Behavior of AgClO$_4$ in Water and in Benzene

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The freezing points and vapor pressures of silver perchlorate in water and in benzene are reported for concentrations up to its solubility limit. The existence of un-ionized dimers and trimers previously reported to exist in benzene has been confirmed, and to much higher concentrations than had previously been measured.

Silver perchlorate, in addition to being extremely soluble in water, is quite soluble in many organic solvents and is therefore one of the few inorganic salts which is experimentally accessible to oil–water partitioning studies. A comprehensive study of the system silver perchlorate–water–benzene was undertaken by Hill (4) more than 50 years ago and has provided us with much of our present knowledge of the phase equilibria in this interesting system. Recently, however, some relevant solvent activity measurements have been made in this laboratory and have been combined with Hill's results to form the basis of this publication.

The octanol–water partition coefficient for any toxic substance is a widely used (6) parameter in physiological transport studies and it would have been interesting to measure its value; however, in view of the tendency of perchlorates to form explosive compounds with alcohols, this measurement was not made. It was, however, possible to predict that it would be about 5 × 10^{-4} on the molar scale.

Experimental Section

There are several cautionary notes in the literature (e.g., ref 1 and 2) stating that silver perchlorate, either by itself or in mixtures with organic solvents, can explode. For this reason, I worked only with very small samples of the salt and always kept the sample behind a heavy transparent shield.

The silver perchlorate used in this study was precipitated from aqueous solution at 0 °C with perchloric acid, dried at 110 °C, and stored over Mg(ClO$_4$)$_2$. Because of the extremely hygroscopic nature of the AgClO$_4$ it was necessary to redry the salt periodically and to make the weighings quickly and at low relative humidity. The experiment was not facilitated by the bulky shielding but was concluded without incident, much to the relief of the author.

Three sets of results are reported here: aqueous freezing point measurements to 1 mol kg^{-1}, aqueous isopiestic measurements at 298 K to 31 mol kg^{-1}, and isopiestic measurements at 293 K in dry benzene to 0.5 mol kg^{-1} and in wet benzene to 6.7 mol kg^{-1}.

The freezing point measurements were made on an Advanced Instruments 3R osmometer (7) which had been calibrated with aqueous sodium chloride. A conventional isopiestic apparatus (8) was used to measure solvent activities over both aqueous and benzene solutions of silver perchlorate. Sodium chloride and calcium chloride were used as reference salts for the aqueous solutions (9), and recrystallized benzil was used for a reference material in the benzene solutions, using osmotic coefficients tabulated in ref 10. The moisture content of the benzene solutions was controlled by the inclusion of a dish of phosphorus pentoxide in the apparatus in the case of the "dry" solutions and by the inclusion of a dish of dilute sodium chloride in the case of the "wet" solutions. In the latter case the relative humidity was kept at greater than 90% but less than 100%,

Table I. Freezing Points of Aqueous AgClO$_4$

m, mol kg^{-1}	θ, mK	$\phi_{F.P.}$
0.012 97	47.6	0.986
0.019 46	70.9	0.979
0.025 68	93.2	0.976
0.051 94	184.0	0.952
0.086 72	304.6	0.944
0.095 26	332.8	0.939
0.146 39	509.0	0.935
0.179 81	621.8	0.929
0.242 3	829.5	0.920
0.302 9	1032	0.917
0.364 5	1235	0.911
0.412 2	1388	0.905
0.826 7	2732	0.889
0.972 6	3205	0.887

Table II. Isopiestic Concentrations of AgClO$_4$ in Water at 298 K

m_{NaCl}, mol kg^{-1}	ϕ_{NaCl}	m_{AgClO_4}, mol kg^{-1}	ϕ_{AgClO_4}
0.1651	0.927	0.1638	0.934
0.2775	0.922	0.2765	0.926
0.3780	0.921	0.3779	0.922
0.4540	0.920	0.4530	0.922
0.6837	0.926	0.6881	0.920
0.8238	0.930	0.8304	0.922
0.8438	0.931	0.8548	0.919
1.0397	0.938	1.0520	0.927
1.2909	0.948	1.3134	0.932
1.7512	0.970	1.7994	0.944
2.1884	0.995	2.2709	0.959
2.4420	1.009	2.5315	0.974
2.7277	1.027	2.8625	0.979
3.3980	1.071	3.6088	1.009
3.7588	1.097	4.0302	1.023
3.9260	1.109	4.2213	1.031
4.4558	1.148	4.8534	1.054
5.0432	1.193	5.5642	1.081
2.778^a	1.672	6.292	1.107
2.975	1.752	6.928	1.128
3.428	1.939	8.450	1.180
3.896	2.136	10.126	1.232
4.559	2.407	12.646	1.302
4.740	2.477	13.319	1.322
5.129	2.621	14.892	1.354
5.295	2.679	15.540	1.369
5.681	2.802	17.080	1.398
6.596	3.021	20.503	1.458
7.217	3.106	22.703	1.481
8.331	3.169	26.145	1.515
8.412	3.171	26.407^b	1.515
8.586	3.175	26.956	1.517
9.613	3.185	30.022	1.530
10.181	3.191	31.595	1.542

^{a} CaCl$_2$ used as reference material at this and higher concentrations. ^{b} Saturated AgClO$_4$.

which could have caused precipitation of water in the benzene. The benzene was thus kept nearly saturated with water, with the latter having a mole fraction of about 0.002.

