the residue was dissolved in acetone and recrystallized from acetone–petroleum ether. The resulting white prisms were soluble in water and most organic solvents; m.p. 120–122°.

Anal. Calcd. for $C_7H_{10}N_2OS$: N, 16.45: Found: N, 16.72.

BELLEVILLE, N. J. RECEIVED JUNE 26, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Systems Ag_2SO_4–Rb_2SO_4–H_2O and Ag_2SO_4–Cs_2SO_4–H_2O at 25°[1]

BY WERNER C. VON DOHLEN[2] AND EDWARD L. SIMONS

The solubility measurements here reported have been made as an extension of the study of the equilibrium relations in aqueous systems involving silver sulfate and the alkali sulfates.[3]

Materials.—C.P. grade silver sulfate was further purified by recrystallization from concentrated sulfuric acid.[4] The rubidium sulfate was prepared from recrystallized rubidium nitrate[5] and the cesium sulfate from cesium dichloroiodide[6] which had been twice recrystallized from 9 molal hydrochloric acid.[7] All salts, after drying at 250°, were stored in glass-stoppered weighing bottles in a calcium chloride desiccator.

Solubility Determinations.—Complexes of known composition were made up by weight in 8-inch ignition tubes fitted with an internal stirrer, similar to that shown by Purdon and Slater.[8] At least two days were allowed for the attainment of equilibrium in a constant temperature water-bath. The 25° solubilities were measured at 25.00 ± 0.05°, the 35° solubilities at 34.90 ± 0.05°. To prevent photochemical decomposition of the silver sulfate, the solubility tubes were wrapped in aluminum foil. Samples for analysis were taken in the usual way by means of pipets fitted with filter paper tips.

The analytical method involved determination of the silver sulfate concentration by titration with ammonium thiocyanate, using the Volhard indicator, and of the water concentration by the loss in weight on evaporation and drying for eight hours at 110° followed by overnight heating at 250°.

TABLE I

SYSTEMS Ag_2SO_4–H_2O– AND Rb_2SO_4 OR Cs_2SO_4 AT 25 OR 35°

Liquid solution			C, Orig. complex, R, wet residue			
Wt. % Ag_2SO_4	Wt. % Rb_2SO_4	Density		Wt. % Ag_2SO_4	Wt. % Rb_2SO_4	Solid phase[a]
		(1) Rb_2SO_4 at 25°				
0.833[b]		1.004[b]				A
0.79	5.85	1.052	C	15.26	5.00	A
0.92	12.99	1.126	C	14.33	11.20	A
1.10	20.45	1.200	C	15.10	17.58	A
1.18	24.41	1.252	C[c]	20.1	19.1	A
1.23	26.13	1.272	C[c]	13.6	22.6	A
1.30	28.95	1.316	C	14.98	25.03	A
1.33	30.85	1.336	C[c]	11.1	27.5	A
1.37	32.93	1.359	C	10.09	29.96	A
1.38	33.66	1.375	C	6.15	33.43	A + B
1.37	33.61	1.373	C[c]	6.2	35.9	A + B
1.38	33.63	1.378	C	2.49	37.47	A + B
1.38	33.63	1.361	C	1.38	38.81	A + B
1.38	33.63	1.372		Average		A + B
0.62	33.72	1.355	C	0.51	45.12	B
	33.77	1.348				B
		(2) Cs_2SO_4 at 25°				
	Wt. % Cs_2SO_4				Wt. % Cs_2SO_4	
0.833[b]		1.004[b]				A
.76	5.93	1.055	C	15.02	5.06	A
.86	13.94	1.136	C	14.96	11.95	A
.98	20.52	1.211	C	15.00	17.61	A
1.07	27.53	1.306	C	14.86	23.69	A
1.19	35.16	1.411	C	15.04	30.15	A
1.22	36.19	1.420	R	90.89	3.69	A
1.28	41.19	1.514	C	14.79	35.52	A
1.38	46.96	1.623	C	14.88	40.37	A
1.43	48.11	1.635	R	84.20	7.78	A
1.43	51.99	1.743	C	14.97	44.84	A
1.53	57.94	1.871	R	84.57	9.16	A
1.57	62.74	2.005	C	15.45	53.79	A
1.57	62.99	2.011	R	77.75	14.22	A
1.57	63.72	2.048	C[c]	8.8	58.6	A + D
1.58	63.71	2.049	C[c]	6.3	65.4	A + D
1.57	63.80	2.054	C[c]	3.1	67.0	A + D
1.57	63.79	2.045	C	1.45	66.60	A + D
1.57	63.76	2.049		Average		A + D
0.57	64.21	2.016	C	0.49	69.45	D
	64.53	2.007				D
		(3) Cs_2SO_4 at 35°				
1.80	64.28	2.057	C[c]	9.8	61.0	A + D
1.80	64.27	2.048	C[c]	6.9	62.5	A + D
1.80	64.22	2.068	C	5.01	65.01	A + D
1.80	64.31	2.059	C[c]	3.2	67.1	A + D
1.80	64.27	2.058		Average		A + D

