Thermodynamics of the Solvation of Lead Nitrate in Mixed DMF-H$_2$O Solvents at 301.15 K

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Authors' contributions

This work was carried out in collaboration between all authors. Authors EAG and EMAE designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors EAG and EMAE managed the analyses of the study. Author EMAE managed the literature searches. All authors read and approved the final manuscript.

Research Article

ABSTRACT

Aims: The aim of this study is to determine thermodynamic energies of the solvation of lead nitrate in mixed DMF-H$_2$O solvents at 301.15 K. The Gibbs free energies as a very important thermodynamic property were evaluated for Pb(NO$_3$)$_2$ in mixed dimethylformamide DMF-H$_2$O solvents at 301.15 K from the experimental solubility measurements. The ratio of the ionic between lead and nitrate ions was used to divide the total Gibbs free energy of the salt into its individual contribution in the mixtures used. Libration Gibbs free energy associated with moving Pb(NO$_3$)$_2$ in standard gas state to standard state in solution was evaluated according to specific cycle for the solvation process using the solubility product. Also the lattice energy for Pb(NO$_3$)$_2$ (cr) was also calculated and used for further evaluation (the symbol (cr) denotes the crystalline phase). The conventional Gibbs free energies for the cation (Pb^{2+}) and anion (NO$_3^-$) were estimated theoretically and also the Gibbs free energy of NO$_3^-$ gas was evaluated and all values were discussed.
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1. INTRODUCTION

For neutral species experimental solvation Gibbs free energies have been tabulated large number of solutes in both aqueous [1-7] and non-aqueous [7,8] solvents. Typically, these solvation free energies are determined experimentally [8] and their uncertainty is relatively low (0.8 kJ mol-1) [9]. Determining accurate values for the Gibbs free energies of ionic solutes like $Pb(NO_3)_2$ is important than that of neutral solutes. Single-ion solvation free energies are well defined in statistical mechanics, and determining their values is an important step in understanding the structure of solutions. Understanding the partitioning of single ions between different liquid phases is important in many areas of biology. For example, the electrical signals sent by nerve cells are activated by changes in cell potential that are caused by the movement of various ions (sodium and potassium) across the neuronal membrane [10]. The division of thermodynamic Gibbs free energies of solvation of electrolytes into ionic constituents is conventionally accomplished by using the single ion solvation Gibbs free energy of one reference ion, conventionally, the proton, to set the single ion scales [11,12].

Sums of solvation free energies of cations and anions are well defined through the use of thermochemical cycles involving calorimetric or electrochemical measurements [13-17]. A number of different extra thermodynamic approximations have been used [18-22] for partition the salt Gibbs free energies into single ion contribution.

The aim of this work is to estimate the single ion Gibbs free energies for Pb^{2+} & NO_3^- ions in mixed DMF-H_2O solvents at 301.15 K.

1.1 Relative and Conventional Solvation Free Energies of Ions

The Gibbs solvation free energies of ions are often tabulated as relative free energies by setting the free energy of solvation of some reference ion equal zero [23]. Proton was chosen as reference ion. For ions, this result in a set of conventional free energies of solvation that the cations are shifted from their absolute values by the value for the absolute Gibbs solvation free energy of the proton. The conventional Gibbs free energies of solvation for anions are shifted by an equal amount in the opposite direction.

1.2 Conventional Gibbs free Energies from Reduction Potentials

When the convention for the absolute Gibbs free energy of the proton is followed, the solution-phase free energy change associated with the half cell for reaction of hydrogen gas is equal to zero. Reduction potentials following this convention for hydrogen electrode are referred as standard reduction potentials. From the half cell reaction for the reduction of metal cation to crystalline phase and the half reduction reaction of hydrogen gas, the redox reaction can be illustrated through the use of thermochemical cycle [12]. This last procedure can be used to estimate the gas free energy of formation of NO_3^- ion, to explain the ionic behaviour.

2. MATERIALS AND METHODS

Lead nitrate $Pb(NO_3)_2$ GCC-laboratory reagent and N-N-dimethylformamide (DMF) from Merck Co. were used.

