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Model for the partition of metal ions in aqueous two-phase systems

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Abstract

A model for the partition of metal ions in aqueous two-phase systems (ATPS) has been developed. The partition coefficient of a metal ion D_M, is a function of several variables of the ion (size, charge and electronegativity), characteristics of the ATPS such as type of salt, salt concentration and PEG concentration and additional inorganic salt present in the ATPS. The model has been tested for complex anions of BiX_4^- ($BiCl_4^-$, $BiBr_4^-$ and BiI_4^-) and cations from groups I and II (Na^+, Cs^+, Ca^{2+}, Sr^{2+} and Ba^{2+}) giving a good correlation in both systems. It was found that for these systems partition coefficient increases with ion size and the variables Y which is a characteristic of the ATPS and Z which is a characteristic of the additional salt present in the system. The partition coefficient of BiX_4^- increases with the variable X which is a characteristic of the electrical interactions of the metal ion. The cations from groups II and I exhibit the opposite behavior, which is attributable to the ion charge. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Traditionally the extraction and recovery of metal ions from aqueous solutions has been carried out by extraction of solvents mixed with water and an organic solvent that form two non-miscible phases. In recent years aqueous two-phase systems (ATPS) have started to be used for the same purpose, particularly those formed by polyethylene glycol–water–inorganic salt. One of the main advantages of these systems is that the partitioning occurs between two non-miscible aqueous phases, which has evident environmental benefits [1].

ATPS composed of polyethylene glycol (PEG) as the polymer and inorganic salts have a great potential to separate metallic ions from aqueous solutions. Most published work focuses on the experimental determination of partition coefficients for metal ions [2,3]. In these systems other components are also added as extractants such as acids, bases or other inorganic ions.

It appears that the use of ATPS for separating metal ions from aqueous solutions has great potential due to their durability, non-flammability and low cost. The phases can be easily separated by centrifugation or sedimentation in mixer-settlers and operation is possible in a wide range of concentrations, pH values and temperatures.

Most of the work on metal ion separation has been focused on experimental measurement of the partition coefficient under different conditions. Different types of acidic or basic extractors have been extensively studied for the extraction of elements such as Am^{3+}, Pu^{4+}, Th^{4+}, Bk^{3+}, UO_2^{2+}, Eu^{3+} [2–5].

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The partition coefficients of transition elements and metals of groups I to V (such as Fe^{3+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, In^{3+}, Zn^{2+}, Sb^{3+}, In^{3+}, Mo^{5+}, Bi^{3+}, Ga^{3+}, Pb^{2+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) have been extensively studied using different PEG concentrations, inorganic salts, acids or base [6–8].

Model

There are a great number of variables that affect metal ion partitioning in ATPS, such as type and concentration of salt, concentration and polymer molecular weight, temperature, metal ion characteristics, concentration and type of extractors, acids, bases or inorganic salts added to the system.

As most of the work on the determination of metal ion partition coefficients in ATPS has been done with polyethylene glycol with an average molecular weight of 2000 and at 20°C, the model has been developed using these systems.

In order to develop the model the following variables, that have been shown to have an important effect on ion partitioning, have been considered.

- Those related to the metal ion: which include r, ion size; q, ion charge; and E, ion electronegativity.
- Those related to the ATPS system: which include C_{PO}, initial concentration of PEG 2000 in ATPS; C_{SO}, initial concentration of phase forming inorganic salt and type of salt.
- Those related to the salt added to the ATPS: which include C_{AO}, additional salt concentration forming ATPS and type of added salt.

It is necessary to consider the type of salt used in the formation of the ATPS, as it directly influences the equilibrium of the system (as shown in Fig. 1) and therefore the metal ion partition coefficient. To develop a mathematical model it is necessary to define in an explicit way the different types of phase forming salts used in the ATPS. For this purpose two variables have been considered. They are, S which is the water solubility of the salt at working tempera-

