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Electrical Conductivity and Thermodynamic Studies on Sodium Diethyldithiocarbamate in Methanol at Different Temperatures

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The conductance data of sodium diethyldithiocarbamate (NaDDC) in methanol at different temperatures (25, 30, 35 and 40°C) are presented. Results were construed by applying the Fuoss-Onsager equation to determine the characteristic parameters: equivalent conductance at infinite dilution Λ_o, association constant K_A, the distance of closest approach of ions å. After calculation of the electrostatic Stokes' radii (R^+ and R^-), their sum is likened to å value. Thermodynamic functions such Gibbs free energy change ΔG^o, enthalpy change ΔH^o, change in entropy ΔS^o and the activation energy (ΔE_s) were estimated.

Keywords: Sodium diethyldithiocarbamate, equivalent conductance at infinite dilution (Λ_o), ion association, activation energy and thermodynamic functions.

1. INTRODUCTION

Thermodynamic and transport properties of electrolyte solutions have significant importance because of their potential applications in different chemical processes and industries as: (i) electrochemical processes (corrosion or electrolysis), (ii) environmental applications including: chemical waste disposal or wastewater treatment, (iii) hydrometallurgical processes, (iv) technologies related to supercritical properties such as synthesis in supercritical fluids and destroying of hazardous agents, (v) separation techniques (e.g., seawater desalination, solution crystallization, bioseparations or extractive distillation) and (vi) production of energy sources. [1-3]

To derive maximum benefit from these applications, multiple models that cover large ranges of composition (organic, aqueous or mixed solvents, concentrated or dilute solutions) and conditions (from ambient temperatures to supercritical conditions) are required. [4]

Measuring the transport properties as conductance at low concentrations facilitates the study of ionic solvation to obtain reliable values of infinite dilution. [5]

It has been found that, the electrolytes behaviour in solution is associated with the dielectric constant of the medium to a certain extent. Several factors can affect the medium dielectric constant of an ion's instant neighbourhood [6]. In very dilute solutions, the dielectric constant of the perspicuous solvent is the suitable value to use for the so-called "limiting law". Moreover, the variations of the dielectric constant of the medium are closely concerned with the congruous changes of the homogeneous reaction rate in solutions [7]. Various three-parameter equations [8-10] and four-parameter equations [11-14] were suggested to explain the relation between Λ_o, å and K_A. All of which are based on charged hard spheres model in a dielectric medium.

This paper reports measurements of the conductance of Sodium diethyldithiocarbamate in methanol at different temperatures (25, 30, 35 and 40°C). Fuoss-Onsager three-parameter equation is applied for the uni-univalent electrolyte (NaDDC). To explicate K_A, The solvent separated-ion pair model [15] is used.

Ultimately, The Thermodynamic data (ΔH^o, ΔG^o, ΔS^o) and energy of activation (ΔE_s) were calculated and interpreted according to interaction of solvent at different temperatures.

Fuoss and Onsager [8] utilized the sphere in the continuum model and the next equation was formulated:

$$\Lambda = \Lambda_o - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + (J - B\Lambda_0) C\gamma - K_A C \gamma \Lambda f^2 \quad (1)$$

Where, Λ is the equivalent conductance $\text{ohm}^{-1}\ \text{equiv}^{-1}\ \text{cm}^2$, equivalent conductance at infinite dilution (Λ_o), C is the concentration (equiv/l) and ion association constant (K_A). γ is the degree of dissociation which is determined by the equation:

$$\gamma = \Lambda/\Lambda_o - S(C\Lambda/\Lambda_o)^{1/2} \qquad (2)$$

S and E are theoretically predicted constants, which depend on the dielectric constant, the medium absolute temperature and the viscosity (D, T and η respectively). J term (which represents the ions and ion-solvent interactions) is given by the equation. [8]

$$J = \sigma_1\Lambda_o + \sigma_2 \quad (3)$$

Where σ_1 and σ_2 are functions of the distance of closest approach of ions å besides η and D.

Since the last century, Dithiocarbamates (DTCs) have widely been used as fungicides besides pesticides. [16] Dithiocarbamates are vastly applied in medicinal chemistry and have potential applications within the field of biomedicine, specifically in the treatment of cancer. [17-19] Furthermore, they have a remarkable role in agricultural industry [20-24]. Although carbamates and dithiocarbamates find an extensive use in agriculture, still overexposure to these chemical has been known to effect adversely on vital organs and most of DTCs are considered to be hazardous according to the World Health Organization (WHO). [25, 26]

The aim of the present work is to study and understand the mobility and association process of the compound “Sodium diethyldithiocarbamate” by measuring its conductance in methanol at various temperatures (25, 30, 35 and 40°C) followed by determining the thermodynamic functions (ΔG^o, ΔH^o, ΔS^o and ΔE_s) to describe how the system responds to changes in its environment and get information about NaDDC behavior in the solvent system studied (Methanol).