Saturated solutions of $Pb(NO_3)_2$ were prepared by dissolving different amounts in closed test tubes containing different DMF-H_2O mixtures. These mixtures were then saturated with nitrogen gas an inert atmosphere. The tubes were placed in a shaking thermostat (Model Gel) for a period of four days till equilibrium reached. The solubility of $Pb(NO_3)_2$ in each mixture was measured gravimetrically by evaporating 1 ml of the saturated solution in small beaker using I. R. lamp. The measurements were done by three readings for each solution at 301.15 K.

3. RESULTS AND DISCUSSION

The molar solubility (S) for $Pb(NO_3)_2$ at 301.15 K were measured gravimetrically with average of the second number after comma in water, dimethylformamide (DMF) and their mixtures. The solubility values for $Pb(NO_3)_2$ are cited in Table 1. The mean activity coefficient ($\gamma_\pm$) of ions which can be estimated from the Debye-Hückel limiting law, as modified by Robinson and Stokes [24 & 25].

$$\log \gamma_\pm = -\frac{AZ_+ Z_- \sqrt{S}}{I + Br°\sqrt{S}} \tag{1}$$

Where Z_+ and Z_- are the charges of ions in solutions, $A = 1.823 \times 106(\varepsilon.T)^{-3/2}$, $B = 50.29$ $(\varepsilon.T)^{-1/2}$, $r°$ is the solvated radius , ε is the dielectric constant of the solvents and S is the molar solubility. The values of ε for DMF-water mixtures were taken from previous publication [26]. These data ($\log \gamma_\pm$) were tabulated also in Table 1. The solubility product was calculated by the use of equation (2) [27-28].

$$pK_{sp} = -4(\log S^3 + \log \gamma_\pm^3) \tag{2}$$

The solubility product (pK_{sp}) data are given in Table 1 from these solubility products, the Gibbs free energies of solvation and the transfer Gibbs free energies from water to organic solvent and mixed solvents were calculated by using equations (3) and (4) [29- 33]. Their values are tabulated also in Table 1.

$$\Delta G = 2.303 \ RT \ pK_{sp} \tag{3}$$

$$\Delta G_t = \Delta G_s - \Delta G_w \tag{4}$$

Where (s), (w) denote solvent and water, respectively.

It was concluded that the Gibbs free energies of transfer (ΔG_t) increase in negativity by increasing the mole fraction of DMF in the mixed DMF-H_2O solvents indicating the spontaneous nature of $Pb(NO_3)_2$ solubilization. This is due to more solvation behaviour in the mixed solvents than that of water where the Gibbs free energy values provide information on whether the process conditions favor or disfavor $Pb(NO_3)_2$ solubilization in the

aqueous carrier solution. Negative Gibbs free energy values indicate favorable conditions. (Fig. 1).

Table 1. Solubility and Gibbs free energies for Pb(NO$_3$)$_2$ in mixed DMF-H$_2$O solvents at 301.15 K.

X$_s$, DMF	S, mol/L	Log $\gamma \pm$	pK$_{sp}$	ΔG , kJmol^{-1}	ΔG$_t$, kJmol^{-1}
0	1.780	-1.1697	1.6737	9.6511	0
0.0250	1.700	-1.1476	1.8250	10.523	0.8720
0.0909	1.720	-1.1498	1.7728	10.222	0.5715
0.1975	1.989	-1.2365	1.3623	7.8556	-1.7954
0.2699	2.350	-1.3440	0.9232	3.2316	-6.4192
0.4828	2.730	-1.4486	0.5604	3.5934	-6.0577
0.7213	2.620	-1.4486	0.9431	5.4381	-4.2130
0.8921	2.103	-1.4486	1.2210	7.0409	-2.6102
1.0000	2.657	-1.4291	0.6237	9.1655	-0.4856

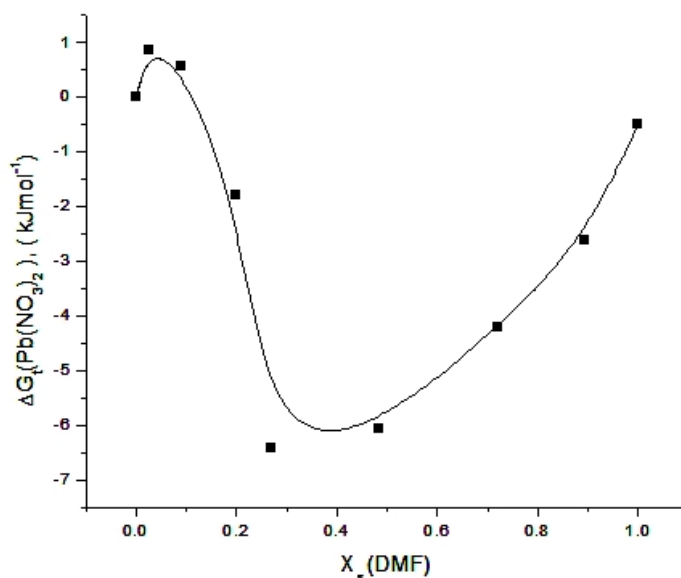**Fig. 1. Gibbs free energies of transfer (ΔG$_t$) for Pb(NO$_3$)$_2$ versus the mole fraction (X$_s$) of DMF at 301.15 K**

