0.0531 *M* solution of diethylaniline are presented in Table V and the average value of the quadrupole formation constant between diethylaniline and water, $K_Q^{D \cdot W} = [Q_{D \cdot w}]/(C_D C_{H_2O})$, was found to be 2.65 ± 0.10. (D = diethylaniline.)

TABLE V

EFFECT OF WATER UPON DIETHYLANILINE (D)

$(C_D)_t = 0.0531$ *M* 2.00 cm. quartz cells

Water, *M*	A_{806}	$[Q_{D.w.}]/C_D$	$K_Q^{D.W.}$
0.274	1.39	0.705	2.58
0.551	0.960	1.47	2.67
1.09	0.580	3.09	2.85
2.08	0.380	5.24	2.62
		Av. =	2.65 ± 0.10

Pyridine solutions in acetic acid are also colorless and the spectrum of pyridine in acetic acid (curve I) and in excess perchloric acid (curve 2) are given in Fig. 6. The molar absorptivities in pure acetic acid were found to be 4.62×10^3 at 255.5 mμ and 3.12×10^3 at 261.0 mμ, while in 0.1 *M* perchloric acid these values at the same wave lengths are 5.48×10^3 and 3.74×10^3. The ratio of the molar absorptivities of pyridine in acetic acid at 255.5 mμ and 261.0 mμ is 1.49, while this ratio is 1.47 in 0.1 *M* perchloric acid This suggests that the two spectra are identical and are caused by similar species. It is reasonable to assume that the base (Py) does not absorb at either of these wave lengths and the observed absorption is caused by PyH^+Ac^- in acetic acid and by $PyH^+ClO_4^-$ in the presence of excess perchloric acid. Experiments using 1.01 and 2.03×10^{-4} *M* pyridine in the presence and absence of excess perchloric acid yielded an average K_i^{Py} of 5.52 ± 0.04 at 255.5 mμ and 5.21 ± 0.09 at 261.0 mμ, assuming that the molar absorptivities of PyH^+Ac^- and $PyH^+ClO_4^-$ are identical at these two wave lengths. These results show that more than 80% of the pyridine is present in the ion-pair form. Adopting the mean value of K_i^{Py} of 5.37 and $K_{Py} = 7.9 \times 10^{-7}$, $K_d^{Py} = 9.4 \times 10^{-7}$.

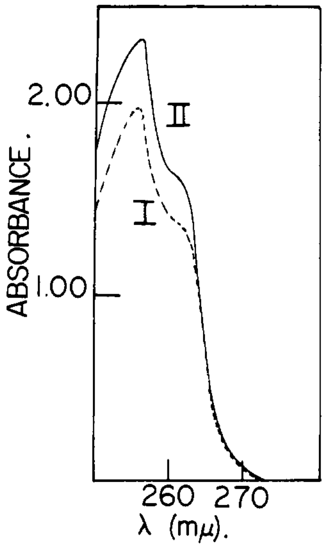

Fig. 6.—Spectrum of pyridine: $(C_{Py})_t = 2.03 \times 10^{-4}$ molar: I, in acetic acid; II, in 0.05 *M* $HClO_4$; 20 mm. cell used.

It was noted that when water was added to pyridine the effect on the spectrum was similar to that produced by perchloric acid, but no quantitative measurements were made to determine the species formed. It may be stated that the "abnormal water effect" is a general phenomenon and it is not restricted to indicator bases.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES OF THE UNIVERSITY OF CHICAGO]

The Outer Sphere Association of Sulfate Ion with Tripositive Cobaltammine Ions

BY FRANZ A. POSEY AND HENRY TAUBE

RECEIVED SEPTEMBER 12, 1955

The equilibrium quotients, *K*, for the outer sphere association of $Co(NH_3)_6^{+++}$ and $Co(NH_3)_5H_2O^{+++}$ with $SO_4^=$ have been measured at several temperatures and ionic strengths by following the changes in optical density in the ultraviolet region of the absorption spectra of the cations as a function of sulfate ion concentration. Values of ΔF^0, ΔH^0 and ΔS^0 at 25° are −4.53 kcal. mole^{-1}, 0.40 kcal. mole^{-1}, and 16.6 e.u. for the association of $Co(NH_3)_6^{+++}$ with $SO_4^=$. The equilibrium quotients calculated are independent of concentrations, of the wave length of light used, and vary with ionic strength in conformity with a Debye–Hückel equation. The quotient for the equilibrium ratio, $(Co(NH_3)_5H_2O^{+++} \cdot SO_4^=)/(Co(NH_3)_5SO_4^+)$, in 1 *M* $NaClO_4$ at 25° has been measured as 0.90 by following changes in the substitution equilibrium using light of wave length 560 mμ. These experiments have also yielded a value for *K* in agreement with that measured using the instantaneous changes in the ultraviolet extinctions as $SO_4^=$ is added to solutions of $Co(NH_3)_2H_2O^{+++}$.