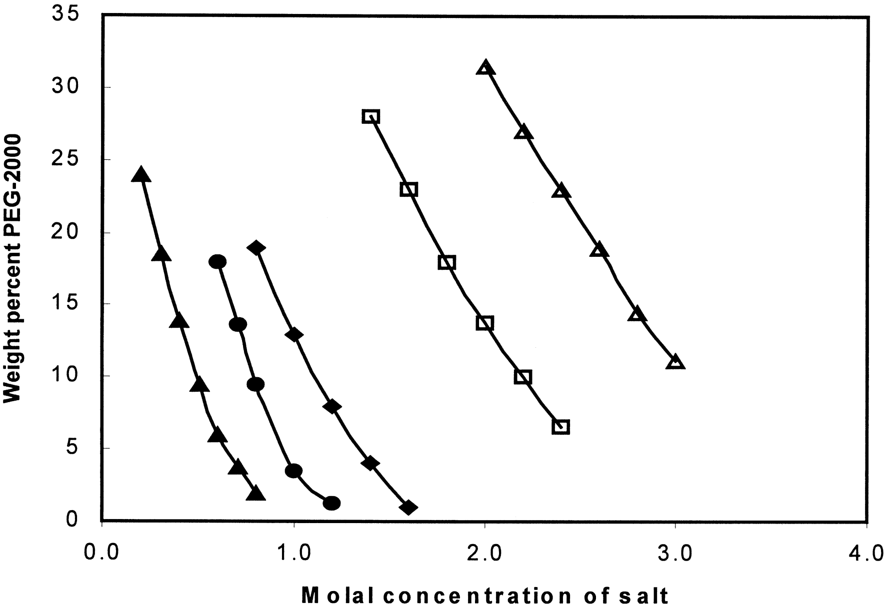

Fig. 1. Phase diagrams for PEG-2000/inorganic salt ATPS for five different salts: (▲) K_3PO_4; (●) K_2CO_3; (♦) $(NH_4)_2SO_4$; (□) NaOH; and (△) KOH. Data from Ref. [12].

ture (salt mass/water mass), and R which is the minimum distance of the ATPS from the binodal curve.

Referring to Fig. 2 and considering the binodal curves for different salts that form ATPS with PEG 2000 (Fig. 1), a nodal point is defined (N in Fig. 2) as the point on the binodal curve that has the least distance from the origin. This minimum distance, R, is a characteristic variable of each salt in a particular ATPS and is given by:

$$R = \sqrt{C_{\mathrm{Se}}^2 + C_{\mathrm{Pe}}^2} \tag{1}$$

where R is minimum equilibrium distance (origin to the nodal point, N in Fig. 2); C_{Se} is salt concentration at the nodal point of the binodal curve; C_{Pe} is polymer concentration at the nodal point of the binodal curve

In Fig. 1 it can be appreciated that R values increase from K_3PO_4 to KOH.

With the purpose of isolating this variable from the units used, a dimensionless variable, R^* which represents the value of R of any system with respect to R of the system with KOH, was defined as follows

$$R^* = \frac{R}{R_{\mathrm{KOH}}} \tag{2}$$

Table 1 gives the values of R^* for the salts in Fig. 1.

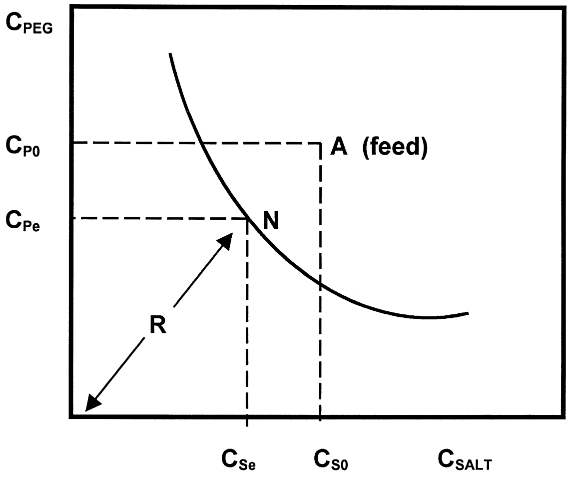

Fig. 2. Definition of the characteristic parameter R of a salt in ATPS.

Table 1
Dimensionless distance, R^*, for different salts

	Salt				
	K_3PO_4	K_2CO_3	$(NH_4)_2SO_4$	NaOH	KOH
R^*	0.250	0.375	0.479	0.666	1.000

With the purpose of isolating the other variables used in the model from the specific units, dimensionless variables were defined related to the metal ion, the ATPS and the added salt.

