

Substituent Effect on the Association Phenomenon of an Aqueous Solution of Benzylidene Substituted Aniline at Different Temperatures

Mohammed A. Al-Iraqi Yaser O. Al-Allaf Kawther H. Al-Naimi

Department of Chemistry

College of Science

University of Mosul

E-mail: maaliraqi_54@yahoo.com

(Received 3 / 6 / 2012 ; Accepted 7 / 1 / 2013)

ABSTRACT

Conductivity parameters of an aqueous solution of benzylidene substituted anilines (I-IV) have been determined at five different temperatures in the range of 283.15-318.15 °K, through accurate conductance measurements. The obtained data were analyzed in accordance to Lee-Wheaton equation taking into account the activity of the electrolyte in the solution. The conductance measurement results were used to determine the association constants (K_A) of ion-pairs, the mean distance between ions in solution, in addition to the molar conductance at infinite dilution (Λ_0) for the free ion in the solution. The dependence of (K_A) values on the temperature has been examined by plotting Log K_A against the reciprocal values of temperature ($1/T$), which showed linear relationship, where (K_A) values decrease with increasing temperature. Moreover, the enthalpy (ΔH), Gibbs free energy (ΔG) and the entropy (ΔS) have been derived from this linear relationship.

Keywords: Ion-association, conductance, Schiff bases, benzylidene substituted aniline, Lee-Wheaton equation.

(I-IV)

(383.15-318.15 °K)

(K_A)

(Λ_0)

extent of charge-transfer character and the role of solvent, protonation and substitution, in altering the energies of these states (El-Bayoumi, 1971).

In this study, we have measured the conductivity of an aqueous solution of a series of benzylidene substituted aniline compounds at different temperatures in order to determine the mechanism of association from the thermodynamic point of view.

EXPERIMENTAL

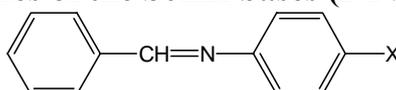
Chemicals and apparatus

All chemicals were obtained from the usual commercial suppliers and used without further purification. Melting points were measured on electrothermal 9300 melting point apparatus and were uncorrected. The IR spectra (as KBr disc) were run with Shimadzu FT/IR spectrophotometer (computerized Bruker Tensor-27). UV-Visible spectra of the ethanolic solutions were measured at room temperature with Zeius PMQ II manual spectrophotometer using matched 10 mm fused silica cells. A thermostated water bath type Haake NK22, with a temperature deviation not greater than ± 0.1 °C, is used. The conductance measurements were performed using Jenawy PCM3 conductivity meter.

Preparation of benzylidene substituted anilines (I-IV):

To a solution of substituted aniline (0.005 moles) in 20 ml absolute ethanol, (0.005 mole, 0.53 g) of benzaldehyde was added. After refluxing for 5 hrs, the reaction mixture was allowed to cool. The resulting solid product was filtered off, dried and recrystallized several times from ethanol to give a pure product (Burgi, 1971). The physical and IR spectral data of the products are summarized in Table (1).

Table 1: The Physical properties of the Schiff bases (I-IV).



Compd. No.	Colour	-X	m.p. °C (Reported)*	U.V. (EtOH) λ_{\max} nm	I.R. (KBr disc), ν (cm ⁻¹)		
					C=N	C=C	C-X
I	Brown	OH	177-179 (183)	346 294 237**	1622 (s)	1580 (s) 1502 (s) 1480 (w)	3350(b)
II	Faint yellow	COOH	189-191 (190-191)	263** 214	1687 (s) 3367(w)	1425 (s) 1498 (w)	1317(s) sym C-O 1595 (s&b) O-H
III	Yellowish white	Cl	63-65 (62-63)	286 241*	1623 (s)	1581 (s) 1483 (m) 1448 (m)	756 (s)
IV	Gray	Br	67-69 (66)	266** 272 287	1620 (s)	1602 (s) 1587 (s) 1479 (w)	819 (s)

* JACS, 75, 910, 1953

** for the λ_{\max}

RESULTS AND DISCUSSION

Correlation of the molecular structure and thermal study of the electrical conductivity of benzaldazine and its nitro derivatives were carried out. The values of activation energies obtained from the measurements, as well as, the energy gaps calculated from UV- visible spectra indicated that all compounds behave like a semiconducting material (El-Sayed *et al.*, 1991). Therefore, a series of benzylidene anilines (I-IV) were prepared and used to estimate their conductivity. These Schiff bases were prepared from the reaction of benzaldehyde with substituted aniline. The structure of these compounds was assigned on the basis of their IR spectral data which are summarized in Table (1). The IR spectra show a characteristic absorption peaks at 1618-1631 cm^{-1} for C=N bond stretching (Criddle and Eilis, 1976).

