1002. *Silver–Hydrocarbon Complexes.*

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Complex formation between silver ions and olefins in aqueous solution varies much more with silver salt concentration than has hitherto been realised. In a dilute solution saturated with olefin, the olefin to silver mole ratio decreases rapidly at first with rising silver concentration and thereafter either rises again sharply or continues to decline gradually. The former behaviour is typical in fluoroborate or perchlorate solution but, in nitrate, the nature of the olefin concerned appears to be much more of a controlling factor. Both types of behaviour have been observed in silver nitrate solution. An explanation of the differing behaviour is put forward. The solubilities of a number of olefins in concentrated silver fluoroborate and nitrate solution are reported.

The solubility of an aromatic hydrocarbon in aqueous silver fluoroborate is much enhanced by addition of an olefin. The longer the carbon chain length of the olefin, the larger the synergistic effect. A possible explanation to account for this effect is suggested.

IT is well known that silver salts form complexes with olefins and aromatic hydrocarbons. The silver salts most commonly used have been the nitrate and perchlorate, whilst straight and branched chain aliphatic olefins, cyclic olefins, di-olefins, oxygenated olefin derivatives and aromatic hydrocarbons have been examined as organic components of the complex. These studies have not been exhaustive, being confined to the simpler or more commonly available olefins, and then only employing a narrow range of silver concentration.[1]

The present investigation extends the range of olefins and silver salt concentrations with the object of (a) correlating complexing ability with olefin structure, and (b) determining the effects, if any, observed on changing the silver salt concentration. Aqueous solutions of silver fluoroborate, nitrate, and perchlorate were used in the investigation.

In the course of this work, it was observed that the solubility of an aromatic hydrocarbon in an aqueous silver salt solution was appreciably raised by the presence of quite small amounts of complexed olefin. It was therefore of interest to investigate the competition between an olefin and an aromatic hydrocarbon in forming complexes with silver ions in aqueous solution.

EXPERIMENTAL

Materials.—Electrolytes. All electrolytes used were A.R. grade with the exception of the sodium fluoroborate (B.D.H. material, 98% pure).

Aqueous silver fluoroborate was prepared as follows: sodium carbonate (162 g.) dissolved in water was added to a solution of silver nitrate (520 g.) in water, and the mixture stirred at room temperature for 30 min. The precipitated silver carbonate was collected, washed and partially dried *in vacuo.*

Fluoroboric acid was prepared by adding boric acid (172 g.) over 10 min. to aqueous hydrofluoric acid (40% w/w, 555 g.) with stirring. The mixture was then stirred at room temperature for a further 30 min. Silver carbonate was added slowly to a stirred solution of fluoroboric acid until evolution of carbon dioxide ceased. After filtration to remove unchanged silver carbonate, the solution was concentrated to the required strength by distillation at reduced pressure. The above procedure yields *ca.* 350 ml. of silver fluoroborate solution containing 805 g. Ag per litre. Addition of hydrogen peroxide (0·5% w/w) stabilises the silver solution.

Hydrocarbons.—The following hydrocarbons were Phillips Petroleum Company, " Pure

[1] (a) Trueblood and Lucas, *J. Amer. Chem. Soc.*, 1952, **74**, 1338; (b) Hepner, Trueblood, and Lucas, *ibid.*, 1952, **74**, 1333; (c) Eberz, Welge, Yost, and Lucas, *ibid.*, 1937, **59**, 45; (d) Lucas, Moore, and Pressman, *ibid.*, 1943, **65**, 227; (e) Lucas, Billmeyer, and Pressman, *ibid.*, 1943, **65**, 230; (f) Winstein and Lucas, *ibid.*, 1938, **60**, 836.

Grade " (99%) material: but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, pent-1-ene, 3-methylbut-1-ene, 2-methylbut-2-ene, hex-1-ene, 4-methylpent-1-ene, *cis*-4-methylpent-2-ene, *trans*-4-methylpent-2-ene, 2-methylpent-1-ene, oct-1-ene, cyclohexene, n-heptane. 2-Ethylbut-1-ene (b. p. 64—66°), 2-ethylhex-1-ene (b. p. 120—122°), dec-1-ene (b. p. 169—171°), tetradec-1-ene (b. p. 126—128°/15 mm.), *m*-xylene (98% pure) were obtained from L. Light and Co. Ltd. A.R. grade benzene, 99·5% pure isobutene and polymerisation grade ethylene and propene were used. Styrene was B.D.H. material (stabilised with 10—20 p.p.m. tert.-butyl catechol). The compositions of the *cis/trans* pent-2-ene and oct-2-ene samples used are given in Table 1.

