



The influence of cation and temperature on the liquid–liquid equilibrium of water + 2-butanone system and its simulation using artificial intelligent-based models

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ABSTRACT

The liquid–liquid equilibrium (LLE) data of the binary 2-butanone/water and ternary 2-butanone/water/salt systems was measured at 298.15 and 303.15 K under 101.1 kPa. The dissolved salts studied in this work were KCl, NaCl, LiCl, CaCl₂, and MgCl₂. For the binary mixture 2-butanone/water, the mutual solubility was measured and compared to those reported data. Through LLE data of the ternary mixtures water/salt/2-butanone, the effect of cation type, and temperature on the LLE data were studied. It was found that the addition of dissolved salts decreases the solubility of 2-butanone in the aqueous phase (i.e., salting-out) for the investigated systems. In addition, no apparent effect of temperature on the LLE data. Furthermore, the influence of the cations on the salting-out efficiency decreases in the following order: Mg²⁺ > Ca²⁺ > Li⁺ > Na⁺ > K⁺ in two temperatures. The linearity of the Setschenow equation was used to study the salting-out effect of salts, and has confirmed its order. The experimental data have been correlated using an artificial neural network (ANN) and a modified extended-UNIQUAC model. Both models correlate the LLE data but the ANN outperformed the modified extended-UNIQUAC model obtaining low modeling errors.

Keywords: Liquid–liquid equilibrium; Salting effect; Artificial neural network; Modified extended-UNIQUAC

1. Introduction

2-Butanone is a common organic compound, it is produced industrially on a large scale but occurs in nature only in trace amounts [1]. Multicomponent mixtures involving water-2-butanone may be found in the extraction of 2-butanone from aqueous solutions in preparative or wastewater treatment units, or in some industrial syntheses, such as plastics, textiles, in the production of paraffin wax, and in household products [2,3]. Thus, the recovery of 2-butanone compounds from aqueous solutions using the aqueous

two-phase extraction (ATPE) method [4]. The ATPE technique is a green separation, industrially, and economically important because of the lower costs and energy required, and particularly suitable for the separation of partially miscible mixtures. The addition of the dissolved salt into the mixture will cause great changes in the solubility (i.e., compositions) and affects the ATPE. The change in the solubility of a non-electrolyte in an aqueous solution that results from the addition of an electrolyte which is known as the salting effect [5]. The salting-out effect is defined as a decrease in the solubility of the non-electrolyte (i.e., organic

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solvent) through increasing concentrations of the added electrolyte (i.e., salt).

In recent years, several studies have been conducted to investigate the salt effects on the liquid–liquid equilibrium (LLE) in partially miscible systems [6–12]. Generally, these studies show that water has a strong solvation effect on anions and cations, but the salting-out effect mainly displays in the solvation of cation in the salts. The salt effect must be considered in both the process design and the unit operations modeling because it can affect to a large extent the thermodynamic phase equilibria. Different thermodynamic models have been also developed for the prediction of LLE conditions in the presence of electrolytes [13,14]. However, these models may show some limitations for fitting and predicting the LLE with salting-out effect.

In this study, LLE data were measured for the system water + butanone at 298.15 and 303.15 K in the presence of KCl, NaCl, LiCl, CaCl₂, and MgCl₂ salts. 2-butanone is a chemical compound widely applied in printing, coatings, glues, resins, paints, and cleaning products [15]. This chemical has been also suggested as a potential biofuel that can be produced from biomasses [16]. LLE of water + 2-butanone + salts mixture has been reported in the literature [17–20]. Specifically, Al-Sahhaf et al. [17] reported the LLE phase diagram of water + 2-butanone at 298.15 K with KI, NaBr, and LiCl where KI exhibited a salting-in effect in contrast to the salts LiCl and NaBr that showed a salting-out effect for 2-butanone. Li et al. [18] measured LLE data of partially miscible systems of water + butanone at 298.15 K with NaCl, KCl, and KBr. In other study, Tang et al. [19] reported the correlation of LLE for the water + 2-butanone at 298.15 K using an extended Setschenow equation. LLE phase diagram of water + butanone system at 296–299 K with CaCl₂ has been also reported by Meissner and Stokes [20]. Note that experimental data reported for these thermodynamic systems has been mainly reported at 298 K, and consequently, there is a lack of phase equilibrium data at higher temperatures. To our best knowledge, the research on the LLE data of 2-butanone/water mixture with lithium and magnesium chloride has not been reported in the literature yet.

Therefore, this paper reports new experimental data for the salting effect on the LLE of water/2-butanone. Setschenow equation was used to analyze the effects of the salt and temperature in the studied ternary systems. Finally, an artificial neural network (ANN) and a modified extended-UNIQUAC model [21–23] have been utilized to calculate the thermodynamic phase behavior of LLE of water/salt/2-butanone where results of both models were compared.

2. Experimental section

2.1. Materials, apparatus, and solutions

For measuring the LLE, 2-butanone (AR, 99.5%), sodium chloride (AR, 99.5%), potassium chloride (AR, 99.5%), lithium chloride (AR, 99.5%), magnesium chloride (AR, 99.6%), and calcium chloride (AR, 99.6%) were supplied from Merck (all are in mass % and of analytical grade). All those dissolved salts used in this work were dried in an oven before being used in the LLE experiments. Distilled water was used in all cases.

2.2. Apparatus and procedure for determining the LLE data

The measurement apparatus employed in this work is essentially similar to the one used in previous works [24,25]. The cloud-point method with refractive index measurement was employed to determine the binodal curves at 298.15 and 303.15 K under 101.1 kPa.

For this purpose, a thermostated miniature cell with about 100 cm³ volume is equipped with a magnetic stirrer and isothermal fluid jacketed. The cell temperature was controlled at a constant temperature with a circulation of water using a thermostat (JULABO model ED, precise to ±0.03 K). As seen in Fig. 1, a schematic diagram of the static apparatus for the LLE data measurement system.

A known composition of the saline solution (water + salt) was titrated with 2-butanone until a turbid mixture was observed, afterward, it was kept for 5 min. After this time, the mixture was stirred gently for few minutes, if the mixture had maintained heterogeneous (turbid) as previously observed, it indicates that a point of the binodal curve had been obtained [26]. Subsequently, the mixture was titrated back by adding water until the heterogeneity vanished [26–28]. The composition and the refractive index measurement of the mixture in each step were measured by a mass using an analytical balance (Model Nahita YP402N, precise to ±0.0001 g) and a refractometer (Atago, model DR-A1, precise to ±0.0002).

For the determination of the experimental tie-lines data of the ternary salt/2-butanone/water systems at each temperature, feed samples were prepared by mixing appropriate amounts of 2-butanone, salt, and water in the equilibrium jacketed cells. At first, the salts were weighed and dissolved in water prior to adding 2-butanone. Afterward, the mixtures of known masses of the components were stirred with a magnetic stirrer for at least 3 h at the desired temperatures and the phases were then allowed to settle for at least 12 h to ensure a complete phase separation into a 2-butanone-rich phase and a water-rich phase. These conditions were sufficient for phase separation and equilibration, as verified by preliminary experiments carried out in this work. The weight of each phase was

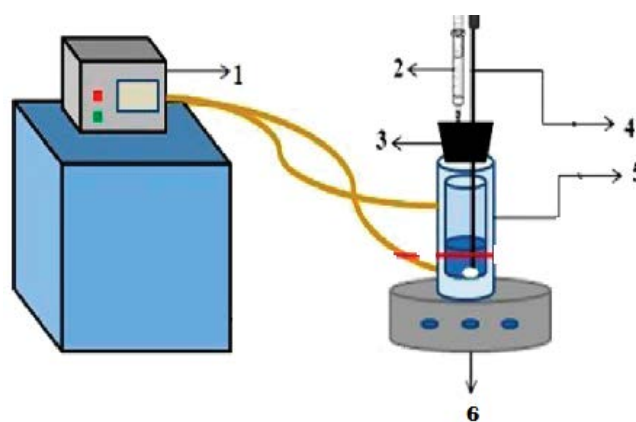


Fig. 1. Schematic diagram for the static apparatus for the LLE measurement: (1) thermostatic water bath, (2) syringe, (3) rubber plug, (4) thermometer, (5) equilibrium cell, and (6) magnetic stirring apparatus.

measured by analytical balance (Model Nahita YP402N, precise to ± 0.0001 g).