Conductivity measurement of aqueous solutions of benzylidene substituted anilines (I-IV) was carried out at five temperatures in the range of 283.15 - 315.15 °K. The values of the molar conductance (Λ) of their solutions were given in Tables (2 A-E). The conductance data obtained were first analyzed in accordance with Lee-Wheaton equation. The correlations between the concentration of the aqueous solution of these Schiff bases and their equivalent conductance are shown in Figs. (1 A-E) which show a non-linear relationships. That means they are weak electrolytes. The brief illustration of those figures was shown in figures (1B_{i-iv}). The oppositely charged ions tend to form ion-pairs in the medium of low relative permittivity. At constant temperature, the concentration of free ions ($C\alpha$) and ion-pairs [$C(1-\alpha)$] are at equilibrium. This state was described by the thermodynamic equilibrium (K) for the ion-association reaction. Since the ion pairs are non-conducting entities and the degree of their dissociation (α) can be given by the ratio between the molar conductivity of the electrolyte (Λ) and the free ion ($\Lambda-C\alpha$). Then the combination of the expressions for K and α can be given as:

$$\Lambda = \frac{(\Lambda - C\alpha)}{1 + K(C/C^\circ)\alpha y^{\pm 2}} \quad \dots\dots\dots (1)$$

Where $C^\circ = 1 \text{ mole dm}^{-3}$, y^\pm is the mean activity coefficient which can be obtained from equation 2:

$$y^\pm = \exp\left(\frac{Kq}{1 + KR}\right) \quad \dots\dots\dots (2)$$

which refers to the dissociated part of the electrolyte, R is the distance parameter which must be the least distance that two free ions can approach before they merge into an ion-pair, or in other words, it is the furthest distance that separates two ions. The parameters K and q can be obtained from equation 3 and 4 respectively:

$$K^2 = 16000 \pi N_A q C\alpha \quad \dots\dots\dots (3)$$

$$q = \frac{e^2}{8\pi\epsilon^\circ\epsilon_rKT} \quad \dots\dots\dots (4)$$

If it is assumed that the dissociated part of the weak electrolyte acts like a completely hypothetical dissociated strong electrolyte of the same type, $\Lambda_{C\alpha}$ can be replaced by any theoretical equation for conductivity in order to make a conductivity model, which was found by the Lee-Wheaton (Lee and Wheaton, 1978) equation (5):

$$\Lambda_{C\alpha} = \Lambda_0 [1 + C_1(KR)(\epsilon K) + C_2(KR)(\epsilon K)^2 + C_3(KR)(\epsilon K)^3] - (\rho K) / (1 + KR)[1 + C_4(KR)(\epsilon K) + C_5(KR)(\epsilon K)^2 + (KR)/12] \quad \dots\dots\dots (5)$$

Where the concentration dependent terms are both the plasma parameter (ϵK) and (KR), while the concentration coefficients ϵ , K and ρ can be obtained from equations 6-8 respectively.

$$\epsilon = |Z_i|^2 e^2 / DKT \quad \dots\dots\dots (6)$$

$$K^2 = 8 \pi N e^2 |Z_i|^2 C / 1000 DKT \quad \dots\dots\dots (7)$$

$$\rho = F \zeta e |Z| / 3 \pi \eta \quad \dots\dots\dots (8)$$

Where F is the Faraday constant (9.6486×10^4), ζ is the conversion factor (volt to e.s.u.) = $1/299.7925$, and all other terms have previously been defined in details (Lee and Wheaton, 1978).

Table 2-A: Molar conductance of aqueous solution of benzylidene substituted aniline as a function of concentration at 283.15° K.

Conc. $\times 10^4$	Λ S. mol ⁻¹ . cm ² p-COOH	Λ S. mol ⁻¹ . cm ² p-OH	Λ S. mol ⁻¹ . cm ² p-Cl	Λ S. mol ⁻¹ . cm ² p-Br
0.196	238.464	75.612	52.346	36.239
0.384	222.656	62.343	47.500	36.072
0.565	203.427	62.438	48.339	36.026
0.909	174.323	58.943	41.386	35.498
1.228	156.889	57.557	38.061	35.365
1.525	145.023	56.318	38.124	34.775
1.803	136.572	54.376	36.672	34.348
2.063	130.964	53.048	36.471	33.639
2.307	123.537	52.379	36.072	33.353
2.537	118.626	52.124	35.947	29.081
2.753	115.118	52.175	35.612	28.197
2.953	111.802	51.660	35.468	26.718

Table 2-B: Molar conductance of aqueous solution of benzylidene substituted aniline as a function of concentration at 288.15° K.

Conc. $\times 10^4$	Λ S. mol ⁻¹ . cm ² p-COOH	Λ S. mol ⁻¹ . cm ² p-OH	Λ S. mol ⁻¹ . cm ² p-Cl	Λ S. mol ⁻¹ . cm ² p-Br
0.196	209.387	56.406	22.746	35.197
0.348	204.843	54.058	22.467	35.082
0.565	195.371	51.582	22.361	34.599
0.909	170.561	50.327	22.236	34.590
1.228	154.104	50.285	22.103	34.260
1.525	145.023	50.118	21.678	33.510
1.803	137.836	50.105	21.497	34.386
2.063	129.859	50.085	20.423	32.491
2.307	125.513	50.075	20.066	31.353
2.537	120.425	48.910	18.127	30.212
2.753	117.602	48.339	17.812	26.718
2.953	114.886	46.530	17.448	23.265

Table 2-C: Molar conductance of aqueous solution of benzylidene substituted aniline as a function of concentration at 298.15 °K.