For the metal ion, r represents the ion size and E the ion electronegativity. The maximum values given in Eqs. (3) and (4) are those obtained for the range of ions studied where X represents electrical interactions of the metal ion and q is the charge of the ion

$$r^* = \frac{r}{r_{\mathrm{max}}} \tag{3}$$

$$E^* = \frac{E}{E_{\mathrm{max}}} \tag{4}$$

$$X = qE^* \tag{5}$$

For the ATPS, C_{p}^* is the dimensionless concentration of PEG and C_{s}^* the dimensionless concentration of salt. They have been defined in Fig. 2 and Eqs. (6) and (7).

$$C_{\mathrm{p}}^* = \frac{C_{\mathrm{PO}}}{C_{\mathrm{Pe}}} \tag{6}$$

$$C_{\mathrm{s}}^* = \frac{C_{\mathrm{SO}}}{C_{\mathrm{Se}}} \tag{7}$$

Y represents a characteristic of the ATPS in the absence of added salt and is given by

$$Y = \frac{R^*S}{C_{\mathrm{p}}^* C_{\mathrm{s}}^*} \tag{8}$$

where S is the solubility of the phase forming salt in water at the system temperature. The other parameters have already been defined (Eqs. (1), (2), (6) and (7) and Fig. 2). C_{A}^* is the dimensionless concentration of salt added to the system:

$$C_{\mathrm{A}}^* = \frac{C_{\mathrm{AO}}}{C_{\mathrm{SO}}} \tag{9}$$

and Z is given by Eq. (10) where S_A is the solubility of the added salt

$$Z = S_A C_A^* \tag{10}$$

Based on all the dimensionless variables defined above and after a careful analysis of the partition behavior given in the literature [9–13] the following equation has been proposed to describe the metal ion partition coefficient, D_M:

$$D_M = D_0 + \frac{a_1 (X)^{a_2} (r^*)^{a_3}}{1 + b_1 \exp(-b_2 Y - b_3 Z)} \tag{11}$$

where D_0 is the metal ion partition coefficient in the absence of additional salt. The variables X and r^* take into account the electrostatic interaction effect and the size of the metal ion (Eqs. (3) and (5)).

The variable Y is a characteristic of each ATPS (Eq. (8)). It describes, with R^* and S, the effect of the type of salt used in the ATPS. The feed is characterized by C_{SO} and C_{PO} (point A in Fig. 2), and gives a specific tie line length which influences the partition coefficient. In general this has not been described before for metal ion partitioning, hence the variables C_s^* and C_p^* are included in the variable Y (Eq. (8)).

The variable Z shows the influence of the addition of additional salt to the original ATPS and its effect on the metal ion partition coefficient (Eq. (10)).

Results

The model was used to describe the partition coefficients of $BiCl_4^-$, $BiBr_4^-$ and BiI_4^- and cations from groups I and II (Na^+, Cs^+, Ca^{2+}, Sr^{2+} and Ba^{2+}) in ATPS.

The experimental information for bismuth, shown in Table 2, was obtained from Rogers et al. [10] working at 25°C in an ATPS formed by PEG-2000 and ammonium sulphate (both prepared with 2 M sulfuric acid). To the initial ammonium sulphate solution different concentrations of NH_4Cl, NH_4Br and NH_4I were added, supplying the chlorine, bromine and iodine to form $BiCl_4^-$, $BiBr_4^-$ and BiI_4^- ions being studied. The bismuth was added to the ATPS from traces of $Bi(NO_3)\cdot nH_2O$ diluted in concentrated nitric acid.

Table 2
Partition coefficients of BiX_4 (X = Cl, Br or I) in ATPS formed by PEG-2000–(NH_4) SO_4–H_2O at 25°C, in the presence of H_2SO_4 and with addition of different concentrations of NH_4X according to Rogers et al. [10]

Conc. NH_4X (mol/l)	X = Cl	X = Br	X = I
0.00	0.07	0.07	0.07
0.01	0.06	0.08	0.20
0.05	0.09	0.70	260.00
0.10	0.15	5.00	270.00
0.50	1.20	49.00	270.00
1.00	2.10	40.00	290.00

In Table 2 it can be observed that for low concentrations of NH_4X the partition coefficients are small for all species of X. At concentrations of 0.05 mol/l and above an increase in the partition coefficients is seen particularly for BiI_4^- and $BiBr_4^-$. At concentrations of NH_4X above 0.05 mol/l there is little change in the partition coefficient of BiI_4^-.

