Competitive Interactions in the Complexing of Ethylene with Silver(I) Salt Solutions

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Conditions which maximise silver(I)–olefin interactions are not suitable for obtaining comparative equilibrium data. Measurements of ethylene absorption efficiencies at 20 °C (C_2H_4: Ag^I ratios) in aqueous silver(I) nitrate, trifluoroacetate, and perchlorate solutions are reported over a pressure and concentration range and with added acid and sodium salts; some results are also given for glycol solutions. The trends in absorption efficiencies are correlated with silver(I)–anion interactions in competition with silver(I)–solvent interactions and with the structure-making influence of ions on the solvent. Single effects cannot explain the experimental observations. Some previous results are reinterpreted, making allowances for anion and solvent effects.

THE interaction of silver(I) cations with olefins has been studied extensively,[1-3] Practical and theoretical objectives, respectively, have been to attain an optimum efficiency in the separation and purification of olefins, and to correlate the extent of silver(I)–olefin interaction with the olefin structure. These objectives are conflicting in that the former requires concentrated solutions of silver(I) salts to maximise the olefin absorption in a given volume, whereas the latter requires dilute solutions to calculate true equilibrium constants. Any review of the literature soon reveals that measurements of the latter kind have been made at comparatively high concentrations of silver(I) salts and that extrapolations to zero concentration have neglected, or incorrectly allowed for, the effect of the counter-ion. Structural differences between silver(I)–olefin complexes deduced from non-comparable formation constants can lead to dubious theory. Theoretical calculations [4,5] have also tended to oversimplify the situation by neglecting interactions other than the silver(I)–olefin interaction. In this paper a more detailed study of the factors influencing the complexing of silver(I) by the simplest olefin (C_2H_4) is presented and some previous results are re-examined.

EXPERIMENTAL

Silver(I) salts were prepared from a suspension of silver(I) carbonate in water and the corresponding acid. The solution of the silver(I) salt was filtered from the excess of carbonate and evaporated to dryness *in vacuo* at 60—100 °C. Silver contents were checked by Volhard's method. Silver(I) perchlorate was maintained as a concentrated stock solution which was analysed and diluted as required. Ethylene (99·9%, B.O.C.) was used without further purification.

A constant-pressure manometric apparatus incorporating greaseless vacuum taps (Figure 1) was used to measure ethylene solubilities in aqueous and non-aqueous solutions. Constant temperature was maintained by pumping water at 20·00 ± 0·05 °C around the apparatus. The ethylene was initially presaturated with vapour of the appropriate solution. The solution (*ca.* 1 cm^3) was placed in the reaction flask, tap B was closed, and taps C and A opened to evacuate and then fill the apparatus with ethylene (*ca.* 1 atm). While the solution was stirred magnetically (*ca.* 20 min), more dry ethylene was admitted *via* A until the final pressure was *ca.* 10 cm above the barometric pressure.

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[1] S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, 1938, **60**, 836.

[2] M. A. Bennett, *Chem. Rev.*, 1962, **62**, 611.

[3] H. W. Quinn and J. H. Tsai, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 217.

[4] H. Hosoya and S. Nagakuru, *Bull. Chem. Soc. Japan*, 1964, **37**, 249.

[5] R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, 1970, **92**, 5589.

When no further change in levels was observed, the gas phase was assumed to be saturated with solvent vapour.

The reaction vessel was removed after closing tap C and replaced by a similar vessel containing a measured volume of the same solution on the surface of which rested a thin foil of Polythene. (The solution volume was chosen to give a gas absorption of 10—20 cm³.) The magnetic follower was held in the neck of the flask by a second external magnet. The flask was quickly evacuated *via* B, then C was opened and the excess of pressure in the reservoir of saturated gas allowed to decrease to within a few cm of atmospheric. By careful manipulation of tap A, the total pressure in the apparatus was set at exactly 1 atm. (Pressures above or below 1 atm could be set in a similar way.) During this short adjustment period, the Polythene foil minimised the gas–liquid interface and prevented solution of gas. The Polythene was then displaced by allowing the magnetic follower to drop into, and stir, the solution. The volume of gas dissolved was measured in the gas burette by maintaining the initial pressure during the process. After deducting the partial pressure of the solution, the volume of ethylene dissolved at n.t.p. was calculated and expressed as moles of ethylene per mole of silver(I). The reproducibility of the technique was checked with 0·1M-$AgNO_3$ (Found: $C_2H_4 : Ag^I$ 0·389, 0·391, and 0·385) at 20 °C and 1 atm. Rates of absorption were in the same order as the equilibrium constants [$AgClO_4$ > $Ag(CF_3CO_2)$ > $AgNO_3$] for the silver(I) salt solutions.