2. EXPERIMENTAL

Sodium diethyldithiocarbamate (NaDDC) is Analar analytical reagent "Sigma-Aldrich", methanol (B.D.H, Analar grade) was used without any further purification**.** The specific conductance of purified methanol at 25, 30, 35 and 40 °C was found to be in range of $5.70 - 6.01 \times 10^{-7}$ ohm^{-1} cm^{-1}. The Preparation of all solutions was performed by weight. NaDDC was weighed on microbalance with a readability of ± 0.1 mg. By dropping the solvent via weighing pipette, dilution into the cell was carried out. Conductivity Bridge instrument model: Crison GLP31 was used to measure the experimental values of conductance (the reproducibility is ±0.1% and Conductivity Measurement error was ≤0.5%) and a cell with platinum electrodes has a cell constant ($K=0.1$ cm^{-1}) for dilute solutions. The calibration of the conductivity meter was done with three conductivity standard solutions provided by Crison (0.001 M KCl, (electrical conductivity)EC=147 $\mu S\ cm^{-1}$ at 25.0 °C; 0.01M KCl, EC=1413 $\mu S\ cm^{-1}$ at 25.0 °C and 0.1 M KCl, EC=12.88 $mS\ cm^{-1}$ at 25.0 °C). Using a water ultra thermostat, the temperature is kept constant to within ±0.1°C. Each measurement is taken three times and then the average of the three measurements is recorded. The solvent constants used in all calculations were taken as reported in references [27-30], i.e., densities ($d25^o$) = 0.7917 g/cm^3, ($d30\ ^o$) = 0.7862 g/cm^3, ($d35\ ^o$) = 0.7815 $g/cm^3$and ($d40\ ^o$) = 0.7762 $g/\ cm^3$ respectively. The viscosities ($\eta 25°$) = 0.5448×10^{-2} Poise, ($\eta 30°$) = 0.5030×10^{-2} Poise, ($\eta 35°$) = 0.4620×10^{-2} Poise and ($\eta 40°$) = 0.4220×10^{-2} Poise respectively. The dielectric constants (D25°) = 33.05, (D30°) = 31.62, (D35°) = 30.08 and (D40°) = 29.98 respectively.

3. RESULTS AND DISCUSSION

3.1.Conductance of sodium diethyldithiocarbamate in methanol at different temperatures:

In order to get the best value of equivalent conductance at infinite dilution (Λ_o), three steps are done. First step, is determining an approximate value of Λ_o by plotting the equivalent conductance (Λ) against ($C^{1/2}$) which gives a straight line and the intercept = Λ_o. The value Λ is calculated from equation (4) [31]:

$$\Lambda = \frac{1000 \cdot \varkappa}{C} \qquad (4)$$

In which ℜ is the specific conductance ($ohm^{-1}\ cm^{-1}$) and C is the concentration (equiv L^{-1}). In Tables 1, 2 the measured equivalent conductance data are represented. Secondly, more rigorous Λ_o values were gained by applying Fuoss, Kraus and Shedlovsky (F.K.S) equation:

$$1 / \Lambda S_{(z)} = 1 / \Lambda_o + C \Lambda S_{(z)} f_{\pm}^2 / K_D \Lambda_o^2 \qquad (5)$$

K_D: the dissociation constant and $S_{(z)}$ is the Shedlovsky's extrapolation function which was represented in table by Daggett [32] for various z values. The linear interpolation in the table was executed to give $S_{(z)}$ for any z in a range of $0.000 \leq z \leq 0.209$ where z can be calculated from the formula**:**

$$z = \alpha (C\Lambda)^{1/2} / \Lambda_o^{3/2} (6)$$

Where α is the limiting Onsager slope. By plotting a graph between $1/\Lambda S_{(z)}$ and $(C\Lambda S_{(z)} f^2)$, straight line was obtained with intercept $(1/\Lambda_o)$ and slope $(1/ K_D \Lambda_o^2)$. Third and last step is calculating the most accurate and precise values of Λ_o, J (a), å and K_A from Fuoss-Onsager equation [8] through the assistance of special computer program (has been developed by Fortran programming) on an IBM-PC, starting by Λ_o value which was taken out from (F.K.S) equation. The agreeable accuracies in these reckonings are ± 0.02 for Λ_o; ± 2 for 'J values lower than 200', ± 5 for 'J = 200 – 1000' and ± 10 for 'J greater than 1000'.

