Electrochemical Studies on Ion Pairs Formation of Sodium Diethyldithiocarbamate in Water

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ABSTRACT: The conductance data of sodium diethyldithiocarbamate (NaDDC) in water solutions at various temperatures (25, 30, 35 and 40°C) are presented. The results were construed by applying the Fuoss-Onsager equation to obtain the parameters: equivalent conductance at infinite dilution (\(\Lambda_0\)), the distance of closest approach (\(\alpha\)) and association constant (\(K_A\)). In the light of the solvent separated-ion pair model, the \(K_A\) trend is discussed. A comparison was done between the value of \(\alpha\) and the sum of calculated electrostatic Stokes' radii \(R^+\) and \(R^-\). Both of thermodynamic functions (\(\Delta H^o\), \(\Delta G^o\), \(\Delta S^o\)) and the activation energy (\(\Delta E_s\)) were determined; the \(\Lambda_0\) values were noticed to increase gradually with the dramatic increase in temperature referring to less solvation or higher ions mobility. Negative values of Gibbs free energy change \(\Delta G^o\) for (NaDDC) indicate that the association process is preferable than the dissociation process. The positive value of (\(\Delta H^o\)) points to that the association process is endothermic. Entropy change (\(\Delta S^o\)) values were positive which means that the solvation of ion-pair decreases emulated to that of the free ion.

KEYWORDS: Sodium diethyldithiocarbamate, limiting equivalent conductance (\(\Lambda_0\)), ion association, activation energy and thermodynamic functions.

INTRODUCTION

Studying the transport and thermodynamic properties of electrolyte solutions is important for its industrial applications in several chemical processes such as: environmental applications (e.g. chemical waste disposal), electrochemical processes (corrosion or electrolysis), hydrometallurgical processes, production of energy sources, separation techniques (solution crystallization, bioseparations) and supercritical technologies (e.g. synthesis in supercritical fluids and destroying of hazardous agents). [1-3]

Measuring the transport properties as conductance at low concentrations helps in exploring the ionic solvation besides obtaining reliable values of conductance at infinite dilution. [4] These properties are affected by (i) size of the ions, (ii) any modulation in the structure of the solvent and (iii) strong ion-solvent interactions. Conductivity method is used to test the process water quality in those applications which require ultrapure water as in microelectronics, pharmaceutical, waste water treatment, sea water desalination, etc. [5,6]

The electrical conductivities study of dilute solutions whether for salts or complexes is considered important method for studying the ion-pair or multiple-ion association in aqueous solutions, non-aqueous or mixed ones [7-10]. Furthermore, measuring conductivity was used to study the solute-solvent interaction of some electrolytic solutions and estimate the hydration free energy [11]. The aim of the present work is to determine sodium diethyldithiocarbamate (NaDDC) conductance values that measured in water at various temperatures (25, 30, 35 and 40°C). The nature of the ion-ion and ion-solvent interaction for NaDDC were discussed by evaluating the limiting equivalent conductance (\(\Lambda_0\)), the association constant (\(K_A\)) and (\(\alpha\)) which expresses the solvation. The effect of temperature mutation on the association constant has been studied. Thus, the thermodynamic functions (\(\Delta H^o\), \(\Delta G^o\), \(\Delta S^o\)) and activation energy (\(\Delta E_s\)) were obtained.
Dithiocarbamates are important organic compounds used in many applications to a large degree and are produced in large amounts around the world. They display worthy biological effects containing antibacterial and antifungal activities besides acting as antioxidant [12]. They have an essential role in agriculture [13-17] and act as linkers in synthesis organic solid phase [18-21]. They are used in industrial rubber processing [22-24] and in techniques related to controlled radical polymerization as well. [25-28] Because they have the capability to bind with metal, they act as enzymes inhibitors. Dithiocarbamates are utilized in medicinal chemistry and have been applied in the treatment of cancer [29-31], also have been upheld in the treatment of acute nickel carbonyl poisoning. [32] Sodium diethyldithiocarbamate has been used as an inhibitor of acquired immune deficiency syndrome progression. [33]