Results and Discussion

The aqueous freezing point results are shown in Table I and the aqueous isopiestic results are shown in Table II, along with the osmotic coefficients of both the reference salt and the

Table III. Isopiestic Concentrations of AgClO₄ in Benzene at 293 K

m_{benzil}, mol kg⁻¹	m_{AgClO_4}, mol kg⁻¹	ϕ_{AgClO_4}	$a_{benzene}$	a_{water}
0.0386	0.0742	0.511	0.9970	0
0.0472	0.0970	0.477	0.9964	0
0.0675	0.1438	0.457	0.9949	0
0.0845	0.1855	0.441	0.9936	0
0.0983	0.2228	0.425	0.9926	0
0.1112	0.2608^a	0.409	0.9917	0
0.1928	0.5159	0.344	0.9862	0
0.2652	1.126^b	0.216	0.9811	0.96
0.4112	1.789	0.206	0.9716	0.94
0.4209	2.98	0.126	0.9710	0.90
0.6786	6.70	0.087	0.953	0.91

^{a} Dry benzene saturated with AgClO₄. ^{b} This and following concentrations are corrected for the presence of a trace of water.

sodium perchlorate at each concentration. Both sets of results are precise to about 0.003 in ϕ. The last three isopiestic results are for solutions which were supersaturated with silver perchlorate. A general equation, developed by Pitzer (5) was fitted to each of these two sets of results. The equation

$$\phi = 1 - \frac{A_\phi \sqrt{m}}{1 + 1.2\sqrt{m}} + (\beta^{(0)} + \beta^{(1)}e^{-2\sqrt{m}})m + Cm^2$$

had coefficients A_ϕ = 0.377, $\beta^{(0)} \simeq$ +0.03, $\beta^{(1)} \simeq$ +0.3, and $C \simeq$ 0 at the freezing temperature, and A_ϕ = 0.392, $\beta^{(0)}$ = +0.0615, $\beta^{(1)}$ = +0.32, and C = -0.0013 at 298 K. Because the Pitzer equation was not intended to fit accurately the inflections and high concentrations which are encountered here, the 298 K coefficients are only usable to about 15 mol kg⁻¹, to which concentrations they will reproduce the experimental values to within 0.05 in ϕ. These same coefficients can be used to calculate mean molal activity coefficients, γ, for the salt, using the following equation, also due to Pitzer (5).

$$\ln \gamma = -A_\phi \left\{ \frac{\sqrt{m}}{1 + 1.2\sqrt{m}} + \frac{2}{1.2} \ln (1 + 1.2\sqrt{m}] \right\} +$$
$$\left\{ 2\beta^{(0)} + \frac{\beta^{(1)}}{2m}[1 - e^{-2m^{1/2}}(1 + 2\sqrt{m} - 2m)] \right\} m + \frac{3}{2}Cm^2$$

The results for silver perchlorate dissolved in benzene are presented in Table III and are plotted in Figure 1. Also plotted are the freezing point data of Hill. Rather than report the results as osmotic coefficients, I have plotted the mole fraction activity coefficients of the benzene against mole fraction of the solute. This plot cannot be linear (3) over its whole concentration range but it is useful in the low solute concentration region for illustrating a deduction already made by Hill, namely, that his freezing point results can be explained by the existence of dimers and trimers of silver perchlorate in benzene. The two solid lines were calculated on the assumption that the solute behaved ideally except for association (the line corresponding to monomers is the abscissa). It can be seen that at concentrations up to 0.5 mol kg⁻¹ AlClO₄ the results can be explained by a mixture of
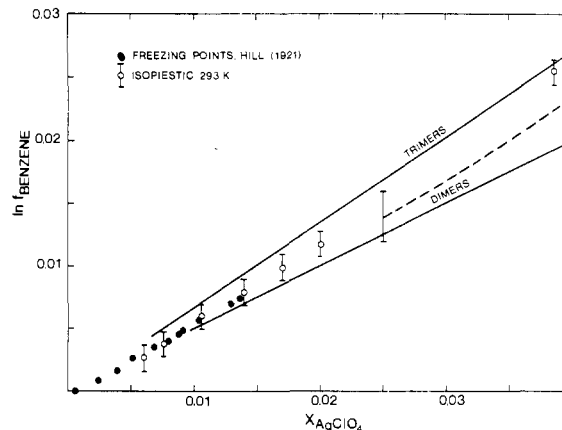

Figure 1. Mole fraction activity coefficient of dry benzene in solutions containing a small fraction of silver perchlorate. The dotted line is an extrapolation of higher concentration results obtained in wet benzene.

predominantly dimers and trimers, with some monomers being present only at the very lowest concentrations. This is what Hill deduced on the basis of his measurements, which extended up to 0.15 mol kg⁻¹ (4). The figure also indicates that the behavior of silver perchlorate in wet benzene is indistinguishable from that in anhydrous benzene. Furthermore, there is no detectable temperature coefficient over the range investigated, in contrast to the behavior of the salt in water, which is characterized by a positive partial molal enthalpy.

Hill (4) has reported the partition coefficient of silver perchlorate between benzene and water as having a value of about 2×10^{-5}. Many of the partition coefficients for salts in the compilation by Leo et al. (6) are about 25 times higher between octanol and water than between benzene and water so that an estimated octanol-water partition coefficient for silver perchlorate would be 5×10^{-4} on the molar scale.

Glossary

θ	aqueous freezing point, in mK
ϕ	molal osmotic coefficient defined as $-1000 \ln a_s/\nu m w_s$, where a_s is the solvent activity, m is the solute molality, w_s is the solvent molecular weight, and ν is defined as 2 in water and 1 in benzene
x	mole fraction
f	mole fraction activity coefficient, a_s/x_s

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