The data given in Table 2 were obtained at constant PEG-2000 and ammonium sulphate concentrations, therefore C_{SO}, C_{PO}, R and S in Eq. (11) are constant and the variable Y is constant as defined in Eq. (8). Eq. (11) can be simplified to:

$$D_M = D_0 + \frac{a_1 (X)^{a_2} (r^*)^{a_3}}{1 + b_1 \exp(-b_3 Z)} \tag{12}$$

In this equation D_0 represents the metal ion partition coefficient in the ATPS without NH_4X. The values of parameters a_i and b_i from Eq. (12) were determined by the Marquardt optimized method in which the objective function, f_{obj}, is given by Eq. (13).

$$\mathrm{Min}\{f_{obj}\} = \mathrm{Min}\left\{\sum_{i=1}^{n} [D_M - D_{Mec}]^2 / D_M\right\} \tag{13}$$

D_M represents the experimental values of the partition coefficient; D_{Mec} the coefficient values obtained from Eq. (12) and n the experimental data number. Table 3 shows the parameter values found using Eq. (13). Fig. 3 shows the experimental and the model values of the partition coefficient as a function of the salt NH_4X (with X = Cl, Br or I) added to the original ATPS.

Table 3
Model parameter values for partition coefficients of $BiCl_4^-$, $BiBr_4^-$ and BiI_4^- in ATPS formed by PEG-2000–$(NH_4)_2SO_4$–H_2O, in the presence of H_2SO_4

a_1	a_2	a_3	b_1	b_3
9.374E+11	4.666E+01	5.986E+01	4.502E+18	5.146E02

Using the parameter values from Table 3 the partition coefficients of BiX_4^- were calculated. The partition coefficient was found to increase with ion size and with variables *Z* and *Y* of the model. Fig. 3 shows a good agreement between the model values and the experimental points especially at the lowest and highest NH_4X concentrations.

It can be observed that given the shape of Eq. (11) the model works for systems in which the partition coefficient shows a strong variation with the concentration of NH_4X. With the purpose of testing this model in systems without alkaline cations and alkaline earth metals (groups I and II from the periodic table) additional systems were investigated. Cations having a low partition coefficient in ATPS, where the variables can take very different values, were studied.

The data for partition coefficients of cations from groups I and II (Na^+, Cs^+, Ca^{2+}, Sr^{2+} and Ba^{2+}) were obtained from Rogers et al. [13] and are shown in Table 4. These coefficients were obtained in ATPS formed by PEG-2000 and inorganic salts (K_2CO_3, $(NH_4)_2SO_4$ and NaOH) at 25°C.

If the data from Tables 2 and 4 are compared, an

Table 4
Partition coefficients of Na^+, Cs^+, Ca^{2+}, Sr^{2+} and Ba^{+2} in ATPS formed by PEG-2000 and different salts at 25°C

Salt	Partition coefficient				
	Na^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
K_2CO_3	0.0170	0.0490	0.0022	0.0043	0.0035
$(NH_4)_2O_4$	0.0270	0.0510	0.0054	0.0074	0.0120
NaOH	0.0980	0.3300	0.0200	0.0220	0.0450

