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Theoretical model for ion exchange of iron (III) in chelating resins: Application to metal ion removal from wine

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Abstract

Equilibrium diagrams have been obtained for the ionic exchange that occurs between Fe^{3+} ions in solution and the protons present in a chelating ion exchange resin, in water, in alcohol and in hydroalcohol solvents. These diagrams have also been obtained for a natural complex solvent (a wine matrix). A mathematical model has been developed to predict this equilibria which gives a good fit for the experimental data in the first three types of solvents studied and, after making some modifications, also in the last case.

It has been observed that the type of solvent influences not only the resin equivalent capacity but also the equilibrium parameters of the system. In the case of the wine matrix used as the solvent it has been found that other factors influence the equilibrium diagram, i.e., the presence of quelating compounds.

Keywords: Food processing; Ion exchange; Mathematical modelling; Metal removal; Phase equilibria; Separations

1. Introduction

The presence of metals in solution in wines, fundamentally iron and copper, even in low concentrations, has a great influence on the oxidative stability of the bottled products (Amerine et al., 1979; Berg, 1953; Berg and Akiyoshi, 1956; Cacho et al., 1995; Kean and Marsh, 1956; Ribereau-Gayon, 1933; Ribereau-Gayon et al., 1998). In this sense, it is known that iron concentrations higher than 5 ppm can cause several stability problems, so above this concentrations it is necessary to treat the product. Depending on the oddities of each industrial process it can be found batches of wine for treatment with concentrations higher than 10–30 ppm (Loubser and Sanderson, 1986; Scollary, 1997). For this reason, demetalisation constitutes an important operation in the oxidative stabilisation stage for wines. This operation is traditionally carried out in the cellar by the addition of potassium ferrocyanide (a well-known practice known as “blue clarification”) (Tarantola, 1963). However, the effectiveness of this treatment is limited to a level of iron elimination in the range 63–80% and copper of 90–95%. It has been proven that the quantity of residual iron after this treatment continues to exercise a remarkable effect on the deterioration in the oxidative stability of the wine in the bottle. Furthermore, this technique can induce the formation of undesirable substances such as hydrocyanic acid and ethyl carbamate (Sánchez-Pineda and Martín López, 1997). On the other hand, cyanurated industrial residues are formed and these are classified as toxic and dangerous residues and require an appropriate disposal regime.

An alternative operation to blue clarification involves the application of chelating resins as those used in the ion exchange techniques. One of the most widely employed types of resin in this respect is reticulated polystyrene resin, which has iminoacetic functional groups (Fig. 1) and shows a high selectivity for the elements iron and copper (Naden and Willey, 1976). Initial experimental results revealed that ion exchange technology with resins of this type is more effective and more economical than the blue clarification

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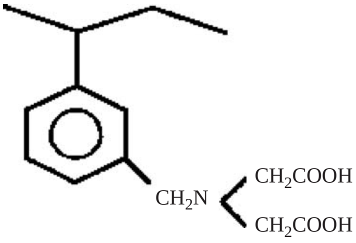

Fig. 1. Structure of the cross-linked polystyrene matrix of the resin with divinylbenzene, containing functional groups of the iminodiacetate type.

technique, especially for the demetalisation of biological ageing wines. The technique also minimizes the problems associated with the generation of residues.

It has been demonstrated that the use of a suitable resin with a high selectivity for the metals iron and copper reduces their concentrations by more than 99.5% in the studied wines (Loubser and Sanderson, 1986). In addition, this technique reduces the cost of the operation by more than 60% and does not produce alterations in the sensorial, physical and chemical properties of the wines, thus improving the stability of the wines against oxidative degradation (Palacios et al., 2001).

Having demonstrated the effectiveness of the ion exchange technique for the industrial demetalisation process of wines, it is important to understand in detail the phenomena that take place during the exchange process and obtain data concerning the equilibrium through which the process occurs. These aspects are necessary in order to carry out an appropriate optimization of the operation variables.

In this way, we have to bear in mind that the ion exchange equilibrium in non-aqueous media was initially studied by several authors (Helfferich, 1962; Marcus, 1973). So initially it was thought that ion exchange in this type of nonaqueous solvent could be explained on the same basis as the process in water, that the resin can be regarded as homogeneous, and that the entire resin capacity is available for the exchange. However, now it is known than they are not (Turner et al., 1966). It was demonstrated that this is not the case and that the resin capacity is not entirely available when a nonaqueous medium is used (Lucas et al., 1996). In short, the available exchange capacity decreases as the polarity of the pure solvent decreases and, in mixtures, this is determined by the most polar solvent in the mixture (Lucas et al., 2001).

In general, several equilibrium models have been developed that consider the resin as a heterogeneous solid with different types of active center for the exchange. Buttersack (1989), defined two kinds of effects, one due to the influence of the morphology of the resin and the other due to the influence of the solvent and adsorbed molecules. Melis et al. (1996), introducing the idea of Myers and Byington (1986), developed a new model by assuming that the effect of mixture nonidealities is smaller than that due to the resin heterogeneity. In the simplest situation, they use only two types of functional groups, which are equally abundant. However, in the case of chelating ion exchange resins, which has a high degree of homogeneity in the particle, these heterogeneous models take less physical sense.

A different model for the ion exchange processes is based on the Gibbs–Donnan ideas (Pesavento and Biesuz, 1998), in which experimental data are treated considering the resin as a solution phase separated from the external solution by an interface. Through this interface a potential is generated, the Donnal potential, and neutral molecules and ions can diffuse, however the groups linked to the mainframe of the resin cannot pass through the interface.