3.1 Single ion Gibbs Free Energies and Conventional Free Energies for Pb^{2+} and NO$_3^-$ Ions

It was well known that the preferential single ion thermodynamic parameters depend on the ionic radii of two ions (cation and anion). Therefore the ionic radii ratio between Pb^{2+} and NO$_3^-$ was evaluated from exact radii values given in literature [34] and found to be (132 nm/179 nm= 0.737). Multiplying this ratio by the Gibbs free energies of Pb(NO$_3$)$_2$ we get the ionic Gibbs free energies of Pb^{2+} ion. This last value was subtracted from the Pb(NO$_3$)$_2$ Gibbs free energy and we obtain the Gibbs free energy for NO$_3^-$ anion. The obtained values for single ions are presented in Table 2. The conventional Gibbs free energies ΔG_s^{*con}

(Pb^{2+}) for Pb^{2+} ion in solvents are shifted from their absolute values by the absolute free energy of the proton [35] according to equation (5)

$$\Delta G_s^{*con}(Pb^{2+}) = \Delta G_s(Pb^{2+}) - 2\Delta G_s(H^+) \tag{5}$$

and for NO_3^- anion is shifted by an equal amount in the opposite direction (equation 6).
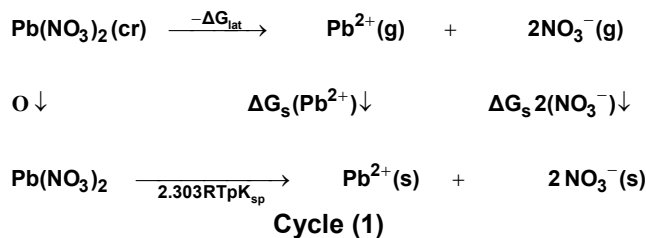
$$\Delta G_s^{*con}(NO_3^-) = \Delta G_s(NO_3^-) + \Delta G_s(H^+) \tag{6}$$

Where ΔG_s^{*con} (Pb^{2+}), ΔG_s^{*con} (NO_3^-) and $\Delta G_s(H^+)$ are the Gibbs free energies of solvation for lead, nitrate and proton in solvents.

From the mean values of proton solvation free energies in water and other solvents in literature [12,35,36] relation between these values and the diameter for each solvent taken from literature [37-38,40], a straight line was obtained. From this line the proton solvation free energies in pure water and DMF were obtained and found to be -252 to -263 kcal/mol ,(this is about -1053 and -1099 kJmol-1), respectively. Multiplying each value by its mole fraction in the mixture and then summing the results. The mixed solvent proton free energies were obtained and their values are given in Table 2. With equations (5) and (6) we get the conventional Gibbs free energies for the cation and anion and their values are given also in Table 2. Cation conventional free energy values are negative indicating exothermic character and anion values are positive indicating endothermic character. Both values increase with increase in the mole fraction of DMF due to more solvation and the sum of them gives the values for the neutral salt.

3.2 Libration Gibbs Free Energies for Pb(NO$_3$)$_2$ in Mixed DMF-H$_2$O Solve~nts

The libration Gibbs free energies for $Pb(NO_3)_2$ in mixed DMF-H$_2$O solvents at 301.15 K were calculated following cycle 1 (thermochemical cycle 1) as done before [12] for silver salts following solubility product concept.

$$Pb(NO_3)_2 (cr) \xrightarrow{-\Delta G_{lat}} Pb^{2+}(g) + 2NO_3^-(g)$$

$$O\downarrow \qquad \Delta G_s(Pb^{2+})\downarrow \qquad \Delta G_s 2(NO_3^-)\downarrow$$

$$Pb(NO_3)_2 \xrightarrow{2.303RTpK_{sp}} Pb^{2+}(s) + 2NO_3^-(s)$$

Cycle (1)