**EXPERIMENTAL**

Sodium diethyldithiocarbamate is Analar analytical reagent "BDH", Conductivity water obtained by passing ordinary distilled water from a tin still over a 60 cm long Elgastat deionizer and guarded against contamination with atmospheric CO$_2$ by soda lime tubes. Its specific conductance ($\sigma_s$) at varied temperatures (25, 30, 35 and 40 °C) amounted to (1.51–1.73 x 10$^{-6}$) ohm$^{-1}$cm$^{-1}$. All solutions were prepared by weight. NaDDC was weighed on microbalance which reads to ±0.1 mg. Dilution into the cell was executed by dropping the solvent via weighing pipette. The experimental values of conductance were measured by Conductivity Bridge instrument model: Crison GLP31 (Conductivity Measurement error ≤0.5% and the reproducibility: ±0.1%) and a cell with bright platinum electrodes has a nominal cell constant for dilute solutions (K=0.1 cm$^{-1}$). The conductivity meter was calibrated with three KCl conductivity standard solutions (0.001 M, EC=147 μS cm$^{-1}$ at 25.0 °C; 0.01M, EC=1413 μS cm$^{-1}$ at 25.0 °C and 0.1 M, EC=12.88 mS cm$^{-1}$ at 25.0 °C) supplied by Crison. The temperature is kept constant to within ±0.1°C using a water ultra thermostat. The dielectric constants (D25°) = 78.54, (D30°) = 76.73, (D35°) = 74.80, (D40°) = 73.15, respectively. In all calculations, the used solvent constants were taken as stated [34-36], i.e., densities ($d_{25°}$) = 0.99707 g · cm$^{-3}$, ($d_{30°}$) = 0.99568 g · cm$^{-3}$, ($d_{35°}$) = 0.99406 g · cm$^{-3}$, ($d_{40°}$) = 0.99220 g · cm$^{-3}$, respectively, the viscosities ($\eta_{25°}$) = 0.8903 × 10$^{-2}$ P, ($\eta_{30°}$) = 0.7975 × 10$^{-2}$ P and ($\eta_{35°}$) = 0.7194 × 10$^{-2}$ P, ($\eta_{40°}$) = 0.6531 × 10$^{-2}$ P, respectively.

**RESULTS AND DISCUSSION**

**A- Conductance of Sodium Diethyldithiocarbamate in Water at several Temperatures:**

The measured equivalent conductance data are shown in Tables (1-2). By plotting the extrapolation of $\Lambda$ against $C^{1/2}$, an approximate value of $\Lambda_o$ was obtained. More precise values of $\Lambda_o$ were resulted from the following Fuoss-Kraus-Shedlovsky (F.K.S) equation:

$$\frac{1}{\Lambda}S_{(a)} = \frac{1}{\Lambda_o} + C \frac{1}{\Lambda_o} \frac{f}{K_o} \Lambda_o^2$$

(1)

<table>
<thead>
<tr>
<th>10$^4$ C $^{(a)}$</th>
<th>$\Lambda$</th>
<th>10$^4$ C $^{(b)}$</th>
<th>$\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5583</td>
<td>97.714</td>
<td>1.6303</td>
<td>107.912</td>
</tr>
<tr>
<td>1.3983</td>
<td>98.601</td>
<td>1.4900</td>
<td>108.811</td>
</tr>
<tr>
<td>1.2747</td>
<td>99.297</td>
<td>1.3698</td>
<td>109.599</td>
</tr>
<tr>
<td>1.1673</td>
<td>99.863</td>
<td>1.2703</td>
<td>110.473</td>
</tr>
<tr>
<td>1.0816</td>
<td>100.29</td>
<td>1.1900</td>
<td>111.200</td>
</tr>
<tr>
<td>1.0019</td>
<td>100.88</td>
<td>1.1102</td>
<td>111.627</td>
</tr>
<tr>
<td>0.9365</td>
<td>101.41</td>
<td>1.0390</td>
<td>112.302</td>
</tr>
<tr>
<td>0.8800</td>
<td>101.67</td>
<td>0.9822</td>
<td>112.914</td>
</tr>
</tbody>
</table>
Electrochemical Studies on Ion Pairs Formation of Sodium Diethyldithiocarbamate in Water