After the separation of the two phases, the concentration of 2-butanone in both phases was determined by refractive index measurements performed at $T = 298.15$ and 303.15 K using a refractometer (Atago, model DR-A1, precise to ± 0.0002).

The salt content in the water-rich phase was carefully measured by evaporating the samples to dryness [29]. The evaporated compounds were completely condensed by the condenser to ensure mass balance. Afterward, the samples were dried in an oven for 24 h to remove any water and 2-butanone completely, then, they were weighed again. Each analysis was performed at least 3 times, and the concentrations' average values were reported. The average uncertainty in the measurements of mass fraction of all components was estimated to be ± 0.001 . It has to be noted that the compositions in the organic phase solution were obtained by a material balance.

In order to determine the solubilities of water and 2-butanone, a synthetic method has been applied. In this regard, the cloud-point technique was used as described in previous works [25]. Table 1 shows a comparison between observed LLE data in this paper with those reported in the literature [17,18,30].

3. Experimental results

3.1. Water/2-butanone

Before examining the salt's effect on the binary water/2-butanone systems, this binary system was measured without salt. The LLE was experimentally determined at 298.15 and 303.15 K under 101.1 kPa, and the resulting data given in Table 1 show excellent agreement with those reported in the literature [17,18,30]. The maximal differences between equilibrium weight fractions of 2-butanone in this work and those reported in the literature are 0.006 for the aqueous phase and 0.01 for the organic phase. The LLE solubility data of the mutual solubility of 2-butanone and water at 298.15 K have nearly the same values compared to those reported [17,18].

3.2. Water/2-butanone/salt

For examining the salt's effect on liquid–liquid phase equilibrium of water/2-butanone mixtures at 298.15 and 303.15 K under 101.1 kPa, different salts were added to achieve this goal. The salts under investigation were NaCl, KCl, LiCl, CaCl_2 , and MgCl_2 .

Our measured LLE data and their absolute standard uncertainty values (u) for the ternary systems 2-butanone/water/salt are given in Table 2 in terms of mass percentage at 298.15 and 303.15 K under 101.1 kPa. In addition, the corresponding LLE phase diagrams for the investigated system are also shown in Fig. 2. It can be seen from these triangular phase diagrams that in the studied temperature span, the temperature has a small effect on the experimental LLE data. The reason might be that the narrow temperature ranges.

On the other hand, It can be observed from Table 2 and Fig. 2 that the mass fraction of 2-butanone in the

Table 1

Experimental data for LLE of 2-butanone/water at 298.15 and 303.15 K and 101.1 kPa^a, with the corresponding literature data

T (K)	w_{21}		w_{23}	
	exp.	lit.	exp.	lit.
298.15	0.2558	0.2540 [30]	0.8820	0.8920 [30]
		0.2560 [18]		0.8820 [18]
		0.2560 [17]		0.8820 [17]
303.15	0.2480	0.2420 [30]	0.8980	0.9030 [30]

^aStandard uncertainties u are: $u(w_{21}) = 0.001$, $u(w_{23}) = 0.0005$, $u(T) = 0.1$ K and $u(P) = 1$ kPa

water-rich phase decreases with increasing salt concentration, this phenomenon is known as salting-out. This can be explained by the fact that when the ions are solvated, some of the water compounds become unavailable for the 2-butanone compounds which are then salted out from the water-rich phase. It should be noted that this behavior was found for all tested electrolytes. From Fig. 3, it is clear that the concentration of 2-butanone in the aqueous phase decreased to <0.049 and 0.06 mass % for MgCl_2 at 298.15 and 303.15 K, respectively, while the other salts decreased this concentration to <0.05 mass % for CaCl_2 , to <0.12 and 0.15 mass % for LiCl, to <0.5 and 1.8 mass % for NaCl and 2.04 and 2.8 mass % for KCl at saturation. At the tested salt concentration range, the salting-out efficiency decreased in the following order: $\text{MgCl}_2 > \text{CaCl}_2 > \text{LiCl} > \text{NaCl} > \text{KCl}$ at two temperatures. This thermodynamic trend can be attributed to the more pronounced solvation degree of Mg^{2+} by water molecules as compared to Ca^{2+} , Li^+ , Na^+ , and K^+ , which decreases the degrees of freedom of the water molecules and, consequently, leads to a butanone solubility decrement in the presence of salts as compared to that in pure water [31,32]. Furthermore, this phenomenon can be more explained by the effect of Gibbs energy of hydration (ΔG_{hyd}) of ions. Accordingly, the hydration Gibbs energies of Mg^{2+} is $-1,830$ kJ/mol, which provides more capability to form the hydration shell than Ca^{2+} , Li^+ , Na^+ , and K^+ with $-1,505$; -475 ; -365 ; and -295 kJ/mol, respectively [33].

For examining the measured precision of LLE data of 2-butanone/water/salt mixtures, the experimental data obtained with NaCl and KCl at 298.15 K were compared with those reported in the literature [18]. The measured equilibrium mass fractions of 2-butanone in the water-rich phase upon addition of KCl and NaCl at 298.15 K (this work) were plotted vs. the corresponding data reported by Li et al. [18] (Fig. 4). Results indicated that the LLE data obtained in this study were in good agreement with the data reported in previous studies. Further, the results of both works indicate that Na^+ causes a stronger salting-out than K^+ .

The experimental LLE data were also analyzed in terms of the Setschenow equation [34]. The Setschenow equation correlates the experimental data of solubility of the organic solvent in water as a function of the concentration of salt. For the water-rich phase, this equation is given by:

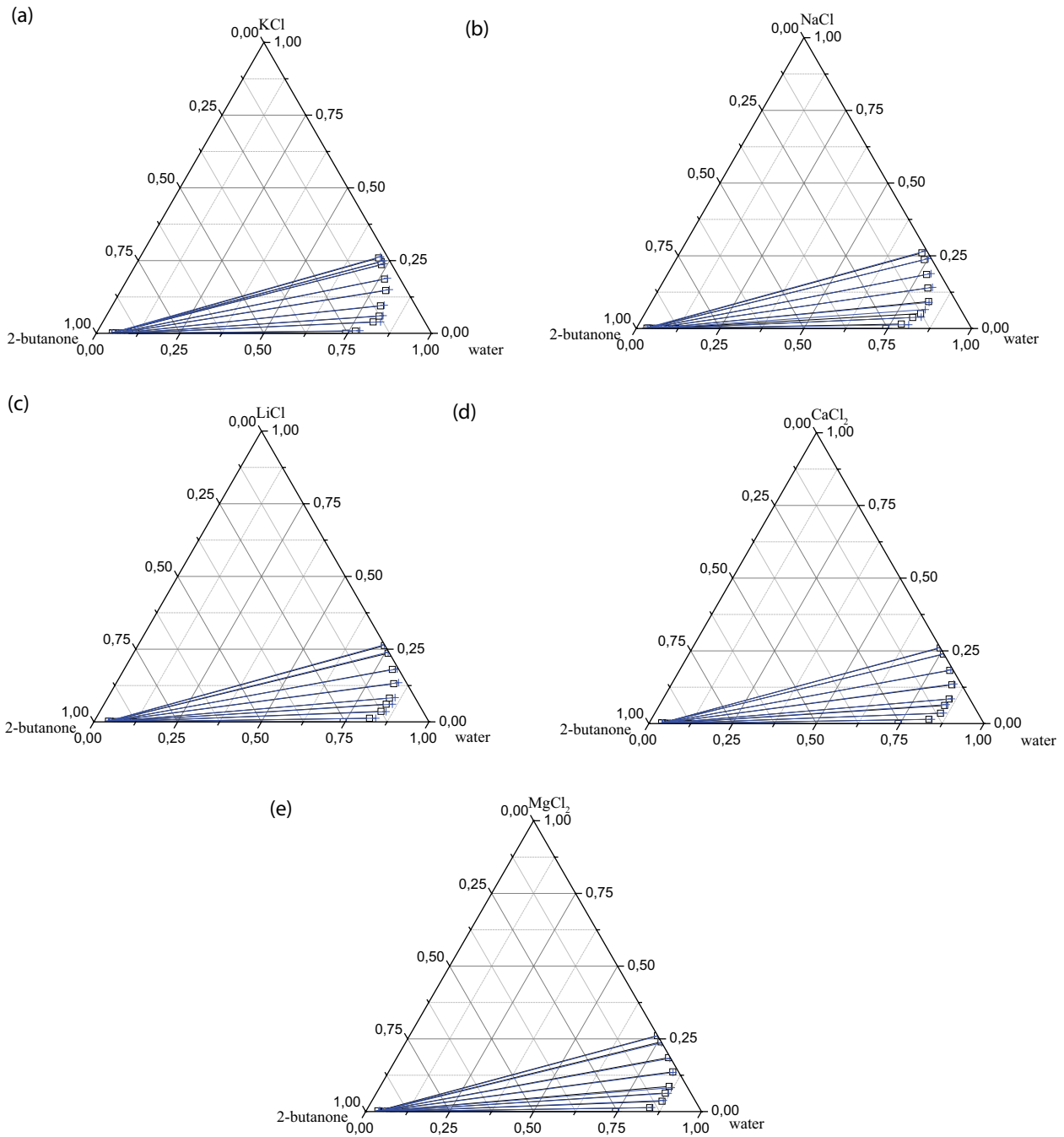


Fig. 2. Phase diagram of the ternary system water/salt/2-butanone in weight fractions: □ and + with solid lines for experimental tie-lines at 298.15 and 303.15 K, respectively.

$$\ln \left\{ \frac{w_2^0}{w_2 / (1 - w_3)} \right\} = k_{s1} w_3$$

and for the alcohol-rich phase, the model is defined as:

$$\ln \left\{ \frac{w_1^0}{w_1 / (1 - w_3)} \right\} = k_{s1} w_3$$

(1) where w_1^0 and w_2^0 are the mass fraction solubilities of water in the solvent-rich phase and of the solvent in the water-rich phase, respectively, in the absence of the salt. Some researchers have suggested that a quadratic term can be required, in some cases, for modeling the solvent-rich phase [34]. This term can be defined as:

$$(2) \quad \ln \left\{ \frac{w_1^0}{w_1 / (1 - w_3)} \right\} = k_{s1} w_3 + k_{s2} (w_3)^2 \quad (3)$$

Table 2
Measured LLE data in terms of mass percentage ($w_i\%$) for water/2-butanone/salt at 298.15 and 303.15 K under 101.1 kPa for the salts NaCl, KCl, LiCl, CaCl₂, and MgCl₂^a

Aqueous phase			Butanone-rich phase		
Water (1) + butanone (2) + NaCl (3) at 298.15 K					
100w ₁₁	100w ₂₁	100w ₃₁	100w ₁₃	100w ₂₃	100w ₃₃
74.42	25.58	0.00	11.8	88.20	0.00
78.28	20.19	1.53	8.84	91.15	0.01
80.54	15.66	3.8	7.90	92.09	0.01
82.24	12.64	5.12	6.51	93.47	0.02
82.55	8.17	9.28	5.64	94.33	0.03
79.99	6.09	13.92	4.82	95.13	0.05
77.31	4.13	18.56	3.86	96.07	0.07
74.06	2.24	23.70	3.56	96.35	0.09
72.17	1.8	26.03	3.14	96.75	0.11
Water (1) + butanone (2) + NaCl (3) at 303.15 K					
75.20	24.8	0.00	10.20	89.80	0.00
80.57	18.13	1.30	8.52	91.46	0.02
83.01	13.08	3.91	7.44	92.53	0.03
82.92	10.56	6.52	6.05	93.91	0.04
82.81	8.22	8.97	5.29	94.65	0.06
81.25	4.60	14.15	4.46	95.47	0.07
78.46	2.67	18.87	3.52	96.39	0.09
75.08	0.92	24.00	3.24	96.64	0.12
72.88	0.50	26.62	2.78	97.08	0.14
Water (1) + butanone (2) + KCl (3) at 298.15 K					
74.42	25.58	0.00	11.8	88.2	0.00
76.95	22.3	0.75	9.90	90.09	0.01
80.67	15.43	3.9	9.72	90.27	0.01
81.46	12.64	5.9	8.35	91.63	0.02
80.10	10.49	9.41	7.05	92.92	0.03
79.00	6.30	14.7	6.39	93.57	0.04
76.72	4.66	18.62	5.86	94.09	0.05
73.33	3.07	23.6	4.95	94.98	0.07
72.70	2.7	24.6	4.89	95.03	0.08
71.30	2.8	25.9	4.78	95.13	0.09
Water (1) + butanone (2) + KCl (3) at 303.15 K					
75.20	24.8	0.00	10.20	89.80	0.00
78.20	20.91	0.89	9.67	90.32	0.01
82.87	13.22	3.91	9.30	90.68	0.02
82.52	11.41	6.07	7.84	92.12	0.04
81.06	9.28	9.66	6.79	93.16	0.05
79.93	5.07	15.00	6.16	93.78	0.06
77.41	3.66	18.93	5.55	94.38	0.07
73.88	2.24	23.88	4.64	95.27	0.09
73.11	1.98	24.91	4.61	95.28	0.11
71.63	2.04	26.33	4.51	95.37	0.12
Water (1) + butanone (2) + LiCl (3) at 298.15 K					
74.42	25.58	0.00	11.8	88.20	0.00
81.64	17.12	1.24	8.10	91.87	0.03
83.88	12.50	3.62	7.16	92.78	0.06
84.200	9.73	6.07	5.85	94.06	0.09
84.11	7.71	8.18	4.97	94.91	0.12
82.93	3.94	13.13	4.40	95.44	0.16