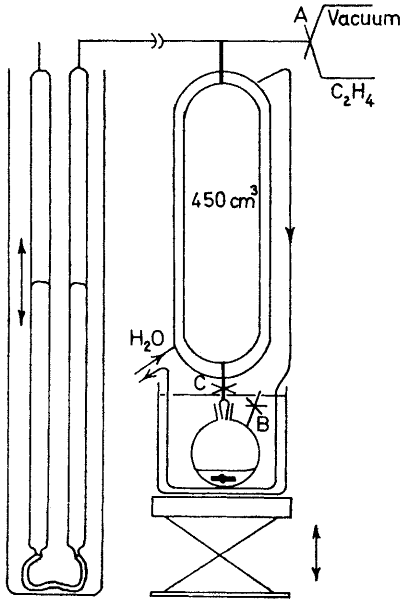

FIGURE 1 Gas-absorption apparatus

RESULTS

Solution vapour pressures were calculated assuming ideality; errors involved were negligible since the partial pressure of ethylene above all solutions at 20 °C only varied from 0·977 to 0·980 atm. An allowance for dissolved but uncomplexed ethylene in solution was obtained by determining the solubility of ethylene in solutions with sodium ions in place of silver(I) ions. Again, because the salting-out effect of the anion is a second-order correction, only sodium nitrate solutions were measured and the interpolated values used for all silver(I) salt solutions.

TABLE 1

Solubility of ethylene in aqueous sodium nitrate solutions at 20 °C and 1 atm total pressure

$[NaNO_3]$/M	$10^3[C_2H_4]$/M
0·00	4·24
0·20	3·56
1·00	2·84
3·00	1·67
7·00	0·00

TABLE 2

Solubility of ethylene in aqueous silver(I) salt solutions at 20 °C and 1 atm total pressure

Initial composition			Final composition	
Concn. / M	Density / kg dm^{-3}	Solute mole fraction	Mole ratio * $C_2H_4 : Ag^I$	Total vol.† of C_2H_4 / Vol. of solution
$AgNO_3$				
0·10	1·00	0·002	0·352	0·89
0·50	1·01	0·009	0·346	4·02
1·00	1·07	0·018	0·339	7·81
3·00	1·14	0·056	0·276	18·95
5·00	1·41	0·098	0·218	25·04
7·00	1·68	0·140	0·194	30·75
8·95	1·94	0·277	0·17	34·10
$Ag(CF_3CO_2)$				
0·10	1·01	0·00178	0·322	0·80
0·50	1·07	0·00928	0·335	3·98
1·00	1·14	0·0191	0·320	7·27
2·00	1·32	0·0395	0·316	14·2
3·00	1·48	0·0618	0·306	20·6
4·00	1·61	0·0901	0·304	27·3
4·75	1·74	0·1123	0·327	34·9
$AgClO_4$				
0·092	1·01	0·00167	0·383	0·89
0·459	1·07	0·00845	0·340	3·64
0·919	1·16	0·01686	0·353	7·44
1·838	1·28	0·0355	0·406	17·05
3·676	1·58	0·0744	0·474	39·71
5·521	1·92	0·1383	0·544	68·80
$Ag(MeSO_3)$				
1·00	1·13	0·019	0·320	7·17
2·00	1·28	0·040	0·290	13·00
3·00	1·43	0·062	0·245	16·47
$Ag(PhSO_3)$				
0·50			0·331	3·71
1·00			0·311	6·97
1·20			0·310	8·34

* Obtained after deducting the ethylene solubility in an equimolar $NaNO_3$ solution. † Includes uncomplexed ethylene; volume reduced to n.t.p.

Effect of Pressure.—Two solutions of each salt were examined over a small pressure range; ethylene exhibits behaviour similar to that of an ideal gas over this range. The correction for uncomplexed ethylene in solution was calculated from the results at 1 atm assuming the validity of Henry's law. The final solution composition is expressed as [(total ethylene − uncomplexed ethylene)/total silver(I)] and assuming a 1 : 1 complex as complexed silver(I)/uncomplexed silver(I). From the latter an equilibrium constant, $K_E = [Ag(C_2H_4)^+]/[Ag(aq)^+]p_{C_2H_4}$, can be evaluated which could be converted to a single-phase constant, using a Henry's law constant appropriate to the pure solvent, when K_E was extrapolated to zero concentration of the silver(I) salt solution.