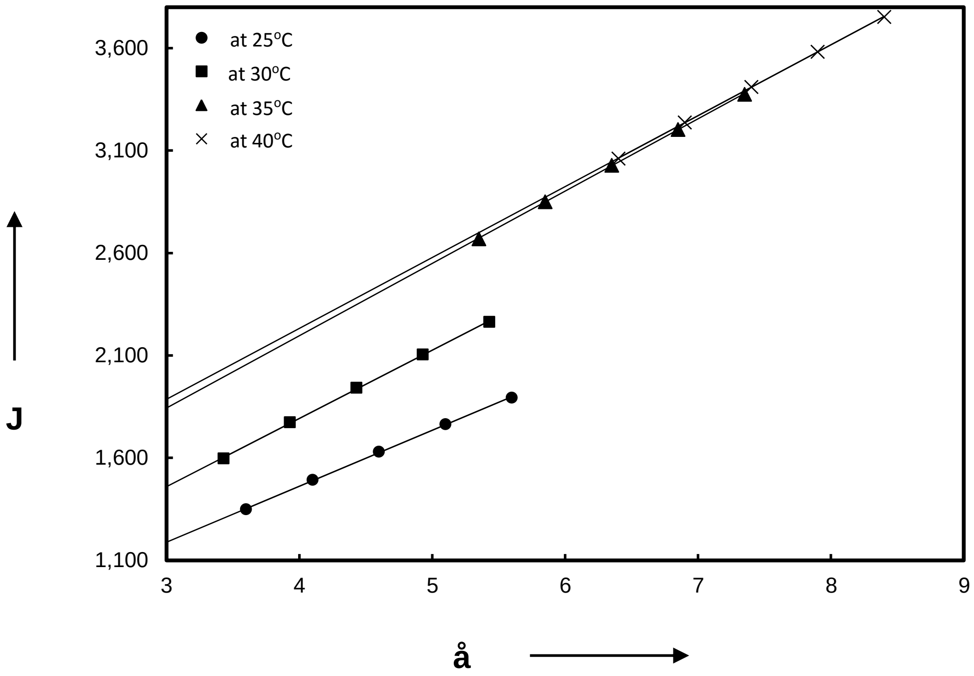


Figure 1. The plot of J versus å for sodium diethyldithiocarbamate in methanol at 25, 30, 35 and 40°C.

The standard deviation of the measured equivalent conductance σ_Λ was calculated using the expression [33]:

$$\sigma_\Lambda = \frac{\{\Sigma\,(\Lambda\ \text{calculated} - \Lambda\ \text{observed})^2\}^{1/2}}{(N-1)^{1/2}} \qquad (7)$$

Where N is the number of experimental points.

Figure 1. displays the linear correlation between å and J, from which the average value of å can be estimated using interpolation by knowing average of J value.

Table 1. Conductance of sodium diethyldithiocarbamate in methanol at 25 and 30°C:

10^4 C$^{*(a)}$	**Λ^{**}**	**10^4 C$^{*(b)}$**	**Λ^{**}**
4.0556	74.218	1.4482	80.564
3.6500	75.508	1.3114	82.003
3.3102	76.823	1.1959	83.655
3.0298	77.992	1.1050	85.017
2.7959	79.007	1.0264	86.264
2.5906	80.021	0.9558	87.400
2.4194	80.804	0.8913	88.570
2.2780	81.386	0.8373	89.618

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

10^4 C$^{*(c)}$	**Λ^{**}**	**10^4 C$^{*(d)}$**	**Λ^{**}**
1.2792	89.304	1.0637	89.773
1.1608	91.110	0.9652	92.039
1.0421	92.997	0.8643	94.056
0.9488	94.910	0.7908	95.590
0.8771	96.063	0.7297	97.425
0.8128	97.313	0.6769	98.799
0.7571	98.499	0.6361	99.971
0.7073	100.42	0.5969	101.18

* equiv L^{-1} ** ohm^{-1} equiv^{-1} cm^{2}

(a) Results at 25°C. (b) Results at 30°C.

(c) Results at 35°C. (d) Results at 40°C.