80.05	1.92	18.03	4.66	95.14	0.20
75.99	0.41	23.60	4.49	95.29	0.22
73.61	0.15	26.24	4.26	95.49	0.25
Water (1) + butanone (2) + LiCl (3) at 303.15 K					
75.20	24.8	0.00	10.20	89.80	0.00
83.49	15.27	1.24	7.96	92.01	0.03
85.42	11.07	3.51	7.02	92.90	0.08
86.05	7.88	6.07	5.67	94.23	0.10
85.70	5.95	8.35	4.79	95.06	0.15
84.19	2.34	13.47	4.26	95.56	0.18
81.43	0.38	18.19	4.48	95.29	0.23
75.86	0.20	23.94	4.38	95.36	0.26
73.38	0.12	26.50	4.13	95.59	0.28
Water (1) + butanone (2) + CaCl ₂ (3) at 298.15 K					
74.42	25.58	0.00	11.80	88.20	0.00
82.87	15.69	1.44	7.70	92.27	0.03
85.29	11.17	3.54	6.60	93.34	0.06
85.15	8.63	6.22	5.50	94.41	0.09
85.41	6.16	8.43	4.58	95.30	0.12
83.78	2.90	13.32	4.03	95.81	0.16
80.67	1.07	18.26	3.92	95.90	0.18
76.03	0.12	23.85	3.85	95.95	0.20
73.94	0.05	26.01	3.70	96.08	0.22
Water (1) + butanone (2) + CaCl ₂ (3) at 303.15 K					
75.20	24.8	0.00	10.20	89.80	0.00
83.57	14.98	1.45	7.49	92.47	0.04
86.10	10.30	3.60	6.35	93.6	0.05
85.50	7.99	6.51	5.17	94.75	0.08
85.99	5.52	8.49	4.47	95.42	0.11
84.19	2.19	13.62	3.98	95.88	0.14
80.87	0.68	18.45	3.93	95.91	0.16
75.97	0.05	23.98	3.98	95.83	0.19
73.81	0.05	26.14	3.81	95.98	0.21
Water (1) + butanone (2) + MgCl ₂ (3) at 298.15 K					
74.42	25.58	0.00	11.8	88.20	0.00
83.93	14.74	1.33	7.34	92.62	0.04
86.48	9.98	3.54	6.23	93.70	0.07
86.03	7.59	6.38	5.14	94.76	0.10
86.07	5.29	8.64	4.25	95.61	0.14
84.64	1.72	13.64	3.71	96.12	0.17
80.95	0.52	18.53	3.71	96.10	0.19
75.99	0.05	23.96	3.59	96.20	0.21
73.841	0.049	26.11	3.52	96.25	0.23
Water (1) + butanone (2) + MgCl ₂ (3) at 303.15 K					
75.20	24.8	0.00	10.20	89.80	0.00
84.46	14.15	1.39	7.25	93.85	0.04
86.72	9.45	3.83	6.08	94.93	0.07
86.9	6.82	6.28	4.98	95.61	0.09
86.89	4.91	8.20	4.27	95.99	0.12
84.81	1.75	13.44	3.88	95.99	0.13
81.44	0.28	18.28	3.83	95.72	0.18
76.31	0.06	23.63	4.08	95.85	0.20
73.98	0.06	25.96	3.93	92.71	0.22

^aMaximal standard uncertainties u are: $u(w) = 0.003$, $u(n_D) = 0.0005$, $u(T) = 0.1$ K, and $u(P) = 1$ kPa.

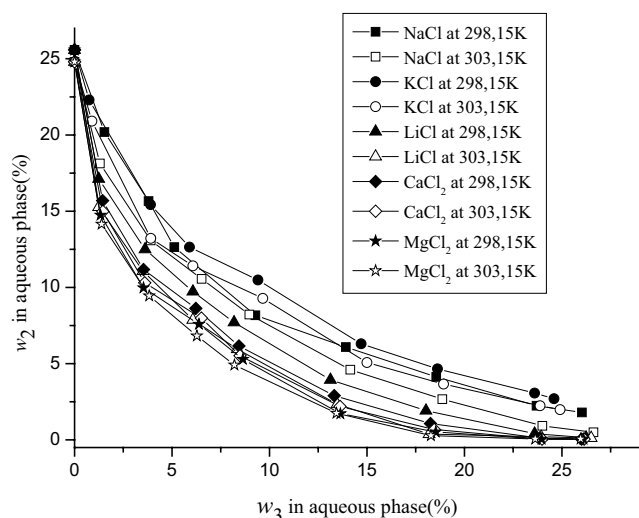


Fig. 3. Comparison of salting-out efficiency for water + 2-butanone with different salts at 298.15 and 303.15 K.

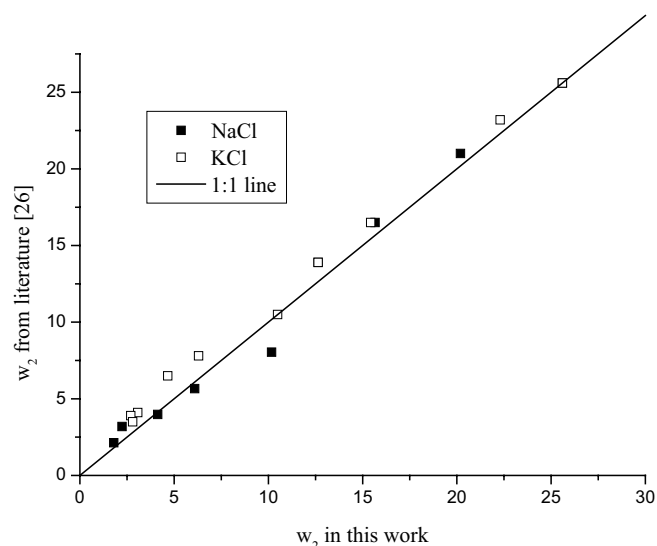


Fig. 4. Comparison of the measured LLE data for 2-butanone in aqueous phase and data reported in the literature [26].

where w_1 and w_2 represent the mass fraction solubilities of water in the alcohol-rich phase and of the alcohol in the water-rich phase, respectively, in the presence of the salt. Note that x_3 is the mass fraction of the salt and k_{s1} is the Setschenow parameter:

The Setschenow plots (i.e., $\ln\left\{\frac{w_2^0}{w_2/(1-w_3)}\right\}$ vs. w_3) are

given in Figs. 5–9 for the systems under investigation and the calculated values of the Setschenow coefficient (k_{s1}) are reported in Table 3. Determination coefficients (R^2) for all correlations were approximately the unity and the linearity of the plots indicated the degree of thermodynamic consistency of the measured LLE values for tested ternary systems. The comparison of the effect of cation and

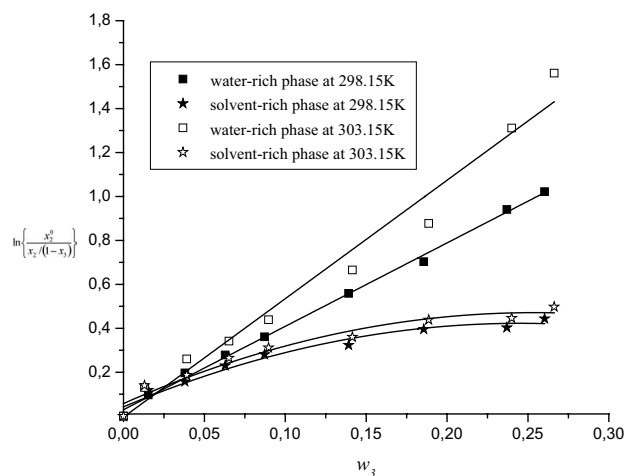


Fig. 5. Correlation of the liquid-liquid equilibrium data with Setschenow equation for the ternary system water + butanone + NaCl at 298.15 and 303.15 K.

