Summary

1. Silver chloride precipitated at room temperature and aged in the mother liquor is subject to a rapid decrease of the surface as measured by the adsorption of wool violet. The aging is most pronounced in 0.001 *M* chloride in water as well as in ethanol, less as an equivalent body and the least in 0.001 *M* silver solution.

2. An explanation has been offered of the fact that silver chloride ages more rapidly as a "chloride body" than as an "equivalent body." Evidence has been presented that the Ostwald ripening is of subordinate significance.

3. Ammonia promotes the aging, the effect increasing with the concentration of ammonia.

4. Freshly precipitated silver chloride adsorbs about twice the amount of wool violet from a solution containing an excess of silver as from a solution containing an excess of chloride on the saturated surface. After one hour of aging the amount of dye adsorbed on the saturated surface is independent of the kind of lattice ion present in excess in the solution. An interpretation of this behavior has been presented.

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[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

The Vapor Pressures and Activity Coefficients of Aqueous Solutions of Ammonium Chloride at 25°[1]

BY J. N. PEARCE[2] AND G. G. PUMPLIN

Continuing the investigation of activity coefficients of salts in aqueous solution by the dynamic vapor pressure method devised by Pearce and Snow, as previously discussed,[3,4] the results on ammonium chloride solutions are here reported. The attempt to apply the method to cupric sulfate solutions gave anomalous results. The apparatus used was exactly the same as reported by Pearce and Blackman.[4]

Reagent grade ammonium chloride, purified by three recrystallizations, was made up into a nearly saturated solution, which was carefully analyzed gravimetrically for its chloride content by precipitation as silver chloride. Solutions of the required molality were made up on the weight-molal basis by dilution of the concentrated solution with conductivity water.

The essential data are collected in Table I. The values of p given are the mean of three or more independent determinations, with a maximum deviation of 0.004 mm. from the mean. The symbols used have their familiar significance. The activity of the water, a_1, is calculated directly from the fact that $a_1 = p/p^0$.

The geometric mean activity coefficients of the ions, $\gamma_\pm$, were calculated from the activity of the solvent by means of the relation[5]

$$\log \gamma_\pm = \frac{-h}{2.303} - \frac{2}{2.303}\int_0^{m^{1/2}} \frac{h}{m^{1/2}}\, dm^{1/2}$$

where $h = (55.51 \ln a_1/\nu m) + 1$, and νm is the total number of ions furnished by m moles of solute.

Randall[6] has shown that for uni-univalent salts, a plot of $h/m^{1/2}$ against the square root of the molality has the limiting value of 0.394 at $m = 0$ for 25°. This plot is shown in Fig. 1. To calculate the value of the activity coefficient of any solution of molality m, the value of the integral from $m = 0$ to m was determined, using a polar planimeter.

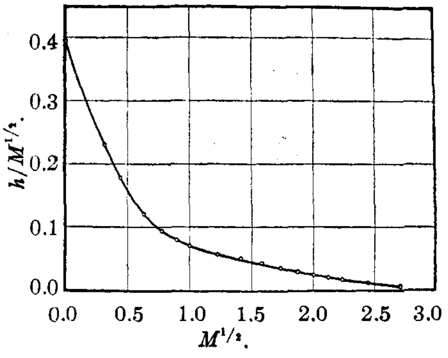

Fig. 1.

The change in free energy accompanying the transfer of one mole of ammonium chloride from

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(1) Part of the dissertation presented to the Graduate College of the State University of Iowa by Gerald G. Pumplin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Deceased Nov. 14, 1936.

(3) Pearce and Nelson, THIS JOURNAL, **54**, 3544 (1932); **55**, 3075 (1933).

(4) Pearce and Blackman, *ibid.*, **57**, 24 (1935).

(5) Randall and White, *ibid.*, **48**, 2514 (1926).