Effect of Added Electrolyte.—Three series of observations were carried out with 0·5M-silver(I) nitrate, trifluoroacetate, and perchlorate solutions. The respective acids or sodium salts of the acid were added in increasing amounts to these solutions and the mole ratio of complexed ethylene to total silver(I) determined after correcting for uncomplexed ethylene.

Effect of Solvent.—The glycol ethane-1,2-diol was used as solvent in place of water. Because its vapour pressure only reaches 1 mm at 53 °C, the partial pressure of ethylene after equilibration with glycol solutions was taken as equal to the total pressure.

TABLE 3

Effect of pressure on ethylene solubility in aqueous silver(I) salt solutions at 20 °C

Initial composition			Final composition		
Concn. of salt M	Total pressure atm	Partial pressure of C_2H_4 atm	Mole ratio Complexed C_2H_4 : total silver(I)	$\frac{[Ag(C_2H_4)^+]}{[Ag(aq)^+]}$	K_E
0·1 ($AgNO_3$)	1·053	1·03	0·367	0·580	0·56
	1·026	1·00	0·356	0·553	0·55
	1·000	0·98	0·352	0·543	0·55
	0·934	0·91	0·334	0·506	0·56
	0·686	0·66	0·264	0·359	0·54
	0·488	0·47	0·191	0·236	0·50
7·0 ($AgNO_3$)	1·079	1·056	0·191	0·235	0·22
	1·053	1·031	0·192	0·237	0·23
	1·000	0·978	0·178	0·217	0·22
	0·921	0·899	0·176	0·214	0·24
	0·641	0·619	0·103	0·115	0·19
	0·395	0·373	0·071	0·076	0·20
2·0 [$Ag(CF_3CO_2)$]	1·233	1·210	0·378	0·607	0·50
	1·000	0·977	0·316	0·462	0·47
	0·717	0·694	0·255	0·342	0·49
	0·412	0·368	0·100	0·111	0·30
4·0 [$Ag(CF_3CO_2)$]	1·220	1·198	0·356	0·553	0·46
	1·000	0·979	0·304	0·437	0·45
	0·680	0·659	0·238	0·312	0·47
	0·556	0·535	0·188	0·231	0·43
0·5 ($AgClO_4$)	1·134	1·112	0·370	0·586	0·53
	1·000	0·978	0·345	0·527	0·54
	0·647	0·625	0·235	0·307	0·49
	0·568	0·546	0·199	0·248	0·46
2·0 ($AgClO_4$)	1·418	1·396	0·522	1·093	0·78
	1·000	0·978	0·415	0·709	0·73
	0·749	0·727	0·350	0·539	0·74
	0·514	0·492	0·219	0·281	0·58

TABLE 4

Effect of added electrolytes on ethylene solubility in 0·5M-silver(I) salt solutions at 20 °C and 1 atm total pressure

Salt	Concn. of added sodium salt or acid M	Mole ratio Complexed C_2H_4 : total silver(I)	Ion product $[Ag^+][Anion^-]$
$AgNO_3$	0	0·345	0·25
	1·00 ($NaNO_3$)	0·281	0·75
	2·00 ($NaNO_3$)	0·237	1·25
	3·00 ($NaNO_3$)	0·219	1·75
	1·51 (HNO_3)	0·333	1·25
	3·02 (HNO_3)	0·354	1·76
	4·53 (HNO_3)	0·393	2·51
$Ag(CF_3CO_2)$	0	0·335	0·25
	1·00 $Na(CF_3CO_2)$	0·315	0·75
	2·00 $Na(CF_3CO_2)$	0·286	1·25
	3·00 $Na(CF_3CO_2)$	0·276	1·75
	1·28 $H(CF_3CO_2)$	0·364	0·89
	2·56 $H(CF_3CO_2)$	0·422	1·53
	3·84 ($H(CF_3CO_2)$	0·565	2·17
$AgClO_4$	0	0·349	0·25
	1·00 $NaClO_4$	0·349	0·75
	2·00 $NaClO_4$	0·351	1·25
	3·00 $NaClO_4$	0·377	1·75
	1·17 $HClO_4$	0·424	0·83
	2·34 $HClO_4$	0·502	1·42
	3·51 $HClO_4$	0·583	2·00

DISCUSSION

Our results with silver(I) nitrate solutions can be compared directly with those of Featherstone and Sorrie [6] obtained by a transpiration technique (Figure 2).

