[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, HARVARD UNIVERSITY]

Solubility of Salts in Deuterium Oxide[1]

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Large differences between the solubilities of various salts in light and heavy water have been observed by Shearman and Menzies,[3] Eddy and Menzies,[4] and Eddy, Machemer and Menzies.[5] They concluded that the effect may be due, in part, to the persistence of molecular association to higher temperatures in heavy water. LaMer and Noonan[6] observed a considerable difference in the activity of potassium chloride in light and heavy water from measurements of a cell with transference. Deviations in the behavior of electrolytes dissolved in light and heavy water are of special interest with respect to the Debye–Hückel theory which takes no direct account of water structure but lays particular emphasis on dielectric effects. Wyman and Ingalls[7] have shown that light and heavy water are nearly isodielectric. They determined the dielectric constant of water at 25° as 78.54 and that of deuterium oxide as 78.25. It is therefore impossible to attribute the relatively large differences in electrolyte activity to dielectric effects.

For a complete understanding of electrolyte behavior in light and heavy water a body of data is needed on the solubility and activity behavior of various electrolytes in the isotopic solvents. This paper reports solubility data for a number of salts. They were selected with several points in mind. First, salts were chosen which do not form solid hydrates in the range explored. Thus the activity of the solid phase would be the same in both solvents. Second, the salts employed all possess a high temperature coefficient of solubility. The viscosity of water changes rapidly with temperature, indicative of a corresponding alteration of its macromolecular structure. Part of the high temperature coefficient of solubility can conceivably be assigned to the influence of water structure, another part to the heat of dissociation of the ionic lattice. The former should be sensitive to the structural differences between light and heavy water. Finally, such factors as freedom from supersaturation, ease of purification, and stability toward hydrolysis and oxidation by air were considered.

Experimental

A. **Preparation of Materials: Deuterium oxide** was purified before each solubility determination by consecutive distillation from alkaline permanganate and then from a crystal of potassium dichromate or chromic anhydride. Water treated in this manner was found to have a conductance of 2×10^{-6} mho or better.

Salts.—Thallous nitrate was made by dissolving thallium metal in concentrated nitric acid, evaporating to dryness and taking the crystals up in water. Thallic hydroxide was removed with hydrogen peroxide. Thallous perchlorate was made by evaporating thallous nitrate three times with perchloric acid or by dissolving thallium metal in perchloric acid. Silver chlorate was prepared from sodium chlorate and silver nitrate. These crude salts, as well as C. P. grade materials used for other determinations, were recrystallized from two to five times. Hot solutions were filtered through fritted glass while crystals were submitted to centrifugal drainage. Precautions were taken to avoid hydrolysis when necessary.

B. **Apparatus and Procedure.**—A 16-ml. pyrex pycnometer fitted with platinum electrodes was used to determine the density and conductivity of heavy water. Ground glass joints were used on the pycnometer and on all parts coming in contact with heavy water. All apparatus other than the pycnometer was carefully cleaned, steamed and dried before each determination.

Solubilities were determined by equilibrating solutions with excess salts, evaporating a filtered, weighed portion of solution to dryness and weighing the remaining salt to ±0.05 mg. Weights were calibrated against a B. S. standard and all weighings corrected for the buoyancy of air.

Appropriate excesses of purified salts were introduced into 6–8 ml. pyrex capsules, heavy water was distilled in under vacuum and the ampoules sealed off. Solubility determinations were therefore made under the vapor pressures of the respective saturated solutions. Equilibrium was approached from the high temperature side only by rotating the ampoules end over end twelve to forty-eight hours in a water-bath. The thermostat was fitted with a refrigeration unit and was controlled to ±0.05° or better. Temperatures were read to ±0.01° with a B. S. calibrated thermometer. After settling one hour, 2–5 ml. samples of solution were removed with pipets fitted with glass wool filters. The pipets were kept at the same temperature as the solutions and protected from condensed moisture.