(6) Randall, *ibid.*, **48**, 2512 (1926).

any concentration m to a solution in which its activity is unity was calculated by the relation $\Delta\bar{F}_2 = RT \ln a_2$, where $a_2 = (\gamma_{\pm} m)^2$. The values of $\Delta\bar{F}_2^{0.1}$, the free energy change accompanying the dilution of a solution of concentration m to one exactly 0.1 m, are obtained by subtracting the value of $\Delta\bar{F}_2$ for $m = 0.1$ from the other values of $\Delta\bar{F}_2$. The change in free energy accompanying the transfer of one mole of solvent from the pure solvent to any solution in which its activity is a_1 is calculated by means of the relation: $\Delta\bar{F}_1 = RT \ln a_1$. The activity of the solvent, the activity coefficients, and the free energy data are given in Table I. The variation of the activity coefficients with concentration is shown in Fig. 2, along with those for sodium chloride and potassium chloride. A minimum is noted in each case, the position of which indicates the relative degree of hydration of the cation. The lower the concentration at which the minimum occurs, the higher the degree of hydration. The order $Na^+ > K^+ > NH_4^+$ for the relative degree of hydration of these chlorides agrees with that obtained cryoscopically by Bourion and Rouyer,[7] and by Sugden.[8]

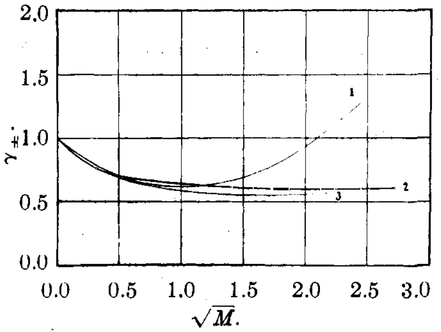

Fig. 2.—The change of activity coefficient with concentration: 1, sodium chloride; 2, ammonium choride; 3, potassium chloride.

TABLE I

VAPOR PRESSURE, ACTIVITY, AND FREE ENERGY DATA OF AQUEOUS SOLUTIONS OF AMMONIUM CHLORIDE AT 25°

m	p, mm.	a_1	$h/m^{1/2}$	$\gamma_{\pm}$	$-\Delta\bar{F}_1$, cal.	$-\Delta\bar{F}_2^{0.1}$ cal.
0.0	23.752	1.0000	0.394	1.000	...	...
.1	23.673	0.9967	.2308	0.765	1.98	0
.2	23.595	.9934	.1787	.721	3.93	752
.4	23.438	.9868	.1209	.686	7.89	1515
.6	23.281	.9802	.0942	.668	11.88	1964
.8	23.125	.9736	.0801	.655	15.86	2282
1.0	22.970	.9671	.0708	.646	19.85	2530
1.5	22.588	.9510	.0573	.628	29.79	2977
2.0	22.215	.9353	.0518	.617	39.66	3298
2.5	21.841	.9195	.0433	.610	49.73	3549
3.0	21.462	.9036	.0357	.605	60.11	3755
3.5	21.084	.8877	.0294	.604	70.63	3935
4.0	20.709	.8719	.0243	.603	81.28	4092
4.5	20.338	.8563	.0203	.604	91.98	4234
5.0	19.974	.8409	.0172	.604	102.69	4360
6.0	19.250	.8105	.0114	.607	124.58	4581
7.3800[a]	18.281	.7697	.0057	.611	155.19	4834

[a] Saturated.

The determination of the activity coefficients of cupric sulfate in solution in the same manner as for ammonium chloride gave results which were not in good agreement with the best e. m. f. data available.[9–11] Hydrolytic effects in the cupric sulfate solutions apparently render this method inapplicable.

Summary

The vapor pressure over aqueous solutions of ammonium chloride is lowered from 23.673 mm. at 0.1 m to 18.281 mm. at 7.3800 m (saturation). The activities of the solvent, the geometric mean activity coefficients of the solute, and the free energies of dilution have been calculated from the vapor pressure data.

The method employed did not give satisfactory results using cupric sulfate.

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(7) Bourion and Rouyer, *Compt. rend.*, **197**, 52 (1933).

(8) Sugden, *J. Chem. Soc.*, **129**, 174 (1926).

(9) Nielson and Brown, THIS JOURNAL, **49**, 2423 (1927).

(10) Getman, *J. Phys. Chem.*, **34**, 1454 (1930).

(11) Wetmore and Gordon, *J. Chem. Phys.*, **5**, 60 (1937).