Table 3. The characteristic parameters (derived from Fuoss-Onsager equation) for sodium diethyldithiocarbamate in methanol at different temperatures

Temperature	**$\Lambda_\circ$ (ohm^{-1} equiv^{-1} cm^{2})**	**J**	**K_A**	**å (Å)**	**σ_Λ**
25°C	99.15	1642.0	1025.3	4.66	0.074
30°C	114.43	2116.8	4077.1	4.98	0.124
35°C	125.87	2906.3	4447.5	6.02	0.300
40°C	130.76	3284.8	6141.3	7.04	0.156

From Table 3, it can be noticed that Λ_o values rise with accretion of the temperature. The same trend is obtained for K_A values which increase with the temperature increment; this can be illustrated as follows: on increasing the temperature, the dielectric constant of solvents decreases as reported in literature [27-30]. Consequently, Ion association process takes place.

In the light of the U term, the association constant (K_A) is evaluated from the equation as follows [34]**:**

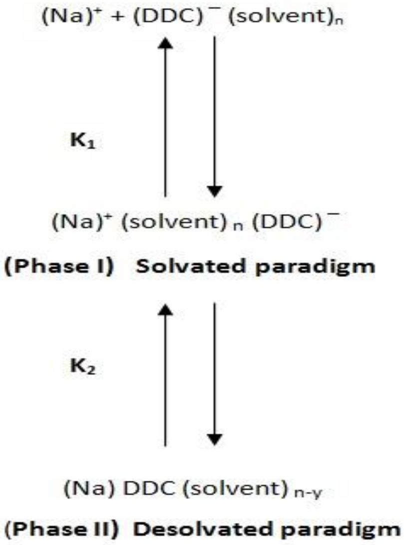
$$\ln K_A = \ln \left(\frac{4 \pi N_A å^3}{3000} \right) + \frac{e^2}{å DkT} + U \qquad (8)$$

Where $U = \Delta S / k - E_s / kT$ (9)

ΔS / k is the entropy/Boltzmann constant ratio which refers to the possibility of surrounding the free ions by the solvent molecules and E_s / kT Gilkerson[35] is an energy relationship where the E_s parameter is the variance between the interaction energies of the solvent-ion and solvent-ion pairs.

As shown in Table 4 the U term (which denotes the change in the internal energy) increases slightly with increasing the temperature which means ion–dipole term for sodium diethyldithiocarbamate is less preponderant than the entropy term.

Ultimately, the solvent-separated ion pair model could be utilized [15] in which a multiple-stages association was proposed as shown in scheme 1:



Scheme 1: Ideation of multiple-stages association process of NaDDC according to the solvent-separated ion pair model.

Where y is the number of solvent molecules flee from solvation.

Hence, the association constant K_A is specified by the expression:

$$K_A = K \quad \Sigma \frac{(C_{(ion\text{-}pairs)})}{(C_{(Na)^+})(C_{(DDC)^-\,(solvent)n})} = K_1 (1 + K_2) \qquad (10)$$

From the conductance measurements, K_A value is gained and since $K_1 = 4 \pi N å^3 e^b /3000$ where $b = e^2 / åDTk$ so K_2 value could be obtained.

It is clearly noticed from Table 4, K_2 values rises with the increase in temperature which is an indication that the desolvated paradigm (Phase II) is more desired than the solvated paradigm (Phase I) for the ion-pair.

Radii of ions

Using Stokes' equation [36], the electrostatic radius for positive and negative ions (R^+ and R^-) can be calculated by knowing the viscosity and the limiting equivalent conductivities of ions as follows:

$$R^{\pm} = \frac{0.8194 \times 10^{-8}}{\lambda_o^{\pm} \eta_o} \qquad (11)$$

Where λ_o^+ or λ_o^- are the limiting ionic equivalent conductance of positive and negative ions respectively.

As shown in Table 5,In case of methanol at 25 and 30°C: the values of å were less than the sum of electrostatic radii ($R^+ + R^-$) obtained from Stokes' equation; this illustrates that ions association occurs. Whereas, In case of methanol at 35 and 40°C: the values of å were higher than electrostatic radii ($R^+ + R^-$) which can be adequately explained by occurrence of ions solvation.

3.2 Thermodynamic functions measurments of sodium diethyldithiocarbamate in methanol

Any rising in thermal energy affects the rotational, vibrational and translational energy of molecules which causes greater frequency and as a result, overstated ionic mobility. As seen in Table 6, Λ_o values increase upon the increase in temperature in an indication of higher mobility of the ions or lower solvation. [37] On increasing the temperature also, the association constant K_A values increase which is explicated by diminution the dielectric constant of the medium when the temperature increases.[38]Svante Arrhenius [39]combined the activation energy concepts and the Boltzmann distribution law into one equation:

$$\Lambda_o = Ae^{-(\Delta Es / RT)} \quad \text{or} \quad \log \Lambda_o = \log A - (\Delta E_s /2.303RT) \qquad (12)$$

Where R is the ideal gas constant, A is the Arrhenius, pre-exponential, collision or frequency factor, ΔE_S is the Arrhenius activation energy (J/mol) and T is the temperature (absolute, Kelvin).