Finally, non-ideal homogeneous models have been developed that use the Debye–Hückel equation for the activity coefficients in the liquid phase and the Wilson equations for the coefficients of the solid phase (Lucas et al., 2001). This type of models have been applied in the case in order to a better prediction of the different situations observed experimentally.

2. Equilibrium mathematical model

The resin used has the iminodiacetic group as the functional group (Fig. 1) and it is believed that the exchange centers are the acid protons of these acetic acid groups (RH). In short, two protons for each iminodiacetic group are available. On the other hand, the molecular structure of this functional group means that the two acetate groups are in close proximity to one another and it is therefore very probable that the chelation of the Fe^{3+} ion occurs only in two coordination positions, to form the ferric iminodiacetato complex (R_2Fe^+). Equally, due to the relative distance between two different iminodiacetic acid groups, the formation of the complex with three coordination positions (R_3Fe) is considered to be improbable. As a consequence, the most likely chemical reaction of exchange is as follows:

$$2RH + Fe^{3+} \leftrightarrows R_2Fe^+ + 2H^+. \tag{1a}$$

On the other hand, in aqueous solution, several chemical species of iron can be present in the medium (Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2{}^+$ and $Fe(OH)_3$). The predominant specie depends on pH. At normal wine pH (3.0–3.5) the predominant specie is $Fe(OH)^{2+}$, thus a more realistic chemical reaction of exchange can be the following:

$$2RH + Fe(OH)^{2+} \leftrightarrows R_2Fe(OH) + 2H^+. \tag{1b}$$

In any case, the combination valence of iron takes the value two, so both equations are analogous in order to express the equilibrium constant of the system. We will represent species $R_2Fe(OH)$ and R_2Fe by the symbol R_2Fe and species $Fe(OH)^{2+}$ and Fe^{3+} by the symbol Fe. Bearing in mind that the system consists of two phases, a solid one (the resin) and a liquid one (the solution), the symbol RH represents the hydrogen in the resin and the symbol H represents hydrogen in solution.

The equilibrium constant (K) of this Eqs. (1a) and (1b) can be generalized with the following expression, where a_i are the activities of the participant compounds in each phase:

$$K = \frac{a_{R_2Fe} a_H^2}{a_{RH}^2 a_{Fe}}. \tag{2}$$

Since the activities can be calculated as the product of the activity coefficient using the corresponding molar concentration ($[i]$), one can express the equilibrium constant by the following expression:

$$K = \frac{\gamma_{R_2Fe}[R_2Fe]\ \gamma_H^2 [H]^2}{\gamma_{RH}^2 [RH]^2\ \gamma_{Fe}[Fe]}. \tag{3}$$

If one defines an activity function in the following way:

$$\Phi = \frac{\gamma_{Fe}\gamma_{RH}^2}{\gamma_H^2 \gamma_{R_2Fe}} \tag{4}$$

and, bearing in mind that the molar concentrations can be substituted by the quotient between the normal concentration (N_i) and the valence coefficient of the compound (val_i), then the equilibrium constant can be expressed as follows:

$$K\Phi = \frac{(N_{R_2Fe}/\mathrm{val}_{R_2Fe})(N_H/\mathrm{val}_H)^2}{(N_{RH}/\mathrm{val}_{RH})^2 (N_{Fe}/\mathrm{val}_{Fe})}. \tag{5}$$

On the other hand, the equivalent fractions of each compound in each phase can be defined in the following way:

$$x_i = \frac{N_i}{N_T}, \quad y_i = \frac{N_i}{Q_T}, \tag{6}$$

where x represents the fraction in the liquid phase and y in the solid phase. N_T is the total normality of the ions in solution and Q_T is the total equivalent capacity of the resin. Introduction of these equivalent fractions in Eq. (5)—bearing in mind that the combination valence coefficients of the compounds are the same ($\mathrm{val}_H = \mathrm{val}_{RH} = 1$; $\mathrm{val}_{R_2Fe} = \mathrm{val}_{Fe} = 2$)—makes the equation

$$K\Phi = \frac{y_{R_2Fe}(x_H)^2 N_T}{(y_{RH})^2 Q_T x_{Fe}}. \tag{7}$$

As there are only two components present in the solution and the resin (Fe^{3+} and H^+), the nomenclature of the equivalent fractions can be simplified in the following way:

$$x_{Fe} = x; \quad x_H = (1-x); \quad y_{RFe} = y; \quad y_{RH} = (1-y).$$

Eq. (7) then becomes

$$K\Phi \frac{Q_T}{N_T} = \frac{y(1-x)^2}{(1-y)^2 x} = \frac{y/(1-y)^2}{x/(1-x)^2}. \tag{8}$$

In this way, the proposed equilibrium model can be denominated as a quadratic model on the basis of the exponent obtained in the fractions. Eq. (8) relates the equivalent fraction of Fe^{3+} in solution (x) with the equivalent fraction of Fe^{3+} in the resin (y), by means of the equilibrium constant (K) and the activity function (Φ), for a given equivalent capacity of the resin (Q_T) and a total equivalent concentration in solution (N_T).