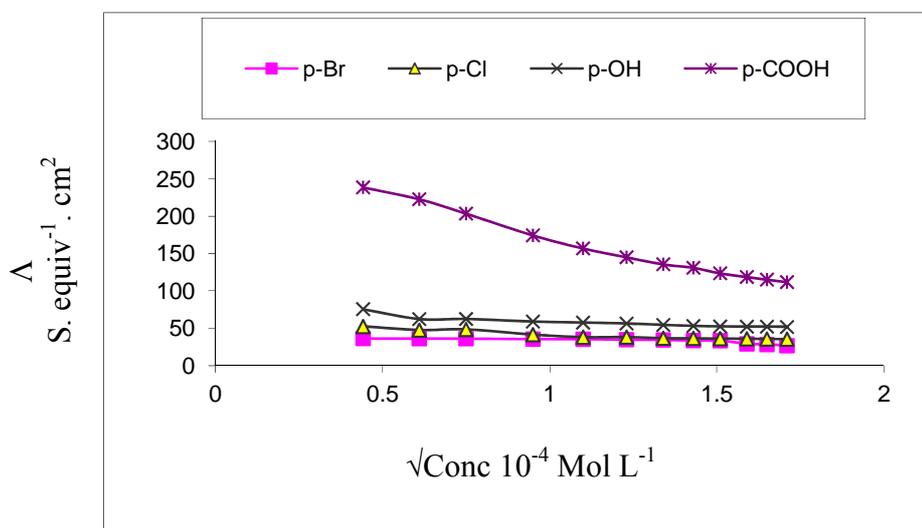
Conc. $\times 10^4$	Λ S. mol ⁻¹ .cm ² p-COOH	Λ S. mol ⁻¹ .cm ² p-OH	Λ S. mol ⁻¹ .cm ² p-Cl	Λ S. mol ⁻¹ .cm ² p-Br
0.196	331.530	69.795	34.897	29.081
0.384	213.498	44.415	21.320	23.688
0.569	195.428	46.325	21.288	20.224
0.909	174.323	44.259	20.423	20.066
1.228	159.674	43.574	19.013	18.566
1.525	142.780	43.357	18.685	18.127
1.803	133.411	43.081	18.330	17.360
2.063	125.930	42.987	18.226	16.445
2.307	118.544	42.723	17.780	15.542
2.537	114.282	42.478	17.714	14.542
2.753	112.305	42.132	17.400	14.132
2.953	110.567	41.855	17.234	13.808

Table 2-D: Molar conductance of aqueous solution of benzylidene substituted aniline as a function of concentration at 308.15 °K.

Conc. $\times 10^4$	Λ S. mol ⁻¹ .cm ² p-COOH	Λ S. mol ⁻¹ .cm ² p-OH	Λ S. mol ⁻¹ .cm ² p-Cl	Λ S. mol ⁻¹ .cm ² p-Br
0.196	187.031	52.175	30.071	34.813
0.384	186.122	52.045	29.557	34.386
0.569	167.173	51.675	29.400	34.348
0.909	150.495	50.897	29.287	34.240
1.228	135.537	50.285	29.084	34.143
1.525	127.082	49.950	28.660	34.096
1.803	118.868	49.337	27.850	33.955
2.063	112.176	48.273	27.659	33.926
2.307	107.230	45.148	23.826	33.861
2.537	103.350	40.262	22.155	33.701
2.753	101.038	35.625	17.812	35.625
2.953	98.694	29.081	17.448	29.081

Table 2-E: Molar conductance of aqueous solution of benzylidene substituted aniline as a function of concentration at 318.15 °K

Conc. $\times 10^4$	Λ S. mol ⁻¹ .cm ² p-COOH	Λ S. mol ⁻¹ .cm ² p-OH	Λ S. mol ⁻¹ .cm ² p-Cl	Λ S. mol ⁻¹ .cm ² p-Br
0.196	187.031	54.820	40.714	33.540
0.384	186.122	54.744	34.348	33.251
0.569	165.159	54.666	34.260	33.155
0.909	142.970	54.570	34.143	33.127
1.228	136.465	53.862	34.096	33.107
1.525	123.344	53.843	33.861	32.878
1.803	120.133	53.743	33.639	31.563
2.063	112.724	53.601	33.541	31.396
2.307	109.206	52.367	33.251	30.099
2.537	105.597	52.346	32.769	28.197
2.753	101.867	50.468	32.656	23.750
2.957	98.694	48.910	32.226	23.265

**Fig. 1-A: Plot of Λ against SQRT of concentration at 283.15 °K.**

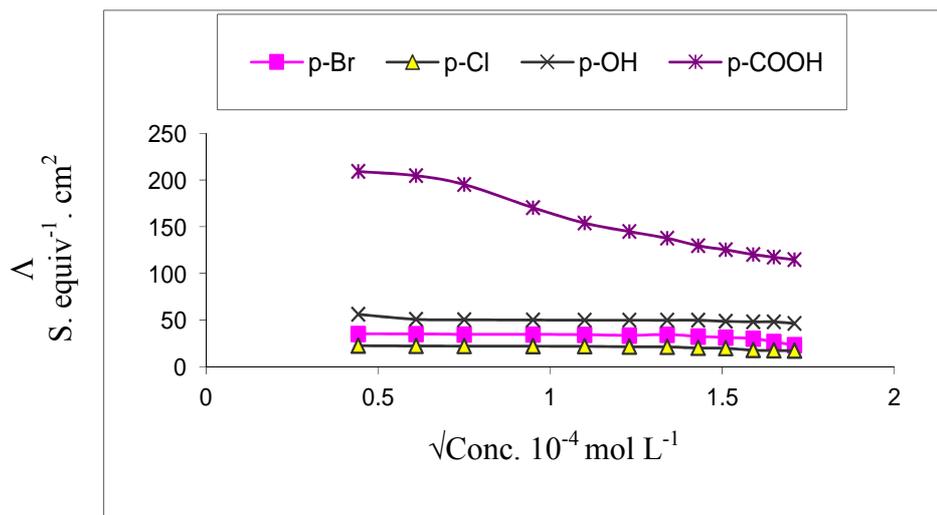


Fig. 1-B: Plot of Δ against SQRT of concentration at 288.15 °K.

