Modeling of Recovery of Tartaric Acid using Various Solvents

Bharat Upadhyay\textsuperscript{1}, Amit Keshav\textsuperscript{2}

Abstract—Extraction of solute into a solvent is understood in terms of its ability to solvate the organic phase species and is affected by different forces such as electrostatic, dispersion, hydrogen bonding etc. It is very rare that the partition coefficient or extraction constants could be correlated with the particular physical properties of diluents (dielectric constant, solubility parameters, and electronic transition energies). Even if correlation were developed it could be for limited group of diluents. So it is necessary to correlate the partition coefficient using interactions of various types like dipole-dipole and/or dipole-induced-dipole interactions, hydrogen bonding etc. Linear solvation energy relationship (LSER) have been a comprehensive tool in this regard and includes the above mentioned interactions in a manageable form using the solvatochromic parameters of the solvents. In the present paper solvent extraction of tartaric acid has been modeled using LSER modeling using the values of solvatochromic parameters hydrogen bond donor acidity (\(\pi^*\)), hydrogen bond acceptor basicities (\(\alpha\), \(\beta\)) of the solvents. Model predicted results were compared with experimental data. It was found that for different solvents there is a good description of the distribution of acid using LSER model with coefficient of linear regression value of above 0.9 in all cases. Thus LSER model successfully predict the equilibrium behavior of acid extraction using different solvents.

Keywords— LSER Modeling, Tartaric acid, Solvents, Extraction.

I. INTRODUCTION

Extraction of tartaric acid by solvent extraction is function of type of solvent employed and operating conditions. Mass action law equilibria model have been used to explain the extraction phenomenon. However, it can be seen for a fixed operating conditions, that there is a relationship between the types of solvent on the extraction of tartaric acid using various diluents. In literature, the difference in extraction of acid by different solvents were tried to be explained on the basis of various physicochemical properties of the diluents, however no generalization could be obtained. The reason for this being that solvation is a very complicated phenomenon and could not be explained by mere one physicochemical property. Thus, a model is required that could correlate the results of extraction with the combined physicochemical characteristics of solvents. In this regard, attempt has been made using the linear solvation energy relationship (LSER) model. Model equations have been generated and presented. In all cases, a good success was obtained.

II. THEORY

The ability of a solvent to donate a hydrogen atom towards the formation of hydrogen bond is an important property. Protic solvents have these properties but some protogenic, albeit aprotic solvents have more recently shown as also potentially having this ability. \(\alpha\) parameter by Taft and Kamlet \cite{1} is the most successful indices that have been proposed to measure the hydrogen bond donor (HBD) ability. The linear solvation energy relationship (LSER) that measures property XYZ, in terms of solvent properties \cite{2} was defined as:

\[
XYZ = XYZ^0 + \text{solvent polarity/polarizability effect} + a\alpha + b\beta
\]

(1)

\(a\) and \(b\) are the susceptibilities of XYZ to changing solvent HBD acidity and hydrogen bond acceptance (HBA) basicity, respectively and \(\beta\) is the HBA basicity of the solvent. \cite{1}

Values of \(\alpha\) have been determined by the use of the solvatochromic comparison method. \cite{1}-\cite{3} In this method, indicator solutes are employed for which XYZ has a negligible susceptibility to the solvent HBA basicity but a high one for the solvent HBD acidity (large a). The (XYZ)_o + solvent polarity/polarizability effect values are obtained for the indicator in solvents devoid of HBD abilities, so that ax for HBD solvents can be calculated from the values of XYZ in the latter kind of solvents. Finally, an averaging procedure for several indicator solutes and a normalization procedure are used in order to obtain values of o~ that are in the range of 0 to 1. Many linear solvation energy correlations involving the solvent HBD acidity scale have been reported and the limitations of this scale have been discussed. \cite{2}-\cite{4} Interactions of various types: dipole-dipole and or dipole-induced dipole, hydrogen bonding etc. are responsible for the extraction of carboxylic acid from aqueous solutions. The general linear solvation energy relationship (LSER) is a comprehensive tool to include the above mentioned parameters of the diluents. Schmidt \cite{5} presented a systematic