On the other hand, it is proposed that the activity coefficients in the liquid phase can be calculated using the Debye–Hückel law limit (Praustnitz et al., 2000). This model is known as the "ionic atmosphere" and is valid for dilute solutions of strong electrolytes. This theory includes relative concepts concerning the structures of the solutions of electrolytes as well as other thermodynamic concepts. For solutions of up to 1 mol/Kg in concentration, the proposed expression is as follows:

$$\ln \gamma_i = \frac{A z_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}} + \beta I, \tag{9}$$

where I is the ionic force of the solution, which can be calculated as

$$I = \frac{1}{2} \sum z_i^2 m_i. \tag{10}$$

In Eqs. (9) and (10) m refers to the molality of each ion present in solution and z_i to their charge. A and B are constants that depend on the temperature and the nature of the solvent, while a_i is a parameter that is related to the ionic radius of each ion. Lastly, β is an adjustment parameter that also depends on the type of solvent.

It is proposed that the activity coefficients in the resin can be calculated using Wilson equations (Tester and Modell, 1997). The Wilson model (Wilson, 1964), is an empirical extension of the Flory and Huggins model and incorporates concepts that consider the combined effects of the differences in molecular size and the intermolecular forces. For a binary system, their adjustment parameters are based on the probability of finding a molecule of type A in the vicinity of another of type B. The equation finally developed is the following:

$$\begin{aligned} \ln \gamma_{AB} &= 1 - \ln\{y_A + (1-y_A)\Lambda_{AB}\} - \frac{y_A}{y_A + (1-y_A)\Lambda_{AB}} \\ &\quad - \frac{(1-y_A)\Lambda_{BA}}{(1-y_A) + y_A\Lambda_{BA}}, \\ \ln \gamma_{BA} &= 1 - \ln\{y_A + (1-y_A)\Lambda_{BA}\} - \frac{(1-y_A)}{(1-y_A) + y_A\Lambda_{BA}} \\ &\quad - \frac{y_A\Lambda_{AB}}{y_A + (1-y_A)\Lambda_{AB}}, \end{aligned} \tag{11}$$

where Λ_{AB} and Λ_{BA} are the Wilson coefficients. In this case, A and B would be the respective species present in the resin, i.e., R_2Fe^+ and RH.

3. Materials and methods

3.1. Ion exchange resin

The resin used in all cases was a weakly acidic, macroporous cation exchange resin with chelating functional groups

Table 1
Characteristics of the exchange resin employed

Ionic form, as shipped	Na^+
Functional group	Iminodiacetic acid
Matrix	Crosslinked polystyrene
Structure	Macroporous
Appearance	Beige, opaque
Bulk weight (g/mL)	0.800 (±5%)
Density in sodic form (g/mL)	1.18
Water retention (%)	50–55
Total capacity (H^+ form) (eq/L)	2.4
Volume change ($Na^+ \rightarrow H^+$) (%)	−30
Temperature stability range (°C)	−20 to 80
pH stability range	0–14
Product storability (min. years)	2

Data taken from the product information.

Table 2
Analytical composition of the wine employed as the matrix

Alcohol grade (°GL)	15.5
Total acidity (g tartaric ac./L)	4.84
Volatile acidity (g acetic ac. /L)	0.21
pH	3.28
Total sulphurous (mg/L)	86
Fe (ppm)	0.0
Cu (ppm)	0.0
Na (ppm)	18
K (ppm)	480
Ca (ppm)	71
Mg (ppm)	51
Color (Optical density 470 nm) (ua)	0.092

(Fig. 1). This resin consists of a matrix of cross-linked polystyrene with divinylbenzene (8%) and contains functional groups of the iminodiacetate type (Lewatit TP 207, of Bayer, 1997). It has a high selectivity for the heavy and transition metals and absorbs them in cationic form. The resin conforms to German law for the food industry (08/07/1993) in that it contains total soluble organic substance levels below the limit of 1 ppm. Its general characteristics are outlined in Table 1. The stability of the resulting complexes varies from one metal to another. For divalent ions, for example, the selectivity is in the following order:

$$Cu^{2+} > Hg^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}.$$

The resin also retains trivalent ions such as Al^{3+}, Fe^{3+}, Cr^{3+} and Co^{3+}.

3.2. Solutions

The solutions used to determine the equivalent capacity of the resin and some of the equilibrium diagrams were prepared with iron (III) chloride (quality PA, Panreac), in demineralised water or in absolute ethanol (assay 99.5%, Panreac) depending on the case. On the other hand, the equilibrium diagrams corresponding to low iron concentrations were obtained using a standard solution of iron of 1 ± 0.002 g/L (quality AA, Panreac) due to the higher convenience to obtain the necessary concentrations in the laboratory.

The experiments for the wine matrix were carried out with the same standard iron solution but in this case the solvent was a typical wine of the area of Sherry wine. The characteristics of the wine are given in Table 2.

The resin was regenerated using a 10% solution of 37% HCl (quality PRS, Panreac) in demineralised water.

3.3. Operation conditions and experiments

The equivalent capacities of the resin were determined using the iron elution curves obtained through a set of glass columns with the appropriate resin. In each case, an iron solution 0.2 N (in water or ethanol) was eluted through the medium (resin) until column saturation was achieved. The pH of the aqueous and the hydroalcohol solutions of Fe^{3+} were set at 3.3, which is the normal wine pH. Contrary, the pH of the absolute alcohol solutions were not adjusted, due to the chemical species of iron in this media are different than those in water and the aim of the experiment is to determine the equivalent capacity of the resin in these conditions.

All this works were carried out in the appropriate resin columns (high 0.40 m; diameter 0.02 m; total volume 125 mL) and the experiments were always performed according to the following steps:

- Service phase, in which a feed flow of 5 L/h/L resin was used.
- Regeneration phase, with an HCl solution (10%), using a flow of 2 L/h/L resin, and a total volume of 2 L/L resin.
- Clearing phase, with demineralised water, until the exit pH current was about 3, and with a flow of 5 L/h/L resin.