[a] A = Ag_2SO_4; B = Rb_2SO_4; D = Cs_2SO_4. [b] Ref. 3. [c] These complexes were not prepared directly from the pure components, but by the addition of salts and water as needed to other complexes. No extrapolation errors were calculated for these data.

Results.—The data (in weight per cent.) are shown in Table I. Both systems are simple, the only solid phases being the pure salts, as determined by the algebraic extrapolation[9] of the tie lines through the original complexes or wet residues. The extrapolation errors averaged 0.30 and 0.26% for the rubidium and cesium systems, respectively. The density values, obtained by using calibrated pipets in the sampling of the saturated liquids for analysis, are relatively less precise and dependable than the analytical results themselves. At 35° only the isothermally invariant point was determined for the cesium system.

Summary

1. The ternary systems silver sulfate–rubidium

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(1) Abstracted from a dissertation submitted by Werner C. von Dohlen in May, 1950, to the School of Chemistry of Rutgers University in partial fulfillment of the requirements for the degree of Bachelor of Science with Special Honors in Chemistry.

(2) Department of Chemistry, Brown University, Providence, R. I.

(3) Simons and Ricci, THIS JOURNAL, **68**, 2194 (1946).

(4) Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 66.

(5) Ref. 4, p. 50.

(6) Ref. 4, p. 52.

(7) Bender and Strehlow, THIS JOURNAL, **70**, 1996 (1948).

(8) Purdon and Slater, "Aqueous Solution and the Phase Diagram," Edward Arnold and Co., London, 1946, p. 68.

(9) Hill and Ricci, THIS JOURNAL, **53**, 4306 (1931).

sulfate–water and silver sulfate–cesium sulfate–water have been studied at 25°. The only solid phases observed were the pure salts.

2. The isothermally invariant solutions saturated with the two salts have the compositions:

	T, °C.	Ag_2SO_4, %	Alkali sulfate, %	Density
I	25	1.38	33.63 (Rb_2SO_4)	1.372
II	25	1.57	63.76 (Cs_2SO_4)	2.049
III	35	1.80	64.27 (Cs_2SO_4)	2.058

NEW BRUNSWICK, N. J. RECEIVED JULY 24, 1950

NOTES

The Interaction of Chlorine with Benzene and *m*-Xylene[1,2]

BY L. J. ANDREWS AND R. M. KEEFER

By employing the same ultraviolet absorption techniques used to demonstrate 1:1 complex formation between iodine,[3] bromine[4] and iodine monochloride[5] and a variety of benzene derivatives it has now been shown that chlorine also undergoes interaction with aromatic substances. The chlorine complexes, like those of the other halogens, display high intensity absorption maxima at wave lengths in the vicinity of 290 mμ. In the present study the spectra of solutions of chlorine in solvent mixtures of carbon tetrachloride and benzene or *m*-xylene have been investigated. Typical spectrophotometric data for these solutions at the absorption maxima of the complexes are given in Table I.