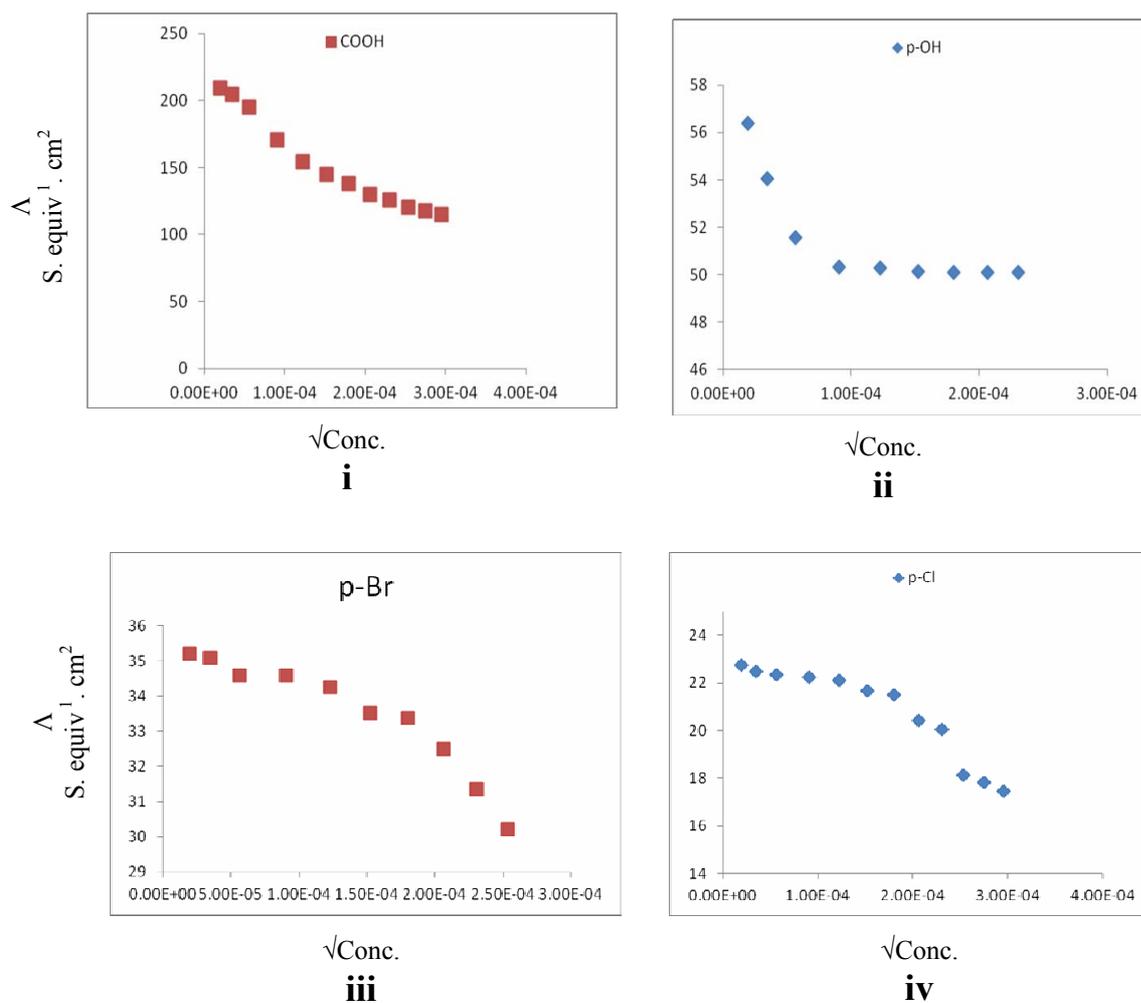


Fig 1B_{i-iv}: The illustration of figure 1-B.

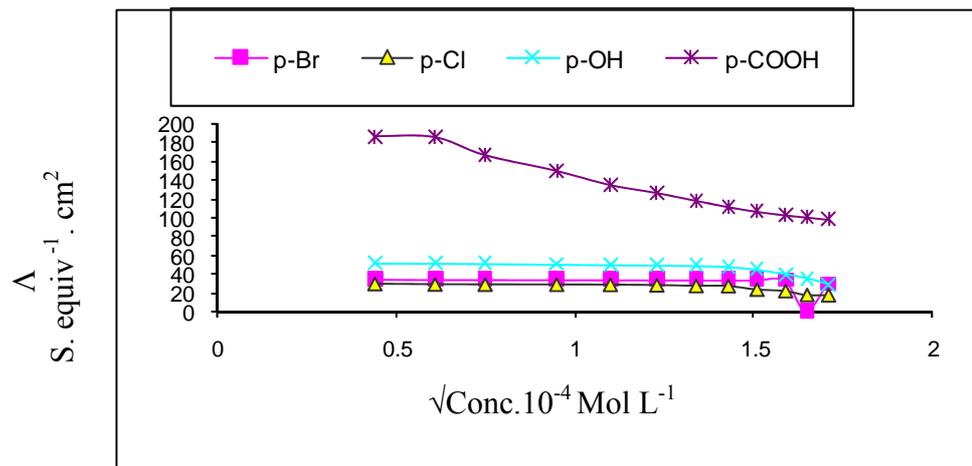


Fig. 1-C: Plot of Λ against SQRT of concentration at 298.15 °K.