Using the data of the elution curves the integral quantity of iron mass retained was computed and the equivalent capacities of resin in the different conditions was established.

On the other hand, several equilibrium diagrams were obtained using an experimental set-up that consisted of 100 mL flasks with a certain quantity of resin and a certain volume of iron solution of known normality. These quantities were varied so that the largest possible range for the equilibrium diagram it was covered. The initial pH of aqueous and hydroalcohol solutions was settled near to 3.3 in order to ensure that the predominant chemical species of iron in the media were the normal species in wine. The final pH obtained in each flask were different depending on the evolution of the equilibria, the mass of iron adsorbed and the mass of protons desorbed.

To attain the equilibrium state between resin and solutions the mixtures were agitated for 24 h in an automatic agitator at a constant speed of 200 rpm. This reaction time was considered adequate after the monitorization of several batch experiments. The contents of each flask were filtered to separate the solid phase from the liquid and the iron concentration was measured in each case. The quantity of iron retained in the resin was calculated as the difference between the initial concentration of the solution and that obtained after the equilibrium. All these experiments were carried out at 25 °C.

In the case of the equilibrium diagrams obtained for wine solutions, the wine alcohol level was adjusted to 15.5% prior to the experiment in order to give comparable results with those obtained in the hydroalcohol mixture. The solution for the wine matrix was previously demetalized by elution through a loaded column with the same resin as used in the rest of the experiments. The desired quantity of iron was later adjusted in solution.

3.4. Analytical procedures

Metal analysis was carried out by atomic absorption spectrophotometry (Philips, model PYE UNICAM SP9) using an apparatus equipped with hollow cathode lamps (Philips, 1984).

The pH determinations were carried out using a digital pH-meter (Crison) equipped with a combined electrode with temperature compensation.

The alcohol grade was determined by distillation and measurement of the density of the distillate, according to the official methods of analysis in wines (OIV, 1990).

The wine used as the wine matrix was characterized as follows: the total SO_2 content, total acidity and volatile acidity were measured using the official methods of analysis in wines (OIV, 1990). The colour measurement was carried out by determining the optical density at 470 nm using a Hitachi spectrophotometer (U 2001 model).

3.5. Data treatment

The calculations and the development of the equations used in the mathematical model were performed using a range of computational programs implemented in the program Matlab 6.5, version 12, from Math Works. The parameters of the model are obtained from the data by an iterative calculation algorithm based on the procedure of square minima (Mathews and Fink, 1999).

4. Results and discussion

4.1. Resin equivalent capacity

The effective equivalent capacity of the resin, both in water and in absolute ethanol, was determined using the experimental data shown in Fig. 2 and applying the integration procedure indicated previously. The experiment gave values of 1.38 eq/L of resin in the case of water and 1.10 eq/L of resin for absolute ethanol. It can be seen that the capacity in the alcohol medium is only 80% of that in water. This result confirms the previous hypothesis that the capacity of the resin is affected by the nature of the solvent and decreases in less polar media. Consequently, as far as the industrial application of the exchange technique is concerned, this indicates that the demetalization process would be less effective as the alcohol level of the treated wine increases.

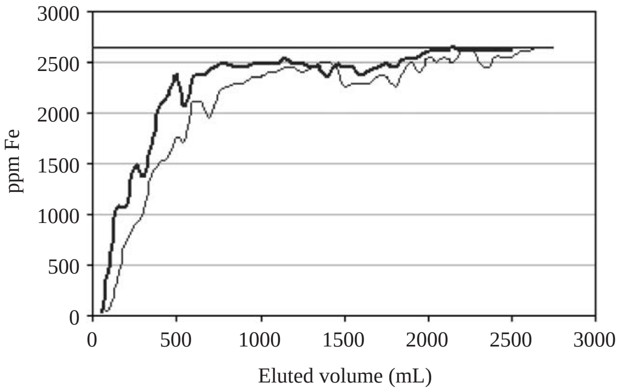

Fig. 2. Elution curves of Fe^{3+} in water (——) and in alcohol media (——). Fe concentration in the eluted media (ppm Fe) vs eluted volume (mL). The straight line shows the initial concentration of iron solutions.

4.2. Equilibrium diagrams

4.2.1. Results in aqueous solutions

The previously described experimental procedure was used to obtain the equilibrium diagrams for Fe^{3+}/H^+ in aqueous solution at five different normalities: 0.002; 0.067; 0.166; 0.333 and 0.667 N. The results are shown in Fig. 3.

These experimental data were used to adjust the proposed mathematical model in the following way. Firstly, the values of the Debye–Hückel parameters A and B (Eq. (9)) for water were taken from the literature, $A = 1.05$ and $B = 3.17 \times 10^9$ (Lucas et al., 1996). Secondly, the parameter "a_i" (Eq. (9)) was calculated as the average ionic radius of the ions in solution in each case, with values of 0.64×10^{-10} m for Fe^{3+}, 1.54×10^{-10} m for H^+ and 1.81×10^{-10} m for Cl^- (Weast, 1975). The parameters N_T and Q_T are known (Eq. (8)) and they reflect the operation conditions of each experiment. Therefore, only four parameters remain to be determined in the proposed model and these are: the equilibrium constant K (Eq. (8)), Debye's β parameter (Eq. (9)) and the Wilson coefficients $\Lambda_{\mathrm{Fe-H}}$ and $\Lambda_{\mathrm{H-Fe}}$ (Eq. (11)).