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[6] W. Featherstone and A. J. S. Sorrie, *J. Chem. Soc.*, 1964, 5235.

TABLE 5

Solubility of ethylene in ethane-1,2-diol solutions at 20 °C and 1 atm total pressure

Initial composition			Final composition	
Concn. / M	Density kg dm^{-3}	Solute mole fraction	Mole ratio C_2H_4 : Ag	Total vol. of C_2H_4 / Vol. of solution
$AgNO_3$				
0·50	1·15	0·0283	0·184	2·05
1·00	1·21	0·0563	0·160	3·56
2·00	1·36	0·1084	0·162	7·21
4·00	1·62	0·2087	0·160	14·24
$Ag(CF_3CO_2)$				
0·10	1·12	0·0056	0·208	0·46
1·00	1·24	0·0573	0·170	3·79
2·00	1·37	0·1178	0·180	8·04
4·00	1·68	0·2374	0·175	15·60
$AgClO_4$				
0·09	1·12	0·0050	0·272	0·56
0·46	1·16	0·0254	0·234	2·41
0·92	1·25	0·0511	0·226	4·53
1·84	1·40	0·1007	0·356	14·62
2·76	1·54	0·1502	0·431	24·63
3·68	1·71	0·1941	0·580	47·79
4·66	1·89	0·2382	0·642	67·02

There is satisfactory agreement except at the lowest molarities. Repeated measurements in 0·1M-solutions gave concordant results and the previous value was considered incorrect. This discrepancy is due partly to the neglect of uncomplexed ethylene in solution, but mainly to the increasing inaccuracy inherent in the previous method at low concentrations (*i.e.* minimal weight change and loss of transpired water vapour).

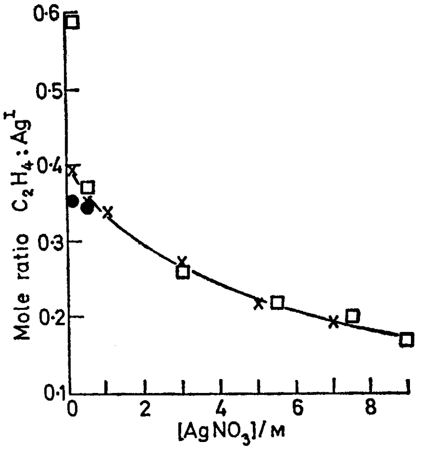

FIGURE 2 Absorption efficiency of silver(I) nitrate solutions: (●), corrected for uncomplexed C_2H_4; (□), ref. 6

Results for other salts are summarised in Figure 3. The absorption efficiency, defined by the ratio of either dissolved or complexed ethylene to total silver(I), can have a negative concentration dependence [$AgNO_3$, $Ag(MeSO_3)$, and $Ag(PhSO_3)$], a positive dependence ($AgClO_4$ and $AgBF_4$), or be almost invariant [$Ag(CF_3CO_2)$]. The cause of this variation needs to be interpreted if meaningful equilibrium constants are to be assigned and hence the strength of silver(I)–olefin interactions compared.

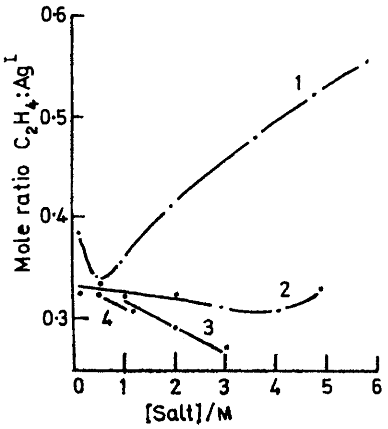

FIGURE 3 Absorption efficiency of silver(I) salt solutions: 1, $AgClO_4$; 2, $Ag(CF_3CO_2)$; 3, $Ag(MeSO_3)$; 4, $Ag(PhSO_3)$

Featherstone and Sorrie advanced the following explanation in terms of equilibria (1)—(3) (X = NO_3 and ClO_4).

$$Ag^+ + \text{olefin} \rightleftharpoons [Ag(\text{olefin})]^+ \quad (1)$$

$$Ag^+ + [Ag(\text{olefin})]^+ \rightleftharpoons [Ag_2(\text{olefin})]^{2+} \quad (2)$$

$$[Ag(\text{olefin})]^+ + HX \rightleftharpoons Ag^+ + (H\text{olefin})^+ X^- \quad (3)$$