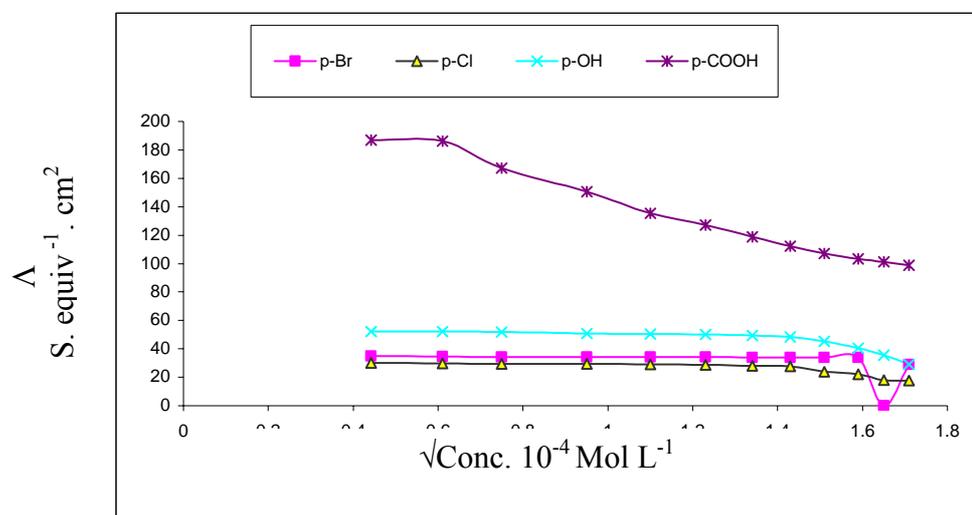


Fig. 1-D: Plot of Λ against SQRT of concentration at 308.15 °K.

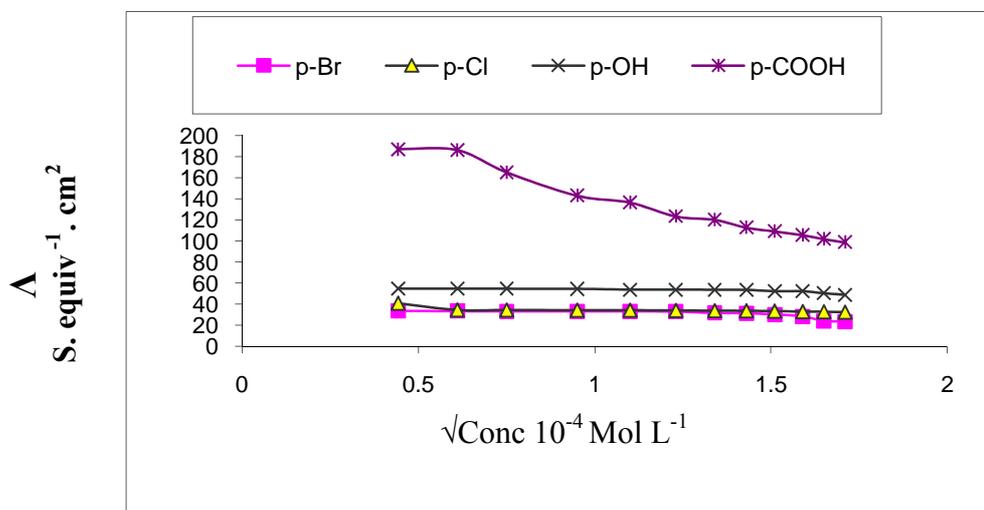


Fig. 1-E: Plot of Λ against SQRT of concentration at 318.15 °K.

The values of K_A , Λ_0 , R of the aqueous solution of Schiff bases (I-IV) at 283.15-318.15 °K are shown in Table (3). Close inspection of this table shows that all values of K_A were decreased with increasing temperatures, which were parallel to decrease of the values of the dielectric constant and viscosity with increasing temperature (Hikmat, 2002). This diversity of the values of K_A may be attributed to the short range interaction and the H-bonding that are formed at low temperature [5].

On the other hand, the substituents on the anilino ring may play an important role and afford obvious differences in the K_A values. The results, as represented in Table 3, show that the K_A values decreased in the order of:



The difference in the K_A values with respect to the above substituents are explicable in terms of their abilities to form hydrogen bonding and ion-solvent interaction, in addition to their electron withdrawing and electron donating abilities, since the increase in donor properties of the substituents will lead to the decrease of association and vice versa. The electron withdrawing ability of any group, results in delocalization of the electron density between the substituents and the rest of the molecule, and accordingly the polarizability of the molecule will be enhanced, giving rise the more association to take place.

Table 3: Fittest parameters on analysis of conductance data for aqueous solution of benzylidene substituted aniline at different temperatures.

