

Series (b)		
$C-C-C-C-C-C-C-C$	125.7	125.7
$C-C-C-C-C-C-C$ C	117.7	118.0
$C-C-C-C-C-C-C$ C	119.0	119.0
$C-C-C-C-C-C-C$ C	117.7	117.5

The appreciation of the author is due to Pro-

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Summary

The boiling points of the paraffins may be correlated with structure by means of the equation $\Delta t = (98/n^2) \Delta w + 5.5 \Delta p$, where Δw and Δp are structural variables which provide simple numerical measures of the effect produced on all atoms simultaneously by a change in position of an atom or of a group. The average deviation between calculated and observed values is less than one degree for the 94 paraffins considered.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Raman Spectra of Aqueous Solutions of Potassium Thiocyanate

By JEN-YUAN CHIEN

Introduction

The Raman spectrum of water, the most conspicuous example of molecular association in the liquid state, has been subjected to numerous studies, especially on the modification of the main band between $\Delta\bar{\nu}$ 3200–3600 cm^{-1} at different temperatures,¹ by the effect of solutes² and in the crystalline field.³ The presence of ions usually increases the intensity of Raman scattering, shifts the maxima and alters the relative intensities of band components, and is in general parallel to the effect of increased temperature. These effects have been explained as due to a gradual change of the water structure, pictured either as a change in a quasi-lattice arrangement of water molecules,^{1c} or as a dissociation of water polymers.^{1a} The temperature and solute effects on water structure have also been studied by X-ray diffraction,⁴ infrared absorption spectra,⁵ magnetic susceptibility measurements,⁶ and investigation of the thermodynamic properties of water and aqueous solutions of electrolytes. Recent calorimetric measurements⁷ have shown that the heat of vaporization of water from concentrated potassium thiocyanate solutions at 30° is about 2% lower than that from pure water. This indicates the breaking of hydrogen bonds of liquid water in the ionic field created by the solute. The Raman spectrum of potassium thiocyanate in aqueous

solution has previously been reported,⁸ but since no information on the modification of the Raman band of the water was included the present investigation was carried out.

Experimental Details

The 4358 Å. line of mercury was employed for excitation. Two experimental arrangements were used, one with six G.E. H-2 mercury vapor lamps and a horizontal Raman tube, the other with seven water cooled d. c. mercury arcs and a vertical Raman tube. The arcs⁹ were made of 10-mm. Pyrex tubing, gave an effective arc length of 9", and operated at 5–8 amperes at 80–90 volts. The water-cooled arcs gave lower light output, but relatively less background and yielded cleaner spectra. The filter solution¹⁰ used to isolate the λ 4358 Å. line consisted of 4% *p*-nitrotoluene and 1/10,000 crystal violet R B bluish, (Cassella Color Co.), in 95% ethyl alcohol.

The spectrograph used was a Steinheil type GH, with three glass prisms and f/3 195 mm. f.l. collimator and camera lenses. Spectra were taken on Eastman 103J plates, developed in D19, and then traced by a photoelectric microdensitometer. An iron arc comparison spectrum was taken on each plate and traced alongside the Raman spectrum. Displacements of peaks on the tracing were measured to within 0.03 mm. by means of a special comparator constructed by Mr. L. K. Henke, laboratory chief mechanician, and frequencies were determined by linear interpolation of the wave numbers of the two nearest iron lines. Rayleigh scattering of the mercury λ 4916 or λ 4078 Å. line was used for correction of any lateral displacement between the Raman and comparison spectra occurring either during picture taking or during tracing. All wave numbers were reduced to those in vacuum by means of Kayser's table.¹¹

Solutions were prepared from reagent potassium thiocyanate and conductivity water. Controlled exposures ranging from two minutes to two hours were used, at a

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- (2) (a) J. H. Hibben, *J. Chem. Phys.*, **5**, 166 (1937); (b) P. A. Leighton and J. Burnham, *THIS JOURNAL*, **59**, 424 (1937); (c) Th. G. Kujumzels, *Z. Physik*, **110**, 760 (1938).
- (3) P. G. N. Nayar, "Raman Jubilee Volume," p. 419 (1938).
- (4) (a) J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938); (b) G. W. Stewart, *ibid.*, **7**, 869 (1939), **11**, 72 (1943).
- (5) E. Ganz, *Ann. Physik*, **28**, 445 (1937).
- (6) Cf. N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corp., New York, N. Y., 1940, p. 166.
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- (9) The author is indebted to Dr. Paul Bender and Messrs. Philip Lyons and Paul Reinker for the development of the arcs used in this work.
- (10) B. Uribe-Vergara, Thesis, University of Wisconsin, 1945.
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slit width of 0.06 mm. (For the iron arc comparison spectra, a slit width of 0.025 mm. was used.)