Samples of solution were transferred to tared 30-ml. platinum crucibles contained in suitable weighing bottles and immediately weighed to the nearest milligram. Heavy water was evaporated in the apparatus shown in Fig. 1. A condensing bulb cooled with Dry Ice–acetone is attached below the section holding the crucible, while a glass "hat" covers the assembly. A flat glass joint was used at this point because tapered joints of this diameter tended to split or stick. Heat was supplied by an infrared bulb mounted above the "hat," the ground glass joint being protected by a radiation shield of aluminum. After evacuation distillation occurred quickly and smoothly provided no air had dissolved in the solution during weighing and transfer operations. Otherwise the solutions spattered hopelessly when a vacuum was applied. Before opening the apparatus, air was admitted slowly to prevent blowing salt out of the crucible. All salt samples were dried to constant weight in an oven or desiccator. For cyanide solutions porcelain crucibles were used.

All solubility determinations were performed in duplicate. Determinations were repeated in the event of discrepancies greater than 0.5%. In some instances only enough water of high deuterium content was available to fill one capsule, but two samples of solution were always distilled.

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[1] Presented at the Atlantic City meeting of the American Chemical Society, April, 1946.

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[3] Shearman and Menzies, THIS JOURNAL, **59**, 185 (1937).

[4] Eddy and Menzies, *J. Phys. Chem.*, **44**, 207 (1940).

[5] Eddy, Machemer and Menzies, *ibid.*, **45**, 908 (1941).

[6] LaMer and Noonan, THIS JOURNAL, **61**, 1487 (1939).

[7] Wyman and Ingalls, *ibid.*, **60**, 1182 (1938).

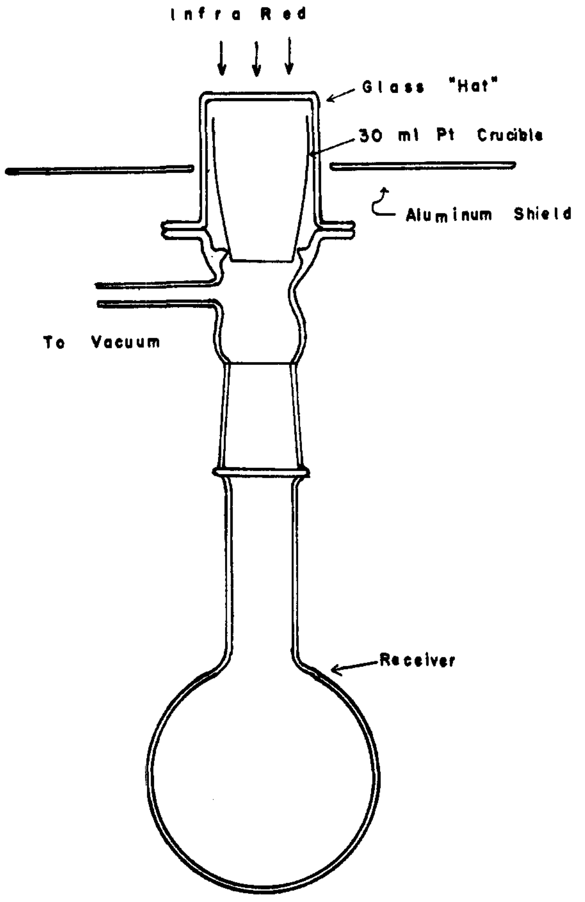

Fig. 1.—Evaporating apparatus.

C. **Experimental Results.**—Deuterium contents of the heavy water mixtures were computed from the density increment over unity at 25° and the d^{25}_{25} value for heavy water of 1.10764 as determined by Stokland, Ronaess and Tronstad.[8] This is in very close agreement with the value 1.10763 ± 0.00005 given by Johnston.[9] Solubility data in terms of gram moles of salt per 100 gram moles of H_2O or H_2O–D_2O mixture are presented in Tables II and III. The columns headed "Diff. Obs." refer to the difference in solubility between H_2O and the H_2O-D_2O mixture in question. Columns labelled "Diff. Pure D_2O" give the solubility difference observed extrapolated to pure D_2O assuming a linear variation of solubility with the deuterium content of the solvent. "Diff. Per cent." represents the solubility difference between light and heavy water expressed as a percentage of the solubility in light water. Sources of light water solubility data are indicated in the tables.