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study on the effect of diluents on amine extraction of acids. He distinguished among three types of solvation: solvation of acid anion, alkylammonium cation or complex as a whole and found that the solvation of cation was not common in the case of tertiary amines. The solvation of the whole amine: acid complex is based on dipole-dipole interaction and was found to play an important role in the neutralization reactions between acid and amine which are promoted by the increasing polarity of the diluent. Empirical parameters, $DP^\ast$, have been introduced to quantify this influence according to the equation based on the linear free energy principle
\[ \ln K = \ln K_0 + a DP^\ast \]

where $K_0$ and $K$ are the extraction constants for standard and given diluent, respectively, and $a$ is constant for given extractant and solute. The values of $DP^\ast$ were estimated for about 25 diluents. Solvation of acid anion, which is based on specific interactions with the proton-donating diluent, is typical for the reaction of acid with alkylammonium salt. The hindering effect of the diluent can be explained as a competition between diluent and acid for the bonding with amine salt. Other empirical parameters, $DP$, were introduced to quantify this type of solvation according to the following equation, similar to equation (2)
\[ \ln K' = \ln K_0' + a' DP^\ast \]
The $DP$ values were estimated for about 30 diluents. If both types of solvation occur simultaneously, the combined equation is to be used in the form
\[ \ln K = \ln K_0 + a DP^\ast + a' DP \]

Using this concept Schmidt (1980) described the effect of diluents on the extraction of mineral acids by various tertiary amines with a comparatively good fit. The attempts were also made to correlate the values of $DP^\ast$ and $DP$ with various physicochemical properties of the diluents. The main disadvantage lies in the fact that the parameters $DP^\ast$ and $DP$ were obtained on the base of the same data set as the extraction constants which were correlated with them. This seems to increase the empirical character of these parameters.

Bizek et al. [6] modified equation (1) to adopt to describe the effect of diluents on the values of partitioning coefficients $K_D$ in the form
\[ \ln K_D = \ln K_{D_0} + P \left( \delta_b \right)^2 + \frac{1}{100} + s \left( \pi^\ast + d \delta \right) + b \beta + a \alpha \]

where $\delta_b$ is the Hildebrand’s solubility parameter and $\pi^\ast$, $d$, and $\delta$ are the solvatochromatic parameters that measure the solute + solvent, dipole + dipole, and dipole + induced dipole interactions, respectively. $K _{D_0}$ represents the extraction constant for an “ideal inert” diluent. The solvatochromatic parameter $\alpha$ scale of solvent HBA (hydrogen-bond donor) acidities describes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond. The $\beta$ scale of HBA (hydrogen-bond acceptor) basicities provides a measure of the solvent’s ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond, respectively. The coefficients $p, s, d, a$ and $b$ include the properties of solute. Rather than $p, s, d, a$ are regression coefficients. The values of solvatochromatic parameters $\pi^\ast$, $\delta$, $\alpha$, $\beta$ have been found several hundreds of compounds. The second term of eq 19 which contains the solubility parameter $\delta_b$ does not affect the values of the objective function significantly. Thus equation (5) reduces to
\[ \ln K_D = \ln K_{D_0} + s \left( \pi^\ast + d \delta \right) + b \beta + a \alpha \]

III. MATERIAL AND METHOD

Tartaric acid (99%) (Himedia, India) and the diluents MIBK, hexane, 1-octanol, 2-octanol, 1-decanol, 1-hexanol and tri-n-butylphosphosphate are of technical grade and were used without pretreatment. These diluents were used to see the effect of alcohols, ketone, aliphatic hydrocarbon and organophosphorous compound on the solvation of the acid in the extraction process. Distilled water was used to prepare the solutions of various concentrations of acid solutions. NaOH used for the titration is of analytical grade and was supplied by Ranbaxy, India. For the standardization of the NaOH, oxalic acid (99.8%) was obtained from S. D. Fine Chem Ltd., India. Phenolphthalein solution (pH range 8.2–10.0) was used as indicator for titration and was obtained from Ranbaxy, India. The range of pH of the feed solutions for the experiment was 2.65–3.14 at 305 K. Low concentration of tartaric acid was used because in waste streams and in fermentation broths, its concentration is not expected to be greater than 0.5 kmol/m³.

IV. RESULTS AND DISCUSSION

Physical extraction of tartaric acid using various solvents is shown as point data in Figure 1. TBP has been found to provide the highest extraction among different chosen solvents. Strongly solvating extractants like organophosphorous compounds have primarily been used in inorganic analysis for the extraction and separation of inorganic acids or metal species. The distribution of acidic compounds is governed by a number of distribution equilibria for distributing species and by secondary chemical equilibria which determine the concentrations of distributing species in each phase. The reaction leading to the extraction of an aqueous phase species into the less polar organic phase is the formation of hydrogen bonds to extractant molecules.