Linhard[1] has demonstrated that the presence in solution of certain anions can cause marked changes in the absorption spectra of tripositive Co(III) and Cr(III) complex ions in the wave length region of the strong ultraviolet band. In an earlier paper[2] we reported that this effect occurs when $SO_4^=$ is added to a solution containing $Co(NH_3)_5H_2O^{+++}$. The changes in question occur immediately on mixing the reagents, in contrast to changes in the two bands in the wave length region of visible light, which for the ions in question take place quite slowly at room temperature, concomitant with substitution in the inner sphere of coördination of the central metallic ion. Therefore, if the changes of spectrum in the ultraviolet region are caused by the association of the cation with the anions, this interaction must be of such nature that the anion does not become equivalent to the six ligands in the

[1] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

[2] H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953).

complex cation. It was the purpose of the work reported here to learn whether the rapid changes in spectrum can be interpreted by an equilibrium between the free ions and the "outer sphere" complexes[3] implied by the structural restriction mentioned.

We have chosen to work with $SO_4^=$ as the anion, both because of its charge and because it is essentially transparent in the spectral region of interest, and the cations, $Co(NH_3)_6^{+++}$ and $Co(NH_3)_5H_2O^{+++}$. The existence of outer sphere complexes was strongly suggested if not proven by the previous work,[2] in which the slow spectrum changes in the visible region were studied. These data have now been amplified to yield a value for the outer sphere association quotient to compare with that obtained measuring the instantaneous changes in extinction. Data with $Co(NH_3)_6^{+++}$ are included to furnish some generalization of the results on outer sphere association.

Experimental

A Beckman Model DU Quartz Spectrophotometer was used for spectral measurements. It was fitted with a cell compartment, the temperature of which was controlled to within ±0.1° by circulating fluid. Standard chemicals were of A. R. quality. The compounds $Co(NH_3)_5H_2O(ClO_4)_3$ and $Co(NH_3)_6(ClO_4)_3$ were used as sources for the complex cations and were purified by repeated crystallization. Solutions of $NaClO_4$ and $Mg(ClO_4)_2$ were prepared by the reaction of perchloric acid with the corresponding carbonate. Measurements of extinction of solutions containing the Co(III) complexes were made against blanks containing all the reagents except the Co(III) salts. The blanks showed significant extinction compared to water only when considerable $NaClO_4$ or Na_2SO_4 was present, perhaps caused by residual Fe(III) in the salts.

Equilibrium with respect to changes in the ultraviolet extinction of $Co(NH_3)_6^{+++}$ on adding $SO_4^=$ was reached immediately on mixing and no further change was noted even after 24 hours had elapsed. With $Co(NH_3)_5H_2O^{+++}$ and $SO_4^=$, after the immediate change on mixing, there is a slow change caused by the replacement of complex-bound H_2O by $SO_4^=$ which is detectable after several minutes at room temperature. For both systems, the ultraviolet measurements were made immediately after temperature equilibrium was established, *ca.* 10 min. after mixing. The changes in the visible spectrum at 25° required the solutions to be stored for 6 to 8 weeks before equilibrium was reached. There was no detectable change during this time in a companion solution containing $Co(NH_3)_{55}H_2O^{+++}$, Na^+, H^+, ClO_4^- but no $SO_4^=$. Equilibrium measurements at 25° were confirmed by approaching the equilibrium distribution from the opposite side, that is, starting with a system containing initially $Co(NH_3)_5SO_4^+$ in excess of the equilibrium amount.

Definitions and Treatment of Data

The outer sphere complex between the cation, M^{+++}, and $SO_4^=$ is represented as $M^{+++}\cdot SO_4^=$.

$D = \log(I_0/I)$ (measured against a blank omitting the Co(III) salt) is referred to as the optical density. The units are l. mole^{-1} cm.$^{-1}$.

The equilibrium quotient, K, refers to the outer sphere association of $Co(NH_3)_6^{+++}$ or $Co(NH_3)_5H_2O^{+++}$ with $SO_4^=$.

$$M^{+++} + SO_4^= = M^{+++}\cdot SO_4^= \qquad (1)$$

With the aquo ion, the additional equilibrium

$$Co(NH_3)_5SO_4^+ + H_2O = Co(NH_3)_5H_2O^{+++}\cdot SO_4^= \qquad (2)$$

is necessary to interpret some of the data. The equilibrium quotient for this reaction is represented by K'. Both K and K' are concentration quotients.

