

Molal Solubility, Dissociation, Association and Solvation Parameters for Saturated O-Chlorobenzoic Acid Solutions in Various Solvents at 298.15 K

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Abstract The molal solubility for saturated solutions of O-chlorobenzoic acid at 298.15 K in various solvents was determined. The solvents used are, water (W), ethanol (Et), dimethylsulphoxide (DMSO), acetonitrile (AN), methanol (Me), 1-4, dioxane (Di) and N, N-dimethylformamide (DMF). From the experimental data for solubility, pH, densities, the different volumes, free energies, dissociation constants, association constants and solvation parameters were estimated. Also the free energies of dissociation and association were also evaluated. Other solvation parameters like the solvation numbers were cited here to help explaining the solubility trend. This work give a lot of data for the solubility of orthochlorobenzoic acid which help the biologist for using it as food preserver. The results were also discussed.

Keywords Solubility, Dissociation Constants, Association Constants, Different Volumes, Solvation Parameters, Free Energies, Orthochlorobenzoic Acid

1. Introduction

The solubility of an electrolyte is influenced by a wide range of factors, including ion association, variation in ionic activity coefficients, complexation and temperature. Solubility is an equilibrium property enable to thermodynamic parameters through the standard state free energy. Ion pairing can occur in dilute solutions for many electrolytes, particularly these with multivalent ions and for all electrolytes in concentrated solutions. Ion pairing is generally more pronounced in non-aqueous solvents which have lower dielectric constants than water. In effect, the ion pairs represent a reservoir of electrolyte in the solution and increase the solubility. The complexity of the system increases for unsymmetrical electrolytes or in mixed electrolyte systems[1].

Bjerrum[2] proposed that the motion of ions would be coupled when the energy of attraction between them exceeded the thermal energy. For solely columbic interactions his theory predicts a distance within which the electrostatic attraction between ions is greater than $2kT$. Which will be sufficient to couple the motions of the ions. The treatment takes account of only electrostatic interactions and neglects the molecularity of solvent. Nevertheless in low concentration interactions between ions and solvent molecules resulting in ion pair formation. The three commonly

assumed structures are the first in which the ion retains their individual solvation shells, and so is separated by two solvent molecules. The second in which the ions share some part of their solvation shells so are separated by one molecule and the third where the ions are in contact and share a common solvation shell.

The presence of species such creates an experimental difficulty; the different techniques will have different sensitivities to the species present. Thus the conductance will see on the dissociated ions and the presence of ion pairs is determined by difference from experimental molar conductance and that expected for strong electrolyte[3].

The formation of complexes (complexation) provides a route to increased solubility. Several equivalent representations of the speciation in these systems have been used[4].

Many publications have appeared on the behaviour of weak acids in anhydrous solvents. Interesting work has been done by Kolthoff et al.[5,6]. Aleksandrov et al.[7,8] studied the dissociation of salicylic acid in butane-2-one. Kreshkov et al.[9] studied the dissociation of amino acids (as weak acids) in mixtures of formic and ethylmethylketone and in mixtures of acetic acid-ethylmethylketone.

Gomaa et al.[10] studied association, dissociation and hydrogen bonding of salicylic acid in water-N,N-dimethylformamide mixtures from solubility measurements.

The aim of this work is to evaluate the solubilities of O-chlorobenzoic acid in different solvents and discuss in detail the solvation parameters for the solubility process for O-chlorobenzoic acid which is one of the most widely used preservation materials. O-chlorobenzoic acid has the ad-

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vantage of low cost, ease of in- corporation into products. Lack of colour and relatively low toxicity.

Also knowing the other factors affecting the solubility is very important here. Is the electrostatic energy play important role in the solubility or not.

Many authors like Bjerrum and other reported that the electrostatic energy plays important role in the solvation energy. In this work more effort was done to explain the main factors affecting the solubility of orthochlorobenzoic acid in different solvents[11]

2. Experimental

The Q-chlorobenzoic acid 98 % m.p type Cambrian Chemicals was used. The solvents, ethanol (ET), dimethylsulphoxide (DMSO), acetonitrile (AN), methanol (Me), 1-4 dioxane (Di) and dimethylformamide (DMF) were supplied from Merck. The saturated solutions of Q-chlorobenzoic acid were prepared by dissolving it in the solvents used. The solutions were saturated with N₂ gas in closed test tubes. The tubes were placed in a shaking water bath of the type assistant for a period of four days, followed by another two days without shaking to reach the necessary equilibrium.