3,3-Dimethylbut-1-ene, 2-methylpent-2-ene, 4-methylhex-1-ene, 2,4-dimethylpent-1-ene were obtained from the American Petroleum Institute (purity >99%).

*Procedure.—Solubility of Gaseous Olefins.—*A stream of gaseous olefin was passed through a drying tube packed with pellets of potassium hydroxide and into a bubbler immersed in a thermostatically controlled bath and containing a weighed volume of the selected silver salt solution. The bubbler was connected to an absorption tube packed with pellets of potassium hydroxide, which was in turn linked to a small catchpot cooled to −50°. Gas was passed through the system until no further increase in the combined weight of bubbler plus absorption tube was recorded. The solubility of the gaseous olefin in the particular silver salt solution was then calculated.

*Solubility of Liquid Olefins and Aromatic Hydrocarbons.—*The solubilities of liquid olefins and aromatic hydrocarbons were determined in stoppered 15 or 20 mm. diameter tubes contained in air jackets, which were immersed in a thermostatically controlled bath. After the addition by pipette of a known volume of silver salt solution, each tube was weighed before the addition of an excess of hydrocarbon. The contents were then shaken vigorously at half-hourly intervals over a period of 2 hr. and finally allowed to settle for 1·5—2 hr. before the undissolved hydrocarbon was separated with a micropipette. The tube was re-weighed to determine the amount of olefin absorbed and the solubility calculated.
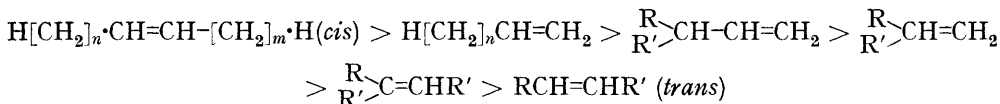
The same procedure was followed in obtaining the figures for the ternary and quaternary systems; in these cases, a mixture of olefin–aromatic hydrocarbon or olefin–aromatic hydrocarbon–paraffin was shaken with the silver salt solution.

*Analysis.—*Silver concentrations were determined by titration with potassium thiocyanate solution.

Analysis of the hydrocarbon mixtures before and after extraction with the silver salt solution was carried out by infrared or ultraviolet spectroscopy or gas–liquid chromatography.

RESULTS AND DISCUSSION

Complex Formation between Olefins and Silver.—Effect of olefin, molecular weight, and structure. The results in Table 1 show that the solubility of the various olefins at 1 atm. and 20° generally decreases with increasing molecular weight, but varies very considerably with structure for a given molecular weight. The position of the double bond in the chain, the steric configuration and the branching of side chains all have an effect on the solubility, which decreases, for a given homologue, in the following order,

$$H[CH_2]_n \cdot CH{=}CH{-}[CH_2]_m \cdot H(cis) > H[CH_2]_n CH{=}CH_2 > \underset{R'}{\overset{R}{>}}CH{-}CH{=}CH_2 > \underset{R'}{\overset{R}{>}}CH{=}CH_2$$

$$> \underset{R'}{\overset{R}{>}}C{=}CHR' > RCH{=}CHR' \ (trans)$$

The three lowest olefins are apparently anomalous in that their solubility at atmospheric pressure increases from ethylene to propene to the butenes. The solutions of these olefins, however, are not saturated under their own vapour pressure, as are those of the higher ones, and the solubilities are not strictly comparable.

A more fundamental way of comparing the various olefins would be in terms of an equilibrium constant for the reversible reaction

$$\text{Olefin} + \text{Ag ion} \rightleftharpoons \text{Complex}$$
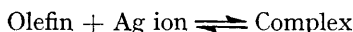
which would be of the form

$$K = \frac{(\text{Concentration of complex})}{(\text{Concentration of uncomplexed olefin}) (\text{Ag ion})}$$

Unfortunately, the solubility of uncomplexed olefin is not readily measured, and the reaction is not as simple as shown. The very strong effect of the anion would have to be allowed

TABLE 1.

Solubilities and relative complex stabilities of olefins in silver fluoroborate and nitrate.