Data on the optical density in the ultraviolet region as a function of $SO_4^=$ concentration at constant ionic strength were treated according to the method outlined by Newton and Arcand.[4] If, in the equilibrium represented by equation 1, the free cation and the 1:1 outer-sphere complex have extinction coefficients independent of $(SO_4^=)$, the relation

$$D = D_1 - \frac{(D - D_0)}{K(SO_4^=)} \qquad (3)$$

is obeyed for a series of experiments in which the activity coefficients of the ions involved in the equilibrium remained constant. D_0 is the optical density of a solution containing no $SO_4^=$, D is that of a solution with $SO_4^=$ present, D_1 that for a solution in which M^{+++} is completely converted to the 1:1 complex, and $(SO_4^=)$ is the concentration of free $SO_4^=$ at equilibrium. D_0 is evaluated by direct measurement, D_1 and K by plotting D against $(D - D_0)/(SO_4^=)$. In most experiments, $(SO_4^=)$ was much in excess of (M^{+++}) and the approximate values of D_1 and K obtained by using stoichiometric $SO_4^=$ in the first plot of these data served to fix $(SO_4^=)$ sufficiently well to make the second plot final.

The optical densities of solutions in the study of the substitution equilibrium at low $(SO_4^=)$ were measured, as in the earlier work at high $(SO_4^=)$, at the wave length 560 mμ. At this wave length, and in fact for the whole region comprised of the two absorption bands in the visible, the species $Co(NH_3)_5H_2O^{+++}$ and $Co(NH_3)_5H_2O^{+++}\cdot SO_4^=$ have the same extinction, but the spectra of these ions differ markedly from that of $Co(NH_3)_5SO_4^+$. Then for a series of experiments in which K' and K, as well as the extinction coefficients of the colored species, remain constant

$$\frac{D_1' - D}{D - D_0} = \frac{(Co(NH_3)_5H_2O^{+++}) + (Co(NH_3)_5H_2O^{+++}\cdot SO_4^=)}{(Co(NH_3)_5SO_4^+)} = K' + \frac{K'}{K(SO_4^=)} \qquad (4)$$

D_1' and D_0 represent the optical densities of solutions having all the Co(III) in the sulfato and aquo forms, respectively, and D that of the solution at equilibrium with respect to inner sphere substitution as well as outer sphere association. K' and K are evaluated by plotting $(D_1' - D)/(D - D_0)$ against $1/(SO_4^=)$, iterating if necessary to fix K', K and $1/(SO_4^=)$ to the accuracy the data justify. In contrast to the situation which obtains when the labile equilibrium (1) is studied, the constancy of D_1' and D_0 with electrolyte composition can be checked directly, nor is constancy of these values essential to the analysis of the system, because the quantities appropriate to any particular solvent composition can be measured directly.

---

(3) The term "outer sphere association" is preferred by the authors rather than "ion-pair formation" since the latter term is not defined with respect to the constitution of the complex ion and offers no distinction between inner sphere and outer sphere forms of the associated species. The term is also of value in describing complex-ion equilibria in exchange-labile systems for which the two forms are difficult to characterize separately but in which there is a need for a term to define the type of association in question.

(4) T. W. Newton and G. M. Arcand, THIS JOURNAL, **75**, 2449 (1953).

Both types of experiments make use of data at varying ($SO_4^=$), but with K' and K constant. The series used to evaluate the parameters D_1, K' and K were performed at constant ionic strength, replacing $NaClO_4$ by Na_2SO_4. This procedure undoubtedly suffices for K', which describes an equilibrium between forms of the same net charge. The internal consistency of the data treated according to equations 3 and 4 is evidence that K also is sufficiently constant for the changes in composition at constant ionic strength.

Results

$Co(NH_3)_6^{+++}$ and $SO_4^=$.—Figure 1 shows the nature of the results obtained when equation 3 is applied to data on the optical density of solutions of $Co(NH_3)_6^{+++}$ with varying ($SO_4^=$). The results in the figure were obtained at λ 235 mμ, which proved to be the optimum wave length for the concentration of M^{+++} chosen, 1.00×10^{-4} M. Data at wave lengths up to 250 mμ were useful, but decreasingly so as the optical densities became too small to provide a dependable basis for evaluating K. The data at $\mu = 0.0094$ are at a concentration of $SO_4^=$ low enough so that a straight line is obtained when they are plotted according to equation 3, yet the maximum concentration of sulfate allowed is high enough so that D approaches D_1. These data were used to define D_1 and the values thus obtained are consistent with the requirements of the data at higher μ in the range of low sulfate concentration, although not defined as accurately by them.

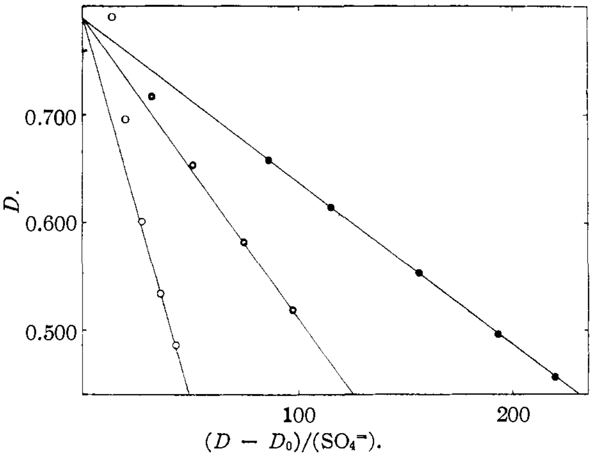

Fig. 1.—Variation of D with ($SO_4^=$): ●, $\mu = 0.0094$; ○, $\mu = 0.0303$; ◦, $\mu = 0.0903$; ($Co(NH_3)_6(ClO_4)_3$) = ($HClO_4$) = 1.00×10^{-4} M; temperature = 24.5°.

