309. *The Conductivity of Silver Salts in Non-aqueous and Mixed Solvents. Part VI.*[1]

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The effects of *cyclo*pentadiene, di*cyclo*pentadiene, polystyrene, and benzene on the conductivity of silver perchlorate in acetone have been observed.

Silver ions are preferentially solvated by nitrogenous basic components of binary non-aqueous solvent mixtures.[1b–e] The extent of this depends upon the mobility of the π electrons on the nitrogen atom of the bases concerned. This property of silver ions was demonstrated conductometrically and accounted for on the basis of their electrophilic nature. Similar solvent–ion interaction occurs between silver ions and olefinic or aromatic solvents.[2,3] Conductometric measurements at 1500 cycles/sec. detected qualitatively an interaction between benzene and silver ions [1e] but the apparatus used was not sufficiently sensitive for quantitative measurements.

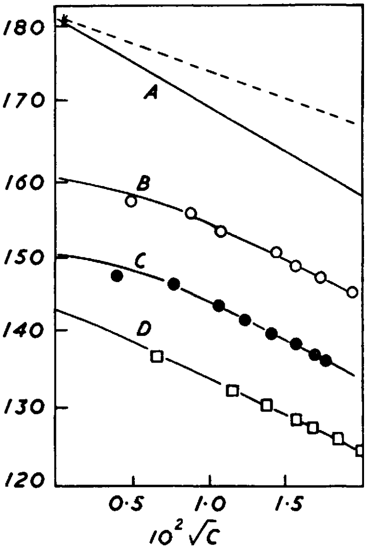

Fig. 1. *Equivalent conductivity of silver perchlorate in: A, pure acetone; B, 1%* cyclo*pentadiene in acetone; C, 1% di*cyclo*pentadiene in acetone; D, the polystyrene suspension. The broken line is the theoretical Onsager slope.*

It was felt that interaction involving an olefin might be measurable by this method if the molecular weight of compound was high enough for the mobility of any complex ions formed to be severely impaired. Polystyrene was chosen, as some specimens of this polymer, although theoretically saturated, do contain olefinic groups. Certain difficulties were encountered. Owing to the extremely low solubility of polystyrene in acetone the conductivity of " saturated " solutions, which were formed by prolonged shaking of polystyrene with pure acetone, was not reproducible. However, addition of a solution of polystyrene in benzene to a large excess (1 : 100) of acetone, gave a " fine suspension " of polystyrene. The conductivity of such mixtures was reproducible and although the system now unfortunately becomes more complex, the large effect of the addition of a benzene–polystyrene mixture on the conductivity of silver perchlorate in acetone is most striking in view of the extremely small effect of benzene.[1e]

Moffitt's theoretical investigations,[4] later confirmed by Pfab and Fischer [5] and Eiland

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[1] (*a*) Part I, *J.*, 1954, 686; (*b*) Part II, *J.*, 1955, 1208; (*c*) Part III, *ibid.*, p. 2797; (*d*) Part IV, *J.*, 1956, 473; (*e*) Part V, *J.*, 1957, 3243.

[2] Winstein and Lewis, *J. Amer. Chem. Soc.*, 1938, **60**, 836.

[3] Taufen, Murray, and Cleveland, *ibid.*, 1941, **63**, 3500.

[4] Moffitt, *ibid.*, 1954, **76**, 3386.

[5] Pfab and Fischer, *Z. Naturforsch.*, 1952, **7b**, 377.

and Pepinsky,[6] showed that " sandwich molecules " are formed between *cyclo*pentadiene and transition-element atoms which contain two vacant or singly occupied *d* orbitals. Although silver ions do not fulfil these electronic requirements, it was expected that some form of complex-ion formation should occur with *cyclo*pentadiene; study of di*cyclo*pentadiene should indicate whether this is of the " sandwich molecule " type. Hence the conductivity of silver perchlorate in the above polystyrene mixture and in 99% acetone–1% *cyclo*pentadiene and in 99% acetone–1% di*cyclo*pentadiene was investigated and compared with that in pure acetone [1e] (Fig. 1).