As the concentration of silver(I) salt increases, the solubility of the olefin declines because of reaction (2) and hence the olefin : silver(I) ratio falls initially. As the concentration of silver(I) is further increased, the acidity due to hydrolysis favours reaction (3) and releases more silver(I) ions for complexing; the olefin : silver(I) ratio then increases. The minimum in the latter was held to depend on the acidity of HX and the basicity of the olefin. Thus, for a given olefin, the stronger the acid the lower the concentration at which this minimum should occur. This explanation is untenable for the following reasons. (*a*) Perchloric acid is fully dissociated in water and is only about twice as strong as nitric acid, but a minimum in the $C_2H_4 : Ag^I$ ratio is found with the perchlorate and not with the nitrate salt. The strongest acids are levelled in aqueous solutions and are not differentiated. (*b*) Previous work indicates that the 1 : 1 complex is predominant and the influence of equilibrium (2) is irrelevant, except perhaps at the highest concentrations of silver(I) or at low partial pressures of olefin. (*c*) The extent of hydrolysis is small;[7] it is of the order of 0·1% in aqueous silver(I) nitrate. In 1M-solutions the hydrolysis reaction (4) is reported for which p*K* = 11·52 and pH 3.

$$2Ag^+ + 2H_2O \rightleftharpoons (AgOH)_2 + 2H^+ \quad (4)$$

Appreciable protonation of olefins is not encountered at such weak acidities and indeed the authors[6] found that olefins were not soluble to any extent in more strongly acid solutions (4·5M-fluoroboric acid). The displacement reaction (3) is even less probable than

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[7] 'Gmelin Handbook of Inorganic Chemistry, Silver,' 1970, Part B1, p. 227.

direct protonation, since water protonation is much more favoured than olefin protonation.

That the different behaviour of the various silver(I) salts was not caused by formation of complexes with different stoicheiometries, was demonstrated by following the pressure dependence of olefin absorption, for each of the three types of silver(I) salts, at two concentrations chosen to be above and below the reputed minimum $C_2H_4 : Ag^I$ ratios. An experimental equilibrium constant can be calculated at each concentration for reactions of type (5). When $n = 1$, $K_E = [Ag(\text{olefin})^+]/[Ag(aq)^+]p_{\text{olefin}}$, where p_{olefin} is the partial pressure of the olefin in atm. Hence the ratio of complexed olefin to uncomplexed silver(I) should be linearly dependent on the olefin partial pressure. This was confirmed with two silver(I) nitrate solutions at the extremes of the concentration range. The lowest points deviate slightly as would be expected when the $Ag^I : C_2H_4$ ratio is maximised [Figure 4(*a*)]. Similar results hold for silver(I) perchlorate and trifluoroacetate solutions, except that for the latter a single curve fits the results at both concentrations because the $C_2H_4 : Ag^I$ ratio is almost independent of concentration [Figure 4(*b*)].

$$Ag^+ + n(\text{olefin}) \rightleftharpoons [Ag(\text{olefin})_n]^+ \qquad (5)$$

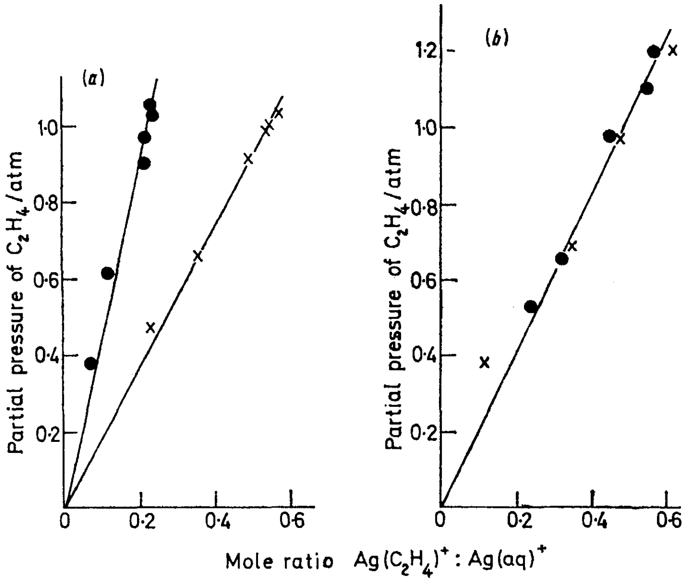

FIGURE 4 Effect of pressure on absorption efficiencies in (*a*) silver(I) nitrate solutions: (●), 7M; (×), 0·1M, (*b*) silver(I) trifluoroacetate solutions: (●), 4M; (×), 2M