Table I shows values of the ratio ($M^{+++}\cdot SO_4^=$)/(M^{+++}), calculated at various wave lengths, applying to data at lower ionic strength the values of D_1 obtained as described. For the experiments in Table I the concentration of sulfate could not be varied over a useful range to obtain an extrapolated value of D_1, and measurements were made on solutions from which $NaClO_4$ was omitted. The data show that the ratio ($M^{+++}\cdot SO_4^=$)/(M^{+++}), and hence the equilibrium quotient, is independent of the wave length at which the measurements were made. This is true also for the more extensive data of the type illustrated in Fig. 1. Thus the value of $K \times 10^{-2}$ at 24.5° calculated for $\mu = 0.0094$ at λ 235, 240, 245, 250 and 255 mμ are 6.65 ± 0.1, 6.8 ± 0.1, 6.7 ± 0.2, 6.6 ± 0.2 and 6.8 ± 0.5.

TABLE I

THE DISTRIBUTION OF Co(III) BETWEEN THE OUTER SPHERE SULFATE COMPLEX AND $Co(NH_3)_6^{+++}$ AS CALCULATED AT VARIOUS WAVE LENGTHS

(Temperature = 24.5°, 1.00×10^{-4} M $HClO_4$, 1.00×10^{-4} M $M(ClO_4)_3$).

(Na_2SO_4) × 10^4	μ × 10^4	Values of the ratio, ($M^{+++}\cdot SO_4^-$)/(M^{+++}), computed at various wave lengths 235 mμ	240 mμ	245 mμ	250 mμ	255 mμ	K × 10^{-2}
3.00	14.4	0.390	0.387	0.395	0.37	0.4	14.4
7.50	26.9	0.75	0.78	0.77	0.76	0.8	10.8
15.00	48.5	1.29	1.27	1.27	1.2	1.4	8.9

In Fig. 2 the equilibrium quotients are shown as a function of ionic strength. The upper line represents the equation

$$\log K = 3.322 - \frac{6.102\sqrt{\mu}}{1 + 2.00\sqrt{\mu}} \qquad (5)$$

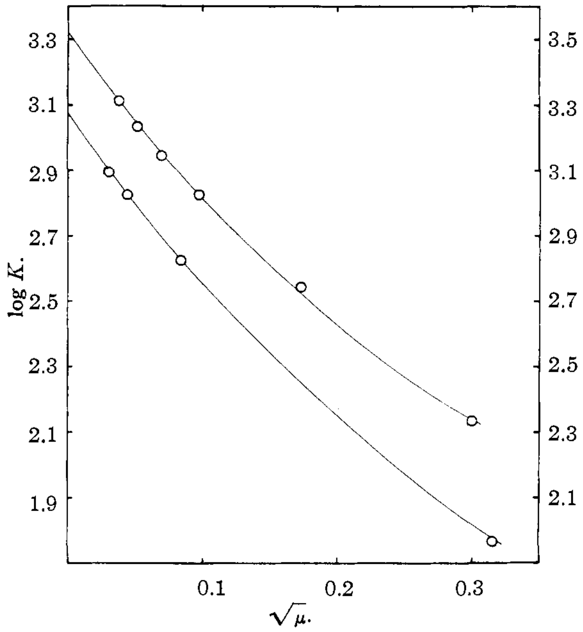

Fig. 2.—Equilibrium quotients as a function of ionic strength. Upper curve for $Co(NH_3)_6^{+++}$ with ordinate scale on the left. $Co(NH_3)_5H_2O^{+++}$ on lower curve with ordinate scale on the right.

Some experiments were done in which the composition of the neutral electrolyte was changed. Table II presents data obtained in a series of experiments at constant Na_2SO_4 and ionic strength, changing the ratio of $NaClO_4$ to $Mg(ClO_4)_2$, as well as another series at constant Na_2SO_4 and concentration of ClO_4^-.

