The Infrared Spectra of Alkane-1-sulfonates

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Several investigations have been made on the characteristic infrared absorptions of sulfur-oxygen compounds such as sulfones or sulfone amides, and 1350∼1300 cm^{-1} and 1160∼1120 cm^{-1} bands were attributed to $-SO_2-$ group[1,2]. On sulfonic acids or their salt, however, there can not be found any systematic studies on their characteristic infrared absorptions. Bellamy[3] proposed 1200∼1160 cm^{-1} and 1060∼1030 cm^{-1} bands as the characteristic infrared absorptions of $-SO_3-$ group based on his results for aromatic sulfonates. Simon and Kriegsmann[4] investigated Raman and infrared spectra of alkali metal salts of methanesulfonic acid, and discussed these spectra under the assumption that methanesulfonate ion has the symmetry property of C_{3v}. Houlton and Tartar[5] investigated Raman spectra of several *n*-alkane-1-sulfonates in aqueous solution, compared these spectra with those of other sulfur compounds, and proposed some assignments.

Since the assignments so far given seem not to be decisive, the author studied infrared spectra of alkane-1-sulfonates where carbon numbers are 1—8 and 12 in the solid state. Taking into account the theoretical result given in the succeeding paper[6] and the spectra of CXY_3 type molecules, the spectra of methanesulfonate ion were assigned. Furthermore, the characteristic infrared absorptions of sulfonic group and C–S bond in the sulfonic acids were assigned for higher sulfonates.

Results and Discussion

The infrared spectra of sulfonates are shown in Figs. 1—9.

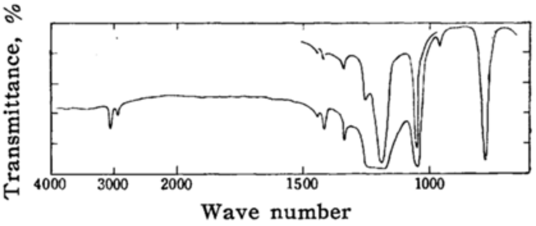

Fig. 1. Methanesulfonate.

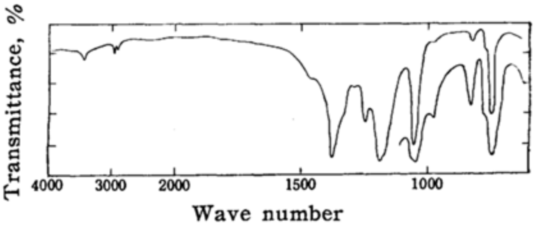

Fig. 2. Ethanesulfonate.

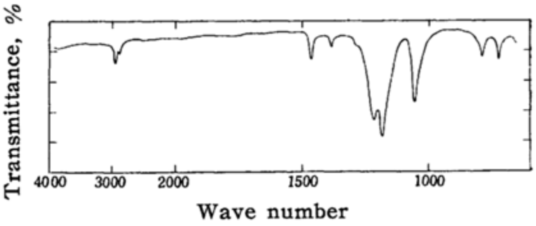

Fig. 3. *n*-Propane-1-sulfonate.

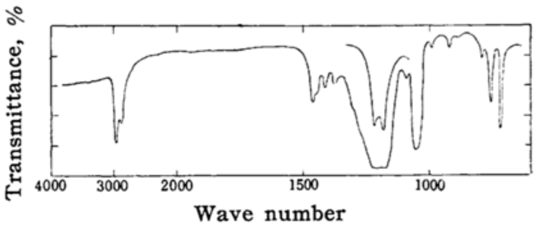

Fig. 4. *n*-Butane-1-sulfonate.

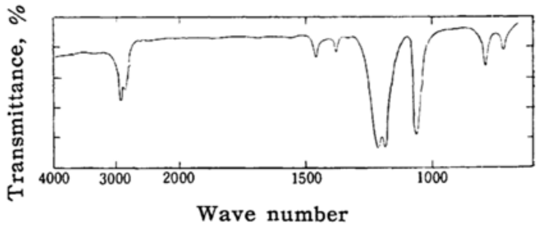

Fig. 5. *n*-Pentane-1-sulfonate.

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[1] K. C. Schreiber, *Anal, Chem.*, **21**, 1169 (1949).

[2] L. J. Bellamy "The Infrared Spectra of Complex Molecules", Methuen & Co., Ltd., London, (1954), p. 297. And also see references cited there.

[3] Idem., ibid., p. 301.