TABLE I

SOLUBILITY OF POTASSIUM DICHROMATE IN H_2O–D_2O AT 25° AS A FUNCTION OF DEUTERIUM CONTENT

D_2O, per cent.	Solubility, moles of salt per 100 moles of H_2O–D_2O
0.0	0.9136
48.5	.788
91.8	,6903
98.0	.6781

Discussion of Results

Lange and Martin[10] found that the difference in integral heat of solution of sodium chloride in water and in water–deuterium oxide mixtures was a linear function of the deuterium content of the solvent when the concentration is expressed in terms of moles of salt per 100 moles of water. In order to extrapolate the solubility results obtained in heavy water mixtures to pure deuterium oxide a linear variation of solubility with deuterium content was heretofore assumed.[4] Since potassium dichromate shows a large difference in solubility in the two solvents, the amount dissolved at three different deuterium concentrations was measured at 25°. Results are given in Table I and plotted in Fig. 2. The curve is not quite linear

TABLE II[a]

SOLUBILITY OF VARIOUS SALTS IN H_2O–D_2O MIXTURES AT SEVERAL TEMPERATURES

		Moles salt per 100 moles H_2O–D_2O				
Temp., °C.	D_2O, %	Soly. H_2O	Soly. H_2O–D_2O	Diff. obs.	Diff. pure D_2O	Diff. per cent.
		1. Silver Chlorate[11]				
5.0	98.3_8	0.8017	0.6532	0.148_5	0.1509	18.8
15.0	98.3_8	1.148_1	0.9567	.1914	$.194_6$	17.0
25.0	98.3_8	1.604_0	1.3578	$.246_2$	$.250_3$	15.6
35.0	98.1_8	2.235_3	1.9076	$.327_7$	$.333_8$	14.9
		2. Thallous Perchlorate[11]				
5.0	99.7	0.3978	0.304	.094	0.094	23.6
15.0	99.7	.615	.488	.127	$.127_4$	20.7
25.0	91.6	.921	.763	.158	$.172_5$	18.7
35.0	91.6	1.337	1.129	.208	.227	17.0
		3. Potassium Permanganate[11,12]				
5.0	91.5_9	0.400_2	0.302	0.098	0.107	26.8
15.0	90.8_6	.600	.471	.129	.142	23.7
25.0	90.8_6	$.869_6$	.700	.170	.187	21.5
35.0	90.8_6	.1224	.1010	.214	.235	19.2
		4. Thallous Nitrate[13]				
5.0	92.3_6	0.328	0.263_2	0.065	0.070	21.3
15.0	92.3_6	.517	$.414_6$	.102	.110	21.3
25.0	92.3_6	.792	$.638_5$	.153	.166	21.0
28.37	90.8_6	.905	.739	.166	.183	20.2
30.11	90.8_6	.970	.793	.177	.195	20.1
35.0	91.5_9	1.175	$.961_2$	.214	.234	19.9
		5. Potassium Dichromate[11,14]				
5.0	91.8_3	0.364_5	0.252_5	0.112_0	0.1220	33.5
15.0	91.5_6	$.597_7$	$.428_6$	$.169_1$	$.184_7$	30.9
25.0	91.8_3	$.913_6$	$.690_3$	$.223_3$	$.243_2$	26.6
25.0	98.0	$.913_6$	$.678_1$	$.235_5$	$.240_0$	26.3
35.0	91.8_3	1.325_2	1.045_4	$.279_8$	$.304_7$	23.0

[a] Sources of light water solubility data, refs. 11, 12, 13, 14.

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[8] Stokland, Ronaess and Tronstad, *Trans. Faraday Soc.*, **35**, 312 (1939).

[9] Johnston, THIS JOURNAL, **61**, 878 (1939).

(10) Lange and Martin, *Z. physik. Chem.*, **A178**, 214 (1937).

(11) Author.

(12) Baxter, Boylston and Hubbard, THIS JOURNAL, **28**, 1336 (1906).

(13) Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, 3rd. ed., D. Van Nostrand, New York, N. Y., 1940, p. 1555.

(14) Flöttmann, *Z. anal. Chem.*, **73**, 1 (1928).

