

Structural studies of vanadium soaps in solid state by X-ray diffraction analysis

SULEMAN, F.M*. PRASAD, SUSAN VERGHESE P and HEMANT KULSHRESHTHA

School of Chemical Sciences. Department of Chemistry, St. John's College Agra - 282 002 (India).

(Received: April 12, 2007; Accepted: June 04, 2007)

ABSTRACT

The structure of vanadium soaps (palmitate, stearate) in solid state was studied using x-ray diffraction analysis technique. The x-ray diffraction analysis confirmed that the vanadium soaps possess single layer structure and metal divalent ions are arranged in a parallel plane.

Keywords: Vanadium carboxylates, X-ray diffraction, layer structure etc.

INTRODUCTION

The study of metallic soaps is becoming increasingly important in technological and academic fields. The metallic soaps have high metal contents, which lend them unique properties and make them useful for many applications in industries. The characteristic & structure of metal soaps depend largely on the method and conditions of their preparations. Therefore, studies of metal soaps are of great significance for understanding their characteristics under different conditions and for their use in industry. While major development has taken place in the study of alkali and alkaline earth metal and some transition metal soaps, the vanadium soaps⁽¹⁻¹⁵⁾ have not been thoroughly investigated.

The present work deals with the study of vanadium soap (palmitate, stearate) in solid state using x-ray diffraction analysis technique.

EXPERIMENTAL

All chemicals used were of BDH/AR grade. Vanadium soaps (Palmitate & Stearate) were prepared by direct metathesis of the corresponding potassium soap with slight excess of the solution of vanadium pentoxide under vigorous stirring.

The purity of the soaps was checked by elemental analysis and determination of their melting points [Vanadium palmitate : 66.0°C, Vanadium Stearate 69.0°C].

The X-ray diffraction analysis of vanadium soaps were obtained with RIGAKU Geiger flex RBRU 200. The Cu – K α radiation was used over the range of diffraction angle, $2\theta = 380^\circ$ (where θ is the Bragg's angle). The XRD curves were recorded under the applied voltage of 35 KV using scanning speed 50/minute. The readings of the diffraction angle were made up to 0.01° and the wavelength of radiation was taken as $1.542 \text{ \AA}$.

RESULTS AND DISCUSSION

Generally, the crystals of metal soaps do not grow up to an extent to give a large single crystal sufficient for a detailed single crystal X-ray examination and so the powder diffraction patterns of vanadium soaps (palmitate and stearate) were analysed to characterize the structure of these soaps in solid state.

The intensities of the diffracted X-rays as a function of diffraction angle 2θ for vanadium soaps are measured over the range of 360° with the help of x-ray spectrophotometer and the interplanar

spacing, α have been calculated from the position of intense peaks using Bragg's relationship.

$$n\lambda = 2d \sin \theta$$

Where λ is the wavelength of radiation. The calculated spacings together with the relative intensities with respect to the most intense peak for vanadium soaps are recorded in Table 1, 2. The X-ray diffraction of stearic acid was measured as a check of apparatus and its long spacing was 39.84 Å Table 1, which was in good agreement with that (39.75 Å) reported by Francis and Tiper² for stearic acid.

The X-ray diffraction analysis of vanadium soaps (palmitate and stearate) show numerous peaks over the range of 3-60° of Diffraction angle.

The peaks are attributed to the diffraction of X-ray by planes of metal-ions known as basal plane.

The appearance of diffractions up to 20th and 24th order for palmitate and stearate of vanadium suggested good crystallinity for these soaps. The order of diffraction (i.e. crystallinity of soaps) increases with increasing chain length of the soap molecules.

The average planner distance i.e. long spacings for palmitate and stearate of vanadium are 44.28 and 49.07 Å respectively Table 1 and 2 differences in long spacings of vanadium palmitate and stearate is 4.79 Å corresponds to double the length of the methylene (- CH₂) groups in the fatty acid radical constituent of the soap molecules. It is, therefore, suggested that the zig-zag chain of the

Table 1: X-ray diffraction analysis of vanadium palmitate

S. No.	2θ	θ	Sinθ	D(A°)	d (A°)	η	I/I°
1.	7.451	3.725	0.0649	14.91	44.73	3	0.16
2.	10.082	5.041	0.0878	11.02	44.10	4	0.22
3.	12.624	6.312	0.1099	8.80	44.03	5	0.28
4.	17.581	8.791	0.1528	6.33	44.37	7	0.39
5.	20.521	10.260	0.1781	5.43	43.51	8	0.45
6.	20.054	15.028	0.2592	3.73	44.84	12	0.66
7.	43.510	21.755	0.3706	2.61	44.43	17	0.96
8.	50.995	25.498	0.4304	2.21	44.20	20	0.13