Table 4. K_2 and U values for sodium diethyldithiocarbamate in methanol at different temperatures

Temperature	**K_A**	**K_1**	**K_2**	**U**
25°C	1025.3	9.693	104.776	4.661
30°C	4077.1	10.300	394.834	5.981

35°C	4447.5	10.973	404.326	6.005
40°C	6141.3	11.010	556.816	6.324

Table 5. Calculation of the radii for sodium diethyldithiocarbamate ions in methanol at different temperatures

Temperature	$^{(1)}\Lambda_\circ$	$\lambda_\circ^- \eta_\circ$ $^{(2)}$	$\lambda_\circ^+$ $^{(1)}$	$\lambda_\circ^-$ $^{(1)}$	R^+ (Å)	R^- (Å)	$R^+ + R^-$	å(Å)
25°C	99.15	0.2942	45.17	53.98	3.329	2.785	6.114	4.66
	114.43	0.3207	50.67	63.76	3.215	2.555	5.770	4.98
30°C	125.87	0.3165	57.37	68.50	3.091	2.589	5.681	6.02
35°C	130.76	0.3022	59.15	71.61	3.283	2.712	5.994	7.04
40°C								

(1) ohm^{-1} $equiv^{-1}$ cm^2 (2) ohm^{-1} $equiv^{-1}$ cm^2 p

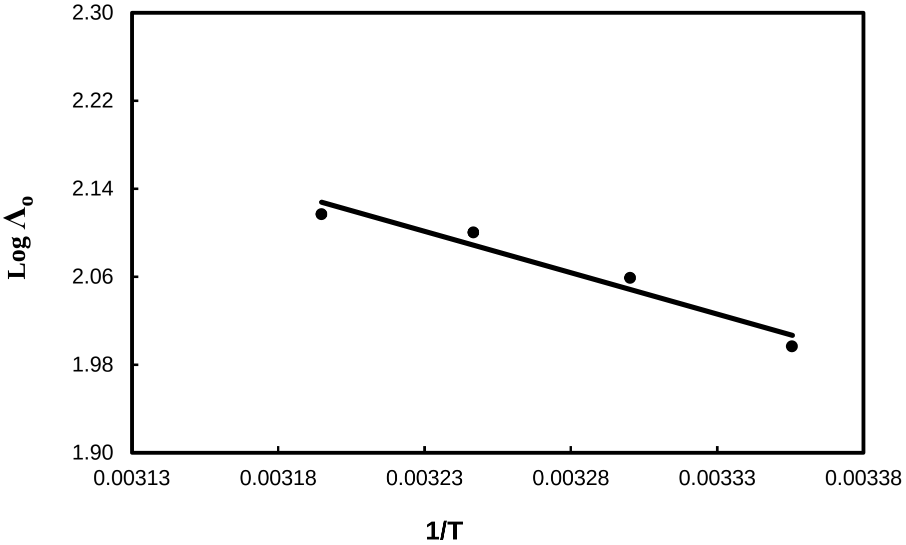


Figure 2. The plot of log Λ_o versus 1/T for sodium diethyldithiocarbamate in methanol at different temperatures.

By plotting a graph between log $\Lambda_o$and 1/T as displayed in Figure 2. , straight line is obtained with slope ($-\Delta E_S/2.303R$) from which ΔE_S value is computed and recorded as seen in Table 6. As shown, the activation energy (ΔE_s) has a positive value which points to the high mobility of ions in the solution and thus high Λ_o values.

The change in Gibbs free energy ΔG^o upon the process of association is obtained from equation (13): [38]

$\Delta G^o = -RT \ln K_A$ (13)

As observed in Table 6, values of ΔG^o are negative for NaDDC in methanol which is associated with a reaction that happens spontaneously; this means that the association process was chosen as favorite process better than dissociation in the solvent system studied.