TABLE 1. *Dielectric constant* (ε), *equivalent conductivity at infinite dilution* (Λ_0), *Stokes radius* (r_+), *and Bjerrum parameter* (a) *determined as in Part V.*[1e]

Solvent	$10^4\varepsilon$	Λ_0	r_+ (Å)	a (Å)
Pure Acetone	5·4	181·5	2·86	2·14
1% *cyclo*Pentadiene	16·9	160	3·87	2·64
1% Di*cyclo*pentadiene	14·1	150	4·54	2·55
Polystyrene suspn.	26·2	143	3·66	9·46

We attempted to measure quantitatively the effect of benzene on the conductivity of silver perchlorate in acetone which was detected with a 1500 c./sec. bridge by using a 10,000 c./sec. transformer ratio-arm bridge [7] with an oscilloscope as detector, and a special conductivity cell (Fig. 2). In order rapidly to mix the benzene added to a solution of silver perchlorate in acetone contained in this cell, a slow stream of nitrogen pre-saturated with acetone vapour could be introduced just above the electrodes. Benzene could be added dropwise through a capillary tube, one drop weighing 0·050 ± 0·0005 g. for the capillary used, so the oscilloscope screen showed the effect of a given mass of benzene on the conductivity of a quantitatively-prepared solution of silver perchlorate in acetone.

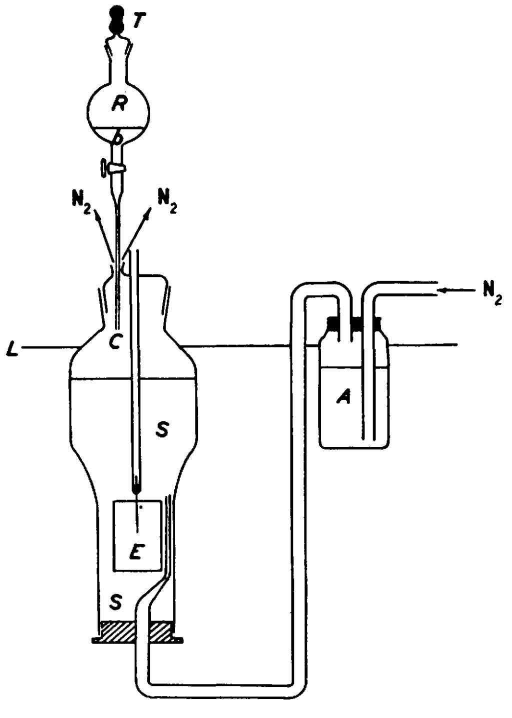

FIG. 2. *Apparatus*: *T, Rubber teat*; *R, reservoir*; *b, benzene*; *C, fine capillary*; *L, oil level in thermostat*; *S, solution*; *A, pure acetone*; *E, electrodes.*

Photographic paper was moved past the oscilloscope screen by a powered camera to

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[6] Eiland and Pepinsky, *J. Amer. Chem. Soc.*, 1952, **74**, 4971.

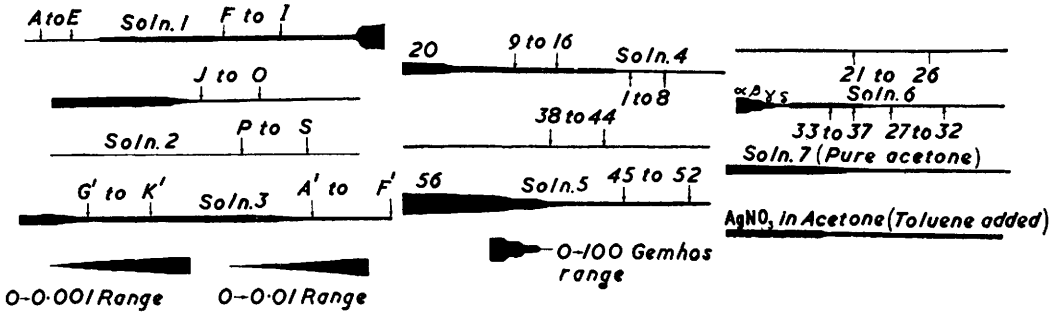
[7] Calvert, Cornelius, Griffiths, and Stock, *J. Phys. Chem.*, 1958, **62**, 47.

record traces (Fig. 3) whose thickness, determined with a travelling microscope, measured the degree of " off balance " of the bridge and hence, by calibration, quantitative changes in conductivity.

