Conductometric study on the benzoic acid in water+methanol systems at different solution temperatures

Narasimha Raghavendra

Department of Chemistry, K.L.E. society’s P. C. Jabin Science College (Autonomous) Vidyanagar, Hubballi-580031

This research article explores the results of the ion-solvent interaction with the aid of electrical conductivity law of benzoic acid in triple distilled water and different amounts of methanol at 293 K, 303 K, 313 K, and 323 K. The specific conductance obtained from the conductivity meter was examined using Shedlovsky and Kraus-Bray plots. The limiting molar conductance ($\lambda_m^0$) values obtained using the Shedlovsky and Kraus-Bray models. The $\lambda_m^0$ values obtained from the Shedlovsky and Kraus-Bray models were found to be in good agreement with each other. The association constant ($K_a$) values obtained from the Shedlovsky plots, whereas dissociation constant ($K_d$) values obtained from the Kraus-Bray plots. The thermodynamic parameters such as activation energy ($E_a$), free energy of adsorption ($\Delta G_a$), adsorption enthalpy ($\Delta H_a$) and adsorption entropy ($\Delta S_a$) values are evaluated in order to study the nature of ion-solvent interaction. The negative $\Delta G_a$ values showed the spontaneous ion-pair association process.

KEYWORDS
Electrical conductivity
Shedlovsky model
Association constant
Adsorption free energy
Adsorption enthalpy

ARTICLE INFORMATION
Received: 27 November 2018
Received in revised: 18 January 2019
Accepted: 17 February 2019
Available online: 20 March 2019
DOI: 10.26655/AJNANOMAT.2019.2.3.8
Introduction

Room-temperature The examination of electrical conductivity of electrolyte in solvent systems is of significant importance, because it can provide vital information about the behavior of the solvent structural effects, ions in the solution, and the ion-solvent interaction. The study of electrolytes in solvent systems is found to be useful for different chemical and electrochemical investigations.

Thermodynamic properties are very much essential to study the geometrical effects and intermolecular interactions in the systems. The study of the electrical conductive property of the electrolyte in aqueous solution provides insights into the electrolyte solution properties [1–3]. Thermodynamic properties are needed in many theoretical and applied areas of research and employed in many industrial sections. Exploring the information about the transport property (conductance) of electrolytes in aqueous environment gives hints about the ion-solvent and ion-ion interaction in the studied environments. The Shedlovsky and Kraus-Bray theories are used to examine the many electrolytes in the aqueous solutions [4–7]. The physical properties of binary mixed solvents can be altered to make them further favor to the solvent system for the investigation of ion association in the systems. The conductance studies in mixed solvents explore the information about the specific, preferential and nonspecific solvation effects on the ion-association phenomenon.

The measurement of conductance is of a great importance in examination of ion-pair formation in the studied systems under the existing condition. Study of conductometry behavior of different compounds in various solvents has a wide range of applications in analytical chemistry. Conductometry is a vital classical approach which provides precious information regarding the ion-solvent and ion-ion interactions in the solution.

Examination of the solvation process in the binary environment where one of the solvent as water throws light on the process of ion solvation [8–10]. Benzoic acid (C₇H₆O₂) is versatile and important compound and has a wide range of applications in several
pharmaceutical, chemical, engineering and agrochemical industries. The electrical conductivity of benzoic acid in water with different percentage of methanol at different solution temperatures is not available in the literature. This made us explore the solvation property of benzoic acid in water with different percentage of methanol at different solution temperatures.

These points strongly motivated us to explore the ion-ion interaction and ion-solvent interaction in water + different percentage of methanol mixtures containing different benzoic acid as a solute. The present research article explores the effect of different parameters on the transport properties of benzoic acid in water + methanol systems at different solution temperatures, namely 293 K, 303 K, 313 K and 323 K by employing the Shedlovsky and Kraus-Bray equations.