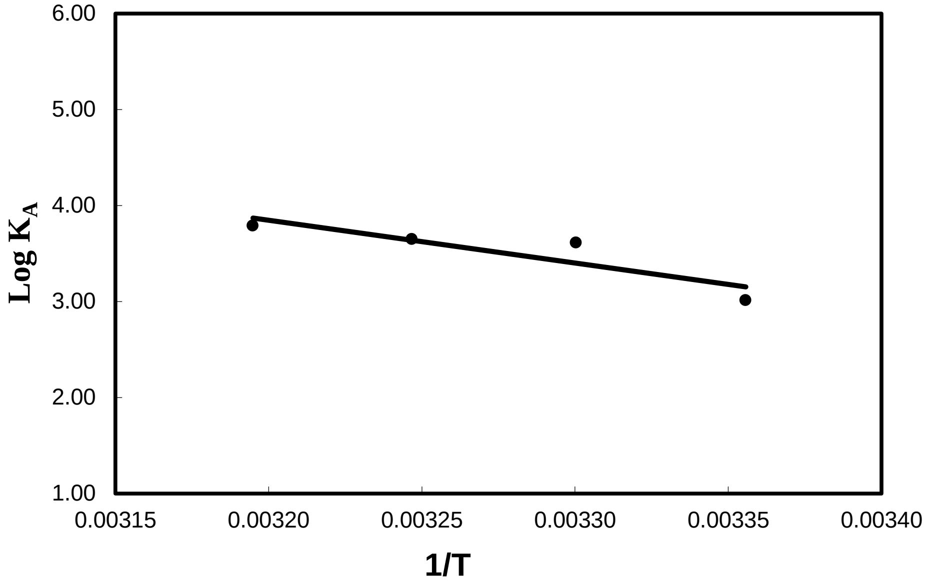


Figure 3. The plot of log K_A versus 1/T for sodium diethyldithiocarbamate in methanol at different temperatures.

With increasing the temperature, an increase in negative values of ΔG^o was observed because of releasing solvent molecules from the solvation shell into the bulk solvent. The association between ions becomes more strength at high temperature where the permittivity of the solvent decreases. [40]

Table 6. Thermodynamic functions of sodium diethyldithiocarbamate in methanol at different temperatures

T (K)	$\Lambda_\circ$ (ohm^{-1} equiv $^{-1}$ cm^2)	K_A	ΔE_s° (kJ mol $^{-1}$)	ΔH° (kJ mol $^{-1}$)	ΔG° (kJ mol $^{-1}$)	ΔS° (J mol $^{-1}$ K^{-1})
298	99.15	1025.3	14.41	85.17	-17.179	285.85
303	114.43	4077.1			-20.946	281.15
308	125.87	4447.5			-21.514	276.58
313	130.76	6141.3			-22.703	272.17

As resulted in Table 6, the enthalpy change or heat of association (ΔH^o) has been calculated where ($-\Delta H^o/2.303R$) is the slope obtained from plotting a graph of log K_A versus 1/T as shown in Figure 3. by applying the Van't Hoff's isochore expression:

$$d \ln K_A/dT = \Delta H^o/RT^2 \qquad (14)$$

Then,

$$2.303 \log K_A = -(\Delta H^o/R)(1/T) + \Delta S^o/R$$

$$\text{or } 2.303 \text{ R} \log K_A = \Delta S^o - \frac{\Delta H^o}{T} \qquad (15)$$

ΔH^o positive value for sodium diethyldithiocarbamate refers to endothermic (endergonic) association process because the enthalpy of the products is higher than the enthalpy of the reactants of the system. [41]

Gibbs-Helmholtz equation was applied to estimate ΔS^o values (The change of entropy) where:

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \qquad (16)$$

For sodium diethyldithiocarbamate in methanol, the positive values of ΔS^o reveal the disorder of ions (randomness). As obviously seen in Table 6, the entropy change values (ΔS^o) were positive because the ion-pair solvation is diminished if they are matched to that of the free ion. [42-44]

Paul et al., [45] have determined the conductance of lithium bromide in methanol solvent over a temperature ranged from 20° to −50°C for several concentrations. The limiting equivalent conductances were obtained by extrapolation of Λ versus $C^{1/2}$. It was observed that, the experimental conductance results comply with the theoretical results for lithium bromide in dilute solutions of methanol. The plot of log Λ_o against 1/T in methanol over the range 20° to −50°C was found to be linear.

The conductance of diammine bis-1-amidino-OMethylurea Cobalt (III) monochloride in methanol - water mixtures at different temperatures has been measured by Bag, et al.,[46] At a certain temperature, the free energy change (ΔG^o) became more negative with temperature increasing where the dielectric constant of medium decreases. This signs that ion-pair association is preferred. Positive ΔS^o can be interpreted on the postulate that iceberg structure surrounding the cation is cracked when association process occurs so the degree of disorder of ions is increased [47].