Table 2: Conductance of sodium diethyldithiocarbamate in water at 35 and 40°C

<table>
<thead>
<tr>
<th>$10^4$ C</th>
<th>$\Lambda$</th>
<th>$10^4$ C</th>
<th>$\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6817</td>
<td>109.43</td>
<td>2.2939</td>
<td>94.896</td>
</tr>
<tr>
<td>1.5447</td>
<td>110.53</td>
<td>2.1006</td>
<td>97.012</td>
</tr>
<tr>
<td>1.4249</td>
<td>111.61</td>
<td>1.9239</td>
<td>99.113</td>
</tr>
<tr>
<td>1.3211</td>
<td>112.58</td>
<td>1.7873</td>
<td>100.70</td>
</tr>
<tr>
<td>1.2371</td>
<td>113.44</td>
<td>1.6573</td>
<td>102.62</td>
</tr>
<tr>
<td>1.1590</td>
<td>114.52</td>
<td>1.5543</td>
<td>104.09</td>
</tr>
<tr>
<td>1.0889</td>
<td>115.09</td>
<td>1.4686</td>
<td>105.19</td>
</tr>
<tr>
<td>1.0265</td>
<td>115.69</td>
<td>1.3808</td>
<td>106.66</td>
</tr>
</tbody>
</table>

(a) Results at 25°C. (b) Results at 30°C. (c) Results at 35°C. (d) Results at 40°C.

Where $K_D$ is the dissociation constant and $S(z)$ is a function of $z$ called Shedlovsky’s function that was tabulated by Daggett. The $z$ value could be determined from the expression:

$$z = \alpha \frac{(CL)^{1/2}}{\Lambda_0^{3/2}} \quad (2)$$

Where $\alpha$ is the limiting tangent (Onsager slope). The plot of $1/\Lambda S(z)$ versus. $(CL S(z))^2$ gives $1/\Lambda_0$ as the intercept and $1/ K_D$ as the slope. More accurate values of $\Lambda_0$, $J(a)$, $\lambda$ and $K_A$ were obtained from Fuoss-Onsager equation. [37] The starting $\Lambda_0$ value was resulted from Fuoss-Kraus-Shedlovsky equation by the assist of specific computer program that was programmed on an IBM-PC. The desired accuracies in these calculations are ± 0.02 for $\Lambda_0$; ± 2 for (J less than 200), ± 5 for (J with values range from 200 to 1000) and ± 10 for (J more than 1000).

The standard deviation $\sigma_\Lambda$ was calculated using the equation [38]:

$$\sigma_\Lambda = \left\{ \frac{\Sigma (\Lambda \text{ calculated} - \Lambda \text{ observed})^2}{N - 1} \right\}^{1/2} \quad (3)$$

Where $N$ is the number of experimental points.

Fig. 1 displays the variation of $J$ with $\lambda$ for sodium diethyldithiocarbamate in water at 25, 30, 35 and 40°C. Through the knowledge of the average value of $J$, The average value of $\lambda$ could be calculated by interpolation. This $J$ value was obtained from the computer reading, where $J$ is being a function of $\lambda$ and has the following equation [37]:

$$J = \sigma_1 \Lambda_0 + \sigma_2 \quad (4)$$
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Fig. 1: Variation of $J$ and $\Lambda$ for sodium diethyldithiocarbamate in water at 25, 30, 35 and 40°C

Where $\sigma_1$ and $\sigma_2$ are the functions of $J$. The derived constants are represented in Table 3 and it is observed that with increasing the temperature, the $\Lambda$ values increase. The values of $K_A$ increase with increasing the temperature where the dielectric constant of solvents decreases with increasing the temperature as reported in literature [34-36] thus, ion association occurs.