Temp °K	p-Br				p-Cl			
	K_A	Λ_0	RA^0	$\sigma \Lambda$	K_A	Λ_0	RA^0	$\sigma \Lambda$
283	1452	38	10	0.014	3107	53	4.0	0.013
288	1028	27	10	0.019	1020	24	3.0	0.01
298	469	30	10	0.01	1042	41	14.0	0.052
308	237	35	18	0.01	948	32	2.0	0.023
318	108	36	20	0.018	520	37	3.0	0.011

Temp °K	p-OH				p-COOH			
	K_A	Λ_0	RA^0	$\sigma \Lambda$	K_A	Λ_0	RA^0	$\sigma \Lambda$
283	2810	71	10.0	0.022	15145	305	4.5	0.032
288	3860	53	5.0	0.011	9752	250	20.0	0.039
298	2842	60	6.0	0.04	5364	370	3.0	0.073
308	1420	55	4.0	0.039	1981	228	10.0	0.040
318	288	56	1.0	0.012	949	225	20.0	0.037

The electronic effect of the substituents can be exhibited through inductive and resonance. The latter depends upon the co-planarity of the molecules. In fact, the 3D-structures and the data obtained from the minimized geometry data, i.e., the charge, bond length, bond angle, interatomic distance and the twist angle (as a representative model Fig. 2 and Table 4 for compound I) for the Schiff bases (I-IV), show that these Schiff bases are not planar in which the two phenyl rings and the imino group are in different planes, i.e. the imino group is out the plane of each of the benzylidene and anilino phenyl rings as indicated

by the selected twist angle for compound I as a representative model (Table 4) ($C_2C_3C_7N_9 = -8.6$, $C_7N_9C_{10}C_{11} = 152.8$, $C_3C_7N_9C_{10} = 174.9$, $C_2C_3C_{10}C_{11} = -34.2$). These values indicate that there are a series of steric congestions around C=N group which is surrounded by the two phenyl rings, and the steric congestion exerted by anilino ring is more than that exerted by benzylidene ring, as a result of the valence shell electron-pair repulsion. Consequently, it can be concluded that the π - frameworks consisting of the two phenyl rings and the C=N group are not in the same plane. This means that the π - clouds of the two phenyl rings and the C=N group are extensively not delocalized, i.e. the substituents can not affect the whole system through the resonance, but they can affect only the anilino ring because these groups are in the same plane of this ring as it is indicated by the bond angle $O_{16}C_{13}C_{12} = 0.0$ (Fig. 2).

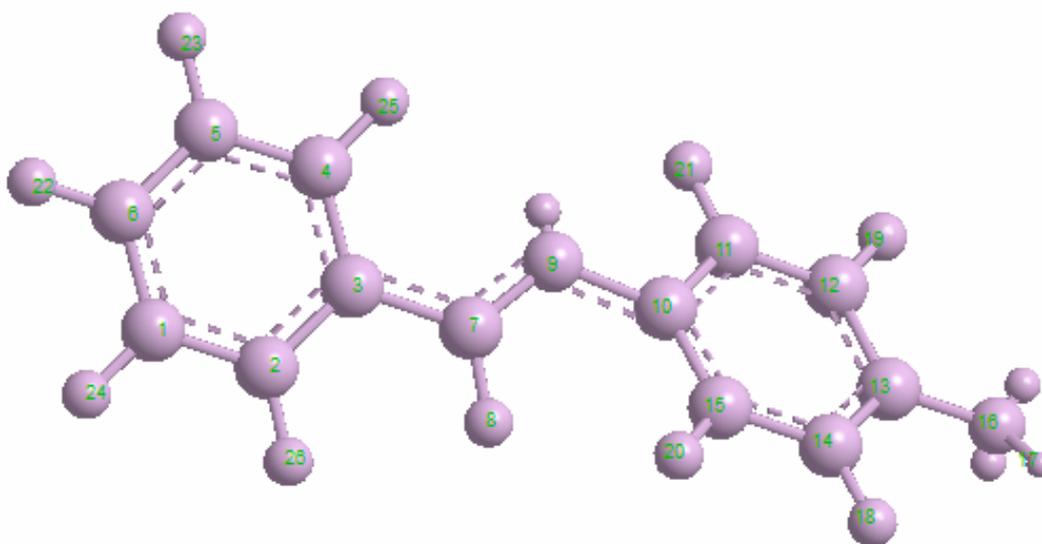


Fig. 2: The 3-D structure of benzylidene p-hydroxyaniline.

Table 4: Twist angles and dipole of benzylidene substituted aniline.

Compd. No.	X	Twist angle				Bond angle $XC_{13}C_{12}$	Dipole
		$C_2C_3C_7N_9$	$C_7N_9C_{10}C_{11}$	$C_3C_7N_9C_{10}$	$C_2C_3C_{10}C_{11}$		
I	OH	-8.6	152.8	174.9	-34.2	0.0	0.817
II	COOH	172.6	-37.4	178.7	-41.9	0.0	3.175
III	Br	172.4	-123.3	31.0	179.2	0.0	3.088
IV	Cl	-6.9	-24.5	177.8	150.9	0.0	2.243

The other factor exhibited by the substituents is the inductive effect, which leads to increase the polarizability of the molecules. The dipole of the molecules (I-IV) (Table 4) obtained from the minimized geometry calculation with respect to the substituents was decreased in the following sequence:



This sequence was in a good agreement with the order of the substituent constants (σ_m values) of these substituents that attributed to the inductive effect, but this sequence does not coincide with the order K_A values. On the light of these results, it appeared that K_A values did not depend only on the electronic effect of the substituents, but on other factors, such as hydrogen bonding, which play an important role in the determination of K_A values.