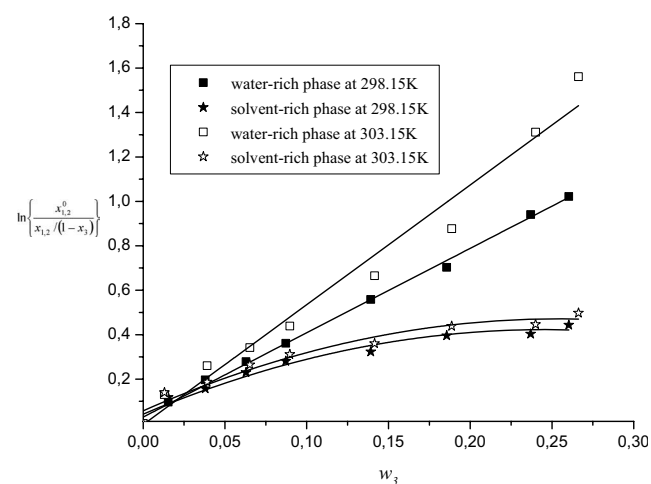


Fig. 6. Correlation of the liquid-liquid equilibrium data with Setschenow equation for ternary system water + butanone + KCl at 298.15 and 303.15 K.

temperature on the values of the Setschenow parameter (k_{s1}) in the aqueous phase is plotted in Fig. 10. According to this Fig. 10, the highest values of k_{s1} are achieved when $MgCl_2$, $CaCl_2$, and $LiCl$ are used as a salt (i.e., indicate higher salting-out effect) for both temperatures. Additionally, the influence of temperature on k_{s1} values is negligible. On the other hand, the values of k_{s1} were calculated from the experimental data reported by Li et al. [18] for NaCl and KCl at 298.15 K and they were compared with results obtained in this study, see Table 3. The differences in k_{s1} (NaCl and KCl) were not significant indicating a high agreement between both sets of LLE experimental data.

4. Modeling of the LLE data

In this paper, two modeling approaches were used for the prediction of the measured data, modified extended

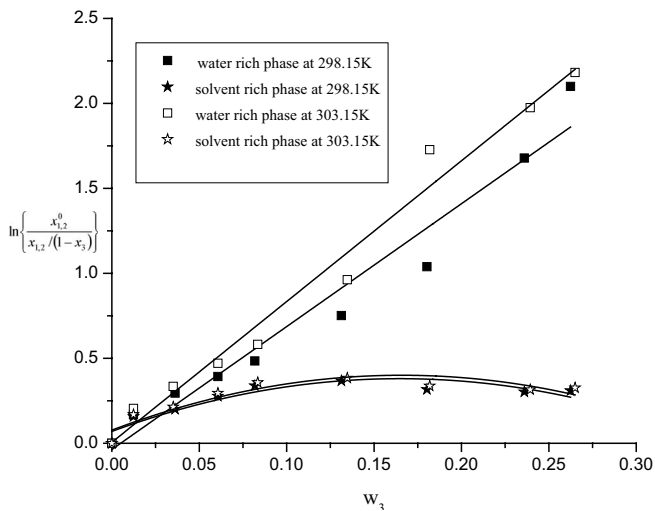


Fig. 7. Correlation of the liquid-liquid equilibrium data with Setschenow equation for ternary system water + butanone + LiCl at 298.15 and 303.15 K.

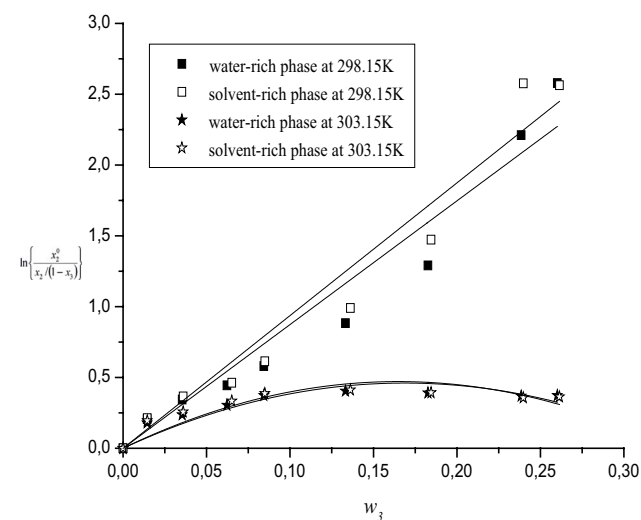


Fig. 8. Correlation of the liquid-liquid equilibrium data with Setschenow equation for ternary system water + butanone + CaCl₂ at 298.15 and 303.15 K.

UNIQUAC and the ANN-based approach. The modified extended-UNIQUAC model was used in a semi-predictive approach in order to quantitatively describe the experimental LLE data. That is, ion-specific binary-interaction parameters between ions-solvent and ions-ions were applied are universally valid, irrespective of the kind of salt. In contrast to that, the ANN model was applied to predict the phase behavior without using the binary interaction parameters.

4.1. Modified extended UNIQUAC

In order to correlate the LLE data for the system water + 2-butanone + salt, a modified extended UNIQUAC model

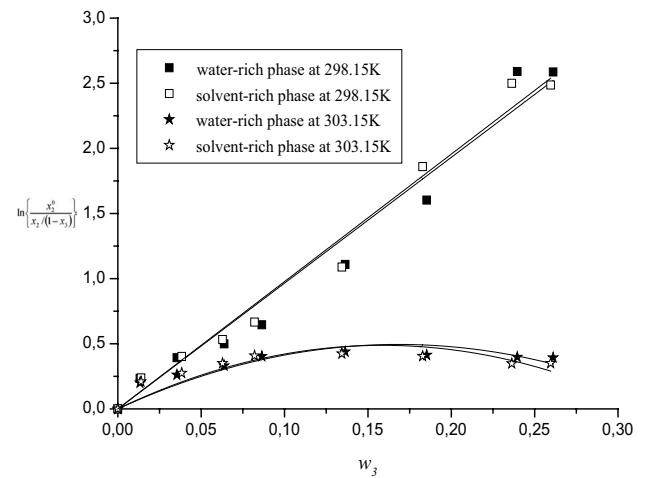


Fig. 9. Correlation of the liquid-liquid equilibrium data with Setschenow equation for ternary system water + butanone + MgCl₂ at 298.15 and 303.15 K.

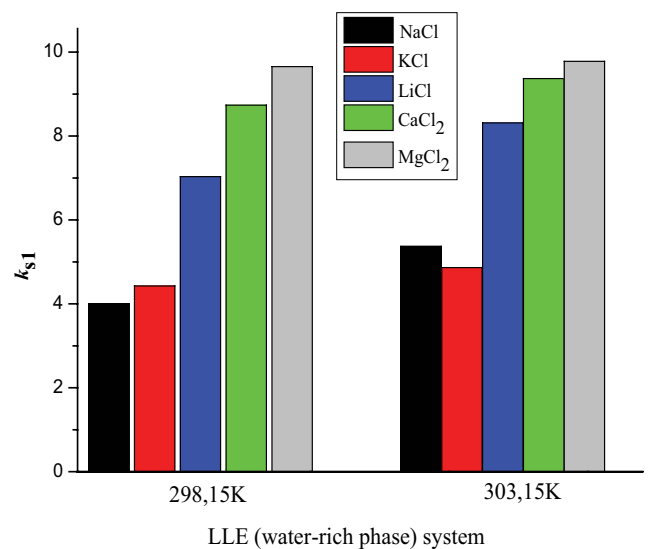


Fig. 10. Comparison of Setschenow coefficient (k_{S1}) for water/salts/2-butanone mixtures, in the LLE water-rich phase at 298.15 and 303.15 K under 101.1 kPa.

was employed. This model is a local composition equation derived by adding a Debye-Hückel term [22] and the Born term [23] to the original UNIQUAC [21]. The activity coefficients of ions and solvents can be separated into two terms arising from the relevant contributions [35].