![Physical extraction of tartaric acid using different solvents](image-url)

Fig. 1 Physical extraction of tartaric acid using different solvents

Since phosphoryl can form hydrogen bonds to proton donors, TBP can be successfully used for the extraction of acidic organic compounds. The driving forces of the extraction are then the solvation of ionic species and the neutralisation of their charge by ion-pairing. The species
distributed into the organic phase will therefore be undissociated molecules of the weak acid solvated by the formation of hydrogen bonds to extractant molecules, possibly still carrying a few molecules of hydration water. The high polarity of the phosphoryl group in tributyl phosphate (TBP) enables it to act as a strong Lewis base and as a result it can form acid base complex when contacted with tartaric acid. The extraction reactions are ionic in nature.

**TABLE I**

<table>
<thead>
<tr>
<th>Diluents</th>
<th>$\pi^*$</th>
<th>$\delta$</th>
<th>$\beta$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MIBK</td>
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<td>1</td>
<td>0.12</td>
<td>0</td>
</tr>
<tr>
<td>hexanol</td>
<td>0.45</td>
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<td>0.66</td>
</tr>
<tr>
<td>1-octanol</td>
<td>0.4</td>
<td>0</td>
<td>0.81</td>
<td>0.77</td>
</tr>
<tr>
<td>2-octanol</td>
<td>0.41</td>
<td>0</td>
<td>0.82</td>
<td>0.78</td>
</tr>
<tr>
<td>1-decanol</td>
<td>0.45</td>
<td>0</td>
<td>0.82</td>
<td>0.70</td>
</tr>
<tr>
<td>TBP</td>
<td>0.65</td>
<td>0</td>
<td>0.95</td>
<td>0</td>
</tr>
</tbody>
</table>

The extraction reactions are ionic in nature.

The Solvatochromic parameters: hydrogen bond donor acidity ($\pi^*$, $\delta$) and hydrogen bond acceptor basicities ($\alpha$, $\beta$) for different diluents used are given in Table I.

LSER have been fitted to the data and the model $\ln K_D$ have been reported in Tables III for acid concentration of 0.05, 0.1, 0.2 and 0.4 mol/l, for extraction of tartaric acid using different solvents. Experimental and modeled $K_D$ values are given in Figure 2 and it was found than the model fits the data very well. The model parameters have been computed using Matlab 7.0 solver and the model equations for determination of $K_D$ are given in Table II.

**V. CONCLUSION**

A mathematical model for the extraction of tartaric acid was presented and model values were presented with the experimental results. A close resemblance of the two values suggested that the model could successfully be used for the future interpretations of the extraction of tartaric acid.

**REFERENCES**


TABLE III
EXPERIMENTAL AND LINEAR SOLVATION ENERGY RELATIONSHIP MODEL VALUES FOR EXTRACTION OF TARTARIC ACID USING DIFFERENT SOLVENTS

<table>
<thead>
<tr>
<th>Diluent</th>
<th>[HA]₀ = 0.05</th>
<th>[HA]₀ = 0.1</th>
<th>[HA]₀ = 0.2</th>
<th>[HA]₀ = 0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lnKᵩ₀&lt;sub&gt;exp&lt;/sub&gt;</td>
<td>lnKᵩ₀&lt;sub&gt;model&lt;/sub&gt;</td>
<td>lnKᵩ₀&lt;sub&gt;exp&lt;/sub&gt;</td>
<td>lnKᵩ₀&lt;sub&gt;model&lt;/sub&gt;</td>
</tr>
<tr>
<td>MIBK</td>
<td>-0.62913</td>
<td>-0.62906</td>
<td>-0.65848</td>
<td>-0.65853</td>
</tr>
<tr>
<td>hexane</td>
<td>-0.45199</td>
<td>-0.45280</td>
<td>-0.65848</td>
<td>-0.65870</td>
</tr>
<tr>
<td>1-octanol</td>
<td>-0.68781</td>
<td>-0.64507</td>
<td>-0.59607</td>
<td>-0.59108</td>
</tr>
<tr>
<td>2-octanol</td>
<td>-0.68773</td>
<td>-0.65992</td>
<td>-0.65606</td>
<td>-0.61548</td>
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<td>decanol</td>
<td>-0.71939</td>
<td>-0.69713</td>
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<tr>
<td>1-hexanol</td>
<td>-0.52906</td>
<td>-0.63510</td>
<td>-0.49714</td>
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<td>TBP</td>
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<td>-0.45072</td>
<td>-0.16952</td>
<td>-0.16060</td>
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</table>