Experimental

The purified benzoic acid, triple distilled water, and non-aqueous methanol were used in this research study. Chemical structure of the benzoic acid is shown in Figure 1a and b. The binary mixtures were prepared by mixing the methanol and benzoic acid. The conductance measurement (model CM 180) was carried out by varying different amounts of methanol (0%, 20%, 40%, and 80%) in benzoic acid-water systems at four different solution temperatures, namely 293 K, 303 K, 313 K, and 323 K with the aid of thermostat with an accuracy of ± 0.01 °C. The known concentration of solution was taken in the double walled vessel and stored in the thermostat at a specific temperature for about 30 min and specific conductivity of the resulting solution was recorded.

\[ \frac{1}{\lambda_m} = \frac{1}{\lambda_m^0} + \frac{\lambda_m C}{\lambda_m^0 K_C} \]  

(Kraus-Bray model)  

\[ \frac{1}{S(z)\lambda_m} = \frac{1}{\lambda_m^0} + \frac{S(z)\lambda_m C^2 f^2 \mp K_a}{\lambda_m^0} \]  

(Shedlovsky model)  

Where, \( K_C \) = Dissociation constant, \( C \) = Concentration, \( \lambda_m^0 \) = limiting molar conductance, \( \lambda_m \) = molar conductance, \( K_a \) = Association constant, \( S \) =Onsagar slope. \( Z = S (\lambda C)^{1/2} / \lambda_0^{3/2} \)

\( S = a + \lambda_0 b \)

\( a = 82.4 / \eta (DT)^{1/2} \)

\( b = 8.20 \times 10^{-5} (DT)^{3/2} \)

\( \log f_\pm = -A (ac)^{1/2} / 1 + Ba^0(\alpha c)^{1/2} \)

\( \alpha = \lambda S(z) / \lambda_0 \), \( a^0 = \) ionic size parameter, B and A are Debye Huckel constants.

\( \lambda_m^0 \) and \( K_C \) values obtained from the plot of \( \frac{1}{\lambda_m} \) (Y-axis) against \( \lambda_m C \) (X-axis) with the help of Kraus-Bray theory.

The limitation of Kraus-Bray theory was overcome by Shedlovsky model. From the plot of the \( \frac{1}{S(z)\lambda_m} \) (Y-axis) against \( S(z)\lambda_m C^2 f^2 \mp \) (X-
Conductometric study on the benzoic acid-water system (1) by Shedlovsky model, the $\lambda_m^0$ and $K_a$ values are calculated.

The activation energy ($E_a$) was calculated from the Arrhenius equation,

$$\lambda_m^0 = A e^{-\frac{E_a}{RT}}$$  \hspace{1cm} (3)

The adsorption energy can be calculated from the equation below,

$$\Delta G = -RT \ln K_a$$  \hspace{1cm} (4)

From the plot of $\log K_a$ vs. $1000/T$, the $\Delta H$ values can be calculated.

The $\Delta S$ values can be obtained from the below equation,

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$  \hspace{1cm} (5)

Results and Discussion

The effects of the different percentage of methanol in the benzoic acid-water system were extensively screened with the aid of conductivity meter. The $\lambda_m^0$ values of benzoic acid in water with different percentage of methanol (0%, 20%, 40%, 60% and 80%) were obtained from the specific conductance values. The specific conductance values are obtained from the digital conductivity meter at four different solution temperatures (293 K, 303 K, 313 K, and 323 K). The $\lambda_m^0$, $K_a$, and $K_d$ values obtained from the Kraus-Bray and Shedlovsky plots are presented in Table 1 and 2.

Table 1. Limiting molar conductance for Benzoic acid in Water (1)+methanol (2) from T (293 to 323) K

<table>
<thead>
<tr>
<th>Property</th>
<th>Methanol (0%)</th>
<th>Methanol (20%)</th>
<th>Methanol (40%)</th>
<th>Methanol (60%)</th>
<th>Methanol (80%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_m^0$ (Kraus-Bray)</td>
<td>5.281</td>
<td>5.354</td>
<td>6.451</td>
<td>5.182</td>
<td>4.904</td>
</tr>
<tr>
<td>$\lambda_m^0$ (Shedlovsky)</td>
<td>5.339</td>
<td>5.413</td>
<td>6.522</td>
<td>5.239</td>
<td>5.409</td>
</tr>
<tr>
<td>$\lambda_m^0$ (Kraus-Bray)</td>
<td>6.809</td>
<td>6.938</td>
<td>7.633</td>
<td>7.311</td>
<td>6.166</td>
</tr>
<tr>
<td>$\lambda_m^0$ (Shedlovsky)</td>
<td>6.880</td>
<td>7.018</td>
<td>7.720</td>
<td>7.395</td>
<td>6.263</td>
</tr>
<tr>
<td>$\lambda_m^0$ (Kraus-Bray)</td>
<td>8.837</td>
<td>9.394</td>
<td>8.901</td>
<td>9.425</td>
<td>8.488</td>
</tr>
<tr>
<td>$\lambda_m^0$ (Shedlovsky)</td>
<td>8.947</td>
<td>9.512</td>
<td>9.013</td>
<td>9.543</td>
<td>8.594</td>
</tr>
<tr>
<td>$\lambda_m^0$ (Kraus-Bray)</td>
<td>8.871</td>
<td>8.864</td>
<td>8.519</td>
<td>8.360</td>
<td>8.076</td>
</tr>
<tr>
<td>$\lambda_m^0$ (Shedlovsky)</td>
<td>8.987</td>
<td>8.975</td>
<td>8.631</td>
<td>8.465</td>
<td>8.177</td>
</tr>
</tbody>
</table>