Where ΔG_{lat} is the lattice free energy, (g) and (s) denote the gas and solution cases. The lattice energy was calculated following Bartlett's relationship following equation (7) [40].

$$\Delta G_{lat} = \frac{232.8}{\sqrt[3]{V}} + 110 \ kJ\,mol^{-1} \tag{7}$$

The volume of $Pb(NO_3)_2$ was calculated by dividing its molecular weight by the density of solid given in literature [37] and apply it in equation (7) to obtain 165.675 kJmol^{-1} as ΔG_{lat} for $Pb(NO_3)_2$. On the use of equation (8) after cycle (1), the libration free energies for $Pb(NO_3)_2$ was obtained (82.837 kJmol^{-1}).

$$\Delta G_s\,(Pb^{2+}) + 2\Delta G_s\,(NO_3^-) = 2.303\,RTpK_{sp} - \Delta G_{lat} - 2\Delta G^{0\rightarrow *} \tag{8}$$

The $\Delta G^{0\rightarrow *}$, the free energy change associated with moving $Pb(NO_3)_2$ from standard gas phase of 1 atmosphere to solution phase. This free energy change has been referred as "compression" work of the gas or libration free energy.

3.3 Conventional Free Energies from Reduction Potentials

The absolute Gibbs free energy of the proton is followed solution phase free energy change associated with the following half cell.

$$H_2(g) \rightarrow 2H^+(s) + 2e^-(g) \tag{9}$$
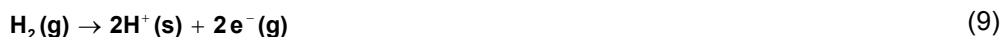
The half cell reaction for the reduction of cation is:

$$Pb^{2+}(s) + 2e^- \rightarrow Pb(cr) \tag{10}$$
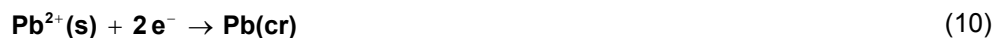
The symbol (cr) denotes the crystalline phase the sum of the two half cells is:

$$H_2(g) + Pb^{2+}(s) \rightarrow Pb(cr) + 2H^+(s) \tag{11}$$

Through the use of thermochemical cycle 2, the conventional free energy for Pb^{2+} can be written as:

$$\Delta G_s\,{}^*con(Pb^{2+}) = 2\,\Delta f G(H^+)g - \Delta f G(Pb^{2+})g - 2FE_c \tag{12}$$

Where $\Delta f G(H^+)g$, $\Delta f G(Pb^{2+})g$ are the gas free energy of formation for H^+ and Pb^{2+} ions. F is Faraday constant, equal 96.485 kJ per volt gram equivalent and E_c is the standard reduction potential of Pb^{2+} $\Delta f G(Pb^{2+})g$ is difficult to evaluate because of the lack of exact gas $\Delta f G(H^+)g$ value.

$$H_2(g) + Pb(NO_3)_2(cr) \xrightarrow{\ \Delta G_g\ } Pb^{2+}(cr) \quad + \quad 2NO_3^-(g) \quad + 2H^+(g)$$

$$0\downarrow \qquad\qquad 0\downarrow \qquad\qquad 0\downarrow \qquad\qquad 2\Delta G_s(NO_3^-)\downarrow \quad 2\Delta G_s(H^+)\downarrow$$

$$H_2(g) + Pb(NO_3)_2(cr) \xrightarrow[-2FE_c]{} Pb^{2+}(s) \quad + \quad 2NO_3^-(s) \quad + 2H^+(s)$$
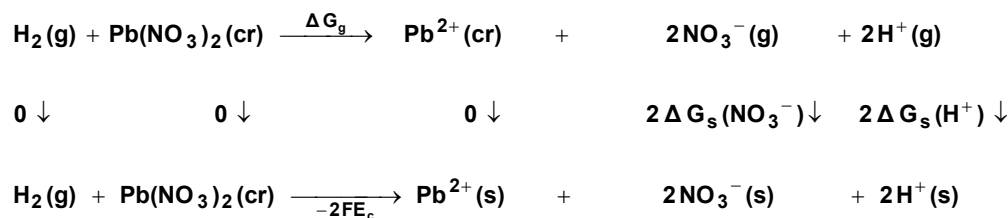
(Cycle 2)