The solubility of Q-chlorobenzoic acid in each solution was determined gravimetrically by taking 1 ml of the saturated solution and subjecting it to complete evaporation using small aluminium disks heated by an infrared lamp.

The pH readings of the saturated solutions were measured using a pH-meter of the type Tacussel/Minis 5000. The densities were measured by using weighing bottle 1 ml and analytical balance (4 digits) of the type Mettler Toledo DA.

3. Results and Discussion

Determination of the dissociation constants of organic acids in aqueous and non aqueous solutions by different methods like conductometric method during a period of 100 years was discussed. From time of pioneering works of Arrhenius and Ostwald the conductometric method provide simple method for the determination of the dissociation constants of organic solvents in water. This method is based on the assumption that strong electrolytes are completely dissociated while weak electrolytes attain this state only at infinite dilution. At fixed temperature, an equilibrium exists in solutions of weak electrolytes between ions and undissociated molecules to which the law of mass action and the Ostwald dilution law can be applied. Therefore complete study need more work for this field which is the target of this work.

The calculated molal solubilities (m) for Q-chlorobenzoic acid saturated solutions were given in Table (1) from at least three average measurements. Also the measured densities and pH values of the acid used are also listed in Table (1).

The molar volumes (V_M) of benzoic acid were obtained by dividing the molar mass by the densities and their values are

listed in Table (2). The packing density as reported by Kim et al.[11] and Gomaa et al.[12], i.e. the relation between Van der Waals volume (V_W) and the molar volume (V_M) of relatively large molecules (above 40) was found to be a constant value and equal to 0.661.

$$P = \frac{V_W}{V_M} = 0.661 \pm 0.017 \quad (1)$$

The electrostriction volume (V_e) which is the volume compressed by the solvent, was calculated by using equation (2) after Gomaa[13].

$$V_e = V_W - V_M \quad (2)$$

The molar, Van der Waals and electrostriction volumes of Q-chloro- benzoic acid in various solvents at 298.15 K were tabulated in Tables (2).

The apparent molar volumes V_φ[14,15] were calculated using equation (3)[16].

$$V_\phi = M/d_o - (d-d_o/dd_o) 1000/m \quad (3)$$

Where M is the molar mass of benzoic acid, m is the concentration, d and d_o are the densities of saturated solution and pure solvents, respectively.

The values of V_φ for Q-chlorobenzoic acid in various solvents at 298.15 K are presented in Table (2).

Table 1. Molal solubilities (m), densities (d) and pH values for saturated Q-chlorobenzoic acid solution in different solvents at 298.15 K

Solvent	m/(g.mol/kg solvent)	d	pH
H ₂ O	1.3319x10 ⁻²	1.00527	6.24
Ethanol (Et)	1.9168	0.95137	2.12
DMSO (Dimethyl sulphoxide)	1.1721	1.2527	3.25
AN (Acetonitrile)	0.6035	0.82307	3.14
Me (Methanol)	1.7169	0.91787	1.89
Di (1,4 dioxane)	3.1219	1.12743	9.01
DMF (dimethylformamide)	3.1431	1.16610	9.01

Table 2. Molar volumes (V_M), Van der Waals volumes (V_W), electrostriction volumes (V_e) and apparent molar volumes (V_φ) for saturated solutions of Q-chlorobenzoic acid in different solvents at 298.15 K (in cm³/mole)

Solvent	V _M	V _W	-V _e	V _φ
H ₂ O	155.780	102.972	52.808	-454.940
Et	164.625	108.817	55.8087	83.445
DMSO	152.075	82.674	42.401	46.077
AN	190.287	125.779	64.508	29.793
Me	170.534	112.789	57.845	93.156
Di	138.917	91.824	47.093	123.715
DMF	134.310	88.778	45.5329	101.718

The activity coefficient was calculated by using the relation $\log \gamma_{\pm} = -0.5062 \sqrt{m}$ [17].

K_{ass} values were calculated[18] from the ratios of association constant to dissociation constant (i.e., K₁/K₂) for the dimers of Q-chlorobenzoic acid which form a complex ion ((HA₂⁻) and hydrogen ion (H⁺), and the values of K['] (where K['] is the dissociation constant of the associated acid complex, H₂A₂) are given by the following equations

$$K' = a^2 H^+ / m^2 \quad (4)$$

$$PaH^+ = \frac{1}{2} \log \frac{K_1}{K_2} - \log m = pH - \log \gamma_{\pm} \quad (5)$$

$$\frac{K_1}{K_2} = K' K_{ass} \quad (6)$$

Where a is the activity and γ_{\pm} is the activity coefficient. The values obtained K_1/K_2 , K' and K_{ass} are reported in Table (3).