Dash, et al., [37] measured the conductance of trans-dichloro-bis(ethylenediamine) Co(III) chloride and trans-dibromo-bis(ethylenediamine) Co(III) bromide in various component of water-Alcohols mixtures (water-methanol, water-ethanol and water-n-propanol) at different temperatures. The limiting molar conductance, K_A and the thermodynamic functions have been estimated. It was observed that there is noticeable increment of K_A values for Cobalt (III) chloride and Cobalt (III) bromide complexes with the increase in temperature. For both association constants in all solvents, the activation energy (E_S) is positive and free energy change (ΔG^o) values are negative which means that the association process is selected over dissociation process. ΔH^o positive values for each complex are attributed to the endothermic association processes. Positive entropy change (ΔS^o) can be thought of as entailing some randomness of ions. These experimental data are found to be in good agreement with the results obtained by the present study.

Pura [42], has measured the conductance of Iron (III) chloride [$FeCl_3$] in methanol, ethanol, n-Propanol and n- butanol at different temperatures. Upon increasing the temperature, the ΔG^o values decrease to more negative values which can be attributed to releasing the solvent molecules into the bulk solvent and thus, smaller ΔG^o values are obtained. For all alcohols (MeOH, EtOH, n-PrOH and n-BuOH), ΔH^o values were positive. High and Positive ΔH^o refers to the interaction between ions. It was found that, ΔS^o values were positive which is interpreted by diminishing the solvation of the ion pairs compared to that of the free ions.

El-Hammamy et al.[48], have measured the electrical conductivity of 1:1 s-acetylthiocholine chloride, bromide and perchlorate salts in methanol at 25, 30, 35 and 40^{o}C. The conductivity data have been analyzed using Fuoss-Onsager equation [8], from which the values Λ_o, K_A and å were resulted. It was reported that the increase in Λ_o and K_A is involved with rising the temperature. ΔE_S values and thermodynamic functions have been evaluated for all salts. The negative $\Delta G^o$for the three association rate constants (K_A) indicates that the reaction is spontaneous and ion association process is energetically favored over dissociation process. For the three salts, the positive values of ΔH^o signalize a process or reaction in which the system absorbs energy from its surroundings (endergonic in nature) and ΔS^o positive values are characteristic of the disorder of ions.

4. CONCLUSIONS

This paper aims to shed light on the limiting equivalent conductance (Λ_o) and the association process of the compound: sodium diethyldithiocarbamate [NaDDC] in methanol at different temperatures. In order to get the best value of equivalent conductance at infinite dilution (Λ_o), three steps were done. First step, is determining an approximate value of Λ_o by plotting the equivalent conductance (Λ) against ($C^{1/2}$). Secondly, more rigorous Λ_o values were gained by applying Fuoss, Kraus and Shedlovsky (F.K.S) equation. Third and last step is calculating the most accurate and precise values of Λ_o, J (a), å and K_A from Fuoss-Onsager equation. For sodium diethyldithiocarbamate, the values of (Λ_o) increase orderly with the temperature increase. It is evident that less solvation or higher mobility of the ions occurs in the solvent system studied (Methanol). A comparison between the closest distance of approach å and stokes' radii ($R^+ + R^-$) was done.

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References

1. K. S. Ashwini, A. S. Rajesh and D. P. Snehal, *J. Chem. Eng. Data*, 41 (1996) 431.
2. A. Anderko, P. Wang and M. Rafal, *Fluid Phase Equilibria*, 194 (2002) 123.
3. S. Masood, R. Saeed and S. R. Khan, *Journal of Materials Physics and Chemistry*, 1 (2013) 69.
4. P. Wang, A. Anderko and R. D. Young, *Fluid Phase Equilibria*, 203 (2002) 141.