Also the conventional free energy of the nitrate anion NO_3^- can be written following Truhlar [41] explanation as:

$$\Delta G_s\,{}^{*con}(NO_3^-) = -\,\Delta f G_g - FE_c - 2\Delta G^{0\rightarrow *} \tag{13}$$

Applying equation (13) the $\Delta f\, G_g$, the gas free energies of formation for the anion NO_3^- was estimated in the mixed DMF-H_2O solvents and their values are given in Table 3 and Fig. 2. the $\Delta f\, G_g$ value increase by increasing the mole fraction of DMF favouring less solvation.

Table 2. Single ion Gibbs free energies for Pb^{2+} and nitrate and their half conventional free energies at 301.15 K. in mixed DMF-H_2O solvents (in $kJmol^{-1}$)

X_s , DMF	$\Delta G(Pb^{2+})$	ΔG (NO_3^-)	$\frac{1}{2}\Delta G_s^{*con}(Pb^{2+})$	$\frac{1}{2}2\Delta G_s^{*con}(NO_3^-)$	ΔG_s^* (H^+)
0	1.2585	8.3923	-1521.00	1531.00	-1052.3
0.0250	1.3722	9.1504	-1521.21	1532.15	-1052.3
0.0909	1.3330	8.8893	-1521.34	1531.88	-1052.3
0.1975	1.3244	6.8312	-1527.97	1535.83	-1052.9
0.2699	1.4214	2.8102	-1544.08	1536.81	-1053.4
0.4828	1.4686	3.1248	-1550.33	1555.12	-1055.2
0.7213	1.3802	3.5624	-1551.71	1559.56	-1055.2
0.8321	1.2686	3. 4561	-1553.33	1561.32	-1055.2
1.0	1.2195	3.3703	-1559.05	1568.97	-1056.1

Table 3. Gas formation free for NO_3^- anion in mixed DMF-H_2O solvents at 301.15 K

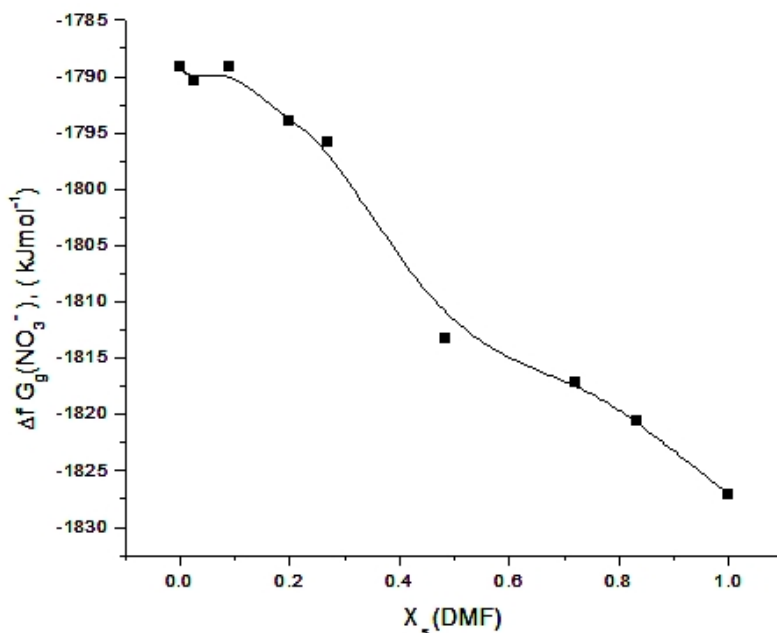| X_s , DMF	$\Delta f G_g$
0	-1789.21
0.0250	-1790.36
0.0909	-1789.21
0.1975	-1794.04
0.2699	-1795.82
0.4828	-1813.33
0.7213	-1817.14
0.8321	-1820.56
1.0	-1827.18

Fig. 2. Relation between $\Delta f G_g (NO_3^-)$ **against the mole fraction (X_s) of DMF at 301.15 K**