Results and Discussion

The experimental results are summarized in Table I.

TABLE I

RAMAN FREQUENCIES OF WATER AND POTASSIUM THIOCYANATE SOLUTIONS

Solution	Mole ratio	Molality	Temp., °C.	Raman frequencies		
KSCN:	H ₂ O			H ₂ O		(SCN) ⁻
Pure water		12	1649	3202 (40) ^a	3409 (60)	
Pure water		25	..	3223 (37)	3428 (63)	
Pure water		85	..	3254 (30)	3445 (70)	
1:40	1.4	25	..	3241 (35)	3440 (65)	750 2069
1:15	3.7	25	1645	3260 (32)	3450 (68)	746 2069
1:6	9.3	25	1633	3272 (25)	3460 (75)	751 2069
1:3	18.5	25	..	3260 (19)	3452 (81)	735 2069
1:3	18.5	12	1625	..	3452	745 2067
1:3	18.5	85	1624	..	3472	745 2067

^a The numbers in parentheses indicate the relative intensities of the two components of the main water band.

The frequencies of the band components were determined by graphical resolution of the band, assuming symmetrical configurations, from the tracings shown in Fig. 1. The spectra employed for the frequency determinations were so chosen that the main water band had been satisfactorily exposed, and was of approximately equal density for all the solutions. This permits a more legitimate comparison of both frequency shifts and band shapes for different solutions, as Cross, *et al.*,^{1c} have pointed out that the apparent band maxima shift with length of exposure, especially when overexposed.

The accuracy of the frequencies of the band components is estimated at 10 cm.⁻¹, due to the extreme broadness of the band and the arbitrariness of resolution. The frequencies for the thiocyanate ion, except one, are in good agreement with those given in the literature,⁸ and tabulated in Table II.

TABLE II

RAMAN FREQUENCIES FOR THE THIOCYANATE ION

Observers	Year	Frequencies cm. ⁻¹	
Dadieu and Kohlrausch	1930	750	2067
Krishnamurti	1930	747	2050
Langseth, Nielsen and Sorensen	1934	750 796	2066
Goubeau and Gott	1940	747	2066

For the Raman frequencies of liquid water, considerable differences of opinion have been recorded in the literature, especially with regard to frequencies below 1000 cm.⁻¹.¹² In Fig. 1 there is a suggestion of a band in the 130 cm.⁻¹ region, but its origin is questionable since it was not observed with λ Hg 4047 Å. excitation. In the 450 cm.⁻¹ region humps on tracings of highly exposed plates are regularly observed due to scattering in the spectrograph and halation caused by the exciting line. (Even slight halation is enough to

(12) I. R. Rao and P. Koteswaram, *Phil. Mag.*, **25**, 90 (1938).

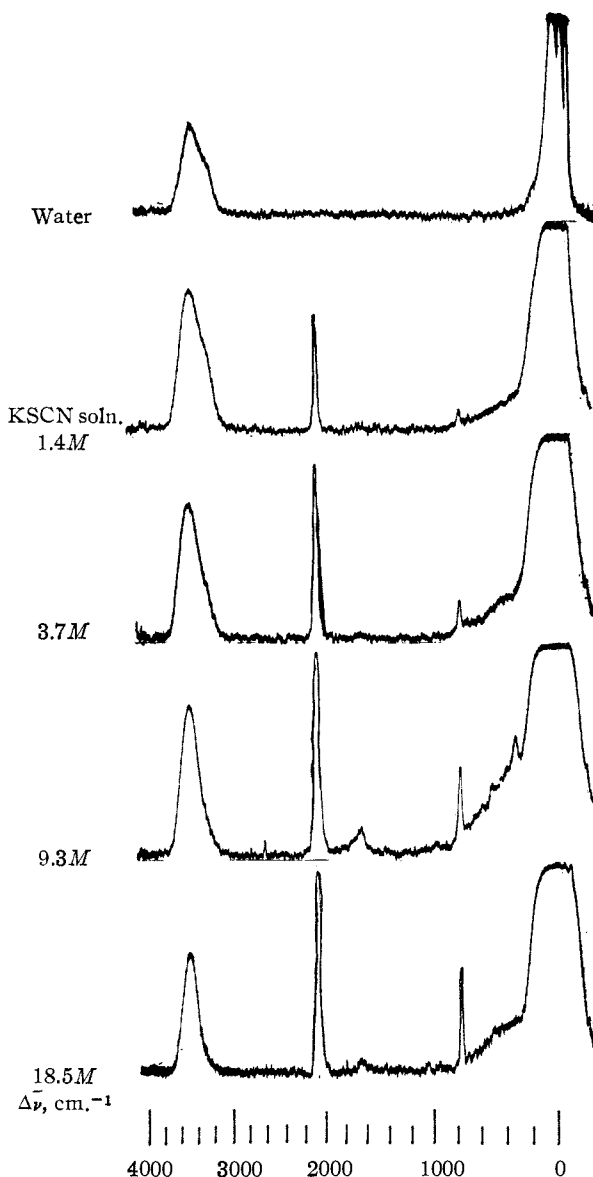


Fig. 1.—Raman spectra of water and aqueous solutions of potassium thiocyanate.

bring out the inevitable continuous background from the light source.) The broad 1650 cm.⁻¹ band is quite definite, while the 3600 cm.⁻¹ component of the main band is not apparent even at 85°.