The iterative adjustment procedure outlined previously was used to determine the values of these parameters and

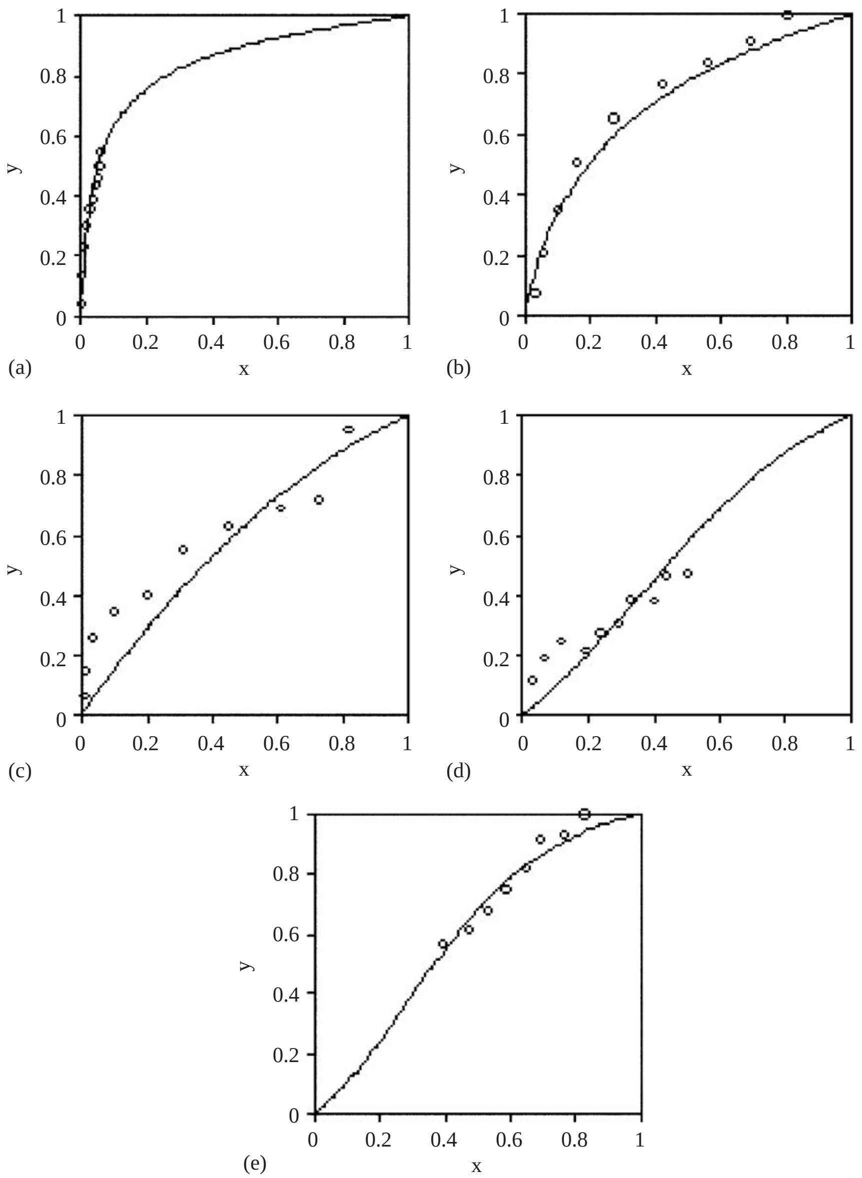

Fig. 3. Equilibrium diagrams of Fe^{3+}/H^{+} in water: (a) 0.002 N, (b) 0.067 N, (c) 0.166 N, (d) 0.333 N, (e) 0.667 N. (-) theoretical diagrams, (o) experimental data.

they were found to be

$$K = 2.16;\ \beta = 0.624;\ \Lambda_{\mathrm{Fe-H}} = 1.12;$$
$$\Lambda_{\mathrm{H-Fe}} = 0.662.$$

The regression coefficient obtained for these values is high ($r^2 = 0.922$). A graphical representation of the theoretical curves is also shown in Fig. 3. It can be observed that the curves are lower in the diagram as the solution becomes more concentrated. However, at a certain concentration of Fe^{3+} (between 0.333 and 0.667 N) the curves are higher again. This effect is a result, according to the applied model on starting from a certain concentration, of the activity coefficient in aqueous solution reaching a minimum and then increasing again.

4.2.2. *Results in absolute ethanol*

The aforementioned experimental procedure was also used to obtain the equilibrium diagrams for Fe^{3+}/H^{+} in absolute ethanol at three different normalities: 0.002; 0.067 and 0.333. The results are represented in Fig. 4.

As in the case for aqueous systems, this data was used to adjust the proposed mathematical model. The corresponding calculations in this case were carried out as follows. Firstly, the values of the ionic radii (a_i) were similar to those used in the previous case, since these are supposedly independent of the solvent. Secondly, new values for the parameters