*cyclo*Pentadiene, di*cyclo*pentadiene, and polystyrene all decrease Λ_0 and increase the dissociation constant of silver perchlorate in acetone. A comparison of the values of the dissociation constant, Λ_0, and Stokes's radii (Table 1) for the 1% *cyclo*pentadiene solution with those of a 1% pyridine solution [1c] indicates that the *cyclo*pentadienyl complex ion is the more bulky and that preferential solvation is more extensive in this solvent. Hence the *cyclo*pentadienyl complex ion probably contains more than one *cyclo*pentadiene molecule.

The effect of di*cyclo*pentadiene is also of interest. A greater decrease in Λ_0 is produced than for the monomer whereas the dissociation constant does not increase to the same extent. Thus it now appears that the di*cyclo*pentadienyl complex ion is more bulky than the *cyclo*pentadienyl ion and yet that preferential solvation of the latter is the more extensive. We have already deduced that the *cyclo*pentadienyl ion probably contains more than one organic molecule and if this applies to the dimer we should expect a larger, not smaller, dissociation constant for the latter. Hence it is most likely that the di*cyclo*pentadienyl complex ion contains only one di*cyclo*pentadiene molecule and that the relatively greater mobility of the *cyclo*pentadiene complex, which on this basis is of virtually the same mass, is due to easy packing of the monomeric molecules round the silver ion such as would occur for a " sandwich molecule " structure. This structure is further supported by r_+ and a for the two mixtures. Although the Stokes radius increases in going from the *cyclo*pentadiene to the di*cyclo*pentadiene complex, as is consistent with the conception of a compact rather than a diffuse complex, the values of the Bjerrum parameter are approximately the same. This is reasonable because the " sandwich molecule " structure shields the ion from approach in any direction whereas any structure formulated for a complex between one silver ion and one tricyclic, and hence necessarily uniplanar, molecule, must allow easy approach of the ion in at least one direction.

FIG. 3. *Examples of photographic traces.*



The complex nature of the conducting system in the polystyrene suspension makes the conclusions most tentative. Although the decrease in conductivity appears at first sight to be very large, closer examination, particularly of the unusually high dissociation constant, reveals that it is not so large as might be expected. This is reflected in the relative values of the Bjerrum parameter and Stokes radius, the former being exceptionally large in this solution. The decrease in conductivity may be partly due to the adsorption of silver ions on undissolved polymer particles. However this is at variance with the observation that large variations in the concentration of polystyrene in the solvent mixture had little or no effect on the decrease in conductivity. An alternative, more likely, explanation is that one polystyrene molecule can form a complex with more than one silver ion; one complex ion may be quite highly charged and this would so affect its mobility as to compensate partially for its large bulk. It will also be uncertain whether the Bjerrum parameter measures the distance of closest approach of the large complex ions or the mean distance of separation of silver ions within the large complex ions.

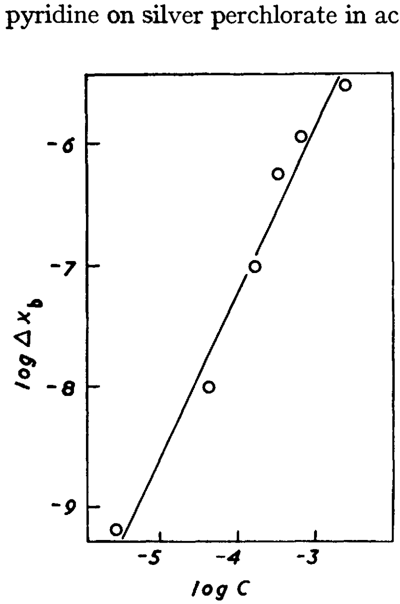


FIG. 4.

The value of the conductometric results at 10,000 c./sec. for the effect of benzene and pyridine on silver perchlorate in acetone (Table 2; κ_i and κ_f are the specific conductivities before and after addition of masses m_b or m_p of benzene or pyridine respectively and C the molar concentration of silver perchlorate) is impaired by the large errors involved. For example, although the maximum error involved in the gross conductivity measurements made was probably 0·05—0·5%, this becomes a possible error of 40% when a difference factor such as $\Delta\kappa_b$ is considered.