Average value of α = 44.28 Å

Table 2: X-ray diffraction analysis of vanadium stearate

S. No.	2θ	θ	Sinθ	D(A°)	d (A°)	η	I/I°
1	4.451	2.226	0.0338	24.96	49.93	2	0.29
2	8.852	4.426	0.0772	12.47	49.89	4	0.59
3	11.221	5.610	0.0977	9.90	49.54	5	0.74
4	16.231	8.115	0.1412	6.86	48.03	7	0.82
5	29.875	13.938	0.1408	4.02	48.26	12	0.85
6	32.588	16.294	0.2805	3.45	48.34	14	0.17
7	41.911	20.956	0.3576	2.70	48.74	18	0.79
8	55.672	27.837	0.4669	2.07	49.77	24	0.71

Average value of d = 49.07 Å

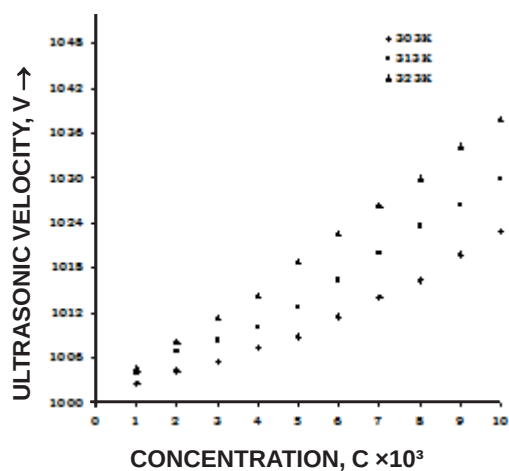


Fig. 1: Ultrasonic velocity vs soap concentration

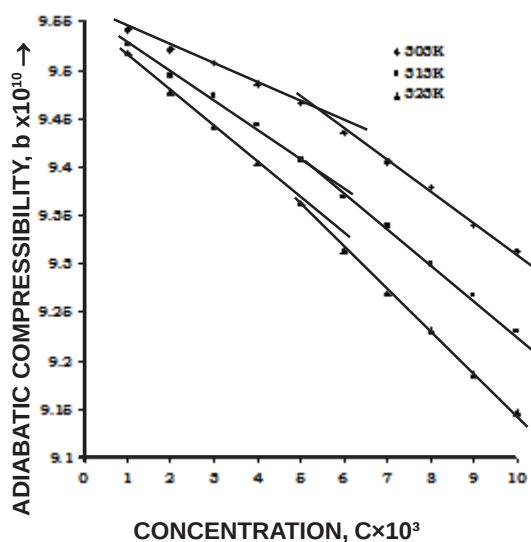
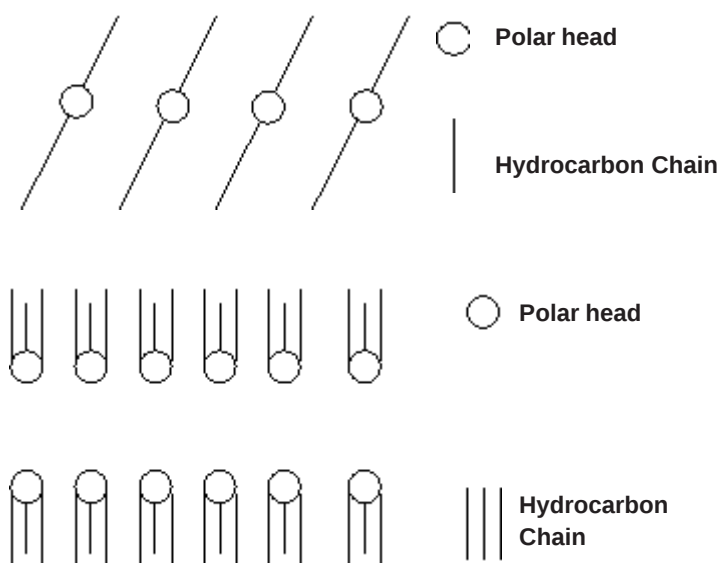


Fig. 2: Adiabatic compressibility vs soap concentration

fatty acid radical constituent of the soap molecules extend straight forward on both sides of each basal plane. The values of long spacings for vanadium soaps are somewhat smaller than the calculated dimension of anions. (palmitate: $47 \text{ \AA}$ and stearate $52 \text{ \AA}$) from Pauling's values of atomic radii and bond angles. It is, therefore, concluded that the molecular axes of these soap molecules are somewhat inclined to the basal planes. The metal ions fit into spaces

between oxygen atom of the ionized carboxyl group without a large strain of the bonds. The X-ray long spacings of homologous vanadium soaps (stearate, palmitate, myristate, laurate) suggest that there are no abrupt changes in the manner of crystallization but the angle of inclination of the basal plane. Increase slightly with decreasing number of carbon atom of fatty acid radicals.