The OH group has an inductive effect as electron withdrawing, but it is suitable to form strong hydrogen bonding, while Br and Cl groups have a higher inductive effect, as electron withdrawing than OH group but they cannot form hydrogen bonding, and accordingly, compound II has a higher K_A value than that of compound III and IV.

Moreover, the carboxy group was expected to exert larger K_A value, but the results showed the contrast. This observation can be explicable in terms of formation of dimers of benzylidene p-carboxyaniline (Burgi and Dunitz, 1971) which results in packing arrangement completely different from that of other substituted anilino compounds and therefore, compound II has a lower K_A value than compound III.

The values of Λ_o , as shown in Table (3), are decreased with increasing temperature. This change is expected, since the forces between ions are decreased, and hence the mobility of ions increased in accordance with increasing the dielectric constants of the medium (Al-Sattar, 2002).

The values of distance parameter (R) are almost more than $3A^\circ$ (according to Bjerrums physical concept of ionic association), which means that the electrolytes form solvent separated ion pairs in water. Furthermore, it can be noted from Table (3), that (σ_Λ) possesses small values which give an indication about the fittest values.

The temperature dependence of the association of the Schiff bases solutions is the most important key toward association description. It has been suggested that the conductance is proportional to the strength of association between Schiff base and the solvent (El-Sayed *et al.*, 1991). Hence, according to Arrhenius equation, the molecule must have acquired certain critical enthalpy ΔH° . This enthalpy can be obtained simply by plotting $\text{Log } K_A$ against the reciprocal of the absolute temperatures. The linearity of the slope provides strong evidence for the consistence of the conductivity with Arrhenius equation. The plot of $\text{Log } K_A$, using the data listed in Table (5), versus $1/T$ over a range of 35° was carried out, and gave excellent straight lines (Fig. 3).

The thermodynamic parameters ΔH° , ΔG° and ΔS° are determined as follows:

The standard enthalpy of ion association reaction (ΔH°) of the charge transport was evaluated by the least-square treatment of the above data. The standard deviation of each enthalpy was derived from the standard deviation of the corresponding slope. The standard Gibbs free energy (ΔG°) was determined from the values of K_A ($\Delta G^\circ = -RT \ln K_A$), while the entropy of ion-pair formation was determined from the linear combination of the two previous variables (Tominić *et al.*, 2004) as follows:

$$\Delta S = (\Delta H - \Delta G) / T$$

The thermodynamic results obtained are tabulated in Table (6).

It can be noted from Table (6) that the values of ΔH° of the ion association in water are negative, i.e., the process is exothermic and the evolution of heat was attributed to the ion-solvent interaction, in addition to the short-range interactions such as hydrogen-bond formation.

The order of ($-\Delta H^\circ$) corresponding to the Schiff bases (I-IV), related to the substituents is decreased in the following sequence:



Compound I has higher ($-\Delta H^\circ$) value than that of other compounds despite its K_A value is lower than that of compound II. This observation is easily accounted in the terms of hydrogen bond formation, in which the association between OH and water is more than that

between COOH and water, as it is mentioned previously that the COOH compound present in a dimer form through intermolecular hydrogen bonding, and hence the intermolecular hydrogen bonding with water was reduced and accordingly ($-\Delta H^\circ$) become smaller. The p- Br and p- Cl compounds have low interaction with the solvent due to the absence of H-bonding, so they have low ($-\Delta H^\circ$) values. On the other hand, the ΔS° values of the interaction of the Schiff bases (I-IV) with water represented by their groups are decreased in the following order: p- OH > p- Br > p- COOH > p- Cl

Table 5: The calculated values of Log K_A vs 1/T.

1 / T	Log K_A p-Br	Log K_A p-OH	Log K_A p-COOH	Log K_A p-Cl
0.00353	7.260	9.990	9.625	8.041
0.00347	6.935	8.258	9.185	7.390
0.00335	6.150	7.952	8.531	6.948
0.00324	5.465	7.258	7.591	6.854
0.00314	4.682	5.662	6.822	6.822

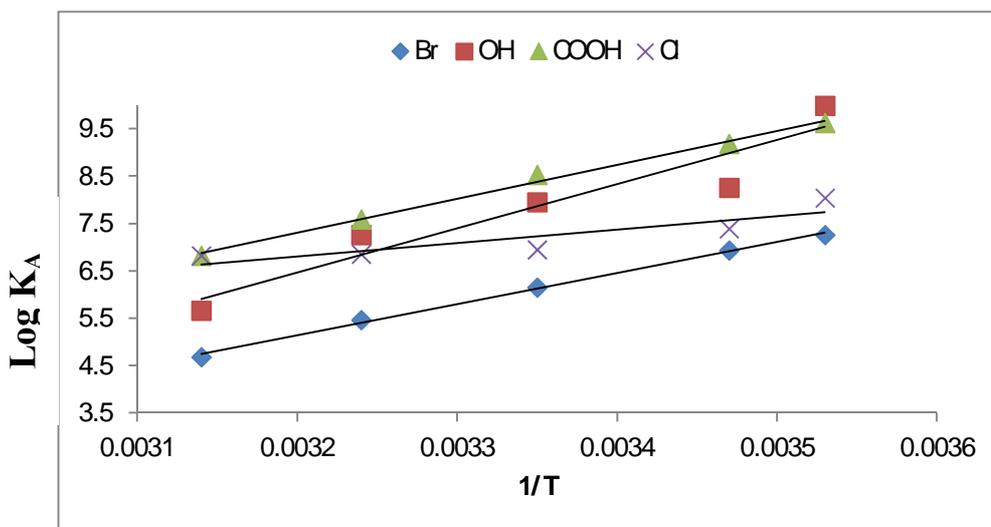


Fig. 3: Plot of Log K_A against 1/T for benzylidene substituted aniline in water at different temperatures.