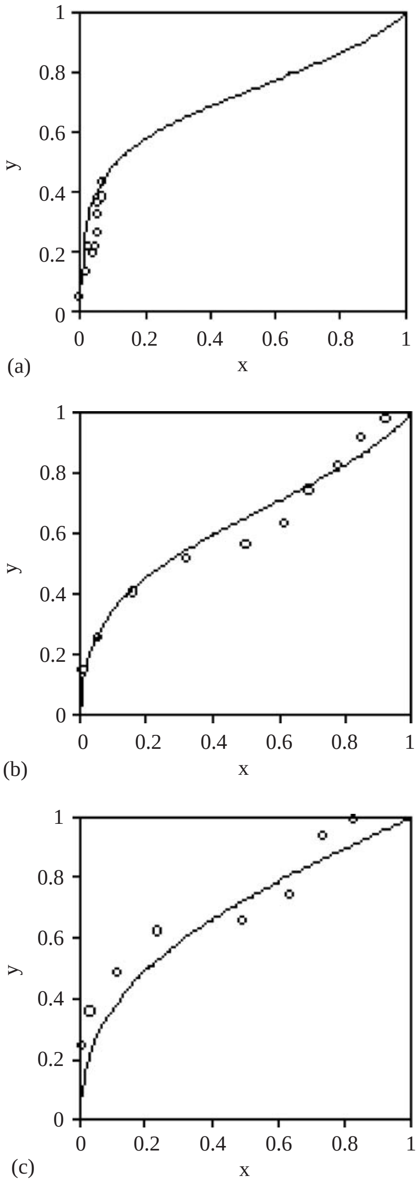

Fig. 4. Equilibrium diagrams of Fe^{3+}/H^+ in absolute ethanol: (a) 0.002 N, (b) 0.067 N, (c) 0.333 N. (-), theoretical diagrams, (o), experimental data.

N_T and Q_T were taken as appropriate for the new conditions (i.e., in ethanol) since they are different to those used in water. Finally, the value of the parameter K was taken as that determined previously in water, as this constant is supposedly independent of the nature of the solvent, which is included in the Φ factor.

On the basis of the above information, there are five unknown parameters in the model and these are as follows: the constants A and B from the Debye–Hückel equation, the Debye–Hückel β parameter and the two parameters $\Lambda_{\text{Fe}-\text{H}}$ and $\Lambda_{\text{H}-\text{Fe}}$ from the Wilson equations. All of these parameters need to be recalculated for alcohol media since they are dependent on the nature of the solvent used.

The iterative adjustment procedure previously outlined gave the following values:

$$A = 1.85;\ B = 1.96 \times 10^9;\ \beta = 3.38;\ \Lambda_{\text{Fe}-\text{H}} = 2.08;\ \Lambda_{\text{H}-\text{Fe}} = 1.35.$$

The regression coefficient obtained was slightly lower than that obtained for the aqueous systems but was nevertheless high ($r^2 = 0.853$). A graphical representation of the corresponding theoretical curves is shown in Fig. 4.

In a similar way to the aqueous solutions, the curves initially become lower upon increasing the solution normality and, at a certain concentration, they rise again. However, the different values of A, B and valid β in this case mean that the minimum point occurs at a lower normality of Fe^{3+}.

On the other hand, if we compare the range of curves obtained in water with the range of curves corresponding to ethanol, a negative displacement is observed in the case of the ethanol curves. This effect indicates that the solvent has a major influence on the exchange process and reduces the effectiveness of the exchange process in the nonaqueous media.

4.2.3. Results in hydroalcohol solutions

Having validated the model for the pure solvent systems (water and ethanol), it was decided to test the applicability in solvent mixtures. In this case, the equilibrium data were determined using 15.5% hydroalcohol solutions in order to mimic the typical composition of the industrial products under investigation.

The values of the parameters used in the theoretical model are as follows. Firstly, the values of K and a_i were taken to be the same as in the pure solvents, since they are not dependent on the nature of the solvent. As previously, the value of N_T corresponds to the specific experimental conditions employed, 0.002 N in this case, to mimic the real conditions in wine. Finally, the values of the remaining parameters were taken as all being proportional to the alcohol content (15.5%) starting from the known values for the pure solvents. Consequently, the values used are as follows:

$$A = 1.17;\ B = 2.98 \times 10^9;\ \beta = 1.04;\ \Lambda_{\text{Fe}-\text{H}} = 1.27;\ \Lambda_{\text{H}-\text{Fe}} = 0.769;\ Q_T = 1.142.$$

The above values allow the value of y to be calculated for different values of x. Since the y data experimentally obtained are known, it is possible to compare the predictions obtained using the proposed model with the real experimental data. The results of this comparison are presented in Fig. 5. The value of the regression coefficient obtained in this case is also high ($r^2 = 0.912$).

It is clear that, in general, the proposed model agrees quite well with the experimental data for the values of the indicated parameters. These results serve to validate the

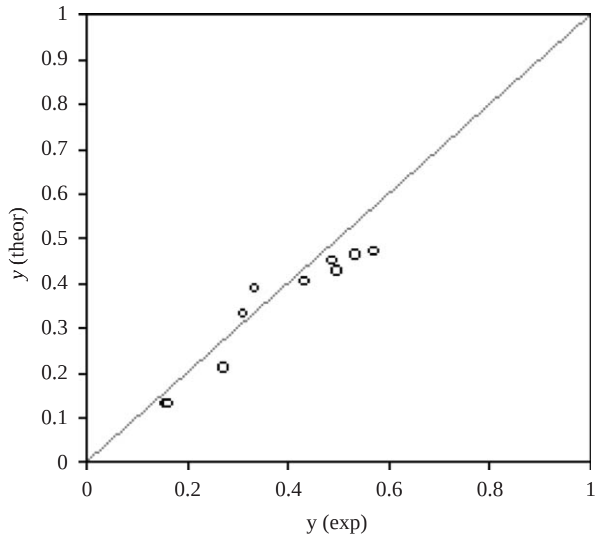

Fig. 5. Adjustment of theoretical data [y (theor)] versus experimental data [y (exp)], in 15.5% hydroalcohol solution.