It would seem reasonable to correlate the drop in absorption efficiency with rising silver(I) nitrate concentration to self-complexing of silver(I) nitrate in solution. The structure of solid silver(I) nitrate[8] shows how complexing can occur; each silver(I) ion has a seven- or eight-fold oxygen-atom co-ordination consisting of two bidentate nitrate groups and three or four other monodentate nitrate groups. A saturated solution of silver(I) nitrate at 20 °C has only 4·36 water molecules available for each silver(I) ion, and hence in strong solutions there is barely enough water to form primary aquation shells for ion separation; some type of aggregation of silver(I) ions *via* linking bidentate nitrate groups is possible and has been confirmed by Raman spectroscopic observations on melts and solutions.[9] Recent ion-transport results in silver(I) nitrate solutions, treated by the formalism of non-equilibrium thermodynamics, show the increase in cation–anion interaction with increasing concentration.[10]

This explanation is not applicable when the absorption efficiency has a minimum, or rises with increasing concentration. The types of curve in Figure 3 are also encountered with curves of molal depression of freezing point against concentration for different aqueous electrolytes, and it seems reasonable to invoke similar interpretations couched in variable activity terms.[11,12] A thermodynamic equilibrium constant would be of the form $K = [Ag(\text{olefin})^+]\gamma_{Ag(\text{olefin})^+}\alpha_{H_2O}/[Ag(aq)^+]\gamma_{Ag(aq)^+}$ at an atmosphere pressure of olefin, to allow for water displacement on complexing [equation (6)]. The activity of water (α_{H_2O}) in silver(I) salt solutions equilibrated with olefins has not been reported. However, if our experimental equilibrium constants for silver(I) nitrate are approximately corrected with water activities derived from freezing-point data, the inconstancy which remains above 3M concentrations requires the activity-coefficient ratio to increase with increasing concentration, *i.e.* nitrate complexing of $[Ag(H_2O)_m]^+$ is greater than that of $[Ag(H_2O)_{m-1}(\text{olefin})]^+$. In general one cannot assume, as have previous workers, that the silver(I) ion activity ratio is always unity and that K_E is dependent on water activity any more than the converse. In concentrated solutions, especially with polarising electrolyte additions, the water activity term is likely to predominate.

$$[Ag(H_2O)_m]^+ + \text{olefin} \rightleftharpoons [Ag(H_2O)_{m-1}(\text{olefin})]^+ + H_2O \qquad (6)$$

where $m = 2$—4

The physical basis for activity variation arises from competition of Ag^+–anion, Ag^+–solvent, and anion–solvent interactions with the Ag^+–olefin interaction. From our results, the Ag^+–anion interaction decreases in the sequence $NO_3^- > CF_3CO_2^- > ClO_4^-$, accepting this interaction as the main competing interaction. In the absence of specific hydrogen-bonding interactions, this sequence can be controlled by the availability of electron density at donor oxygen sites on the oxo-anions. A charge sequence on the oxygen atoms of NO_3^- (0·33 e), $CF_3CO_2^-$ (*ca.* 0·33 e), and ClO_4^- (0·25 e)

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[8] P. F. Lindley and P. Woodward, *J. Chem. Soc.* (*A*), 1966, 123.

[9] R. E. Hester and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 769.

[10] N. Roessler and H. Schneider, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 1225.

[11] R. W. Gurney, 'Ionic Processes in Solution,' McGraw-Hill, New York, 1953, ch. 16.

[12] J. Hildebrand, *J. Chem. Educ.*, 1971, **48**, 224.

can be estimated, using reasonable resonance contributions, by Pauling's method.[13] Similarly the observed sequences $ClO_4^- > BF_4^- > SbF_6^-$ and $MeCO_2^- > NO_3^- > CF_3CO_2^-$ are expected allowing for the less polarisable nature of fluorine donor sites. The anion–water interaction, given by lyotropic and similar series[14] with a decreasing order of anion interaction $RCO_2^- > NO_3^- > ClO_4^- > PF_6^-$, acts in unison with the silver(I)–anion interaction. The Ag^+–solvent interaction is considered later.