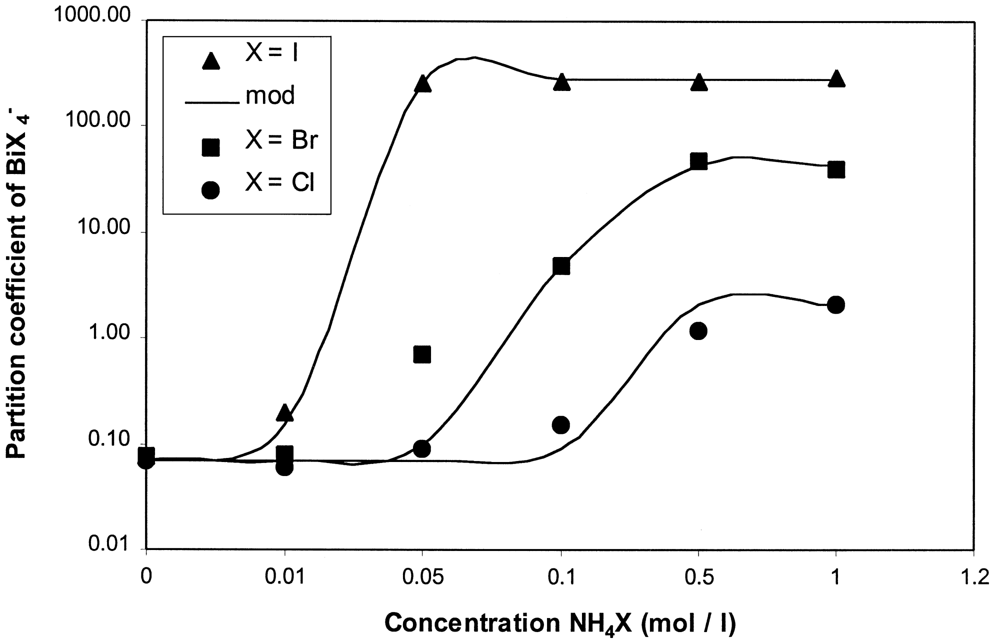

Fig. 3. Partition coefficients in BiX_4^- in ATPS formed by $(NH_4)_2SO_4$+PEG-2000+H_2O with increasing concentration of added NH_4X. Experimental values (▲, NH_4I; ■, NH_4Br; ●, NH_4Cl) and model.

Table 5
Parameter values obtained by optimization of Eq. (13) for Na^+, Cs^+, Ca^{2+}, Sr^{2+} and Ba^{2+} in ATPS formed by PEG-2000 and different salts (K_2CO_3, $(NH_4)_2SO_4$ or NaOH) at 25°C

D_0	a_1	a_2	a_3	b_1	b_2
0.000626	1.68	−2.57	1.72	160.0	8.06

important difference between them can be observed. The partition coefficients for BiX_4^- reach much higher values than those of cations from groups I and II. Table 4 shows that the elements of group I (Na^+ and Cs^+) have larger partition coefficients than cations from groups II, and that within each group the partition coefficients increase with atomic number. This implies that the partition coefficients are affected by ion size, charge and electronegativity and therefore with variable X in Eq. (11). It is also observed that for the same ion the partition coefficient changes when the salt used for ATPS formation varies, which implies a change in variable Y in Eq. (11).

As there is no added salt in the original ATPS, the variable Z in Eq. (11) is zero and the model can be represented by Eq. (14):

$$D_M = D_0 + \frac{a_1(X)^{a_2}(r^*)^{a_3}}{1 + b_1 \exp(-b_2 Y)} \tag{14}$$

The parameters from Eq. (14) were determined by optimization of Eq. (13), the values of the parameters obtained are shown in Table 5. In Fig. 4 the experimental partition coefficients are shown as points and the model is shown with a continuous line.

The parameter values shown in Tables 5 and 3 are rather different as they correspond to very different ion types (cations and anions) and different salts used in the ATPS. Fig. 4 shows that the model follows well the effect of the parameter R on the partition coefficients of Na^+, Cs^+, Ba^{2+}, Ca^{2+} and Sr^{2+}. Charge effects from different ions are included in the variable X. As the exponent of X in the model (a_2) is positive for BiX_4 anions, when the partition coefficient increases X increases. On the other hand, for ions from groups I and II, a_2 is negative (Table 5)