The decrease in conductivity observed when benzene is added to a solution of silver perchlorate in acetone being assumed to be due to the formation of stoicheiometric complex ions, the concentration of the ionic complex should depend linearly on the concentration of both benzene and silver ions. For present purposes this means that the decrease in conductivity caused by the benzene, $\Delta\kappa_b$, should be proportional to the concentration of silver ions, C, and, since the volumes of the solutions used were always the same to within 2 or 3%, to the mass of benzene added, m_b. Hence $\Delta\kappa_b/C$ and $\Delta\kappa_b/m_b$ should both be constant for all solutions used. Table 3 shows that although $\Delta\kappa_b/C$ is constant to within a factor of ten, $\Delta\kappa_b/m_b$ is not, since it varies by more than three thousandfold. Thus, the large errors being borne in mind, $\Delta\kappa_b/C$ is probably constant (see Fig. 4), and this merely indicates that the reduction in conductivity is due to a reduction in the mobility of the silver ions. The large variation in $\Delta\kappa_b/m_b$ however shows that the conductometric effect of the benzene is not continuously dependent on the quantitative composition of the binary solvent mixture.

TABLE 2.

Soln.	1*a*	1*b* *	2*a*	2*b* •	3	4	5	6	7 †
10^5C	17·13	17·13	64·39	64·39	280·9	30·54	3·927	0·253	0
m_b (g.) ...	0·220	0·0	0·356	0·220	0·238	0·238	0·238	0·238	0·238
m_p (g.) ...	0·05	0·05	0·05	0·10	0·10	0·10	0·10	0·50	0·10
κ_i	$3·57 \times 10^{-5}$	$3·56 \times 10^{-5}$	$1·33 \times 10^{-4}$	$1·35 \times 10^{-4}$	$3·62 \times 10^{-4}$	$4·97 \times 10^{-5}$	$6·89 \times 10^{-6}$	$5·58 \times 10^{-7}$	$5·045 \times 10^{-8}$
κ_f	$3·39 \times 10^{-5}$	$3·39 \times 10^{-5}$	$1·28 \times 10^{-4}$	$1·28 \times 10^{-4}$	$3·53 \times 10^{-4}$	$4·71 \times 10^{-5}$	$6·775 \times 10^{-6}$	$5·63 \times 10^{-7}$	$5·515 \times 10^{-8}$

* No trace taken. † Addition of benzene caused a measured increase of $2·43 \times 10^{-9}$ mho.

TABLE 3.

Soln.	10^5C	m_b (g.)	$\Delta\kappa_b$	$\Delta\kappa_b$ (%) *	$10^3\Delta\kappa_b/C$	$10^8\Delta\kappa_b/m_b$
6	0·2534	0·238	$6·98 \times 10^{-10}$	0·125	0·276	0·294
5	3·927	0·238	$1·00 \times 10^{-8}$	0·145	0·255	4·21
1	17·13	0·220	$9·64 \times 10^{-8}$	0·270	0·563	43·8
4	30·54	0·238	$7·77 \times 10^{-7}$	1·54	2·54	323
2	64·39	0·356	$1·13 \times 10^{-6}$	0·846	1·75	317
3	280·9	0·238	$2·50 \times 10^{-6}$	0·691	0·890	1050

* $\Delta\kappa_b$ (%) = $\Delta\kappa_b$ expressed as a percentage of κ_i.

These facts are therefore not consistent with the formation of stoicheiometric complex ions as claimed by Taufen, Murray, and Cleveland.[3] It is possible that silver ions, moving through a solution under the influence of an applied potential, tend to drag benzene molecules with them owing to the affinity between the electrophilic ions and the π bonds of the aromatic molecules. Apparently here again the effect should depend in some way on the benzene concentration but in this case it need not be of a linear nature. The " toluene trace " (Fig. 3) supports this. Toluene, when added to a silver nitrate solution, causes an increase in conductivity which is consistent with the effects of organic bases on solutions of this salt [1c] and suggests that it is the aromatic nature of benzene which is responsible for its effect on silver ions. The theory of the formation of loose benzene–silver ion aggregates in solution, although basically different from the theory of stoicheiometric complex-ion formation as suggested by Taufen, Murray, and Cleveland, need not be totally incompatible with their results.

Experimental.—The use of the 1500 c./sec. bridge was described earlier.[1a] Di*cyclo*pentadiene was purified by two distillations and *cyclo*pentadiene was prepared by "cracking" the dimer in a 14 in. glass tube packed with glass helices. Benzene was purified by Rybicka and Wynne-Jones's method.[8] Polystyrene was reprecipitated from carbon tetrachloride with methyl alcohol.

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[8] Rybicka and Wynne-Jones, *J.*, 1950, 3671.