Olefins	Solubility,* moles/mole silver salt in		Olefin vapour pressure, atm./20°	B. p.°/ 1 atm.
	Silver fluoroborate	Silver nitrate		
Ethylene	0·68	0·225	1	−102·4
Propene	0·78	0·23	1	−47·7
But-1-ene.............................	0·976	0·374	1	−6·47
cis-But-2-ene	1·04	0·39	1	3·73
trans-But-2-ene	0·61	0·09	1	0·5
Isobutene	0·94	0·21	1	−6·6
Pent-1-ene	1·066	0·29	0·7	30·1
3-Methylbut-1-ene	0·94	0·35	1	20
Pent-2-ene{90% *cis*/10% *trans*}*cis*	0·99 †	0·34 ‡	0·537	37
Pent-2-ene{85% *trans*/15% *cis*}*trans* ...	0·616 †	0·29 ‡	0·549	35·85
2-Methylbut-2-ene	0·9	0·245	0·506	38·6
Hex-1-ene	1·03	0·036	0·197	63·5
4-Methylpent-1-ene	0·83	0·03	0·291	53·8
3,3-Dimethylbut-1-ene	0·87	—	0·201	41·2
cis-4-Methylpent-2-ene	0·7	0·041	0·2604	56·4
trans-4-Methylpent-2-ene	0·25	—	0·237	58·6
2-Methylpent-1-ene	0·57	0·025	0·207	62
2-Ethylbut-1-ene	0·7	0·03	0·186	64·7
2-Methylpent-2-ene	0·35	—	0·166	67·3
4-Methylhex-1-ene.................	0·73	—	0·0766	86·7
2,4-Dimethylpent-1-ene...........	0·017	0·0054	0·0986	81·6
Oct-1-ene............................	0·97	0·009	0·0173	121·3
Oct-2-ene{50% *cis*/50% *trans*}	0·12	—	—	—
2-Ethylhex-1-ene	0·033	—	0·0196	120
Cyclohexene	1·03	0·26	0·088	83·2
Styrene	1·15	0·18	0·0063	146

* Solubilities were measured at 20°; silver nitrate of concentration 600 g./l. Ag and silver fluoroborate of 650 g./l. Ag were used. † Assuming solubilities are additive this corresponds to values of 1·04 and 0·54 moles/mole for pure *cis*- and *trans*-pent-2-ene, respectively. ‡ From these results, values of 0·35 for pure *cis*- and 0·28 for *trans*-pent-2-ene were calculated.

for, as well as changes in the composition of the complex with varying silver concentration. However, a tentative general conclusion may perhaps be drawn: the solubility of uncomplexed olefin should decrease appreciably with molecular weight and, since the solubility of complexed olefin of the same structure decreases but little, one may infer that the equilibrium shifts, if at all, in the direction of the complex as the molecular weight increases.

Silver Concentration and Complex Formation.—The variation of the solubility of an olefin with silver concentration in solutions of silver fluoroborate, perchlorate, and nitrate saturated with olefin is shown in Table 2. In dilute solution (0·1—*ca.* 2·0N) the olefin : silver mole ratio decreases rapidly with rising silver concentration and is independent of the anion employed. In fluoroborate and perchlorate, this ratio then increases steadily as the solution becomes more and more concentrated. The position of the minimum in fluoroborate or perchlorate solution depends only on the anion employed and is unaffected by the olefinic constituent of the complex. For perchlorate, this conclusion is based on a study of only two olefins, but is considered to be justified because silver perchlorate and fluoroborate are isomorphous. It is also of interest that the silver concentration at which the olefin : silver mole ratio was a minimum does not alter with temperature in the range 0—35° (see Fig. 1).

In nitrate solution much more variable behaviour was observed. With some olefins,

e.g., but-1-ene, cyclohexene, and styrene, the olefin : silver ratio passed through a minimum with rising silver concentration. Furthermore, the silver concentration at which the minimum occurred changed with the olefin. With other olefins, however, the above ratio decreased steadily with increasing silver concentration (see Table 2).

TABLE 2.

Relationship between solubility and silver concentration.