[4] A. Simon and H. Kriegsmann, *Chem. Ber.*, **89**, 1718 (1956); *Z. physik. Chem.*, **209**, 369 (1955).

[5] H. G. Houlton and A. V. Tartar, *J. Am. Chem. Soc.*, **60**, 544 (1938).

[6] K. Fujimori, This Bulletin, **32**, 621 (1959).

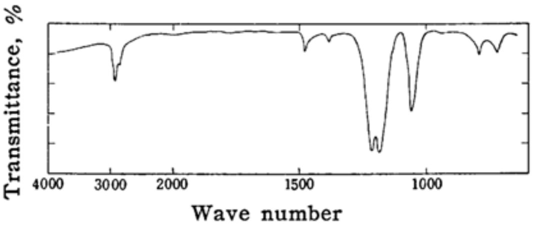

Fig. 6. *n*-Hexane-1-sulfonate.

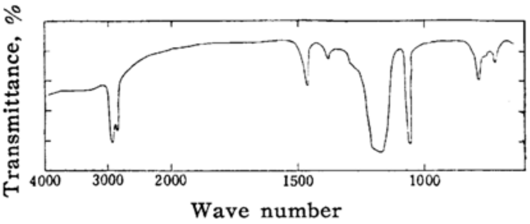

Fig. 7. *n*-Heptane-1-sulfonate.

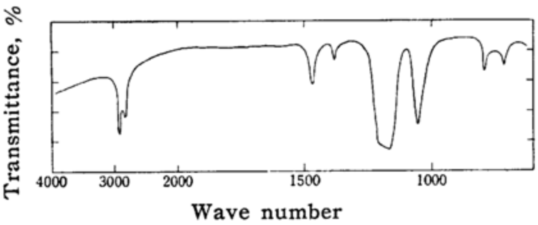

Fig. 8. *n*-Octane-1-sulfonate.

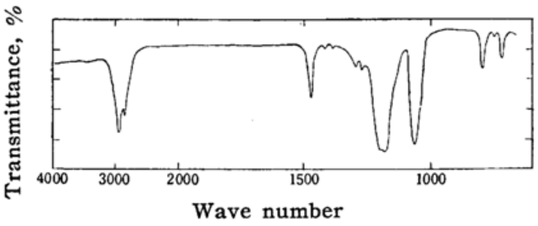

Fig. 9. *n*-Dodecane-1-sulfonate.

For lower homologues the C–H stretching frequencies have wave numbers higher than 2950 cm^{-1}. For higher homologues they decrease and gradually approach to those of hydrocarbons. This result is shown in Table I.

TABLE I. C–H STRETCHING VIBRATIONS (in cm^{-1})

N_C	Wave No.	Wave No.	N_C	Wave No.	Wave No.
1	3024 (w)	2944 (w)	6	2935 (s)	2850 (s)
2	2988 (w)	2944 (w)	7	2926 (s)	2855 (s)
3	2960 (m)	2880 (m)	8	2926 (s)	2855 (s)
4	2944 (s)	2880 (m)	12	2924 (s)	2855 (s)
5	2940 (s)	2870 (s)			

The C–H deformation vibrations are found at 1450∼1470 cm^{-1} and at 1380 cm^{-1} and are summarized in Table II.

TABLE II. C–H DEFORMATION VIBRATIONS (in cm^{-1})

N_C	Wave No.	Wave No.	N_C	Wave No.	Wave No.
1	1436 (m)	1418 (m)	6	1462 (m)	1380 (w)
2	1450 (m)	1383 (m)	7	1467 (m)	1380 (w)
3	1461 (m)		8	1468 (m)	1380 (w)
4	1468 (m)	1378 (m)	12	1468 (m)	1380 (w)
5	1464 (m)	1379 (m)			

As to the assignments of S–O stretching and C–S stretching vibrations methanesulfonate ion was dealt with at first. In this case relatively stronger absorptions at 1192, 1060 and 789 cm^{-1} were found. As shown in the preceding paper⁶⁾, only three stretching vibrations, ν_1, ν_2 and ν_4, are expected to appear in the rock salt region, where ν_1 is S–CH$_3$ stretching, ν_2 S–O symmetric stretching, and ν_4 S–O degenerate stretching vibration. From the result of normal coordinate treatment and the comparison of similar molecules given in Table III, the assignments for the spectra of methanesulfonate ion are determined as shown in the table.