The experiments at $\mu = 0.0094$, which yielded an average value of $K = 6.7 \pm 0.1 \times 10^2$ at 24.5°, were repeated at 4.0 and 49.0°. The corresponding values of $K \times 10^{-2}$ are 6.5 ± 0.1 and 7.2 ± 0.1. This system provides a striking illustration of the errors that can be made in using the spectrophotometric method to measure the variation of K with temperature unless the variation of ϵ with

TABLE II

VARIATION OF D AT CONSTANT (Na_2SO_4) WITH COMPOSITION OF NEUTRAL ELECTROLYTE

Temp. = 24.5°; (Na_2SO_4) = 0.0075 M, except in expt. 1, in which none is present; $M(ClO_4)_3 = 1.00 \times 10^{-4}$ M

Expt. no.	($NaClO_4$)	($Mg(ClO_4)_2$)	Value of D at various wave lengths 250 mμ	245 mμ	240 mμ	235 mμ
1	0.090	....	0.014	0.042	0.132	0.409
2	.0675	....	.067	.129	.269	.613
3	.0525	0.0050	.067	.128	.268	.611
4	.0315	.0120	.067	.128	.266	.606
5	.0165	.0170	.070	.130	.270	.614
6	....	.0225	.075	.138	.282	.625
7	.040	.0138	.065	.124	.258	.602
8	.030	.0188	.066	.125	.261	.603
9	.020	.0238	.067	.128	.263	.603
10	....	.0338	.080	.144	.283	.622

temperature also is measured. The variation of the extinction coefficients with temperature was found to be much greater than that of the equilibrium quotients. Table III shows values of ϵ for $Co(NH_3)_6^{+++}$ and $Co(NH_3)_6^{+++} \cdot SO_4^{=}$ at three different temperatures. The variation with temperature is large because the measurements are made far from the maximum of a strong absorption band. The variation of ϵ with (ClO_4^-) over the range covered in this work is less than 1 or 2%.

TABLE III

THE VARIATION OF ϵ FOR $Co(NH_3)_6^{+++}$ AND $Co(NH_3)_6^{+++} \cdot SO_4^{=}$ WITH TEMPERATURE

$\mu = 0.010$; 1.00×10^{-4} M $HClO_4$.

Wave length (mμ)		235	240	245	250	255
for $Co(NH_3)_6^{+++}$	4.0°	318	95	28	11	5
	24.5°	409	132	42	14	6
	49.0°	533	186	64	24	8
for $Co(NH_3)_6^{+++} \cdot SO_4^{=}$	4.0°	672	330	164	93	50
	24.5°	788	388	208	117	63
	49.0°	938	486	274	162	104

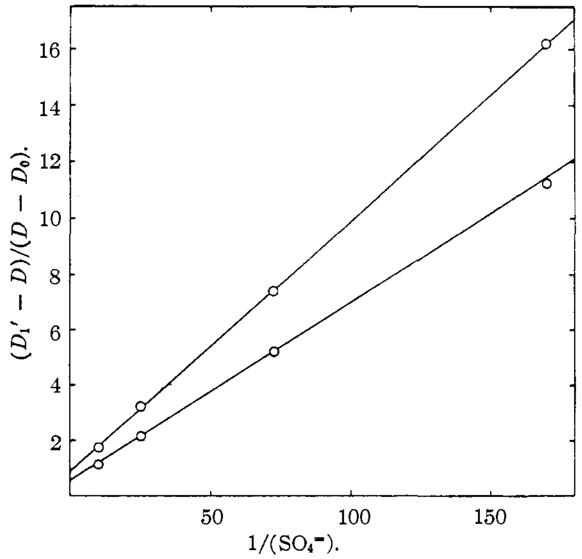

Fig. 3.—Distribution between aquo forms and the sulfato form as a function of sulfate concentration: μ = 1.05, Na_2SO_4 being substituted for $NaClO_4$; upper line at 25.0°; lower line at 44.5°.

$Co(NH_3)_5H_2O^{+++}$ and $SO_4^{=}$.—The nature of the results obtained investigating the ultraviolet spectrum for this system resembles those described for $Co(NH_3)_6^{+++}$ and $SO_4^{=}$. In this system also D, at high ($SO_4^{=}$), increases with ($SO_4^{=}$) more rapidly than equation 3 permits. As before, D_1 was fixed using data at low ionic strength and low maximum sulfate. The results at a variety of temperatures and ionic strengths are summarized in Table IV.

TABLE IV

EQUILIBRIUM QUOTIENTS FOR THE ASSOCIATION OF $Co(NH_3)_5H_2O^{+++}$ WITH $SO_4^{=}$ AT 24.5°

$\sqrt{\mu}$	$K \times 10^{-2}$
0.0304	12.4
.0448	10.6
.0836	6.66
.316	0.92
1.000	0.112

The values of K were evaluated at a number of wave lengths, the range being extended over that covered in the system, $Co(NH_3)_6^{+++} + SO_4^{=}$, by using the cation at 1.00×10^{-3} M as well as at 1.00×10^{-4} M. There is no variation of K with wave length, nor with concentration of the cation. Figure 2 shows the experimental results at 24.8° compared to the equation

$$\log K = 3.276 - \frac{6.10\sqrt{\mu}}{1 + 1.50\sqrt{\mu}} \qquad (6)$$

The equation does not accommodate the experimental result at $\mu = 1.000$, and predicts a value too low by a factor of almost 2.