The presence of the dissolved potassium thiocyanate greatly enhances the intensity of the Raman scattering. The 1650 cm.⁻¹ band is displaced toward lower frequencies with increasing concentration; as reported by Kujumzelis^{2c} it may be as low as 1625 cm.⁻¹ in iodide solutions. The main band is shifted toward higher frequencies with the 3200 cm.⁻¹ component greatly suppressed, so that the band has a sharp and symmetrical appearance for concentrated solutions. The frequency shift of both components shows an increase with increasing salt concentration up to a

concentration of 1:6, and thereafter a slight decrease. Similar behavior has been observed in solutions of zinc chloride^{2b} and hydrogen chloride.¹³

If the relative intensity of the two components of the band can be taken as a measure of the extent of inter-molecular association in water, then water in a 3.7 *M* solution of potassium thiocyanate at 25° has a structural temperature around 60°, and in a 9.3 *M* solution over 100°. This striking effect of potassium ion and thiocyanate ion on the structure of water is in conformity with the low hydration of both ions and the resulting far extending ion-fields, as discussed by Ulich.¹⁴

(13) L. Ochs, J. Guéron and M. Magat, *J. phys. radium*, (8) **1**, 85 (1940).

(14) H. Ulich, *Angew. Chem.*, **49**, 279 (1936).

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Summary

The Raman spectra of aqueous solutions of potassium thiocyanate and of pure water at various concentrations and temperatures have been described. The results show a great increase in the structural temperature of water in potassium thiocyanate solutions caused by the perturbing ionic field created by the solute.

MADISON, WISCONSIN

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An Improved Flow Calorimeter. Experimental Vapor Heat Capacities and Heats of Vaporization of *n*-Heptane and 2,2,3-Trimethylbutane¹

BY GUY WADDINGTON,² SAMUEL S. TODD³ AND HUGH M. HUFFMAN⁴

Introduction

The dearth of reliable heat capacity values for vapors has been emphasized in recent years by the increasing need of the petroleum and allied industries for such information. Theoretical and quasi-theoretical calculations of heat capacities and other thermodynamic quantities from spectral data, by the methods of statistical mechanics, have done much to supplement and to extend existing experimental data. However, as the accuracy and self-consistency of thermodynamic values ultimately rest upon the quality of the available experimental evidence, it is evident that additional accurate measurements are desirable.

To fill this need, the Petroleum and Natural Gas Division of the Bureau of Mines, U.S. Department of the Interior, has instituted, as part of its thermodynamic research program, a project for the development and application of accurate methods for determining heat capacities of hydrocarbon vapors and their derivatives. This paper describes the apparatus and experimental procedure now in use and also presents molal heat capacities and heats of vaporization for *n*-heptane and 2,2,3-trimethylbutane.

Modified versions of Swann's⁵ continuous flow method have given good results in the hands of careful experimenters. Of the early work, that of

Scheel and Heuse⁶ and of Osborne,⁷ *et al.*, may be mentioned, while recent contributors in this field include De Vries,⁸ Felsing,⁹ Pitzer¹⁰ and Scott¹¹ and their co-workers.

The method used by Osborne⁷ and by Scott¹¹ reduced losses to a minimum by creating nearly adiabatic conditions in the calorimeter, while the others involved heat-loss corrections obtained from measurements at several flow rates. In this Laboratory the design due to Pitzer¹⁰ was used as a starting point for the following reasons: (1) the heat losses may be made small and can be corrected for by a linear relationship if all important variables are taken into account; (2) it is well-adapted to the study of compounds the boiling points of which are above room temperature; (3) it permits the incorporation of changes of design and operating procedure, which may lead to improvements in precision.

Very briefly, the method consists of passing a measured constant flow of vapor, generated by electrical evaporation in a cycling vaporizer, through a calorimeter in which the vapor is heated electrically by a measured and constant power input. The apparent heat capacity $C_{p,obs}$ is given by $E/F \Delta T$, where ΔT is the temperature increase produced when E units of energy per unit of time are imparted to a vapor flowing at a rate of F moles per unit of time. The experi-

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(4) Principal Physical Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

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(9) Benjamin P. Dailey with W. A. Felsing, *ibid.*, **65**, 42 (1943).

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