Table 3: The characteristic parameters for sodium diethyldithiocarbamate in water at 25, 30, 35 and 40°C derived from Fuoss-Onsager equation

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\Lambda$ (ohm$^{-1}$ equiv$^{-1}$ cm$^2$)</th>
<th>$J$</th>
<th>$K_A$</th>
<th>$\Lambda$ (Å)</th>
<th>$\sigma_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>108.41</td>
<td>241.81</td>
<td>721.84</td>
<td>4.84</td>
<td>0.063</td>
</tr>
<tr>
<td>30°C</td>
<td>122.97</td>
<td>304.16</td>
<td>925.87</td>
<td>5.40</td>
<td>0.101</td>
</tr>
<tr>
<td>35°C</td>
<td>130.28</td>
<td>383.74</td>
<td>1301.6</td>
<td>6.34</td>
<td>0.111</td>
</tr>
<tr>
<td>40°C</td>
<td>144.92</td>
<td>497.32</td>
<td>3475.6</td>
<td>7.47</td>
<td>0.086</td>
</tr>
</tbody>
</table>

The trend of $K_A$ in the present work was explained in the light of the U term as represented in the following equation [39]:

\[
\ln K_A = \ln (4 \pi N_A \Lambda^3 / 3000) + e^2 / \Lambda DkT + U
\]

(5)

Where $U = \Delta S / k - E_s / kT$  

(6)

$\Delta S / k$ is the entropy Boltzmann constant ratio which explains the eventuality of the orientation of the solvent molecules around the free ions and $E_s / kT$ is an energy relationship which includes the energy of the solvent molecules with respect to the free ions and ion-pairs. In case of water in Table 4 the U term increases with increasing the temperature, i.e. the entropy term is more predominant than ion–dipole term for sodium diethyldithiocarbamate.
Eventually, the solvent separated ion-pair model can be applied [40]. In this model a multiple-step association was suggested as illustrated scheme 1:

\[
\text{(Na)}^+ + \text{(DDC)}^- + (\text{solvent})_n \quad \text{(Condition I) Solvated pattern} \\
K_1 \quad \text{K}_2
\]

\[
\text{(Na)}^+ (\text{solvent})_n (\text{DDC})^- \quad \text{(Condition II) Desolvated pattern}
\]

Where \( y \) = the number solvent molecules that escaped from solvation.

Thus, the association constant was given by the expression:

\[
K_A = K \sum (C_{\text{ion-pairs}}) / (C_{\text{(Na)}})(C_{\text{DDC}})(\text{solvent})_n = K_1 (1 + K_2)
\]

Where \( K_A = K \sum \) is obtained from the conductance measurements and since \( K_1 = 4 \pi N \lambda^2 e^2 / 3000 \), then \( K_2 \) can be calculated and \( b = e^2 / \lambda DTk \).

In case of sodium diethyldithiocarbamate in water at different temperatures, the results compiled in Table 4 indicated that \( K_2 \) increases with increasing the temperature, i.e. ion-pair favored the desolvated pattern (condition II) than the solvated pattern (condition I).

### Radii of Ions

The electrostatic radius \((R^+ + R^-)\) was given by Stokes' equation:

\[
R^+ = \frac{0.8194 \times 10^{-8}}{\lambda_0^2 \eta_0} 
\]

Where \( \lambda_0^+ \) or \( \lambda_0^- \) are obtained from the intercept of the straight line, resulting from the plots of Walden product \( \Lambda_0 \eta_0 \) versus the reciprocal of the molecular weight as previously discussed. [41]
From the data in Table 5, it could be noticed that in case of water at 25, 30, 35 and 40°C, the values of \( \hat{a} \) were greater than electrostatic radii \( (R^+ + R^-) \) obtained from Stokes' equation. This was due to the solvation of ions.