TABLE III. COMPARISON OF THE SPECTRA OF $(CH_3)SO_3^-$ AND SIMILAR MOLECULES (in cm^{-1})

Molecules	ν_1	ν_2	ν_4
CH_3D	2205	2982	3030
CH_3F	1050	2863	3009
CCl_3Br	418	710	765
$SO_3(CH_3)^-$	789	1060	1192

The weak absorption at 970 cm^{-1} may be attributed to the rocking vibration of the methyl radical. Simon and Kriegsmann⁴⁾ and Siebert⁷⁾ reached the same conclusion.

Comparing the absorptions of the higher sulfonates with those of methanesulfonate, the assignments can be made as listed in Tables IV—VI.

About C–S stretching vibration, Simon and Kriegsmann⁴⁾ and Siebert⁷⁾ reached almost the same conclusion for the cases of

TABLE IV. DOUBLY DEGENERATED AND DOUBLET VIBRATIONS OF S–O STRETCHING VIBRATIONS (in cm^{-1})

N_C	Wave No.	Wave No.	N_C	Wave No.	Wave No.
1		1192	6	1216	1180
2		1180	7		1175
3	1224	1182	8		1175
4	1200	1186	12		1175
5	1210	1184			

All absorptions are strong.

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7) H. Siebert, *Z. anorg. u. allgem. Chem.*, **289**, 15 (1957).

TABLE V. SYMMETRIC S-O STRETCHING VIBRATION (in cm^{-1})

N_C	Wave No.	N_C	Wave No.
1	1060	6	1062
2	1056	7	1062
3	1055	8	1062
4	1053	12	1063
5	1060		

All absorptions are strong.

TABLE VI. C-S STRETCHING VIBRATION (in cm^{-1})

N_C	Wave No.	N_C	Wave No.
1	789 (s)	6	787 (m)
2	751 (m)	7	792 (m)
3	783 (m)	8	792 (m)
4	793 (m)	12	798 (m)
5	787 (m)		

TABLE VII. ROCKING VIBRATION OF $-(CH_2)_n-$ group (in cm^{-1})

n	Wave No.	n	Wave No.
2	726 (w)	5	720 (w)
3	759 (m)	6	720 (w)
	723 (m)	7	720 (w)
4	720 (w)	11	721 (w)

methane- and ethane-sulfonates. However, the rocking vibration of $-(CH_2)_n-$ group in the n-alkyl radical is expected to be at about 750 cm^{-1} when n is 2 and at 730～720 cm^{-1} when n is greater than 3. Some irregularity found in Table VI may be due to the coupling of C-S stretching vibration with this CH_2 rocking vibration of $-(CH_2)_n-$ group is summarized in Table VII.

The absorptions at 1250 cm^{-1} of methane- and ethane-sulfonates, at 836 cm^{-1} of ethane-sulfonate may be attributed to overtones or combination tones.

Experimental

Samples. — *Methanesulfonate.* — Methanesulfonic acid (pure reagent grade) was distilled in vacuo (b. p. 160°C at 5 mmHg) and the aqueous solution was neutralized with sodium carbonate and evaporated to dryness. Sodium methanesulfonate was recrystallized from 90% ethanol.

Ethanesulfonate.—Ethyl mercaptane (b. p. 37°C) was oxidized with concentrated nitric acid[8] and the reaction mixture was neutralized with sodium carbonate (10% aqueous solution), the sulfonate solution was evaporated to dryness and extracted with hot ethanol to separate inorganic salts. The sulfonate was recrystallized from ethanol.

Other sulfonates.—Sulfonates other than above described were prepared by Strecker reaction[9]. Corresponding chloride was heated from 180 upto 200°C in a stainless steel autoclave for 10～16 hr. with sodium sulfite (anhydride) and water. The reaction mixture was filtered and evaporated to dryness. The residue was washed with petroleum ether (b. p. 30～40°C) and the sulfonate was extracted with hot ethanol and recrystallized from ethanol.

Absorption Measurement. — The infrared spectra were obtained with a Perkin-Elmer Model 21 double beam infrared spectrophotometer using NaCl prism. The KBr disk method was employed to obtain the spectra in solid state.

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Nippon Mining Co., Funakawa Refinery
Oga-shi, Akita

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[8] D. L. Vivian and E. E. Reid, *J. Am. Chem. Soc.*, **57**, 2559 (1935).

[9] R. M. Reed and H. V. Tartar, ibib., **57**, 571 (1935).