TABLE III[a]

SOLUBILITY OF SEVERAL SALTS IN H_2O–D_2O MIXTURES AT A SINGLE TEMPERATURE

	Temp., °C.	D_2O, %	Moles salt per 100 moles H_2O–D_2O Sol. H_2O	Soly. H_2O–D_2O	Diff. obs.	Diff. pure D_2O	Diff. per cent.
Sodium bromate	5.0	91.59	3.253 (15)	2.899	0.354	0.386	11.9
Potassium argentocyanide	5.0	90.86	1.290 (11)	1.015	.287	.316	24.5
Cesium nitrate	5.0	91.43	1.078 (11)	0.9056	.172	.188	17.4
Potassium chlorate	5.0	91.43	0.5845 (11)	.5182	.0663	.0725	12.4
Mercuric cyanide	5.0	91.43	.537 (11)	.434	.103	.113	21
Sodium oxalate	5.0	91.43	.386 (16)	.340	.046	.050	13.0
Lead chloride	25.0	91.56	.0705 (14)	.0471	.0234	.0256	36.3

[a] Sources of light water solubility data, refs. 11, 14, 15, 16.

but the deviation is not much beyond the experimental error. For less sensitive salts, as sodium chloride, it is doubtful whether the difference would be detectable. In the absence of more complete information, the assumption of linear variation of solubility with deuterium content may be continued.

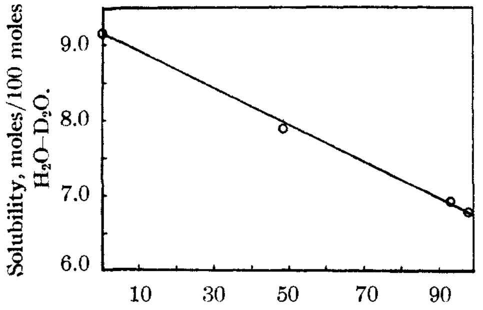

Fig. 2.—Solubility of potassium dichromate as a function of deuterium content of solvent.

Relatively large solubility differences were observed for the five salts which were studied at a series of temperatures. The results are given in Table II and plotted in Fig. 3. In common with most other salts, the solubility difference increases at temperatures giving the lowest concentration. The curve for thallous nitrate appears somewhat anomalous, since it is practically independent of temperature. There appears to be a discontinuity between 25 and 28.4°. Results of duplicate determinations at 25° agreed to 0.16%. The effect does not appear to be due to an error in light water solubility data. Possibly a solid state transition of thallous nitrate occurs in this range, although none has ever been reported. The transition from rhombic form takes place in the neighborhood of 75–80°.

If water structure exercises a critical effect on the behavior of electrolytes, the greatest differences should be observed at the highest dilutions, since under these conditions the water structure should be least disturbed. Eddy, Machemer and Menzies[5] reported that the greatest solubility difference for a given salt occurred at the lowest concentrations, whether or not these appeared at low or high temperatures. The data in Table III are arranged in order of decreasing salt solubility in light water. There seems to be no correlation between total concentration of different salts, and the percentage difference in solubility.

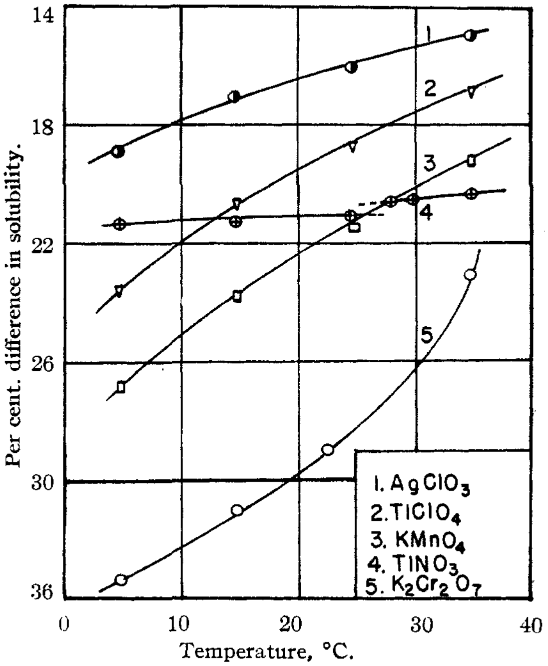

Fig. 3.—Solubility difference of salts in light and heavy water as a function of temperature.

Mercuric cyanide was chosen as an example of an inorganic compound which is nearly un-ionized. The solubility difference apparently extends to this type of compound.

Summary

1. Twelve sparingly soluble salts having high temperature coefficients of solubility have been studied in light and heavy water mixtures.

2. Solubility data at 5–35° in light and heavy water mixtures are given for silver chlorate, thallous perchlorate, potassium permanganate, thallous nitrate and potassium dichromate. Solu-

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(15) Ricci, THIS JOURNAL, **56**, 290 (1934).