$$\ln \gamma_i^* = \ln \gamma_i^{*UNIQUAC} + \ln \gamma_i^{*PDH} + \ln \gamma_i^{*Born} \quad (4)$$

$$\ln \gamma_j = \ln \gamma_j^{UNIQUAC} + \ln \gamma_j^{PDH} + \ln \gamma_j^{Born} \quad (5)$$

where j and i refer to solvent and ions, respectively, and the symbol * indicates that the activity coefficients of the ions are defined using an asymmetric convention. The activity coefficient of solvents and the asymmetrical activity

Table 3
Calculated values of Setschenow parameter (k_{s1}) and determination coefficients (R^2) for the mixtures water (1) + butanone (2) + salt

T (K)	LLE system	Water-rich phase k_{s1} (R^2)	Butanone-rich phase k_{s1} , k_{s2} (R^2)
298.15	Water + NaCl + butanone	3.9988 (0.9933)	3.8374, -8.6838 (0.9808)
		3.74 (0.9983) ^a	2.9535, -5.7500 (0.9841) ^a
	Water + KCl + butanone	4.4247 (0.9968)	2.932, -3.639 (0.9934)
		3.0455 (0.9933) ^a	1.8334, -3.5240 (0.9958) ^a
	Water + LiCl + butanone	7.0325 (0.9800)	4.9018, -14.9504 (0.9536)
	Water + CaCl ₂ + butanone	8.7358 (0.9752)	5.4591, -16.1792 (0.9603)
	Water + MgCl ₂ + butanone	9.6543 (0.9862)	5.8826, -17.48 (0.9654)
303.15	Water + NaCl + butanone	5.3688 (0.9895)	4.1593, -9.1526 (0.9807)
	Water + KCl + butanone	4.8624 (0.9962)	3.2248, -4.3863 (0.9930)
	Water + LiCl + butanone	8.3128 (0.9917)	5.1344, -15.5420 (0.9510)
	Water + CaCl ₂ + butanone	9.3702 (0.9783)	5.7184, -17.3562 (0.9580)
	Water + MgCl ₂ + butanone	9.7783 (0.9918)	6.1530, -19.3950 (0.9540)

^aExperimental data obtained from Li et al. [26].

coefficient of ions can be derived by the straight forward differentiation of the excess Gibbs function. For the case of the solvents, we have that:

$$\ln \gamma_j^{PDH} = \frac{2A_x I_x^{3/2}}{1 + \rho I_x^{1/2}} + \frac{4A_x I_x}{\rho} \ln(1 + \rho I_x^{1/2}) \left[\frac{1}{2M_s} \sum_{\text{solvent}} \frac{(M_j - M_s)}{x_{\text{solvent}}} - \frac{1}{2d_s} \frac{\partial d_s}{\partial x_j} + \frac{3}{2D_x} \frac{\partial D_s}{\partial x_j} \right] \quad (6)$$

where the mole fraction ionic strength I_x is defined as follows:

$$I_x = \frac{1}{2} \sum z_i^2 x_i \quad (7)$$

where A_x is the Debye–Hückel parameter on a mole fraction basis that is given by:

$$A_x = \frac{1}{3} \left(\frac{1,000}{M_s} \right)^{1/2} \left(\frac{2\pi N_A d_s}{1,000} \right)^{1/2} \left(\frac{e^2}{4\pi\epsilon_0 D_s kT} \right)^{3/2} \quad (8)$$

where e is the electronic charge, N_A is Avogadro’s number, ϵ_0 is the vacuum permittivity, and k is the Boltzmann’s constant. On the other hand, M_s , d_s , and D_s are the molar mass, density, and dielectric constant of the mixed solvent, respectively. These parameters are defined as follows:

$$M_s = \sum_j M_j x'_j \quad (9)$$

$$d_s = \frac{M_s}{\sum_j (x'_j M_j / d_j)} \quad (10)$$

$$D_s = \sum_j D_j w'_j \quad (11)$$

where w'_j and x'_j are the salt-free mass fraction and mole fraction of solvent j , respectively.

The Born term is calculated as:

$$\ln \gamma_j^{\text{Born}} = -\frac{e^2}{2kT} \frac{1}{4\pi\epsilon_0 D_s^2} \frac{\partial D_s}{\partial x_j} \sum_i \frac{x_i z_i^2}{\sigma_i} \quad (12)$$

where σ is the Born radius of the ions. Finally, the contribution corresponding to UNIQUAC model is given by:

$$\ln \gamma_j^{\text{UNIQUAC}} = 1 - \frac{\phi_j}{x_j} + \ln \left(\frac{\phi_j}{x_j} \right) - 5q_j \left[\ln \left(\frac{\phi_j}{\theta_j} \right) + 1 - \frac{\phi_j}{\theta_j} \right] + q_j \left[1 - \ln \left(\sum_k \theta_k \psi_{kj} \right) - \sum_k \frac{\theta_k \psi_{jk}}{\sum_l \theta_l \psi_{lk}} \right] \quad (13)$$

The parameters f and θ are the surface and volume fractions, respectively, and they depend on the volume and surface area parameters r and q :

$$\phi_j = \frac{x_j r_j}{\sum_j x_j r_j} \quad (14)$$

$$\theta_j = \frac{x_j q_j}{\sum_j x_j q_j} \quad (15)$$

The parameter ψ_{kj} is defined in terms of the binary energy interaction parameter (a_{kl}):

$$\psi_{kl} = \exp \left(-\frac{u_{kl} - u_{ll}}{T} \right) = \exp \left(-\frac{a_{kl}}{T} \right) \quad (16)$$

where $a_{kl} \neq a_{lk}$ and $a_{kk} = a_{ll} = 0$. For the case of the ions, the model equations are given by:

$$\ln \gamma_j^{\text{PDH}} = -\frac{2A_x z_j^2}{\rho} \ln(1 + \rho I_x^{1/2}) - \frac{2A_x I_x^{1/2} z_j^2}{1 + \rho I_x^{1/2}} \quad (17)$$

$$\ln \gamma_j^{*Bom} = -\frac{e^2}{2kT} \left(\frac{1}{4\pi\epsilon_0 D_s} - \frac{1}{4\pi\epsilon_0 D_w} \right) z_i^2 \quad (18)$$

$$\ln \gamma_j^{*UNIQUAC} = \ln \gamma_i^{UNIQUAC} - \ln \gamma_i^{\infty UNIQUAC} \quad (19)$$

$$\ln \gamma_j^{\infty UNIQUAC} = \ln \left(\frac{r_i}{r_w} \right) + 1 - \frac{r_i}{r_w} - 5q_i \left[\ln \left(\frac{r_i q_{iw}}{r_w q_i} \right) + 1 - \frac{r_i q_w}{r_w q_i} \right] + q_i [1 - \ln \Psi_{wi} - \Psi_{iw}] \quad (20)$$

Regarding the model parameters for the UNIQUAC terms, the molecular volume (r_i) and surface area parameters (q_i) for water, butanone, Na^+ , K^+ , and Li^+ cations, and the Cl^- anion has been taken from the Aspen-Hysys database.