The effect of additions of weakly and strongly polarising cations (Na^+, H^+) on ethylene absorption in 0·5M-silver(I) salt solutions is shown in Figure 5. Addition of acid raises the efficiency in each series, but least for nitric acid; addition of sodium salts is least effective with the perchlorate. The effect produced by perchloric acid represents the uninhibited influence of added hydrogen ions, since the perchlorate anion has no detectable effect. At the other extreme, the nitrate ion competes successfully with ethylene for the silver(I) species in solution. Consequently, with nitric acid addition, the nitrate ion works in opposition to the hydrogen ion. At lower concentrations, the cation and anion additions operate almost independently, as shown when the differences between hydrogen and sodium ion additions are plotted on a common abscissa (Figure 6). These results extend Baker's[15] observations on fluoroborate additions to silver(I) fluoroborate solutions, and have an important bearing on the intercomparison of experimental equilibrium constants determined by different workers who have ignored, or misinterpreted, interactions other than that of Ag^+–olefin.

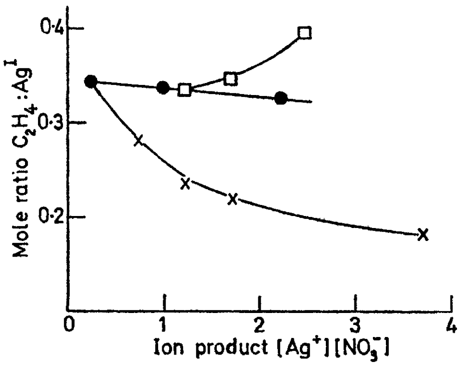

FIGURE 5 Effect of acid and salt additions on absorption efficiencies: (□), HNO_3; (●), $AgNO_3$; (×), $NaNO_3$

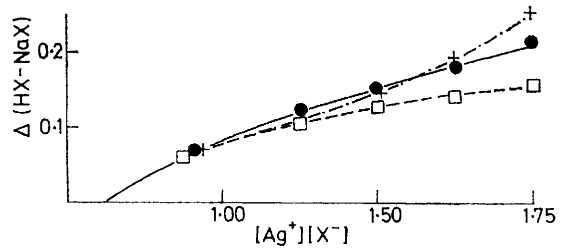

FIGURE 6 Plot of the difference between the acid and salt additions against silver(I)–anion ion product X = ClO_4 (●), CF_3CO_2 (+), and NO_3 (□)

Thus Brandt[16] measured an equilibrium constant between aqueous silver(I) ions and ethylene manometrically. He compared his value for a 1 : 1 complex (94·0 ± 0·5 l mol^{-1} at 25 °C) with that obtained by Trueblood and Lucas[17] (85·3 l mol^{-1}) who partitioned ethylene between carbon tetrachloride and aqueous silver(I) salt solutions. The rough correspondence is deceptive because the aqueous phases were quite different. Brandt used the solution 0·1M-$AgNO_3$–0·875M-CF_3CO_2H–0·025M-CF_3CO_2H whereas Trueblood and Lucas used 1M-$AgNO_3$ and 0·5M-$AgNO_3$–0·5M-KNO_3 solutions. Although all three solutions have unit ionic strengths, our work on electrolyte additions lead us to expect significant differences in the experimental equilibrium constants determined in these solutions. In Brandt's solution, the depression in ethylene absorption caused by NO_3^- ions is roughly cancelled by the acidity contribution. Since the $CF_3CO_2^- : NO_3^-$ ratio is 9 : 1, the solution is similar to a 0·1M-$Ag(CF_3CO_2)$ solution and the equilibrium constant would not change much on extrapolation to zero concentration (see Figure 3).

The ethylene absorption efficiency at 20 °C for 1M-$AgNO_3$ is 0·339 and 0·315 for 0·5M-$AgNO_3$–0·5M-$NaNO_3$ (Figures 2 and 5), and hence the ratio of these values (1·076 : 1) should approximate the ratio of experimental equilibrium constants found by Trueblood and Lucas (98·1 ± 1·0 : 91·7 ± 1·7 = 1·070 ± 0·02 : 1). The latter authors assumed the difference between the equilibrium constants in the two media was caused by the presence of a disilver(I) complex and calculated equilibrium constants of 85·3 l mol^{-1} and 0·15 l^2 mol^{-2} for the formation of 1 : 1 and 2 : 1 complexes. The sequence of equilibrium constants in 1M-$AgNO_3$ (98·1), Brandt's solution (94·0) and 0·5M-$AgNO_3$–0·5M-KNO_3 (91·7 l mol^{-1}) is therefore in the expected order. Other data in the literature can be considered in this manner.[1]