Figure 3 shows equation 4 applied to the new results obtained by following changes in the extent of substitution at equilibrium at $\mu = 1.05$, using light of wave length 560 mμ. The optical densities for solutions containing $Co(NH_3)_5H_2O^{+++}$ and $Co(NH_3)_5SO_4^{+}$ agreed closely (±1%) with those reported earlier.[2] K' at 25.0 and 44.5° is found to be 0.90 and 0.60, and K at the same two temperatures is 10.1 and 9.7. Data published earlier[5] give for K' and K at 31.1° and $\mu \sim 1.0$, 0.80 and 10.6. This value for K' is consistent with the newer values at other temperatures, but K is apparently too high. The old value is less dependable than the newer values, and the deviation may be attributable to failure to approach equilibrium completely in the older work. K' is affected less than K because solutions at high ($SO_4^{=}$) approach equilibrium more rapidly than at low.

Discussion

With the exception of a single effect, the data on the optical density change in the ultraviolet band of the cations with added $SO_4^{=}$ are completely explained by the assumption of an outer sphere complex ion equilibrium. The calculated equilibrium quotient at constant ionic strength is independent of the concentration of $SO_4^{=}$ and M^{+++} over wide ranges, as well as of the wave length over a large range of optical densities. The equilibrium quotients as a function of ionic strength, at low ionic strength (<0.1), are expressible by a Debye–

---

(5) We are grateful to Dr. T. W. Newton for suggesting the treatment of the data embodied in equation 4 and for applying the equation to the data published in the earlier paper.

Hückel equation. The interpretation receives the strongest kind of support from the analysis of data on the substitution equilibrium. The values of K for comparable conditions obtained by the two methods agree well. In face of the strict adherence of the spectrum changes to the mass law requirements of equation 1, it does not seem reasonable or profitable to ascribe them to some indefinite salt effects, and the further discussion will take the equilibrium quotients for reactions (1) and (2) as having been measured in the work described.

The effect which requires additional explanation is that, at high ($SO_4^=$) in the ultraviolet region, D increases more rapidly with ($SO_4^=$) than equation 3 allows. It may be caused in part by changes in activity coefficients as the electrolyte composition is changed (although at constant μ) but must in part at least have a more direct cause. This follows because in some experiments D actually exceeds D_1, the limiting value for the 1:1 complex. The most reasonable assumption is that a second stage of association takes place at high sulfate. The quotient for the second stage of association will be less sensitive to μ than that for the first, so that at high μ the separate stages will be less cleanly resolved than at low μ. Experiments (not reported in this paper) on the changes in the optical density of a solution of $Co(NH_3)_5SO_4^+$ as $SO_4^=$ are added support of the assumption that a second stage of outer sphere association is possible. The experiments summarized in Fig. 3 show that the affinity in the second association stage must be so small at ($SO_4^=$) = 0.1 M that the forms, RH_2O^{+++}, RSO_4^+ and $RH_2O^{+++}\cdot SO_4^=$, are not much depleted, except possibly at the highest concentration of sulfate.

For the outer sphere association of $Co(NH_3)_6^{+++}$ with $SO_4^=$ at 25° and $\mu = 0$, we find

$$\Delta F^0 = -4.53 \text{ kcal. mole}^{-1}$$

$$\Delta H^0 = 0.40 \text{ kcal. mole}^{-1}$$

$$\Delta S^0 = 16.6 \text{ e.u.}$$

The value of ΔH^0 has been assumed to be the same as that of ΔH at $\mu = 0.0094$, this calculated from the values of K at the extreme temperatures, 4 and 49°. For the outer-sphere association of $Co(NH_3)_5H_2O^{+++}$ and $SO_4^=$, $\Delta F^0_{298} = -4.47$ kcal. mole as calculated using the value of K measured by the changes in O.D. in the strong ultraviolet band. The temperature coefficient of K is not well defined. Experiments to determine K at higher temperatures using the instantaneous spectrum changes, indicated a value of $\Delta H^0 = 1.77$ kcal. mole^{-1} but are vitiated by the effect on the spectrum of inner sphere substitution, which though small in extent, makes an appreciable contribution to the O.D. after a few minutes at the higher temperatures. The experiments on the substitution equilibrium suggest that in 1 M $NaClO_4$, K is almost independent of temperature. If ΔH^0 is taken as zero, ΔS^0 is calculated as 16.4 e.u., a value reasonable, in view of the similarity of the ions, in comparison with that obtained for $Co(NH_3)_6^{+++}$.