4. CONCLUSION

Using a combination of experimental gas-phase free energies of formation and solution-phase reduction potentials, we determined conventional solvation free energies of $Pb(NO_3)_2$ in mixed DMF-H_2O solvents at 301.15 K from the experimental solubility measurements. Libration Gibbs free energy associated with moving $Pb(NO_3)_2$ in standard gas state to standard stat in solution was evaluated according to thermochemical cycle for the solvation process using the solubility product. Also the lattice energy for $Pb(NO_3)_2$ was also calculated and used for further evaluation. These conventional solvation free energies were then combined with experimental and calculated gas-phase free energies to determine conventional solvation free energies of ion-solvent clusters containing up to solvent molecules. The values for the absolute solvation free energy of the proton obtained in this work should be useful as standard against which the absolute solvation free energies of other single ions can be derived. For example, Table 2 shows the absolute single-ion solvation free energies of the ions considered in this work.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Gabani S, Gianni P, Mollica V, Lepori L. Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solution. J. Solution Chem. 1981;10:563-595.

2. Abraham MH, Whiting GS, Fuchs R, Chambers EJ. Thermodynamics of solute transfer from water to hexadecane. J. Chem. Soc., Perkin Trans. 1990;2:291-300.

3. Leo A. J. Masterfile from Med Chem Sofware; Biobytc: Claremont, C. A.; 1994.

4. Physical/Chemical property Database (PHYSPROP); SRC Environmental Science Center: Syracuse, NY; 1994.

5. Yaffe D, Cohen Y, Espinosa G, Arenas AA, Giralt F. Fuzzy ARTMAP and back-propagation neural networks based quantitative structure-property relationships (QSPRs) for octanol-water partition coefficient of organic compounds. J. Chem. Inf. Comput. 2002; 42(2):162-83.

6. Kelly CP, Cramer CJ, Truhlar DG. A Density Functional Theory Continuum Solvation Model for Calculating Aqueous Solvation Free Energies of Neutrals, Ions, and Solute Water Clusters. J. Chem. Theory Comput. 2005;1:1133-1152.

7. Rizzo RC, Aynechi T, Case DA, Kuntz ID. Estimation of Absolute Free Energies of Hydration Using Continuum Methods: Accuracy of Partial Charge Models and Optimization of Nonpolar Contributions. J. Chem. Theory Comput. 2006;2:128-139.

8. Cramer CJ, Truhlar DG. In Free Energy Calculation in Rational Drug Design, Reddy, MR, Eds. Kluwer/Plenum: New York; 2001:63–95.

9. Thompson JD, Cranier CJ, Truhlar DG. New Universal Solvation Model and Comparison of the Accuracy of Three Continuum Solvation Models, SM5.42R, SM5.43R, and C-PCM, in Aqueous Solution and Organic Solvents and for Vapor Pressures. J. Phys. Chem. A. 2004;108:6532-6542.

10. Hodgkin AL. Ionic movements and electrical activity in giant nerve fibres. Biol. Rev. 1951; 26: 339.

11. Kelly CP, Cramer CJ, Truhlar DG. Single ion solvation free energies and the normal hydrogen electrode poteutial in methanol, acetonitrile and dimerhylsulphoxide. J. Phys. Chem. B. 2007;111(1):408-422.

12. Klotz IM, Rosenbery RM. Chemical Thermodynamics, 5th ed.; Wiley: New York; 1994;459.

13. Tissandier MD, Cowen KA, Feng WY, Gundlach E, Cohen MH, Earhart AD, Coe JV, and Tuttle TR. Jr. The Proton's Absolute Aqueous Enthalpy and Gibbs Free Energy of Solvation from Cluster Ion Solvation Data. J. Phys. Chem. A 1998;102:7787-7794.

14. Pliego Jr. JR, Riveros JM. New Values for the Absolute Solvation Free Energy of Univalent Ions in Aqueous Solution. Chem. Phys. Lett. 2000;332:597-602.

15. Llano J, Eriksson LEJ. First principles electrochemistry: electrons and protons reacting as independent ions. Chem. Phys. 2002;117:10193.

16. Doménech A, Montoya N, Scholz F. Estimation of individual Gibbs energies of cation transfer employing the insertion electrochemistry of solid Prussian blue. Journal of Electroanalytical Chemistry. 2011;657:117–122.

17. Krestov GA. Thermodynamics of Solvation: Solution and Dissolution, Ions and Solvents, Structure and Energetics. Ellis Horwood Ltd.: New York, 1991.