The positive values of ΔS° for all compounds indicate the higher degree of freedom as a result of decrease in the orientation of the solvent molecules when the ion pair was formed in addition to the salvation of the solute molecules (Kubota *et al.*, 1988), i.e. the molecules were spread in the solvent.

The ΔG° values for conductivity are negative which indicates that the thermodynamic parameter ΔG° for the conductance process of Schiff base salvation have -ve values, hence this process takes place spontaneously due to the interactions as it is suggested above.

Table 6: The thermodynamic parameters calculated from the ion association constants of substituted benzylidene aniline in water at different temperatures.

p-Br				p-Cl		
Temp °K	-ΔH KJ/mol	-ΔG KJ/mole	ΔS J/mol.deg.	-ΔH KJ/mol	-ΔG KJ/mol	ΔS KJ/mol
283.16	6.666	4.122	8.984	4.324	4.553	0.808
288.15		4.025	9.165		4.159	0.225
298.15		3.667	10.058		4.148	0.607
308.15		3.368	10.702		4.224	0.324
318.15		2.970	11.588		3.978	1.087
p-OH				p-COOH		
Temp °K	-ΔH KJ/mol	-ΔG KJ/mole	ΔS J/mol.deg.	-ΔH KJ/mol	-ΔG KJ/mol	ΔS KJ/mol
283.16	11.025	5.657	16.975	7.272	5.450	6.434
288.15		4.765	21.755		5.293	6.867
298.15		4.740	21.075		5.087	7.328
308.15		4.473	21.261		4.678	8.417
318.15		3.662	23.142		4.340	9.215

REFERENCES

- Akrawi, B.A.; Sarsem, L.A. (2001). The electrolytic conductivity of oxime with transition alkaline earth chloride complexes in methanol at 25 °C. *Raf. J. Sci.* **12** (2), 17-27.
- Al-Sattar, A.A. (2002). The electrical conductivity study of 2,5-di(2,4-dichlorophenoxy methyl)-1,3,4-oxadiazole in methanol-water mixtures at 25 °C. *Raf. J. Sci.* **12** (3), 9.
- Burgi, H.B.; Dunitz, J.D. (1971). Molecular conformation of benzylidene anilines. *Helvetica Chem. Acta*, **5415**, 1255.
- Criddle, W.J.; Eilis, G.P. (1976). "Spectral and Chemical Characterization of organic compounds". John Wiley and Sons, Inc., London.
- El-Bayoumi, M.A.; El-Aasser, M.; Abdel-Halim, F. (1971). Electronic spectra and structure of Schiff bases. I. Benzanils. *J. Amer. Chem. Soc.* **93** (1-3), 586-590.
- El-Dossoki, F.I. (2010). Effect of hydrogen bond, relative permittivity and temperature on the transport properties and the association behavior of some 1:1 electrolytes in some binary mixed solvents. *J. molecular Liquid*, **151**(1), 1.
- El-Sayed, B.A.; Shaaban, S.M.; El-Desoky, M.M.; Ahmed, M.A. (1991). The electrical conductivity of some azine compounds. *J. Material Sci.* **2**(1), 11-13.
- Frranis, J.; Cowan, D.O.; Walatka, V.Jr.; Peristsm, J.H. (1973). The electrical conductivity of some fulavlene compounds. *J. Amer. Chem. Soc.* **95**, 984.
- Hikmat, N.A. (2002). Association in tetraethyl ammonium bromide solution in sodium carboxymethyl cellulose-water mixture. *Iraqi J. Chem*, **28** (1), 107-116.
- Jones, G.; Bradshaw, B.C. (1933). The measurement of conductance of electrolytes. *J. Amer. Chem. Soc.* **55**, 1780.

- Kubota, E.; Mochizuki, Y.; Yokoi, M. (1988). Conductivity of Iron (II) sulfate in aqueous solution at various temperatures. *Bull. Chem. Soc. Jp.* **61**(10), 3723.
- Lee, W.H.; Wheaton, R.J. (1978). Conductance of symmetrical, unsymmetrical and mixed electrolytes. *J. Chem. Soc. Faraday Trans. II*, 740.
- Tominic, I.; Tomas, R.; Visic, M.M.; Sokol, V. (2004). Conductometric study of hydrobromic acid in 2-propanol-water mixtures. *Croatica Chem. Acta.* **77**(3), 537.
- Wang, H.; Wang, J.; Zhang, S.; Pei, Y.; Zhuo, K. (2009). Ionic association of the ionic liquids [C4mim][BF4], [C4mim][PF6] and [Cnmim]Br in molecular solvents. *Eur. J. Chemphyschem*, **10**(14), 2516-2523.
- Yokoyama, H.; Ohta, T.; Iida, M. (1992). Conductometric study of ion association between Tris (ethylenediamine cobalt III) and monovalent anions at temperatures from zero to 50 °C. *Bull. Chem. Soc. Jp.* **65**, 2901.