**Table 5:** Calculation of the radii of the ions for sodium diethyldithiocarbamate in water at 25, 30, 35 and 40°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \lambda^+ ) (Å)</th>
<th>( \lambda^- ) (Å)</th>
<th>( \lambda^+ ) (Å)</th>
<th>( R^+ ) (Å)</th>
<th>( R^- ) (Å)</th>
<th>( R^+ + R^- ) (Å)</th>
<th>( \hat{a} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>108.41</td>
<td>0.5191</td>
<td>50.10</td>
<td>58.31</td>
<td>1.837</td>
<td>1.578</td>
<td>3.415</td>
</tr>
<tr>
<td>30°C</td>
<td>122.97</td>
<td>0.5304</td>
<td>56.46</td>
<td>66.51</td>
<td>1.820</td>
<td>1.545</td>
<td>3.365</td>
</tr>
<tr>
<td>35°C</td>
<td>130.28</td>
<td>0.4948</td>
<td>61.50</td>
<td>68.78</td>
<td>1.852</td>
<td>1.656</td>
<td>3.508</td>
</tr>
<tr>
<td>40°C</td>
<td>144.92</td>
<td>0.5008</td>
<td>68.24</td>
<td>76.68</td>
<td>1.839</td>
<td>1.636</td>
<td>3.475</td>
</tr>
</tbody>
</table>

(1) ohm\(^{-1}\) equiv\(^{-1}\) cm\(^2\)

**B- THERMODYNAMIC STUDIES OF SODIUM DIETHYLDITHIOCARBAMATE IN WATER FROM CONDUCTANCE MEASUREMENTS:**

It is evident from Table 6 that, the values of \( \Lambda_0 \) increase regularly with increasing the temperature for sodium diethyldithiocarbamate, indicating lower solvation or greater mobility of the ions in the solvent system studied. This is due to the fact that, the increase in thermal energy causes variance in the vibrational, rotational and translational energy of molecules which leads to higher frequency and hence, farthest ionic mobility [42]. Moreover, the association constant \( (K_a) \) values increase with increasing the temperature, due to the decrease in dielectric constant of the medium [43].

Measuring the ionic conductance depends on the mobility of the ions. So, it is totally sensible to deal with the conductance data in the same manner to that one which related to the processes occur with variation of temperature [43], i.e.

\[
\Lambda_0 = Ae^{-\Delta E_S / RT} \quad \text{Or} \quad \log \Lambda_0 = \log A - (\Delta E_s / 2.303RT), \tag{9}
\]

Where \( A \) is the frequency factor, \( R \) is the ideal gas constant and \( \Delta E_s \) is the Arrhenius activation energy of transport processes.

By plotting \( \log \Lambda_0 \) versus \( 1/T \) as shown in Fig. 2, the slope \( (-\Delta E_s / 2.303R) \) is obtained from which the \( \Delta E_s \) value was computed and recorded in Table 6. From the table, the activation energy \( \Delta E_s \) is positive for sodium diethyldithiocarbamate in water solvent. The activation energy \( \Delta E_s \) positive value refers to the ions high mobility in the solution and as a result high \( \Lambda_0 \) values were obtained.

**Fig. 2:** The variation of \( \log \Lambda_0 \) versus \( 1/T \) for sodium diethyldithiocarbamate in water at different temperatures.
Table 6: Thermodynamic parameters of sodium diethyl dithiocarbamate in water at different temperatures:

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Λ_0 (ohm^-1 equiv^-1 cm^2)</th>
<th>Κ_A</th>
<th>ΔΕ_i (kJ mol^-1)</th>
<th>ΔH (kJ mol^-1)</th>
<th>ΔG (kJ mol^-1)</th>
<th>ΔS (J mol^-1 K^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>108.41</td>
<td>721.84</td>
<td>14.41</td>
<td>78.04</td>
<td>-16.310</td>
<td>261.95</td>
</tr>
<tr>
<td>303</td>
<td>122.97</td>
<td>925.87</td>
<td>16.211</td>
<td>257.63</td>
<td>-17.211</td>
<td>253.45</td>
</tr>
<tr>
<td>308</td>
<td>130.28</td>
<td>1301.6</td>
<td>18.367</td>
<td>253.45</td>
<td>-18.367</td>
<td>249.41</td>
</tr>
<tr>
<td>313</td>
<td>144.92</td>
<td>3475.6</td>
<td>21.222</td>
<td>249.41</td>
<td>-21.222</td>
<td>249.41</td>
</tr>
</tbody>
</table>

The free energy change ΔG° for the association process is calculated from equation (10): [43]

\[
ΔG° = -RT \ln K_A. \tag{10}
\]

As noticed in Table 6, negative values of the free energy change (ΔG°) mean that the reaction is spontaneous and association process is preferable than the dissociation process. The values of (ΔG°) become more negative with increasing the temperature. The solvent molecules are released into bulk solvent that leads to rise in ΔG° values. At high temperature, the permittivity of the solvent is decreased which leading strengthen the association between ions [44].