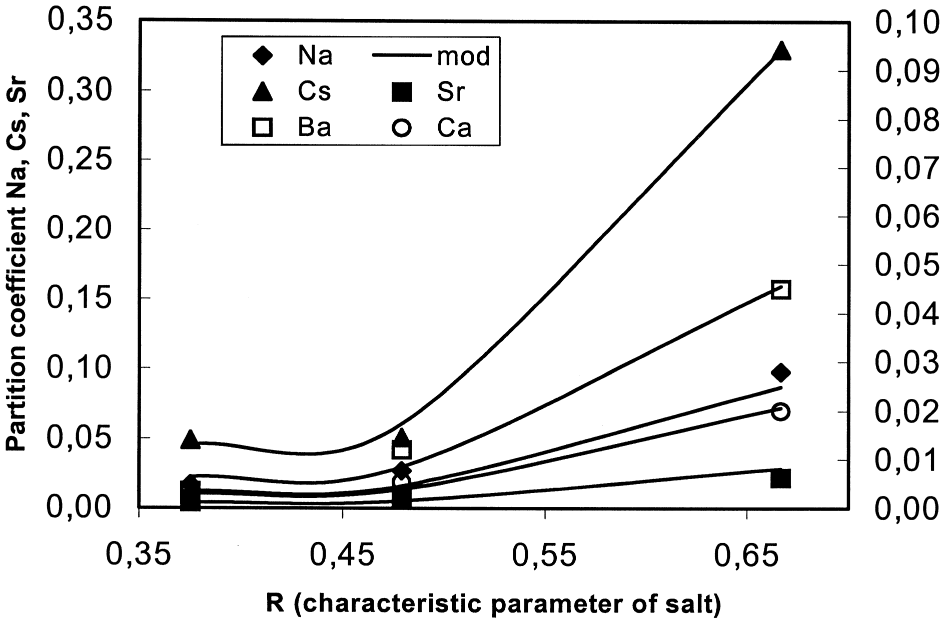

Fig. 4. Effect of the value of R of different salts on the partition coefficients of Na^+ (♦); Cs^+ (▲); Sr^{2+} (■); Ca^{2+} (○); and Ba^{2+} (□) in PEG-2000/salt systems.

and the partition coefficient decreases with an increase in X.

The advantage of this model is that it allows the separation of the effect of ion size from those of charge and electronegativity through the variable X. In accordance with the parameter values from Tables 3 and 5 it can be seen that for both systems studied, the partition coefficients increase with increasing ion size. This is not always easy to appreciate from the experimental data, for example for ions from groups I and II (Table 4) as the water or electronegativity of each ion hides the effect of size. On the other hand, according to Tables 3 and 5 for both systems it was found that the partition coefficients increase with variable Y (type of salt/ATPS composition) and with an increase in variable Z (product of salt solubility and concentration added to the original ATPS).

2. Conclusions

A model for the partition of metal ions in aqueous two-phase systems (ATPS) has been developed. The partition coefficient of a metal ion D_M, is a function of several variables of the metal ion (size, charge and electronegativity), characteristics of the ATPS such as type of salt, salt concentration and PEG concentration and additional inorganic salt present in the ATPS.

The proposed model is able to predict, with the same equation, the partition coefficients of bismuth halide ions ($BiCI_4^-$, $BiBr_4^-$ and BiI_4^-) when different salts are added to the original ATPS of PEG-2000 and ammonium sulphate. The model is also able to predict the partition coefficients of cations from groups I and II (Na^+, Cs^+, Ca^{2+}, Sr^{2+} and Ba^{2+}).

Different behavior was observed in the two systems studied in terms of the charge and electronegativity effects of the ions measured by the variable X which is a characteristic of the electrochemical interactions of the metal ion. It was found that the partition coefficients of BiX_4^- increase with variable X, whereas cations from groups I and II have an inverse behavior attributable to the ion charge.

It was found that for both systems the partition coefficients increase with ion size ($a_3 > 0$).

3. Nomenclature

C_{AO}	Concentration of salt added to the original ATPS
C_A^*	Dimensionless concentration of salt added to the original ATPS (Eq. 9)
C_{PO}	PEG concentration in ATPS
C_p^*	Dimensionless PEG concentration
C_{Pe}	PEG concentration at the nodal point of binodal curve
C_{SO}	Inorganic phase-forming salt concentration
C_{Se}	Salt concentration at the nodal point of binodal curve.
C_s^*	Dimensionless inorganic phase-forming salt concentration (Eq. 7).
D_M	Experimental partition coefficient.
D_{Mec}	Partition coefficient given by the model.
E	Ion electronegativity.
E^*	Dimensionless ion electronegativity.
f_{obj}	Objective function from Eq. (13).
q	Ion charge.
r	Ion size.
r^*	Dimensionless ion size (Eq. 3).
R	Minimum distance of binodal curve from origin (characteristic of each phase forming salt).
S	Salt solubility in water at working temperature (salt mass/water mass).
S_A	Solubility of added salt (salt mass/water mass)
X	Variable characteristic of metal ion electric interactions (Eq. 5)
Y	Variable characteristic of ATPS. (Eq. 8) in the absence of added salt.
Z	Variable characteristic of salt added to the original ATPS (Eq. 10).

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