Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2014, 3 (3): 1134-1138

(International Peer Reviewed Journal)

Activity Coefficient Behaviour of Nonelectrolytes in Sulphuric Acid Solution

Anita Sarin and Rama Pande*

Department of Chemistry, Dr. R.B. Govt. Navin Girls College, Raipur (C.G.), **INDIA**

Email: anitasarin24@gmail.com

Accepted on 20th April 2014

ABSTRACT

Hydroxamic acids behave as nonelectrolytes in the presence of electrolyte solution. The activity coefficient behaviour of N-p-Tolyl-4-Bromobenzohydroxamic acid is investigated by the measurement of its distribution ratio between organic solvent and sulphuric acid-water mixture. Activity coefficients are directly related to the partial molar free energies of organic species in various media, they are important in providing information about typical solute-solvent interactions as a function of medium and about relative solvation energies of various species in a given medium on the basis of activity coefficient data, salting-constants of hydroxamic acids have been evaluated in terms of Setschenow Constant.

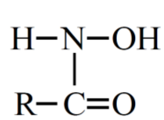
Keywords: Hydroxamic acid, Activity coefficient, Hammett's activity coefficient postulate, Setschenow constant, Distribution ratio.

INTRODUCTION

Hydroxamic acids ($R_1NOH.R_2C{=}O$) are the N-acyl derivatives of hydroxylamine/substituted hydroxylamines. These are versatile metal extractants and have a wide spectrum of agricultural [1-3], biological [4-7], medicinal [8] and technical activities [9-13]. These reagents behave as non electrolyte in presence of electrolyte solution (mineral acid in the present system). Their activity coefficient behaviour is investigated in presence of sulphuric acid solution, by the measurement of their distribution ratios between sulfuric acid-water mixture and an inert solvent, carbon tetrachloride. Such data are useful to understand the solute-solvent interactions. Values of Setschenow constants of these metal extractants evaluated are negative, indicating the salting-in behaviour of the system. It explains the salting co-efficient from cavity formation or interaction. Thus, once a cavity is formed in the electrolyte solution, it is easier to introduce a nonelectrolyte molecule, than it is in pure water. These parameters are of importance in various studies like reaction kinetics, hydrolysis, complexation reactions and extractions.

Hydroxamic acids have exhibited many interesting facets of chemistry since they coerce reported. Extensive work has been carried out on their formation reaction and structure in the ground state. N-acetyl derivatives of hydroxylamine are the

Hydroxamic acid (I), and the



(I)

hydroxamic acid functional group (II) has the outstanding chemical feature. The field of hydroxamic acid is very vast and lots of strenuous work has been already done in different aspects of these versatile metal extractants. These are involved in biological activities and have been reported to be active as pesticides, plant growth promoters and soil enhances. These are used in floatation techniques, as corrosion inhibitors and in photography also. A number of hydroxamic acids are used as antibacterial, antifungal and anticancer agents. [14,15] Hydroxamic acids behave as nonelectrolyte in presence of mineral acid solution. Their activity coefficient behaviour is investigated in sulfuric acid solution to understand the solute-solvent interaction.

MATERIALS AND METHODS

Electronic corporation of India, Hyderabad, Model G5 5700 a DIGITAL Spectrophotometer with 10 mm matched, silica cells was used for the measurement of absorbance.

Hydroxamic acids were prepared according to the method and purified by crystallization thrice from benzene and dried over phosphorus pentaoxide in vacuum desiccator for several hours. Saturated solution of ammonium metavanadate was prepared in glass distilled water. Chloroform used was shaken six times with equal volume of water and distilled. It was stored in dark colored bottle in a cool place. For determining distribution ratios, a solution of hydroxamic acid (20-25 mg) in carbon tetrachloride was vigorously shaken for five minutes with acid solution of increasing acidities (10-55%). The volumes of the two phases to be taken were dependent on the magnitude of D. After separation, the phases were analyzed colorimetrically following the vanadium (V) method.