Table 2. The dissociation constant ($K_c$) and association constant ($K_a$) for Benzoic acid in water (1) + methanol (2) from $T$ (293 K to 323 K)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Methanol (0%)</th>
<th>Methanol (20%)</th>
<th>Methanol (40%)</th>
<th>Methanol (60%)</th>
<th>Methanol (80%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_c$</td>
<td>$K_a$</td>
<td>$K_c$</td>
<td>$K_a$</td>
<td>$K_c$</td>
</tr>
<tr>
<td>293</td>
<td>0.019</td>
<td>55.36</td>
<td>0.007</td>
<td>133.33</td>
<td>0.002</td>
</tr>
<tr>
<td>303</td>
<td>0.03</td>
<td>32.294</td>
<td>0.016</td>
<td>63.864</td>
<td>0.004</td>
</tr>
<tr>
<td>313</td>
<td>0.018</td>
<td>80.66</td>
<td>0.008</td>
<td>132.351</td>
<td>0.010</td>
</tr>
<tr>
<td>323</td>
<td>0.050</td>
<td>21.174</td>
<td>0.034</td>
<td>31.112</td>
<td>0.032</td>
</tr>
</tbody>
</table>

The conductance of the solution mainly depends on the number of ions and mobility of ions. The $\lambda_m^0$ values enhances with a rise in the solution temperature from 293 K to 323 K which is due to the enhance in the mobility of the ions and thermal energy ions. This nature is
due to the enhanced thermal energy and cleavage of weak bonds. The limiting molar conductance reduced with an increase in the methanol percentage (0\%, 20\%, 40\%, 60\%, and 80\%) in the benzoic acid-water system. The decrease in the conductance is due to the enhanced solvent-solvent interaction and ion-solvent interaction in the studied system. As soon as methanol is added to the water, there is exists solvent-solvent interaction instead of ion-solvent interaction. The introduction of methanol leads to the solvent-solvent interaction which leads to the formation of a new solvent mixture molecule having higher size than any pure solvent molecule. The new molecule preferentially solvates the cation and enhances the size of the solvated cation. This leads to a reduction in the conductance. The reduction in the dielectric constant, enhancement in the viscosity of the binary mixtures, enhanced solvated ion size and hydrophobic attraction. The formation of intermolecular and intramolecular hydrogen bond acts as a barrier for ionic mobility which generally decreases the conductivity of the solution. The increase in the limiting molar conductance with a rise in the solution temperature from 293 K to 323 K is due to enhancement of kinetic energy of ions. \( \lambda_{\text{m}} \) values obtained from the Kraus-Bray and Shedlovsky plots are in good agreement. Hence, ion-solvent interaction and solvent-solvent interactions plays vital role in the study of electrical conductivity of benzoic acid in these solvent mixtures. The association constant (\( K_a \)) values under the studied systems are shown in the Table 2. It is observed that, the \( K_a \) values decrease with a rise in the solution temperature from 293 K to 323 K which shows the exothermic association process. Further, with increase in the amount of methanol percentage in benzoic acid-water system, the association constant value increases. The enhancement in the association constant may be related to a reduction in the relative permittivity by enhancing the proportion of methanol and reducing the ion mobility which leads to the association of ions.