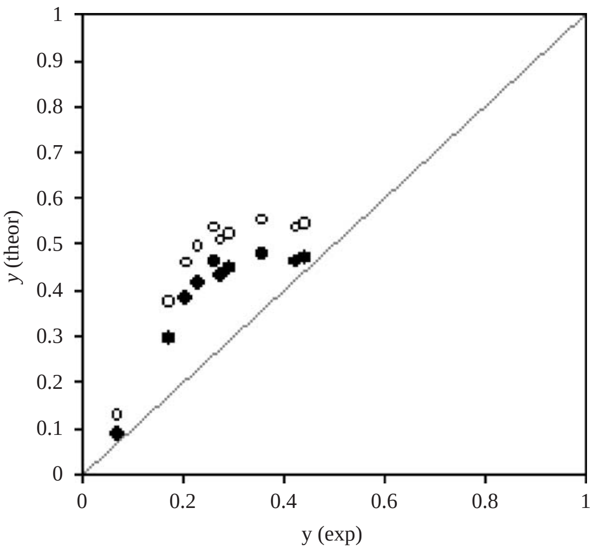

Fig. 6. Comparative representation of theoretical data [y (theor)] with experimental data [y (exp)] in wine media. (o), initial theoretical model, (●), modified theoretical model.

proposed theoretical model for aqueous, alcohol and hydroalcohol media.

4.2.4. *Results in wine media*

Finally, having confirmed the validity of the model in simple solutions, the model was analyzed in a complex natural solution, which in this case was wine as a representative industrial product for treatment, with iron concentration of 0.002 N and 15.5% alcohol grade. The values of the model parameters used in the calculation of the theoretical data were the same as those employed for the hydroalcohol solutions, since these solutions mimic the conditions in the industrial product. A comparative representation of the theoretical values with the experimental ones is shown in Fig. 6.

In this case, however, it is clear that the obtained theoretical values stray considerably off the diagonal. This situation indicates that the initially proposed model is not a good representation in the case of the complex solution (wine media) under investigation.

The deviations from model behaviour observed in these experiments can be explained by considering the diverse range of different components present in the wine matrix, that is likely to modify the equilibrium. In this sense, a major cause of this deviation can be attributed to the high saline concentration in the wine, which is considerably higher than that expected on considering only the iron salts.

As the salts dissolved in the wine are many and varied, the real ionic force is significantly higher than that estimated theoretically considering only the iron salts. Since the ionic force affects the activity coefficients and the calculated values of y, these differences in salinity may well be a key in explaining the observed deviations. In this sense, theoretical y values were recalculated, but in this case an ionic force constant of 0.125, a typical value in this type of wine, was considered. A comparative representation of the new y values obtained using the modified model is shown in Fig. 6.

It can be seen that the modified theoretical values move closer to the diagonal and therefore show a better adjustment than in the case of the initial theoretical model. This result demonstrates that the effect of the real ionic force of the medium must be included in the theoretical calculations, thus relegating Eq. (10) to use in simple solutions of known composition.

Nevertheless, despite the modification to the model, the theoretical y values were not adjusted perfectly to the diagonal and so it seems reasonable that factors other than the salinity must contribute to the deviations found.

4.2.5. *Modification due to complexing compounds*

In order to explain the deviations observed in Fig. 6, it is necessary to consider the existence of substances that are capable of complexing iron in the wine matrix. The presence of this type of substance in the wine has been widely reported in the bibliography. These compounds are usually organic acids, polyphenols, tannins and proteins, amongst others; where the highest quantity of complexes are formed with the organic acids (Ribereau-Gayon et al., 1976; De Rosa, 1997). In this media, the principal acids forming complexes with iron are the citric, malic, tartaric and lactic acids (from highest to lowest stability). However the most abundant acid in wine is tartaric, follow by malic, lactic and citric, been normally reached a total quantity of organic acids between 5 and 10 g/L, where more than 75% is tartaric. The most stable complex formed between iron and tartaric acid is $K(FeC_4O_6H_2)$ (potassium ferritartate) which has 1:1 stequiometry (De Rosa, 1997; Usseglio-Tomasset, 1978).

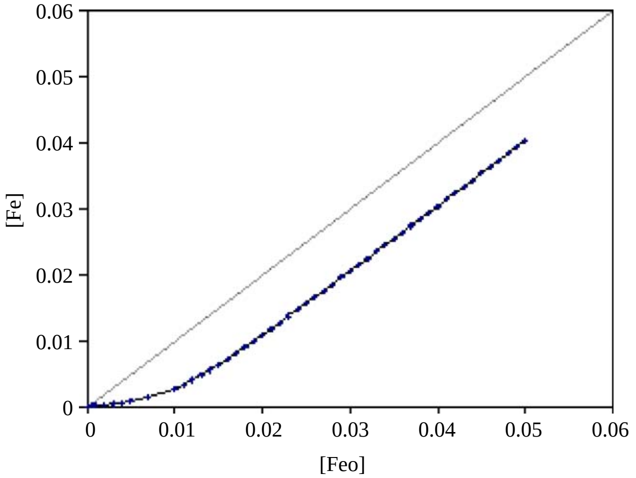

Fig. 7. Free iron concentration in solution [Fe] as a function of total iron concentration [Fe$_0$] (ppm). Quantitative calculate take of Eq. (18). ($K_C = 1 \times 10^3$ L/mol and $C_0 = 1 \times 10^{-2}$ mol/L).