The enthalpy change (heat of association "ΔH°") for water is obtained from the slope of the plot of log Κ_A versus 1/T Fig. 3. The value of (ΔH°) was calculated, where the slope equals (-ΔH°/2.303R). For sodium diethyl dithiocarbamate, the positive value of (ΔH°) indicates that the association processes is endothermic. Positive and high (ΔH°) value can be attributed to the interaction between ions [44].

Fig. 3: The variation of log K_A versus 1/T for sodium diethyl dithiocarbamate in water at different temperatures

The entropy change (ΔS°) was calculated, from Gibbs-Helmholtz equation:

\[
ΔS° = ΔH° - TΔS°. \tag{11}
\]

ΔS° values represent the randomness of ions in the studied solvent system. As shown in Table 6 and because of the decrease in the solvation of ion-pair compared to that of the free ion, [45-47] ΔS° values were positive. This may be attributed to increase in the degree of freedom upon association, mainly due to the release of solvent molecules.

The primary factors which administer the entropy of electrolytes ion association are: the ions shape and size, orientation of the solvent molecules around the ions, ions charge density and to what extent the molecules of solvent penetrate inside the space of ions [48].
El-Hammamy et al., [35] measured the conductance of cobalt (III) complex, chloropentammine chloride, in water at several temperatures starting of 40 to 60°C. The data were interpreted by applying Fuoss-Edelson equation [49]. It was clear that, \( \Lambda_o \) and \( K_o \) increase with increasing the temperature. The positive value of \( \Delta_{E_o} \) was determined. The values of \( \Delta H^o \) and \( \Delta S^o \) are positive at a particular temperature but \( \Delta G^o \) is negative, this may be due to the increase in association of ions and thus solvation process was less. The reaction was endothermic; energy was required to break the bonds around free ion as well as the ion-pairs.

At different temperatures beginning from 25 to 35°C, the conductance of cobalt (III) complex, bromopentammine salts (chloride, bromide and perchlorate) was measured in water by El-Hammamy et al. [50]. Using Fuoss-Edelson equation, results were analyzed. [49] With increasing the temperature, the \( \Lambda_o \) and \( \alpha \) values increased however \( K_o \) value decreased. From the log \( \Lambda_o \) versus \( 1/T \) plot for all complexes of cobalt (III) in water, the \( \Delta_{E_o} \) positive values were estimated and likewise the parameters \( \Delta H^o, \Delta G^o, \Delta S^o \). In the solvents studied at different temperatures, negative \( \Delta H^o \) values manifest the exothermic ion association processes. With increasing the temperature, it was noticed that the limiting equivalent conductance values exceeded. So, higher solvation occurs. [51]

El-Hammamy et al., [52] have measured the electric conductance of 1:1 s-acetylthiocholine halides (Cl\(^-\), Br\(^-\), I\(^-\)) and perchlorate (ClO\(_4\)\(^-\)) in water solvent at 25, 30 and 35°C. Fuoss-Onsager equation was applied and the values \( \Lambda_o, K_o \) and \( \alpha \) were gained. For all salts of s-acetylthiocholine, it was observed that both of \( \Lambda_o \) and \( \alpha \) had the same approach; increased with increasing the temperature unlike \( K_o \) which decreased upon increasing the temperature. \( \Delta H^o, \Delta G^o \) and \( \Delta S^o \) negative values for the whole salts studied, showed that the association step was much more stable and no high energy consumption was required. In short, the reaction was exothermic in nature [53].

References