(16) Seidell, *loc. cit.*, p. 1214.

bility differences varying from 15–33% less than that in light water were observed.

3. Solubilities in water–deuterium oxide of cesium nitrate, potassium silver cyanide, potassium chlorate, sodium bromate, sodium oxalate and mercuric cyanide are given at 5° and that of lead chloride at 25°. The latter is 36.3% less soluble in deuterium oxide than in water.

4. The solubility of potassium dichromate in light and heavy water at 25° has been measured and is a linear function of the deuterium content of the solvent.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Conductivities of Alkylammonium Chlorides in Aqueous Solutions of Their Homologs

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The effect of various salts and acids upon the equivalent conductivity of dodecylammonium chloride has been recently described,[1] the method employed being a determination of the conductivity by difference of the amine salt solutions in the presence of salt solutions of various concentrations. The presence of either salts or acids greatly decreases the equivalent conductivity of dilute solutions of alkylammonium chlorides. The critical concentration is markedly reduced by the presence of salts; however, the effect of acids upon the critical concentration is apparently much less. These results can be attributed to a decreased solubility of the long-chain ions in the presence of such electrolytes and can be related to the salting-out properties of the various ions.

The alkylammonium chlorides range from ordinary uni-univalent electrolytes to typical colloidal electrolytes depending upon the length of the alkyl chain. This transition has been shown[2] to occur at octylammonium chloride, since its lower homologs do not show evidence of micelle formation in aqueous solution, whereas its higher homologs progressively increase in colloidal properties with increase in molecular weight. A low molecular weight alkylammonium chloride, such as hexylammonium chloride, would be expected to affect the conductivity of a cationic colloidal electrolyte in the same manner as a salt. The effect of the presence of lower homologs upon the critical concentrations of anionic colloidal electrolytes has been investigated by Corrin and Harkins,[3] who reported that if the tendency of the components to aggregate is quite dissimilar, the soap with the lower aggregation value acts as a salt toward the other soap.

From the foregoing it is evident that the effect of an electrolyte such as an inorganic salt, an acid, or a lower molecular weight soap or alkylammonium salt upon the electrical conductance of a colloidal electrolyte is generally predictable. Much valuable information can be obtained, however, if the added electrolyte itself is a colloidal electrolyte, and it is the purpose of this paper to present a study of the electrical conductivities of cationic colloidal electrolytes in the presence of various concentrations of other cationic colloidal electrolytes. This has been accomplished by determining the conductivity by difference of an alkylammonium chloride, such as dodecylammonium chloride, in a solution which contains a known concentration of another alkylammonium chloride, for example, tetradecylammonium chloride. It must be clearly realized that since the conductivity by difference is obtained by subtracting the conductivity of the solution employed as the solvent from the conductivity of the solution which contains both electrolytes, the conductivity by difference combines the total conductivity change occasioned by the addition of the second electrolyte. In certain instances, discussed herein, this leads to an unreal value for the conductivity of the added electrolyte. On the other hand, the conductivity by difference does show the mutual effect of the mixed electrolytes, and the proper interpretation of these effects can yield valuable information concerning the colloidal properties of one or both of the components.

Recent work upon the electrical conductivities of mixtures of cationic colloidal electrolytes has shown that both components of such mixtures are included in the micelles and that the change of slope at the critical concentration is as abrupt for mixtures as it is for pure compounds. A study of the equivalent conductivities of mixtures of dodecyl- and octadecylammonium chlorides[4] has shown that the conductance values and also the critical concentrations are intermediate between those of the two amine salts. The critical concentrations of compounds of similar structure are a function of the chain lengths,[1] and it has been observed that dodecylammonium chloride and dodecylammonium acetate and also mixtures of these salts possess identical critical concentrations. If, therefore, one determines the conductivity by difference of a higher alkylammonium chloride in a solution of a homolog which is also a colloidal electrolyte, the concentration of the original solution being below the critical concentration, the curve

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[1] A. W. Ralston and D. N. Eggenberger, THIS JOURNAL, **70**, 980 (1948).

[2] A. W. Ralston and C. W. Hoerr, *ibid.*, **64**, 772 (1942).

[3] M. L. Corrin and W. D. Harkins, *J. Colloid Sci.*, **1**, 469 (1946).

[4] A. W. Ralston and C. W. Hoerr, THIS JOURNAL, **69**, 883 (1947).