### Table 3. Thermodynamic parameters

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>0 %</th>
<th>20 %</th>
<th>40 %</th>
<th>60 %</th>
<th>80 %</th>
<th>0 %</th>
<th>20 %</th>
<th>40 %</th>
<th>60 %</th>
<th>80 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_a ) (kJ/mol)</td>
<td>-14.96</td>
<td>-28.26</td>
<td>-69.06</td>
<td>-38.19</td>
<td>-43.78</td>
<td>-14.96</td>
<td>-28.26</td>
<td>-69.06</td>
<td>-38.19</td>
<td>-43.78</td>
</tr>
<tr>
<td>( \Delta S_a ) (J/mol)</td>
<td>-17.71</td>
<td>-55.77</td>
<td>-184.33</td>
<td>-85.07</td>
<td>-100.4</td>
<td>-33.36</td>
<td>-77.06</td>
<td>-210.9</td>
<td>-109.4</td>
<td>-129.2</td>
</tr>
<tr>
<td>( \Delta G_s ) (kJ/mol)</td>
<td>-9.77</td>
<td>-11.91</td>
<td>-15.05</td>
<td>-13.27</td>
<td>-14.34</td>
<td>-4.85</td>
<td>-4.90</td>
<td>-5.14</td>
<td>-5.04</td>
<td>-4.62</td>
</tr>
<tr>
<td>0 %</td>
<td>20 %</td>
<td>40 %</td>
<td>60 %</td>
<td>80 %</td>
<td>0 %</td>
<td>20 %</td>
<td>40 %</td>
<td>60 %</td>
<td>80 %</td>
<td></td>
</tr>
<tr>
<td>( \Delta H_a ) (kJ/mol)</td>
<td>-14.96</td>
<td>-28.26</td>
<td>-69.06</td>
<td>-38.19</td>
<td>-43.78</td>
<td>-14.96</td>
<td>-28.26</td>
<td>-69.06</td>
<td>-38.19</td>
<td>-43.78</td>
</tr>
<tr>
<td>( \Delta S_a ) (J/mol)</td>
<td>-29.6</td>
<td>-71.56</td>
<td>-202.36</td>
<td>-103.28</td>
<td>-122.0</td>
<td>-28.0</td>
<td>-69.2</td>
<td>-195.8</td>
<td>-100.5</td>
<td>-118.0</td>
</tr>
<tr>
<td>( \Delta G_s ) (kJ/mol)</td>
<td>-5.70</td>
<td>-5.86</td>
<td>-5.72</td>
<td>-5.87</td>
<td>-5.59</td>
<td>-5.89</td>
<td>-5.89</td>
<td>-5.78</td>
<td>-5.73</td>
<td>-5.64</td>
</tr>
</tbody>
</table>

The thermodynamic parameters of the studied systems are presented in the Table 3. The variation in the activation energy values shows that, the activation energy values slightly decrease with rising in methanol percentage in benzoic acid–water system. The decrease in the activation energy values at the initial stage is due to enhancement in the dissociation process,
which leads to the release of several ions and then undergoes solvation. Further, in all the cases, the obtained $\Delta G$ values are negative. The negative sign in the association free energy values shows that, the process of association is spontaneous and indicates the strong ion-pair association process. The process of association is exothermic in nature which is due to positive $\Delta H^\circ$ values. The values of association entropy are in negative for all the studied systems and obtained values are very low, which is due to the presence of steric hindrance. This controls the motion of ions in the studied systems and enhanced disorders.

Conclusions

In this research study, the conductivity measurement of the benzoic acid in the binary mixed solvents (water + different percentage of methanol) at 293 K, 303 K, 313 K and 323 K was reported. The conductivity data were evaluated using the Kraus-Bray and Shedlovsky equations. The limiting molar conductance values obtained from the Kraus-Bray and Shedlovsky models were in good agreement with each other. The limiting molar conductance values enhanced with increasing the solution temperature and decreased with a rise in the methanol percentage in the benzoic acid-water system. The Gibbs free energy of association was negative which indicates the spontaneous association process. The negative enthalpy association values showed the exothermic association process.

References


[5]. EL-Khouly A.A., Gomaa E.A., EL-Ashry S. second conf. in Basic science, Assiut University, Assiut, 2000


How to cite this manuscript: Narasimha Raghavendra*. Conductometric study on the benzoic acid in water+methanol systems at different solution temperatures. Asian Journal of Nanoscience and Materials, 2019, 2(3), 350-355. DOI: 10.26655/AJNANOMAT.2019.2.3.8