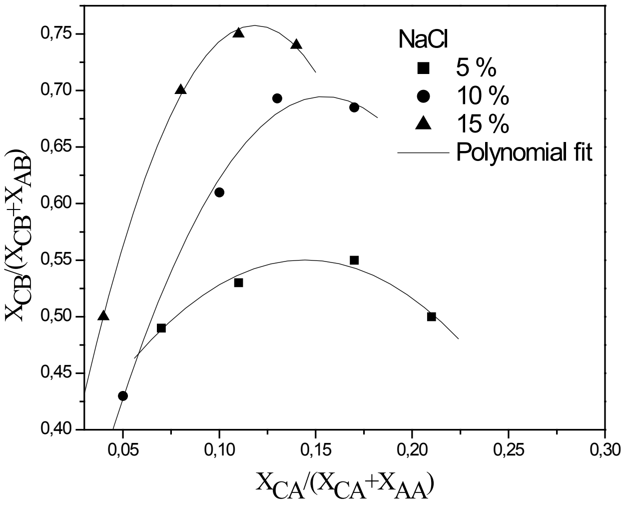

Fig. 7. Selectivity diagram at 20°C for different salt weight percentages for the system water (A)–ethyl acetate (B)–ethanol (C)–NaCl.

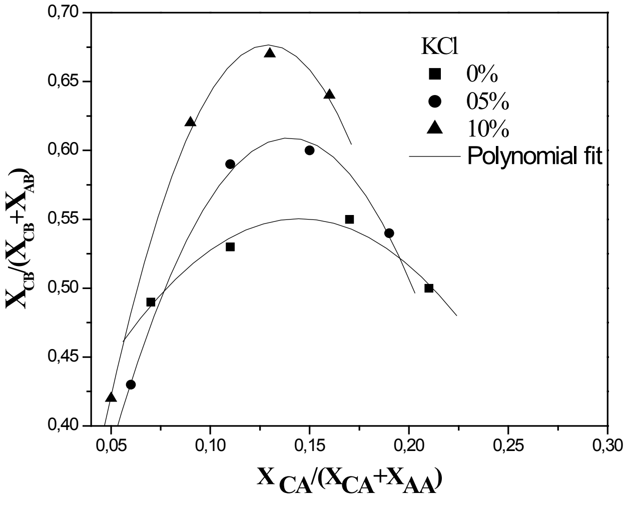

Fig. 8. Selectivity diagram at 20°C for different salt weight percentages for the system water (A)–ethyl acetate (B)–ethanol (C)–KCl.

Table 7
Binary interaction parameters values for quaternary system at 20°C, 5% and 10% KCl

a (K)×10^3	Ethyl acetate	Ethanol	Water	Na$^+$	Cl$^-$
Ethyl acetate	0.00	3.8293	0.3139	9.9758	–7.8203
Ethanol	–5.8681	0.00	–6.6479	–6.5325	7.1050
Water	5.1167	5.9239	0.00	0.2868	–7.3098
Na$^+$	–2.9011	–3.3723	3.5427	0.00	–0.6770
Cl$^-$	–1.5435	–2.6087	–5.8361	–6.7963	0.00

Rmsd KCl: 1.12×10^{-4}

Table 8
Binary interaction parameters values for quaternary system at 20°C, 5% and 10% NaCl

a (K)10^3	Ethyl acetate	Ethanol	Water	Na$^+$	Cl$^-$
Ethyl acetate	0.00	–6.3180	–5.5240	2.5469	–4.4986
Ethanol	9.7829	0.00	8.9116	–1.7681	–2.9093
Water	5.6574	–5.5145	0.00	–3.7612	0.0257
Na$^+$	4.2715	6.7044	–0.1531	0.00	4.3009
Cl$^-$	0.0756	1.7288	–1.9302	8.6008	0.00

Rmsd NaCl: 1.13×10^{-4}

tive mean squared deviations according to Eq. (19) were 1.13×10^{-4} and 1.12×10^{-4} for NaCl and KCl, respectively. The representing points of the experimental and calculated values would be practically confounded.

The quality of the results justifies the choice of the genetic algorithm as the optimization technique for the calculation of the necessary interaction parameters for the used thermodynamic model. Compared to classical methods, the main advantage of the GA is that it does not require any good initial guess.

5. Conclusions

Liquid–liquid equilibrium data for the system water–ethanol–ethyl acetate, in the absence and presence of NaCl or KCl, were measured at 293.15 K and atmospheric pressure. It can be concluded that the salting out of the solute was more important with NaCl rather than with KCl.

The importance of this salting effect was also demonstrated through this study, particularly with the elimination of a solutropy, by acting on the salt mass percentage.

It can be mentioned that the effects of dissolved salts on the distribution of a solute between two partially miscible solvents is a problem having potential engineering applications despite a few negative features like corrosion and recovery problems that are associated with the use of these electrolytic species.

Finally an integrated optimisation–simulation algorithm was used to estimate the interaction parameters required for the thermodynamic model UNIQUAC in order to predict liquid-liquid equilibrium for liquid–liquid systems containing salts.

Symbols

A — Constant in Eq. (6)
b — Constant in Eq. (6)
c — Total number of components
d — Density, kg m^{-3}
F — Objective function, Faraday constant
G — Molar Gibbs free energy, kJ mol^{-1}
I — Ionic strength
k_S — Salt effect parameter
M — Molar mass, kg mol^{-1}
m — Total number of tie-lines, molality
N — Number of constituents
N_A — Avogadro number
N_p — Number of phases [Eq. (19)]
N_t — Number of measured tie lines [Eq. (19)]
n — Solvent
q — UN1QUAC volume parameter
R — Universal gas constant, J mol^{-1} K^{-1}
r — UNIQUAC surface area parameter
T — Absolute temperature, K
u_{ij} — Molar interaction energy between molecules i and j, kJ mol^{-1}
W — Weighing factor
X_{ij} — Mass fraction of component i in phase j on a salt-free basis

x — Experimental mole fraction
$\hat{x}$ — Predicted mole fraction
Z — Coordination number =10
z_i — Ion charge

Greek

ε — Vacuum permittivity, $C^2J^{-1}m^{-1}$
ϕ — Volume fraction
γ — Activity coefficient
θ — Surface area fraction
τ — Interaction parameter

Superscripts

C — Combinatorial
D-H — Debye–Huckel
E — Excess
0 — Salt free condition, vacuum
R — Relative, residual
I, II — Phases
* — Assymetric

Subscripts

i,j — Components
n — Solvent
∞ — Infinite dilution

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