RESULTS AND DISCUSSION

Activity coefficients have been expressed as a sum of individual terms resulting from various types of interaction with the solvent [16]. Information about the effect of electrolytes on the activity coefficient of nonelectrolytes in strong mineral acid solution is of interest [17] and is calculated following the equation,

$$f = \frac{\gamma_0}{\gamma}\left[1 + \frac{h_0}{K_{BH^+}}\right]$$

where, f is the activity coefficient, γ_0 is distribution coefficient of nonelectrolyte in water, γ is distribution coefficient in acid solution, h_0 is Hammett's activity coefficient postulates and is obtained following the relation, $pK_{BH^+} = -\log K_{BH^+}$. The values of distribution ratios as a function of sulfuric acid concentration are presented in table 1.

Table 1 : Activity coefficient Data of N-p-Tolyl-4-Bromobenzohydroxamic acid, $\gamma_0 = 340.34$

Conc. %	**γ**	**γ/γ_0**	**h_0**	**log f**
10	570.00	1.6747	2.0417	0.2213
15	730.50	2.1463	4.5708	0.3260
20	837.25	2.4600	10.2329	0.3785
25	917.33	2.6953	23.4422	0.4027
30	552.83	1.6253	52.4807	0.1507
35	396.41	1.1647	114.8153	-0.0555
40	260.00	0.7639	257.0395	-0.3536

45	116.66	0.3427	707.9457	0.9419
50	40.00	0.1175	2398.8329	-1.8210
55	11.98	0.0352	8128.3051	-2.8538

for solvents, immiscible with water it is equal to the reciprocal of distribution constant as in the following equation -

$$f = \frac{\gamma}{\gamma_0}\left[\frac{K_{BH^+}}{K_{BH^+} + h_0}\right]$$

Setschenow constant (K_S).

The activity coefficient of a nonelectrolyte dissolved in an aqueous electrolyte solution is emperically found to be a function of the concentration of the salt(s) and of the nonelectrolyte(s) [18]

$$\log f = K_S.S + KS$$

where K_S is Setschenow constant.

In low concentration the last term on the right hand side is negligible and the proportionality factor is known as Setschenow constant (K_S). Thus above equation becomes,

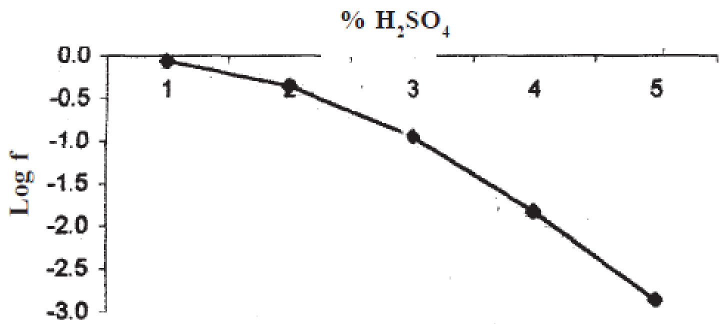
$$\log f = K_S.S$$

Values of K_S are listed in table 2.

Table 2 : Setschenow constant of N-p-tolyl-4-bromobenzohydroxamic acid.

Hydroxamic Acid / % Acid	N-p-tolyl-4-bromobenzo-
10	0.2032
15	0.1931
20	0.1625
25	0.1337
30	0.0403
35	-0.0123
40	-0.0064
45	-0.1520
50	-0.2555
55	-0.3514
Average	**-0.0104**

The activity coefficient behaviour of this nonelectrolytes is presented in figure 1, with increased acidity, values of activity coefficient decreases. This indicates the salting-in behaviour of the system. The solute molecules, which can act as hydrogen-bond donors would be relatively salted out as the acidity is increased, while molecules which can act as hydrogen bond acceptors would be relatively salted-in, salting out and salting - in refer to positive and negative values of activity coefficient respectively.