Prediction of electrolyte activity coefficients is one of the classical problems in physical chemistry and is outlined in classical works[17]. The defining characteristic of ions is that they carry a net charge and so the principle interaction between ions are largest contribution to the activity coefficients are coulombic. Debye and Hückel solved the problem for a system purely electrostatic interactions between point charges surrounded by a dielectric continuum. Therefore the extended Debye- Hückel equation was applied taking account of the ion size[18]

From the activity coefficients γ_{\pm} , calculated using Debye Hückel equation as explained in ref. 16 and from the molal solubility data, values of K' , K_1/K_2 and K_{ass} were evaluated following equations 4 – 6[11,12].

The maximum value of K_{ass} was found to be by using Di where water is the least association parameters.

Table 3. Log activity coefficients ($\log \gamma_{\pm}$), dissociation constants (K') and association constants for *O*-chlorobenzoic acid saturated solutions in different solvents at 298.15 K.

Solvent	$\log \gamma_{\pm}$	Pa_{H^+}	K'	$\frac{K_1}{K_2}$	K_{ass}
H ₂ O	-0.0584	6.2984	2.2361×10^5	7.0106×10^8	3.1352×10^3
Et	-0.7008	2.8208	4.1510	1.6097×10^6	3.8777×10^5
DMSO	-0.5480	3.7980	3.7980	5.4189×10^7	5.1574×10^6
AN	-0.3932	3.5332	34.276	2.0600×10^3	60.099
Me	-0.6633	2.5533	2.2116	6.1380×10^2	277.53^6
Di	-0.8944	9.9044	10.065	2.5054×10^{10}	2.4889×10^9
DMF	-0.8974	10.1774	10.485	4.7288×10^{10}	4.5100×10^9

The free energies of dissociation (ΔG_d), free energies of association (ΔG_A), difference free energies ($\Delta \Delta G$) and free energies of solvation (ΔG_s) for *O*-chlorobenzoic acid saturated solutions in various solvents were calculated by using the following equations and collected in Table (4).

$$\Delta G_d = -RT \ln K' \quad (7)$$

$$\Delta G_{ass} = -RT \ln K_{ass} \quad (8)$$

$$\Delta \Delta G = \Delta G_{ass} - \Delta G_d \quad (9)$$

$$\Delta G_s = -RT \ln K_{sp} \quad (10)$$

$$\ln K_{sp} = -2 \log m - 2 \log \gamma_{\pm} \quad (11)$$

Dissociation of electrolytes introduces two solutes, the anion and the cation into solution. In principle, these solutes have individual activity coefficients but, since there is no experiment that allows the measurement of thermodynamic properties of individual ions. The formation of complexes becomes more important at high concentrations of the complexing ion and is likely to be more extensive in non-aqueous solvents, partially in dipolar aprotic solvents whereas the solvation of anion is weaker leading to stronger complexation[18].

The solvation volumes for *O*-chlorobenzoic acid were evaluated from the difference between Van der Waals of *O*-chlorobenzoic in various solvents. The Van der Waals

volume of *O*-chlorobenzoic acid in solid state, was calculated from the Bondi method[19,20] and found to be $167.537 \text{ cm}^3/\text{mole}$. Subtracting this value from V_w in solvents and dividing the results by the molar volumes of the solvents taken from refs.[19-21], n (the solvation numbers) were obtained and is given in Table (5).

It was concluded that the solute-solvent interaction increased by increasing $\Delta \Delta G$ and ΔG_s due mainly to the increase of the association parameters in the corresponding solvents. Also it was observed that the

association, dissection and microscopic interactions between solute and solvent is important for any solvent individually, whether it is polar, aprotic or amphiprotic.

Increasing of the solvation numbers favor more solute-solvent interactions between orthochlorobenzoic acid and solvents. Also small solvation numbers favour more solute-solute interaction or ion pair formation resulting in the decrease of the solute-solvent interactions in the solvent under discussion. Big positive values for $\Delta \Delta G$ and big negative values for ΔG_s indicate also more solute-solvent interactions.