5. 5. F. I. EI-Dossoki, *J. Mol. Liqs*., 142 (2008)72.
6. P. Debye and L. Pauling, *J. Amer. Chem. Soc*., 47 (1925) 2129.
7. H. S. Harned and N. N. T. Samaras, *J. Amer. Chem. Soc*., 54 (1932) 9.
8. R. M. Fuoss and L. Onsager, *J. Phys. Chem*., 61 (1957) 668.
9. R. M. Fuoss, *J. Amer. Chem., Soc*., 81(1959) 2659.
10. R. M. Fuoss, L. Onsager and J. P. Skinner, *J. Phys. Chem*., 69 (1965) 2581.
11. R. F. Prini and J. E. Prui, *Z. Phys. Chem. (Leipzing),* 228 (1965) 373.
12. K. L. Hsia and R. M. Fuoss, *Proc. Natl. Acad. Sci.U.S.A*., 57 (1967) 1550.
13. J. C. Justice, *J. Chem. Phys*., 65 (1968) 353.
14. A. D'Aprano, *J. Phys. Chem*., 75 (1971) 3290.
15. D. F. Evans and P. Gardam, *J. Phys. Chem*., 73 (1969) 158.
16. WHO, Dithiocarbamate Pesticides, Ethylenethiourea and Propylenethiourea: A General Introduction, WHO, Geneva, (1988).
17. L. Ronconi, C. Marzano, P. Zanello, M. Corsini, G. Miolo, C. Macca, A. Trevisan and D. Fregona, *J. Med. Chem*., 49 (2006) 1648.
18. W. Walter and K. D. Bode, *Angew. Chem. Int. Ed. Engl*., 6 (1967) 281.
19. G. H. Elgemeie and S. H. Sayed, *Synthesis*, 1747 (2001).
20. C. Rafin, E. Veignie, M. Sancholle, D. Postal, C. Len, P. Villa and G. Ronco, *J. Agric. Food. Chem*., 48 (2000) 5283.
21. W. Chen-Hsien, *Synthesis*, 622 (1981)
22. T. Mizuno, I. Nishiguchi, T. Okushi and T. Hirashima, *Tetrahedron Lett*., 32 (1991) 6867.
23. Y. S. Chen, I. Schuphan and J. E. Casida, *J. Agric. Food Chem*., 27 (1979) 709.
24. C. Len, D. Postal, G. Ronco, P. Villa, C. Goubert, E. Jeufrault, B. Mathon and H. Simon, *J. Agric. Food Chem.*, 45 (1997) 3.
25. R. Serio, R. A. Long, J. E. Taylor, R. L. Tolman, R. M. Weppelman and G. Olson,*Toxicol. Appl. Pharmacol*., 72 (1984) 333.
26. WHO, The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification, WHO/IPCS/IOMC, (2005).
27. N. H. El-Hammamy, A. A. Hasanien, M. F. Amira and F. M. Abd El-Halim, *J. Indian Chem. Soc*., 31 (1984) 512.
28. N. H. EI-Hammamy, A. I. Kawana, M. N. EI-Hammamy and H. M. Moharem, *J. Chem. Sci*., 2 (2011) 51.
29. N. H. EI-Hammamy, A. I. Kawana, M. N. EI-Hammamy and H. M. Moharem, *J. Adv. Appl. Sci. Res.,* 2 (2011) 86.
30. N. H. EI-Hammamy, H. A. Hawaty, A. I. Kawana, M. N. EI-Hammamy and H. M. Moharem, *J. Chem. Pharm. Res*., 3 (2011) 729.
31. B. Sivasankar,, Engineering Chemistry, Tata McGraw-Hill Pub. Co. Ltd, New Delhi (2008).
32. H. M. Daggett, *J. Am. Chem. Soc*., 73 (1951) 4977.
33. G. W. Brown, *Am. J. Dis. Child*., 136 (1982) 937.
34. F. Accascina, A. D'Aprano and R. Triolo, *J. Phys. Chem*.,71 (1967) 3469.
35. W. R. Gilkerson, *J. Chem. Phys*. 25 (1956) 1199.
36. R. A. Robinson and R. H. Stokes, "Electrolyte solutions". Butterworths, 2nd ed, London, (1959).
37. U. N. Dash, J. R. Mohatra and B. Lal, *J. Molecular Liquids*, 124 (2006) 13.
38. J. F. Coetzee and C. D. Ritchie, "Solute-Solvent Interaction", Marcel-Dekker, New York, vol. 2 (1976).
39. S. A. Arrhenius, *Z. Phys. Chem*., 4 (1889) 96.
40. O. N. Kalugin, V. N. Agieienko, N. A. Otroshko and V. V. Moroz, *Russian. J. Phys. Chem*. A., 83 (2009) 231.
41. R. H Petrucci, W. S. Harwood, F. G. Herring and J. D. Madura, General Chemistry: Principles and Modern Applications. 9th Ed. Pearson Prentice Hall Inc., New Jersey, 2007.

42. S. Pura, *J. Molecular Liquids*, 136 (2007) 64.
43. H. Yokoyama and H. Kon, *J. Phys. Chem*., 95 (1991) 8956.
44. S. Pura and G. Atun, *J. Solution Chem*., 32 (2003) 341.
45. P. G. Sears, R. L. McNeer and L. R. Dawson, *J. Electrochem. Soc*. 102 (1955) 269.
46. G. C. Bag, N. M. Singh and N. R. Singh, *J. Indian Chem. Soc*., 78 (2001) 294.
47. M. K. De and R. L. Dutta, *J. Indian Chem. Soc*., 52 (1975) 67.
48. N. H. El-Hammamy, M. N. El-Hammamy and A. I. Kawana, *J. Mex. Chem. Soc*., 58 (2014) 11.