N-p-Tolyl-4-bromobenzo hydroxamic acid

Figure 1: Activity Coefficient Behaviour of Hydroxamic Acid

Hydroxamic acid act as hydrogen bond acceptor, in presence of strong mineral acid solution, thus they became salted-in as the electrolyte concentration is increased and therefore activity coefficient values are negative. In the present system, the activity coefficients are considered in connection with acidity function are essentially "medium effect" activity coefficient, because on transferring one mole of the species from its infinitely dilute solution in water to that in the acid solution is the departure of the solute from ideal behaviour to that with the solvent. Values of Setschenow constants for hydroxamic acid represent the contribution to the salting coefficient from cavity formation or interaction. In the present system the negative values of K_S explain that once a cavity is formed in the electrolyte solution, it is easier to introduce a non electrolyte molecules than it is in pure water.

APPLICATIONS

The activity coefficient behaviour in sulfuric acid solution is useful to understand the solute-solvent interaction. Activity coefficients are directly related to the partial molar free energies of organic species in various media, they are important in providing information about typical solute-solvent interactions as a function of medium and about relative solvation energies of various species in a given medium on the basis of activity coefficient data, salting-constants of hydroxamic acids have been evaluated in terms of Setschenow Constant.

REFERENCES

[1] C.C. Figueroa, M.R. Loayza, H.M. Niemeyer, *Bull. Entomol. Res.*, **2002**, 92, 25.
[2] H.R. Bravo, E. Villarroel, S.V. Copaja, V.H. Argandona, *Natur. Forsh.*, **2008**, 63, 389.
[3] Y.S. Mukangan, C.C. Figueroa, J.A. Hasler, H.M. Niemeyer, *J. Insect Physiol.*, **2003**, 49, 223.
[4] G.C. Ooi, , P.L. Khong, W.K. Lam, S.N. Trendell, K.W. Tsang, *Acta Haematol.*, **2002**, 108, 43.
[5] S.A. Kim, Y.L. Jin, H.S. Kim, *Arch. Pharm. Res.*, **2009**, 32, 15.
[6] C. Henderson, M. Mizzau, G. Paroni, R. Maestro, C. Schneider, C. Braneolini, *J. Biol. Chem.*, **2003**, 278, 12579.
[7] N. Mitsiades, C.S. Mitsiades, P.G. Richardson, C. McMullan, V. Poulaki, G. Fanourakis, R. Schlossman, D. Chauhan, N.C. Munshi, T. Hideshima, V.M. Richon, D.A. Marks, K.C. Anderson, *Blood*, **2003**, 101, 4055.
[8] D. Khare, B. Verma, R. Pande, *Asian Journal of Pharmaceutical and Clinical Research*, **2012**, 5.

[9] M.J. Haron, W.M.Z. Wan Yunus, P.C. Yap, M.A. Sukari, M. Sulaiman, *Oriental J. Chem.*, **2001**,17, 173.
[10] J. Telegdi, A. Shaban, E. Kalam, *Electrochimica Acta*, **2000**, 45, 3639.
[11] Y.K. Yang, H.J. Cho, J. Lee, I. Shin, J. Tae, *Org. Lett.*, **2009**, 11, 859.
[12] M. Resmini, A. Servant, F. Rogers, A. Zarbakhsh, *New J. Che.*, **2013**.
[13] D.T.K. Oanh, H.V. Hai, H.J. Kim, B.W. Han, H.S. Kim, T.T. Jong, S.B. Han, V.T.M. Hue, N.H. Nam, *Bio Medical Chem. Liet.*, **2011**, 21, 7509-7512.
[14] P. Kenneth, R.A. Iyer, G. Prasad, T. Liu Gee, E.L. Robert, E. Patrick, *Hanna. Prostate*, **1998**, 34, 92.
[15] J.D. Evans, A. Stark, C.D. Johnson, F. Daniel, J. Carmichael, J. Buckels, C.W. Imria, P. Brown, J.P. Neoptolemos, *British J. Cancer*, **2001**, 85 1865.
[16] N.C. Deno, J. Phys. Chem., **1961**, 65, 179.
[17] T.R. Essig, J.A. Marinksy, *Can. J. Chem.*, **1972**, 50, 2254.
[18] J.F. Coetzee, D.R. Calvin, N.Y. Marcel Dekkar, *Solute-Solvent Interactions*, **1969**, 329.