The fact that the Fe^{3+} cations are perfectly complexed and stabilized in solutions by some compounds would diminish the quantity of free cations in the media. The effective concentration of iron in solution that is able to undergo ionic exchange with the resin would be lower than the total measured concentration of iron. If the measured concentration of iron in solution is higher than the effective concentration, then the normal fraction measured for x would also be higher than the effective normal fraction of x. As a consequence, the theoretical y estimated values using the experimental x values would also be higher than those actual. In general, this would lead to a deviation of the curve for the theoretical y values.

In this sense, it can be considered that a complexing reaction occurs between the free iron ions in solution (that we will represent with symbol Fe) and the different complexing substances (represented with symbol C listlessly of charge) to form a stable iron complex (symbolized by FeC), that we can consider with a 1:1 general stequiometry. This reaction is represented as follows:

$$\mathrm{Fe} + \mathrm{C} \rightleftharpoons \mathrm{FeC}. \qquad (12)$$

If the free iron and free complexing concentrations in solution are expressed as a function of the total concentrations in the media of each of the constituents (Fe$_0$ and C$_0$), respectively, the equilibrium constant for this reaction (K_C) can be calculated as a function of the molar concentrations:

$$K_C = \frac{[\mathrm{FeC}]}{[\mathrm{Fe}][\mathrm{C}]} = \frac{[\mathrm{Fe_0}] - [\mathrm{Fe}]}{[\mathrm{Fe}][\mathrm{C_0}] - [\mathrm{Fe}][\mathrm{Fe_0}] + [\mathrm{Fe}]^2}. \qquad (13)$$

On clearing the concentration of free iron as a function of the concentration of total iron, one has the expression

$$[\mathrm{Fe}] = \frac{-(K_C[C_0] - K_C[\mathrm{Fe_0}] + 1) \pm \sqrt{(K_C[C_0] - K_C[\mathrm{Fe_0}] + 1)^2 + 4K_C[\mathrm{Fe_0}]}}{2K_C}. \qquad (14)$$

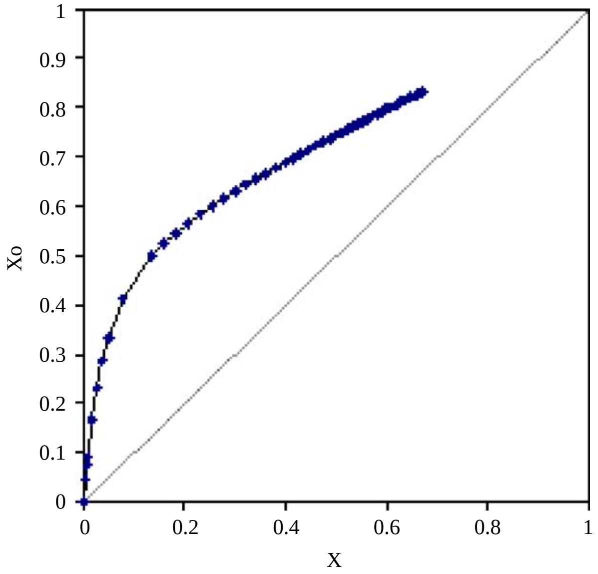

Fig. 8. Total iron fraction (x_0) versus effective iron fraction (x). Calculus take of Eq. (18), which includes the presence of complexing substances in the media. ($K_C = 1 \times 10^3$ L/mol and $C_0 = 1 \times 10^{-2}$ mol/L).

The result of the quantitative study of Eq. (14), is presented in Fig. 7, where we are taking $K_C = 1 \times 10^3$ L/mol and $C_0 = 1 \times 10^{-2}$ mol/L, that are typical values in wines.

In fact, the theoretical calculations should be carried out using the effective iron fraction data (x) rather than the data for the total iron fraction (x_0), which was used in the previous calculations for the model (Fig. 6). Therefore, a quantitative reproduction of the corresponding deviation due to this effect can be obtained using the representation of the total iron fraction against the effective iron fraction (x_0 versus x). This situation is represented in Fig. 8, where K_C and C_0 are the same as in Fig. 7 and pH $= 3.3$.

It can be seen that the form of the resulting curve is similar to that presented in Fig. 6, so it is possible to explain the type of deviations observed in Fig. 6 by considering this modification. In consequence, a complete mathematical model which present good fit to the real system must to include Eq. (14) to obtain the effective values of x.

5. Conclusions

Firstly, it is necessary to point out that the equivalent capacity of the studied resin decreases on changing from water to alcohol media and reaches a level of approximately 80% of the initial value. Therefore, it has been shown that the alcohol grade of the medium significantly affects the ionic demetalisation process, with the yield decreasing as the concentration of alcohol in the medium increases.

The developed theoretical model includes the Debye–Hückel equation for the liquid phase and Wilson equations for the resin phase. It has been demonstrated that the model is sufficiently valid for the process in question both in water and in alcohol or hydroalcohol media. Nevertheless, it is clear that factors exist in the wine matrix that make the ionic exchange process move away from the ideal behaviour initially considered in the model.

Among the factors that cause deviations, it was found that the value of the real ionic strength of the medium, which is higher than that calculated on the basis of the iron salts alone, is extremely important due to the presence of a diverse range of salts dissolved in the medium.

Equally, it was shown that it is necessary to bear in mind, when establishing the theoretical considerations for the proposed model, the presence of iron-complexing substances in the medium. These substances reduce the effective iron concentration in solution and, therefore, diminish the exchange effect and reduce its effectiveness.

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