Using the data of Fig. 3, ΔH for the formation of $Co(NH_3)_5H_2O^{+++}\cdot SO_4^=$ from the free ions in 1 M $NaClO_4$ is -0.3 kcal. mole^{-1} and ΔS for the reaction at 25° is 3.3 e.u. ΔH for reaction (2) in 1 M $NaClO_4$ is -3.95 kcal. mole^{-1} (the value previously[2] obtained with Na_2SO_4 the only salt present was -4.0 kcal. mole^{-1}) and ΔS is -13.0 e.u. at 25°. Thus the over-all change from the free ions to the inner sphere complex in this environment is accomplished with an entropy increase of 16.3 e.u. at this temperature. The comparison of the entropy changes for the two stages of association which have been defined for the system, $Co(NH_3)_5H_2O^{+++}$ and $SO_4^=$, with the value of 17 e.u. for the formation of the $Ce^{+++} - SO_4^=$ complex[4] in the same environment suggests that the latter complex consists largely of the inner sphere form in solution. The value of ΔS measured for association reactions between ions of 3-2 charge type may be considered as diagnostic of the presence of inner sphere forms, except possibly at very high ionic strengths.

Adell[6] has studied the substitution equilibrium in dilute solutions of $Co(NH_3)_5H_2O^{+++}$ and $SO_4^=$, but did not resolve the "aquo" form into the components, $Co(NH_3)_5H_2O^{+++}$ and $Co(NH_3)_5H_2O^{+++}\cdot SO_4^=$. Taking his data (1st experiment in Table II, p. 254) and assuming the ratio, $(RH_2O^{+++}SO_4^=)/(RSO_4^+)$, at equilibrium (= K'), to be 1.12, K is calculated from his data as 288. At the ionic strength prevailing and the same temperature, the same value for K is calculated also from equation 6. The value of K' which gives agreement is fairly reasonable in comparison with 0.90 for this ratio in 1 M $NaClO_4$ as measured in the work reported in this paper.

Referring to our previous work,[2] $((RH_2O^{+++}) + (RH_2O^{+++}\cdot SO_4^=))/(RSO_4^+)$ with $(SO_4^=) = 0.052$ was measured as 1.28 at 25°. If K' for these conditions is taken to be 0.95, K is calculated to be about 90, and μ as 0.108. This is in good agreement with the value of 92 measured at $\mu = 0.100$. It is evident that the approximation made earlier[2] that K' is measured by (A)/(S) at moderate sulfate concentrations is a rough one. This approximation was made in calculating the values of K reported and accounts for their being in error. The previous comparisons show that a consistent interpretation of all the data can be given, using the measured equilibrium quotients for reactions (1) and (2), if one takes account of a slight change in the value of K' with ionic strength. Davies[7] has reported an equilibrium constant of 2.8 to 3.4×10^3 at $\mu = 0$ and 25° for the association of $Co(NH_3)_6^{+++}$ and $SO_4^=$, basing his result on determinations of the solubility of $Co(NH_3)_6\text{-}(Co(NH_3)_2(NO_2)_4)_3$ in K_2SO_4. Jenkins and Monk,[8] on the basis of conductivity measurements, have obtained a value of 3.6×10^3 for the association constant at 25°. Our value of 2.2×10^3 is in moderately good agreement with those of Davies and of Jenkins and Monk, but the difference seems to be too great to be attributed to errors in observation. Gimblett and Monk,[9] using a spectral method similar to that employed in this work, have established a value of 1.8×10^3 for the association constant of $Co(NH_3)_6^{+++}$ with $S_2O_3^=$ at zero ionic strength and 25°. This value is near

---

[6] B. Adell, *Z. anorg. allgem. Chem.*, **249**, 251 (1942). This reference was cited incorrectly in our previous paper.

[7] C. W. Davies, *J. Chem. Soc.*, 2421 (1930).

[8] I. L. Jenkins and C. B. Monk, *ibid.*, 86 (1951).

[9] F. G. R. Gimblett and C. B. Monk, *Trans. Faraday Soc.*, **51**, 793 (1955).

that (~10^3) reported by Katzenellenbogen,[10] also obtained by measurements on the variation of the ultraviolet absorption band of $Co(NH_3)_6^{+++}$ with $(S_2O_3^{=})$.

The simplest interpretation of the experiments with $Mg(ClO_4)_2$ added in small amount is that the affinity of Mg^{++} and $SO_4^{=}$ is small with an equilibrium quotient for the association reaction probably of the order of magnitude of unity at $\mu = 0.091$ and 25°. At higher concentrations, $Mg(ClO_4)_2$ exerts a remarkable effect, enhancing D rather than reducing it as would be expected if depletion of $SO_4^{=}$ were its only effect. The effect appears whether a series at constant μ (expts. 2–6 in Table III) or at constant (ClO_4^-) (expts. 7–10, Table III) is followed and increases sharply in the $Mg(ClO_4)_2$-rich end of the concentration range. It cannot be explained merely by assuming that $Mg(ClO_4)_2$ shifts equilibrium (1), for the different wave lengths respond differently.

There is the possibility that cations of high field intensity can affect the u.v. spectra of forms such as $Co(NH_3)_5^{+++}{\cdot}SO_4^{=}$; if so, the spectral method is not suited to very refined measurements. Alternatively, the effect may merely be to change the distribution between the 1:1 complex, and higher order ones.