The Ag^+–solvent interaction is constant in aqueous solutions and can be neglected when comparing silver(I)–olefin complexes in such solutions. However, if the solvent contains more polarisable oxygen (or nitrogen) sites than are encountered in aqueous Ag^+–H_2O and Ag^+–anion interactions, then the solvent interacts preferentially with silver(I) and olefin cannot displace it from the solvated cation. Thus methyl cyanide solutions which form stable $Ag(MeCN)_4^+$ ions do not absorb ethylene. An order of increasing Ag^+–solvent interactions CH_2Cl_2, $PhNO_2$, PhCl, $MeNO_2$, EtOCOMe, $MeOCH_2{\cdot}CH_2OMe$, $HCON(Me)_2$ is derivable from the range of equilibrium constants obtained in these solvents.[18]

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[13] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, New York, 1960, p. 320.

[14] M. J. Blandamer and M. F. Fox, *Chem. Rev.*, 1969, **69**, 75.

[15] B. B. Baker, *Inorg. Chem.*, 1964, **3**, 200.

[16] P. Brandt, *Acta Chem. Scand.*, 1959, **13**, 1639.

[17] K. N. Trueblood and H. J. Lucas, *J. Amer. Chem. Soc.*, 1952, **74**, 1338.

[18] J. Solodar and J. P. Petrovich, *Inorg. Chem.*, 1971, **10**, 395.

An extensive collection of equilibrium constants have been obtained by passing olefin vapours over silver(I) nitrate solutions in the glycol ethane-1,2-diol on gas-chromatography columns.[19] Because these constants are often compared with data from aqueous solutions, we have made a comparative study of ethylene absorption by silver(I) salts in glycol and water (Figure 7). The behaviour of $AgClO_4$ and $Ag(CF_3CO_2)$ is similar in both solvents, but the $AgNO_3$ absorption in glycol is more uniform in comparison with water, suggesting a suppression of the association present in water. Whilst this justifies the Muhs and Weiss extrapolation method[19] it shows the danger of comparing data at arbitrary nitrate-ion concentrations in the two solvents. An extreme example was encountered by Franzus *et al.*[20] who found that the Ag^+-*syn*-7-acetoxynorbornene complex was more stable than the *anti*-form in 1M-aqueous silver(I) nitrate solution, and suggested that additional co-ordination *via* the acetoxy-group stabilised the former. However, the *anti*-form gives the more stable complex when equilibria are measured in silver nitrate(I)–glycol solutions by the gas-chromatographic method. Our observations would suggest that the Ag^+–glycol interaction is successfully competing with that of Ag^+–acetoxy-group. In the *anti*-complex four co-ordination sites around the silver(I) ion could be occupied in a bidentate manner by the glycol and in a monodentate manner by the nitrate group and the olefin. In the *syn*-complex, further co-ordination from the acetoxy-group would sterically destabilise the complex.

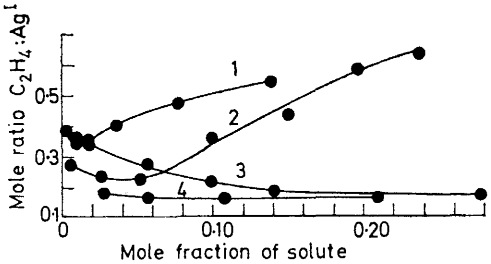
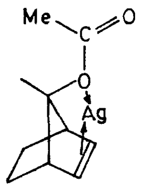
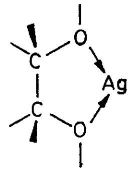


FIGURE 7 Absorption efficiencies in glycol (2, $AgClO_4$; 4, $AgNO_3$) compared with those in water (1, $AgClO_4$; 3, $AgNO_3$)



syn – Acetoxynorbornene complex



Ethane-1,2-diol complex

We conclude that equilibrium constants for silver(I)–olefin complexes in solution can only be meaningfully compared when due consideration is paid to interactions other than that of silver(I)–olefin, especially those due to anion and solvent effects. Silver(I) ion-catalysed rearrangements would also be expected to be influenced by solvent and counter-ion effects.[21]

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[19] M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, 1962, **84**, 4697.

[20] B. Franzus, W. C. Baird, E. J. Snyder, and J. E. Surridge, *J. Org. Chem.*, 1967, **32**, 2845.

[21] L. O. Paquette, *Accounts Chem. Res.*, 1971, **4**, 285.