18. Conway BE. Electrolyte solutions: Solvation and structural aspects. Annu. Rev. Phys. Chem. 1966;17:481-528.

19. Parker A. The effects of solvation on the properties of anions in dipolar aprotic solvents. Quart. Rev. Chem. Soc. 1962;16:163-87.

20. Friedman HL, Krishnan CV. Thermodynamics of Ion Hydration in Water. a Comprehensive Treatise; Franks F. Ed.; Plenum Press: New York, 1973.

21. Marcus Y. Pure Appl. Chem. 1986;58:1721.

22. Krestov, GA. Thermodynamics of Solution; Ellis Horwood; New York; 1991.

23. Lewis GN, Randall M, Pltzer KS, Brewer L. Thermodynamics, 2nd ed.; McGraw-Hill: New York. 1961;R 399.

24. Pradyot P. Handbook of Inorganic Chemicals. McGraw-Hill; 2002, ISBN 049439-8.

25. Robinson RA, Stokes RH. Electroyte Solutions, Wiley, New York. 1968;463.

26. Gomaa EA. and AbouElleef EM. (Thermodynamics of the Solvation of $CaSO_4$ in Mixed DMF-H2O at 301.15 K), International Research Journal of Pure & Applied Chemistry, 2013;3(4):320-329.

27. Gomaa EA. Single ion free energies of some ion and the hydrophobic interactions of $Ph_4 AsBPh^4$ and $Ph_4SbB Ph_4$ in mixed ethanol-water solvents. Thermochimica Acta, 1989;156:91-99.

28. El-khouly AA, Gomaa EA, and Abou El-leef S. (Conductometry and solubility study of Cd^{2+}-Kryptofix-22 complexes in various hydroorganic solvents), (Bulletin of electrochemistry. May 2003;19(4):153-164.

29. El-khouly AA, Gomaa EA, and Abou El-leef S. Apparent association constants of $HgCl_2$ in presence of kryptofix –22 in mixed aqueous-organic solvents. (Bulletin of electrochemistry. May 2003;19(5):193-202.

30. Gomaa EA. Abou Elleef EM, and Mahmoud EH. Gibbs free energies for the solvation of $KClO_3$ in DMF-H_2O at 301.15 K. Eur. Chem. Bull. 2013;2(10):732-735.

31. Gomaa EA. Solubility and solvation parameters of barium sulphate in mixed ethanol-water mixtures at 301.15 K. International Journal of Materials and Chemistry. 2012;2(1):16-18.

32. Gomaa EA,and Al-Jahdali BM. Association of $Cu(NO_3)_2$ with Kryptofix-221 in mixed (MeOH-DMF) solvents at different temperatures. American Journal of Fluid Dynamics. 2011;1(1):4-8.

33. Gomaa EA. Solvation parameters of lead acetate in mixed, N,N-dimethylformamide–water mixtures at 298.15K. Analele Universitate din Bucuresti-Chimie. 2010;19:45-4.

34. Handbook of Chemistry and Physics, 91st ed.; 2010–2011.

35. Marcus Y. Ion Properties, Dekker, New York; 1999.

36. Marcus Y. Solvent Mixtures, Dekker, New York; 2005.

37. Kim JI, Brückl. On the temperature dependence of solubilities of inert Gases from the scaled particle theory. Z. Phys. Chem. Neue Folge. 1978;110:197-208.

38. Tawa GJ, Topol IA, Burt SK, Caldwell RA, and. Rashin AA. Calculation of the aqueous solvation free energy of the proton. J. Chem. Phys. 1998;109: 4852 .

39. Casey P, Kelly Christopher J. Cramer, Donald G. Aqueous solvation free energies of ions and ion-water clusters based on an accurate value for the absolute aqueous solvation free energy of the proton. Truhlar J Phys Chem B. 2007;111(2):408–422.

40. Shen C, Hagiwara R, Mallouk TE, Bartlett N. Inorganic fluorine chemistry; ACS Symposium Series 555; Thrasher JS, Strauss SH, Eds. American Chemical Society: Washington, DC; 1994; Chapter 2.

41.   Kelly CP, Cramer CJ, Truhlar DG. Single-ion solvation free energies and the normal hydrogen electrode potential in methanol, acetonitrile, and dimethyl sulfoxide. J. Phys. Chem. B. 2007;111(2):408-422.

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