Acknowledgment.—This work was given financial support by the Office of Naval Research under Contract N6-Ori-02026.

CHICAGO 37, ILLINOIS

---

[10] E. R. Katzenellenbogen, Paper No. 23, Division of Physical and Inorganic Chemistry, American Chemical Society Meeting, September, 1950.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XI. The Relaxation Times of Three Nearly Spherical Molecules in the Pure Liquid and in Solution[1,2]

BY RUSSELL S. HOLLAND,[3a] GEORGE N. ROBERTS[3b] AND CHARLES P. SMYTH

RECEIVED JUNE 27, 1955

The dielectric constants and losses of 1,1,1-trichloroethane, 2,2-dichloropropane and 2,2-dinitropropane and of their dilute solutions in heptane, a paraffin oil and carbon tetrachloride have been measured at wave lengths of 1.22, 3.22, 6.6, 10.7 and 30 cm. and temperatures between 2 and 60°. The data have been used to calculate the critical wave lengths, the corresponding dielectric relaxation times of the liquids, and the approximate molecular relaxation times. The results indicate a rough proportionality between molecular relaxation time and the macroscopic viscosity of the liquid when molecules of not very different sizes and shapes are compared within a narrow range of viscosity. This is in contrast to the extreme deviations from proportionality previously reported in this series of papers for liquids varying over a wide range of viscosity.

In earlier papers of this series[4-13] the critical wave lengths of *t*-butyl bromide[6], *t*-butyl chloride[10] in the pure liquid and in solution, and 1,1,1-trichloroethane[10] in solution in heptane and nujol have been studied. In a recent paper,[14] the critical wave lengths of these three substances and of 2,2-dichloropropane, dibromodichloromethane and 2,2-dinitropropane have been considered with reference to their molecular relaxation times, τ_μ, and the microscopic or internal viscosities, η_μ, of the liquids. It is the purpose of the present paper to present as briefly as possible the dielectric constants and losses of three of these substances at different temperatures in the pure state and in solution in different solvents and to consider the significance of their relaxation times. These substances have been chosen for consideration together because of the roughly spherical shapes of their molecules.

Experimental Methods and Results

n-Heptane from the Phillips Petroleum Company was used without further purification; $n^{20}_{\rm D}$ 1.3881 (lit. values 1.3877–1.3882). The viscous paraffin oil used was Nujol purchased at a drugstore. Carbon tetrachloride was refluxed over mercury for two hours, washed with concentrated sulfuric acid, distilled water, dilute sodium hydroxide solution and distilled water, dried over anhydrous calcium chloride, and twice fractionated; b.p. 76.2–76.4° (lit. 76.7–76.8°), $n^{20}_{\rm D}$ 1.4602 (lit. 1.4604–1.4608). 1,1,1-Trichloroethane, or methylchloroform, from Matheson, Coleman and Bell was washed three times with concentrated sulfuric acid, distilled water, sodium bicarbonate solution and distilled water, dried over anhydrous calcium chloride, and twice fractionated; b.p. 74.0–74.3° (lit. 73.9–74.1°), $n^{20}_{\rm D}$ 1.4383 (lit. 1.4384). 2,2-Dichloropropane from the Halogen Chemical Company was washed twice with sodium carbonate solution and distilled water, dried over anhydrous calcium chloride, and fractionally distilled; b.p. 69.2–69.5° (lit. 69.3°), $n^{20}_{\rm D}$ 1.4150 ("International Critical Tables," 1.4093). 2,2-Dinitropropane, kindly given us by the Commercial Solvents Corporation, was fractionally crystallized

---

[1] This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents a part of the work submitted by R. S. Holland to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] (a) Procter and Gamble Fellow in Chemistry, 1953–1954; (b) supported by a Grant-in-Aid to the Chemistry Department of Princeton University from E. I. du Pont de Nemours and Company.

[4] W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, THIS JOURNAL, **70**, 4093 (1948).

[5] H. L. Laquer and C. P. Smyth, *ibid.*, **70**, 4097 (1948).

[6] E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, *ibid.*, **70**, 4102 (1948).

[7] W. M. Heston, Jr., and C. P. Smyth, *ibid.*, **72**, 99 (1950).

[8] W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

[9] A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3447 (1950).

[10] A. J. Curtis, P. L. McGeer, G. B. Rathmann and C. P. Smyth, *ibid.*, **74**, 644 (1952).

[11] P. L. McGeer, A. J. Curtis, G. B. Rathmann and C. P. Smyth, *ibid.*, **74**, 3541 (1952).

[12] F. H. Branin, Jr., and C. P. Smyth, *J. Chem. Phys.*, **20**, 1121 (1952).

[13] R. S. Holland and C. P. Smyth, *J. Phys. Chem.*, **59**, 1088 (1955).

[14] C. P. Smyth, *ibid.*, **58**, 580 (1954).