Olefin	Silver salt system	Solubility moles/unit Ag in aqueous solutions of Ag+ concentration at 20° N						
		0·1	0·5	1·0	5·0	5·5	7·5	8·95
Ethylene	AgNO₃	0·69	0·37	0·34	0·26	0·22	0·20	0·17
	AgNO₃–NaNO₃ *	0·21	0·18	0·18	0·16	0·17	0·20	—
	AgBF₄	0·7	0·4	0·46	0·52	0·62	0·84	—
Propene	AgNO₃	0·83	0·42	0·42	0·28	0·22	0·18	0·15
	AgNO₃–NaNO₃ *	0·6	0·14	0·16	0·13	0·15	0·18	—
	AgBF₄	1·07	0·41	0·44	0·47	0·75	0·98	—
	AgBF₄–NaBF₄ †	0·77	0·36	0·39	0·49	0·74	—	—
	AgClO₄	1·4	0·56	0·44	0·5	0·7	0·84	—
But-1-ene	AgNO₃	1·0	0·7	0·57	0·43	0·32	0·39	0·44
	AgNO₃–NaNO₃ *	0·5	0·32	0·17	0·18	0·25	0·39	—
	AgBF₄	1·15	0·8	0·61	0·69	0·92	1·1	—
Isobutene	AgNO₃	1·2	0·54	0·42	0·28	0·20	0·15	0·11
	AgNO₃–NaNO₃ *	0·54	0·2	0·12	0·095	0·12	0·15	—
	AgBF₄	1·4	0·56	0·45	0·5	0·88	1·19	—
	AgClO₄	1·6	0·7	0·5	0·47	0·85	1·1	—
Hex-1-ene	AgNO₃	0·45	0·15	0·13	0·05	0·036	0·041	0·042
	AgBF₄	0·48	0·16	0·15	0·16	0·78	1·3	—
4-Methylpent-1-ene	AgNO₃	0·2	0·16	0·17	0·05	0·03	0·02	—
	AgBF₃	0·6	0·21	0·11	0·11	0·8	1·24	—
2-Methylpent-1-ene	AgNO₃	—	0·095	0·08	0·05	0·03	0·02	—
	AgBF₄	—	0·11	0·11	0·13	0·58	1·12	—
Oct-1-ene	AgNO₃	0·35	0·05	0·04	0·015	0·007	0·002	—
	AgBF₄	0·6	0·06	0·04	0·01	0·86	1·58	—
Cyclohexene	AgNO₃	1·2	0·54	0·46	0·24	0·26	0·46	—
	AgBF₄	1·6	0·24	0·23	0·34	0·94	1·36	—
Styrene	AgNO₃	0·14	0·09	0·13	0·15	0·2	0·3	—
	AgBF₄	0·63	0·19	0·14	0·27	0·95	1·8	—

$* \mu = 7.5. \quad † \mu = 5.5.$

At each silver concentration, the amount of olefin dissolved per unit of silver depends on the anion. Thus, in dilute solution (0·1—*ca.* 2N) $ClO_4^- > BF_4^- \simeq NO_3^-$ whilst in concentrated solution ($\geqslant$5N) the order is $BF_4^- > ClO_4^- \gg NO_3^-$ (see Table 2).

It should be noted that the variation of olefin solubility observed on changing the silver concentration is not due to the change in the ionic strength of the medium; this behaviour was also observed in solutions of constant ionic strength (see Table 2). Addition of sodium nitrate to silver nitrate to maintain constant ionic strength exerted a salting out effect on the olefin, whereas in sodium fluoroborate–silver fluoroborate solutions of constant ionic strength the salting out was mild and only occurred in dilute solution. Addition of fluoroboric acid or its salts to concentrated silver fluoroborate has been shown to enhance olefin solubility.[2]

The following explanation is suggested to account for the behaviour described above. In dilute solution, we need consider only the solubility of the olefin, which determines the concentration of free olefin in the salt solution and the complex forming reactions:

$$Ag^+ + olefin \rightleftharpoons (Ag\ olefin)^+ \qquad (1)$$

$$Ag^+ + (Ag\ olefin)^+ \rightleftharpoons (Ag_2\ olefin)^{2+} \qquad (2)$$
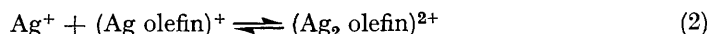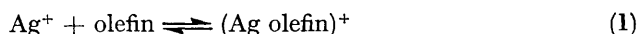
[2] (*a*) Krekeler, Hirschbeck, and Schwenk, Sixth World Petroleum Congress in Frankfurt, 1963, Section IV—Paper 14; (*b*) U.S.P. 3,007,981.