Table 4. Free energies of dissociation (ΔG_d), free energies of association (ΔG_A), difference free energies ($\Delta \Delta G$) and free energies of solvation (ΔG_s) for *O*-chlorobenzoic acid saturated solutions in different solvents at 298.15 K (in k Joule/mole)

Solvent	ΔG_d	ΔG_A	$\Delta \Delta G$	ΔG_s
H ₂ O	-30.538	-19.9590	10.9480	-9.582
Et	-3.5288	-31.9034	-28.3746	-2.0728
DMSO	-5.8312	-38.3192	-32.4880	-2.3740
AN	-8.7627	-10.1549	-1.3922	-3.0355
Me	-1.9677	-13.9481	-11.9804	-4.4507
Di	-5.7247	-53.6389	-47.9142	-6.8814
DMF	-5.8261	-55.1127	-49.2866	-6.9123

Table 5. Molar volumes of solvents (V_s), difference in different Van der Waals volumes (ΔV_w) and solvation numbers (n_s) for *O*-chlorobenzoic acid saturated solutions in different solvents at 298.15 K

Solvent	V_s	ΔV_w	n_s
H ₂ O	18.0724	64.5649	3.5725
Et	58.6804	58.7199	1.0006
DMSO	71.2995	84.8629	1.1902
AN	52.8450	41.7669	0.7904
Me	40.7322	54.7479	1.3441
Di	86.3552	75.7129	0.8767
DMF	77.4118	78.7589	1.0174

REFERENCES

- [1] Apelblat, Alexander, J. Molecular Liquids, 95(2002)99-145.
- [2] Barthel, J., Wachter, R. and Gores, H.-J., in Modern Aspects of Electrochemistry, Coway, B.E., and Bockris, J.O'M., Editors, Vol. 13, pp. 1-179. Plenum Publ. Corp., New York, 1979.
- [3] Barthel, J.M.G., Krienke, H. and Kunz, W., "Physical Chemistry of Electrolyte Solutions, Modern Aspects", Springer, Darmstadt, 1998.
- [4] Bockris, J.O'M. and Reddy, A.K.N., "Modern Electroche-

- mistry”, Plenum Press, New York, 1970.
- [5] Kolthoff, I.M. and Chantooni, M.K., J. Am. Chem. Soc., 87(1965).4428.
- [6] Kolthoff, I.M., Chantooni, M.K. and Bhowmik, S., J. Am. Chem. Soc., 90(1968) 123.
- [7] Aleksandrov, V.V., Zudochkina, A.I., and Sandovinchaya, L.P., Zh. Fiz. Khim., 52(1978) 1295 .
- [8] Alekandrov, V.V., and Burakhovich, Fizicheskaya Khimiya Rastrorov (Physical Chemistry in Solutions), Nauka, Moscow, 1972, p. 154.
- [9] Kreshkov, A.P., Tanganor, B.B., Yarovenko, A.N. and Batoreva, T. Kh., Zh. Fiz. Khim., 54(1980) 105.
- [10] Gomaa, E.A., Mousa, M.A. and El-Khouly, A.A., Thermochimica Acta, 89(1985) 133-139.
- [11] Kim, J.T., Cecal, A., Born, H.J. and Gomaa, E.A., Z. Physikalische Chemie, Neue Folge, 110(1978) 209-227.
- [12] El-Khouly, A.A., Gomaa, E.A. and Abou-El-Leef, S., Bull. Of Electrochemistry, 19(2003) 153-164.
- [13] El-Khouly, A.A., Gomaa, E.A., Abou El-Leef, S., Bull. Of electrochemistry, 19(2003) 193-202.
- [14] Oswal, S.L., Desai, J.S., Ijardar, S.P. and Jain, D.M., journal of Mol. Liquids, 144(2009) 108-114 .
- [15] Dorota Bobicz, Wacław Grzybkowski and Andrzej Lwandowski, J. of Mol. Liquids, 105(2003).93-104.
- [16] Marcus, Y. “The properties of solvents”, Wiley, London, 1998.
- [17] Moelwyn-Hughes, E.A., “Physikalische Chemie”, George Thieme Verlag, Stuttgart, 1970, p. 489.
- [18] Gomaa, E.A., Mousa, M.A. and El-Khouly, Thermochim. Acta, 89(1985).133-139.
- [19] Gomaa, Esam, A., Thermochim. Acta, 120(1987).183-190.
- [20] Bondi, A., J. Phys. Chem., 68 (1964) 441.
- [21] Gomaa, E.A. and Al-Jahdalli, B.M., American Journal of Condensed Matter Physics, 2(2012).16-21 .