A number of diffraction peaks in the intermediate range are also observed in the diffraction pattern of vanadium soaps and are attributed to the diffraction of the X-ray by planes of atoms of much smaller separation than the basal planes. The calculated spacings from those peaks correspond to the shorter side spacings i.e. the lateral distance between one soap molecule and the next in a layer.

The value of long and short spacings for vanadium soaps are in agreement with those reported by Koga and Matsuura^{14,16} for vanadium penta soaps.

It is therefore, suggested that the soaps possess single layer structure as proposed by Hattiangdi and Vold^{17,18} in which metal divalent ions are arranged in a parallel plane, i.e. a basal plane,

equally spaced in a soap crystal, with fully extended zig-zag chains of fatty acid radical on both sides of each basal plane as the double layer structure for penta soap crystals would be energetically difficult due to the considerable strain of bonds in the ionized carboxyl group of soap molecules. However, the double layer structure is well established for fatty acids.

It is also therefore, concluded that these soaps possess single layer structure with molecular axes somewhat inclined to the basal planes.

ACKNOWLEDGMENTS

The authors are thankful to Dr. F. M. Prasad Principal, St. John's College Agra and also thanks to Dr. Rajesh Mishra, Director of Radha Ballabh Education Academy, Agra, India.

REFERENCES

1. Fisel, S. Zhur, Neorg. Khim., **5**: 1090-4 (1960).
2. Piper, D. J., Fleiger, A. G., Smith, C.S. and Kerstein, N.A., *Ind. Eng. Chem.*, **31**: 307 (1939).
3. Shlyapintokh, Y.I. and Emanuel, N. M., *Izv. Akad. Nauk SSSR, Ser. Khim.* 782 (1957).
4. Banerjee, B.C. and Palit, S.R., *J. and Chem. Soc.*, **27**: 385 (1950).
5. Villarreal, E.D., *Rev. Soc. Quim. Mex.*, **8**(6): 155-156 (1964).
6. Malik, W.U., Ahmad, S.I. and Jain, A.K., *Kolloid Z.*, **218**(2): 155-156 (1967).
7. Malik, W.U. and Jain, A.K., *Aust. J. Chem.*, **22**(2): 465-68 (1969).
8. Malik, W.U. and Jain, A.K., *J. Electroanal. Chem. Interfacial Electro. Chem.*, 276 (1968).
9. Mehta, V.P., Hassan M., Mathur, S.P. and Rai, G.L., *Tenside Detergents*, **16**(2): 79-80 (1979).
10. Gel Perin, N.I., Pebalk. V.L. Rozor, V.N. and Zamyshlyayev, V.G., *Tsvetn. Metal*, **38**(10): 41-8 (1965).
11. Yamada, H. and Tanaka, M., *J. Inorg. Nuclear Chem.*, **38**: 501 (1976).
12. Mehrotra, K.N. Singh Suman and Kumar, Anil, *Indian J. Chem.*, **31**(A): 756-59 (1992).
13. Matsuura, R. and Nagasue, K., *Mem. Fac. Sci, Kyushu, Univ. Ser.*, C-3, 49-54 (1958).
14. Mehrotra, K.N., Mehta V.P. and Nagar, T.N. *J. Am Oil Chemists Soc.*, **47**: 329 (1970).
15. Mehrotra, K.N. and Poranchand, Dinah, *Tenside Detergents.*, **27**(6): 393-95 (1990).
16. Koga, Y. and Matsuura, R., *Mem. Fac. Sci. Kyushu Univ., Ser. (C4, C1)*, 44 (1961).
17. Vold, R.D. and Hattiangdi, G.S., *Ind. Engl. Chem.*, **41**: 2311 (1949).
18. Hattiangdi, G.S. and Vold., R.D., *Ind. Engl. Chem.*, **41**: 2320 (1949).