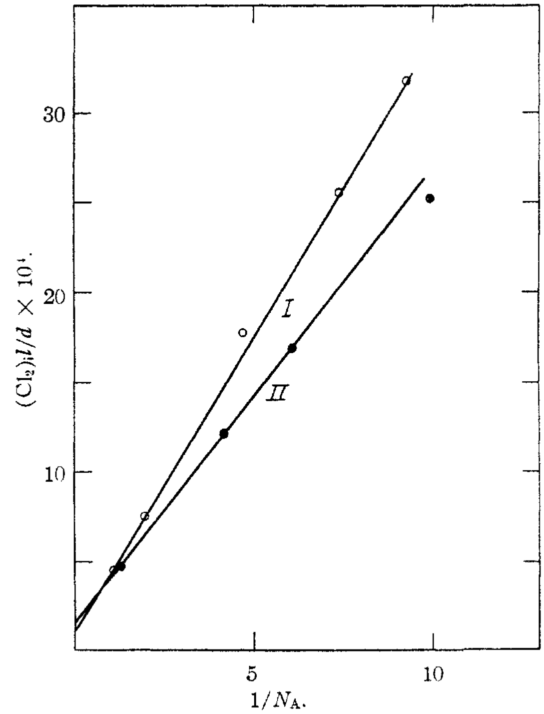

Fig. 1.—The evaluation of ϵ_c and *K*: I, data for benzene; II, data for *m*-xylene.

TABLE I

THE EXTINCTION COEFFICIENT OF CHLORINE IN CARBON TETRACHLORIDE SOLUTIONS OF BENZENE OR *m*-XYLENE

Aromatic substance	N_A mole fractn.	λ_{max}, mμ	ϵ_{max}[a]
Benzene	0.915	278[b]	2220
m-Xylene	.845	290[b]	2180

[a] Based on total chlorine present in the solution as free halogen and in complex form. [b] The extinction coefficient of chlorine in carbon tetrachloride is 6.1 at 278 mμ and 19.5 at 290 mμ.

The changes in the optical density at the complex absorption maximum for these chlorine solutions, as influenced by changes in the mole fraction of aromatic hydrocarbon in the solvent, have been determined. The resultant data have been used to evaluate the equilibrium constants *K* for the reaction between the halogen (X_2) and the aromatic substance (A). As is required for a 1:1 complex[3b]

$$X_2 + A = X_2\cdot A,\ K = \frac{(X_2)(A)}{(X_2\cdot A)} \qquad (1)$$

These data were found to fit equation (2)

$$\frac{(Cl_2)_i l}{d} = \frac{1}{K\epsilon_c} \times \frac{1}{N_A} + \frac{1}{\epsilon_c} \qquad (2)$$

in which

$(Cl_2)_i$ = total molar chlorine concentration
d = maximum optical density of the solution at the complex absorption peak
l = light path length = 1 cm.
ϵ_c = molecular extinction coefficient of the complex at the absorption maximum

That is, a plot of $(Cl_2)_i l/d$ values against $1/N_A$ for both the benzene and *m*-xylene solutions produced straight lines (see Fig. 1 for a plot of data for solutions at 25°). The ϵ_c and *K* values calculated using the ordinate intercepts and slopes of these lines along with corresponding data for the other halogens studied previously are given in Table II. The $(Cl_2)_i l/d$ values as represented in Fig. 1 were corrected for the slight absorption of the free halogen in the manner described in previous papers.[4,5]

In the studies with chlorine, both the degree of complex formation and the ϵ_c values were small. Appreciable error therefore entered into the reading of $1/\epsilon_c$ values from the ordinate intercepts (Fig. 1) which seriously limited the accuracy of reported

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[1] This investigation has been supported by a grant-in-aid from Research Corporation.

[2] Reported in the Symposium on Generalized Acids and Bases before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Chicago, Illinois, September, 1950.

[3] (a) Benesi and Hildebrand, THIS JOURNAL, **70**, 3978 (1948); (b) *ibid.*, **71**, 2703 (1949).

[4] Keefer and Andrews, *ibid.*, **72**, 4677 (1950).

[5] Keefer and Andrews, *ibid.*, **72**, 5170 (1950).