On the other hand, the experimental tie lines data of ternary system water + butanone + salt were used to estimate the binary interactions parameters a_{ij} of the modified Extended UNIQUAC. The water-butanone, water-ion, butanone-ion, and ion-ion interaction parameters were fitted to the experimental tie lines at 298.15 and 303.15 K using an iterative computer program based on the isoactivity criteria along with the equations derived from the summation rules and overall mass balances. Thus, the 12 interactions parameters have been determined by minimizing the differences between the experimental and calculated mass fractions for each of the components overall tie lines using the next objective function [36]:

$$OF = \sum_{j=1}^{M_t} \sum_{i=1}^{N_c} \left[\left(w_{ij}^{\text{cal}} - w_{ij}^{\text{exp}} \right)_I^2 + \left(w_{ij}^{\text{cal}} - w_{ij}^{\text{exp}} \right)_{II}^2 \right] \quad (21)$$

where M_t and N_c are the number of tie lines and the number of components, w^{exp} and w^{cal} indicate the experimental and calculated mass fractions, subscripts I , II , i , and j represent the phases at equilibrium, the constituents, and the tie lines, respectively. The objective function was minimized with Monkey–Krill Herd Hybrid (MAKHA) [37]. For more information, numerical implementation can be found in previous works [24,36]. For each set of variable (i.e., binary interaction parameters) proposed by MAKHA, the Newton–Raphson method was used for the identification of the tie-lines with the corresponding thermodynamic model. In our current work, all parameter settings of MAKHA optimization solver can be found in Khalil et al. [37].

The accuracy of data correlation was quantified via the root mean square deviation (RMSD) of component mass fractions in both phases and this metric was defined as:

$$\text{RMSD} = \left(\frac{\sum_{j=1}^{M_t} \sum_{i=1}^{N_c} \left(\left(w_{ij}^{\text{exp}} - w_{ij}^{\text{calc}} \right)_I^2 + \left(w_{ij}^{\text{exp}} - w_{ij}^{\text{calc}} \right)_{II}^2 \right)^{1/2}}{2M_t N_c} \right) \quad (22)$$

The values of adjusted interaction parameters of the modified extended UNIQUAC model and RMSD values for the electrolyte systems are shown in Table 4. Modeling errors ranged from 10.88% to 36.22% where the ternary

system with salt LiCl showed the highest fit with this thermodynamic model. Note that the modeling errors increased with temperature indicating that the three ternary systems exhibited a more complex phase diagram to be correlated and simulated.

4.2. ANN model

An ANN was also considered to predict the phase behavior of the studied electrolyte mixtures. ANN model is a robust black-box approach capable of establishing non-linear relationships between the inputs and outputs variables of a system under study [38]. The multilayer perceptron (MLP) was utilized as data processing unit in a feedforward ANN model. This model included three types of layers: input, hidden, and output. The number of neurons in input and output layers equals to the corresponding parameters of input and output data sets, respectively. Furthermore, the number of hidden layers and their neurons were obtained by a trial and error method through constructing different networks. Synaptic weights and biases are the parameters of the ANN model. A training algorithm should be applied to adjust these parameters by using the modeling error as a performance metric [39]. Therefore, the ANN model should be trained to reach a minimum value in the squared weights and errors over several iterations [40].

To improve the accuracy of LLE data fitting properties, we used some additional LLE data sets of salts/water/2-butanone systems from some studies in the literature [17,18,20]. In the ANN technique, all LLE data are divided randomly into three subsets: training, validation, and testing sets. In this study, the experimental LLE data (159 tie lines) were randomly divided into train and test sets. 75% of all data points (119 tie lines) were randomly chosen for the train set to construct the MLP neural network. The remaining 25% of data points (40 tie lines) were employed for the test set, which was used to validate the ANN model. Temperature (T), composition of three components (Z_1 , Z_2 , and Z_3), molecular weight of salt (M_w), melting point of salt (M_p), and the refractive index of salt (η) were considered as input parameters. These input data were used to develop the ANN model. Solute distribution coefficient (β) was considered as an output parameter for ANN modeling:

$$\beta = \frac{x_1^{II}}{x_1^I} \quad (23)$$

Where x_1^I and x_1^{II} are the composition of water in 2-butanone-rich phase and water-rich phases, respectively. It should be mentioned that the composition of three components of both 2-butanone-rich and water-rich liquid phases can be obtained from β based on the assumption that the composition of salt in 2-butanone-rich phase is zero. The parameters range of the input and output data are provided in Table 5.

Moreover, input and output data were normalized and scaled between 0 and 1 prior to the ANN modeling. Preliminary calculations were performed to identify the

Table 4

Binary interaction parameters and RMSD values of the modified extended UNIQUAC model for LLE correlation of water + butanone + salt

298.15 K		303.15 K		
Water (1) + butanone (2) + Na ⁺ (3) + Cl ⁻ (4)				
<i>i-j</i>	$a_{ij}(k)$	$a_{ji}(k)$	$a_{ij}(k)$	$a_{ji}(k)$
1-2	268.24	344.05	279.78	315.75
1-3	-1,243.85	-1,045.66	-1,296.23	-1,108.52
1-4	-1,275.21	-122.47	-1,268.92	-137.82
2-4	1,308.92	1,465.54	1,289.88	1,438.15
3-4	-354.81	-406.92	-329.73	387.66
RMSD(%)		0.7562		0.7806
Water (1) + butanone (2) + K ⁺ (3) + Cl ⁻ (4)				
<i>i-j</i>	$a_{ij}(k)$	$a_{ji}(k)$	$a_{ij}(k)$	$a_{ji}(k)$
1-2	124.62	228.34	142.45	312.66
1-3	-1,358.60	-678.05	-1,472.68	-651.47
1-4	1,947.58	1,892.33	1,982.05	1,835.72
2-4	-1,734.25	1,923.58	-1,751.92	1,950.24
3-4	-1,248.49	-1,085.63	-1,182.22	-1,127.89
RMSD(%)		0.5657		0.5893
Water (1) + butanone(2) + Li ⁺ (3) + Cl ⁻ (4)				
<i>i-j</i>	$a_{ij}(k)$	$a_{ji}(k)$	$a_{ij}(k)$	$a_{ji}(k)$
1-2	48.64	345.82	77.58	505.86
1-3	920.33	-229.56	-1,971.25	-722.3
1-4	1,746.24	1,385.24	-1,758.33	1,295.21
2-4	1,499.82	1,846.77	1,657.08	1,784.66
3-4	-1,623.05	-353.09	-1,568.79	-389.45
RMSD(%)		0.5258		0.5428
Water (1) + butanone(2) + Ca ²⁺ (3) + Cl ⁻ (4)				
<i>i-j</i>	$a_{ij}(k)$	$a_{ji}(k)$	$a_{ij}(k)$	$a_{ji}(k)$
1-2	151.44	412.32	138.66	432.18
1-3	853.74	178.05	862.05	169.51
1-4	1,823.92	1,025.71	1,833.55	1,028.65
2-4	1,602.15	1,362.18	1,598.27	1,368.57
3-4	553.92	973.26	568.95	982.04
RMSD(%)		0.4586		0.5215
Water (1) + butanone(2) + Mg ²⁺ (3) + Cl ⁻ (4)				
<i>i-j</i>	$a_{ij}(k)$	$a_{ji}(k)$	$a_{ij}(k)$	$a_{ji}(k)$
1-2	232.80	522.93	238.92	488.53
1-3	1,025.88	269.62	1,108.04	258.62
1-4	1,982.08	1,139.46	1,953.76	1,183.28
2-4	1,801.05	1,418.22	1,829.58	1,456.37
3-4	-186.60	-948.17	-28.37	-1,052.55
RMSD(%)		0.3561		0.3872

best architecture of the ANN model for modeling the phase equilibrium data.

Fig. 11 shows the optimum structure of the ANN model used in this study. It included one hidden layer with 10 neurons. Table 6 provides the synaptic weights and bias obtained for the ANN model. Results of the ANN model for the prediction of β are shown in Fig. 12. The predicted β values were near 45° line for all data points of train and

test sets indicating that the ANN model predicted accurate values of β for studied ternary systems. Moreover, the RMSD for the prediction of LLE of ternary systems was 0.0016 for the ANN model. Modeling errors ranged from 0.022 to 0.258%, which were lower than those obtained with the activity coefficient model. Finally, the efficiency of both approaches has been compared, in terms of the residuals (e_i) plots for all tie lines (Fig. 13). This Fig. 13 shows that

Table 5
Parameters range and type of studied data points

Type of data	Property	Minimum	Maximum
Inputs	Temperature (T , K)	298.15	303.15
	Mass fraction of water (Z_1)	0.02	0.88
	Mass fraction of 2-butanone (Z_2)	0.0003	0.98
	Mass fraction of salt (Z_3)	0	0.27
	Molecular weight of salt (M_w , g/mol)	42.40	111
	Melting point of salt (M_p , K)	878	1,075
	Refractive index of salt (η)	1.4904	1.6800
Output	β	2.9	22.85

Table 6
Synaptic weights and bias values of the MLP-ANN model for LLE correlation of water/salts/2-butanone

Neuron	Hidden layer							Output layer		
	Temperature, K	Z_1	Z_2	Z_3	M_w of salt	M_p of salt	η of salt	Bias	Weight	Bias
1	256.1174	-38.5271	22.1270	-18.5127	27.5536	1.2568	4.259	-0.0347	-144.562	10.5648
2	98.8065	-7.1864	2.4344	3.1093	8.1717	21.5163	3.865	3.2124	-126.305	
3	-88.3521	-11.8674	-1.5863	-2.8528	-15.7602	38.4371	21.6393	-5.3772	55.2541	
4	-48.1816	12.056	17.1432	-0.2265	-19.8301	4.1571	-12.615	0.1235	32.6421	
5	93.3759	-48.8551	-18.1253	-28.9161	-25.608	-15.4589	-12.1683	-0.2182	40.7107	
6	-111.713	-3.1045	9.9348	13.3964	9.1509	27.1312	4.2063	-6.3174	95.229	
7	149.3659	-14.3853	-21.6141	0.4475	2.6827	-12.0551	-1.831	-9.7875	-145.237	
8	-65.2057	-8.4768	32.5085	9.1264	23.5594	-8.1219	-3.0618	0.2504	-8.4674	
9	-239.634	2.1681	7.6541	0.0289	2.8560	58.6167	-2.1281	0.3462	120.062	
10	-78.9771	8.3896	-29.438	-3.4401	-3.4072	43.0124	0.2609	7.3991	62.6814	

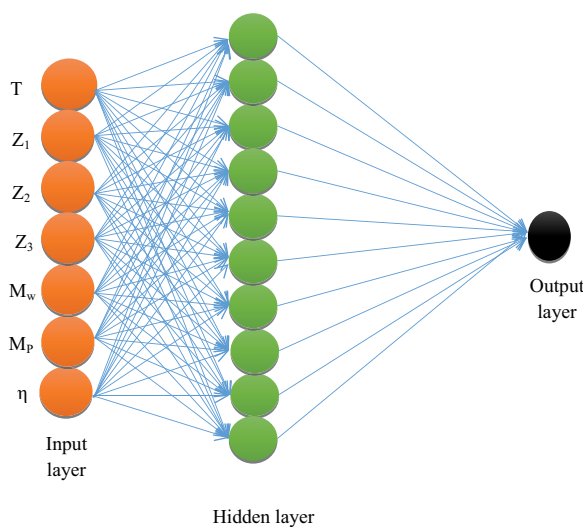


Fig. 11. Architecture of ANN model used for the phase equilibrium modeling of mixtures water + butanone + salt.

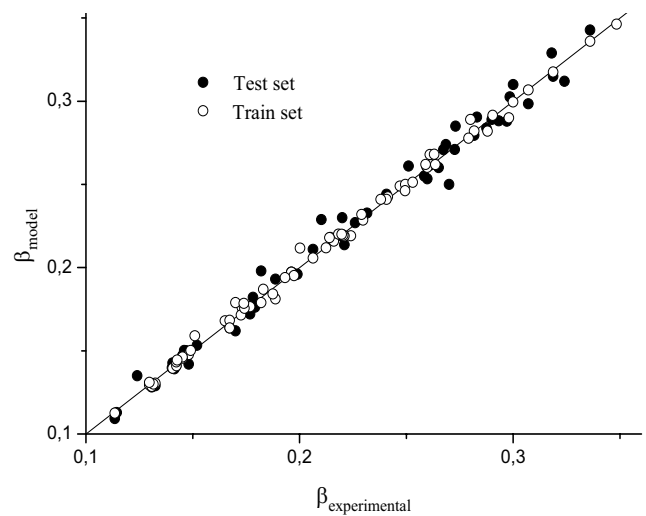


Fig. 12. Cross-plot of predicted solute distribution coefficient by MLP-ANN model vs. experimental data.

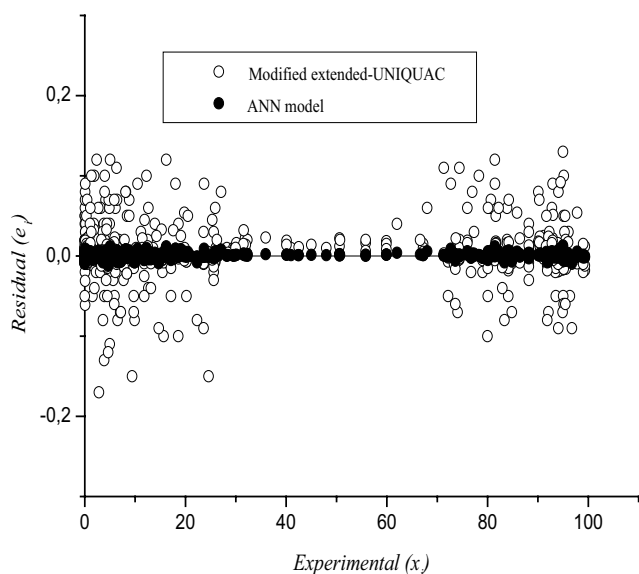


Fig. 13. Residuals (e_i) plots of all LLE compositions of water/salts/2-butanone mixtures modeled with extended-UNIQUAC and MLP-ANN.

the MLP-ANN model was the best option for LLE data fitting of water/salts/2-butanone ternary systems compared to the modified extended-UNIQUAC model.

5. Conclusion

The LLE data of the binary 2-butanone/water and of ternary 2-butanone/water/salt systems have been measured at 298.15 and 303.15 K under 101.1 kPa. The dissolved salts studied in this work were KCl, NaCl, LiCl, CaCl_2 , and MgCl_2 . For the binary mixture 2-butanone / water, the LLE solubility data of the mutual solubility were found in a good agreement compared to those reported data. The effect of different types of salt on the LLE data of the water/2-butanone mixture was studied through the phase diagram, and Gibbs free energy of hydration of ions, and it was found that the addition of the dissolved salts decreases the solubility of 2-butanone in the aqueous phase (i.e., salting-out) and the phase forming ability of the dissolved salt is related to the cations, and Gibbs free energy of hydration of cations. Furthermore, the influence of the cations on the salting-out efficiency decreased in the following order: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+$ at two temperatures. The linearity of the Setschenow equation was used to study the salting-out effect of salts, and it has confirmed the salting-out effect order of different salts. Moreover, the effect of the temperature on the phase diagrams was discussed, and it was found that the temperature has a small effect on the LLE data.

On the other hand, the experimental data have been correlated using an ANN and a modified extended-UNIQUAC model. Both models correlated the LLE data but the ANN outperformed the modified extended-UNIQUAC model obtaining low modeling errors.

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