As the silver salt concentration is raised, the solubility of the olefin in the solution declines, the contribution of reaction (2) increases and thus the olefin : silver mole ratio falls. As the silver salt concentration continues to increase, however, the acidity of the solution will also rise, because hydrolysis and protonation of the complexed olefin will then start:

$$(Ag \ olefin)^+ + HBF_4 \rightleftharpoons Ag^+ + (olefin \ H)^+BF_4^-$$
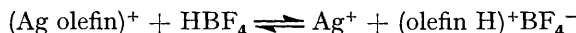
The freed ion can then complex with more olefin. On this basis, the silver concentration at which the minimum olefin : silver ratio occurred would depend on the acidity of the parent acid and the basicity of the complexed olefin. The stronger the acid, the lower the silver concentration at which the minimum occurred, *i.e.*, $AgBF_4 < AgClO_4 < AgNO_3$; furthermore, if the basicity of the olefin involved was not important relative to the strength of the acid, protonation would then occur at the same concentration for each olefin, as has been found for fluoroborate and perchlorate. With nitrate, the basicity of the individual olefin is presumably not negligible compared with the acid strength, and the concentration at which protonation begins will vary with the olefin employed. We postulate
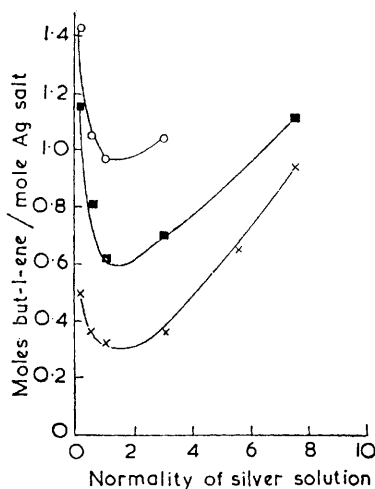

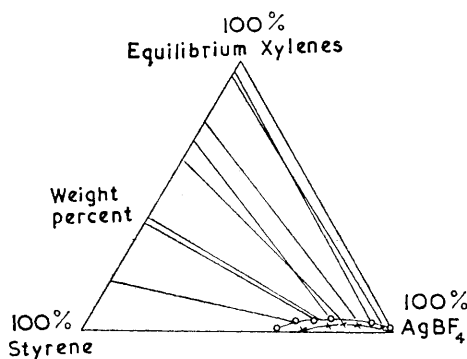FIG. 1. Solubility of but-1-ene in $AgBF_4$ solution at 0° (○), 20° (■), and 35° (×).

FIG. 2. Ternary system: styrene–xylenes–$AgBF_4$.

○ $AgBF_4$ contained 810 g./l. Ag. Extraction temperature 23°.
× $AgBF_4$ contained 590 g./l. Ag. Extraction temperature 5°.

protonation of the olefin *via* its complex, because the olefins examined were not soluble to any extent in *ca.* 4·5N fluoroboric acid.

Complex Formation between Olefin–Aromatic Hydrocarbon and Silver Fluoroborate.— During the investigation of the olefin–silver complexes an attempt was made to extract styrene from admixture with xylenes. The results showed that the solubility of xylenes in the aqueous phase was enhanced by the presence of complexed olefin. It was therefore thought desirable to study this phenomenon in more detail with other olefin–aromatic hydrocarbon mixtures.

Complex Formation between Aromatic Hydrocarbons and Silver Fluoroborate.—Before the competition between olefin and aromatic hydrocarbon in forming complexes with silver ions was studied systematically, the solubilities of benzene and *m*-xylene in aqueous silver fluoroborate were determined (see Table 3).

The results show that benzene is much more soluble in aqueous silver fluoroborate than is *m*-xylene, and that temperature has little effect on the solubility of either. Other workers have also shown that benzene is more soluble than *m*-xylene in silver solutions, and have calculated that *m*-xylene complexes more strongly than does benzene.[3]

[3] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1949, **71**, 3644.

Enhancement of the Solubility of Aromatic Hydrocarbons in Aqueous Silver Fluoroborate by Addition of an Olefin.—The data collected during the study of olefin–aromatic hydrocarbon–silver fluoroborate systems are shown in Figs. 2, 3, and 4 in the form of ternary diagrams. Although not indicated, where oct-1-ene was present, three phases were

TABLE 3.

The solubility of benzene and *m*-xylene in aqueous silver fluoroborate.

Aromatic hydrocarbon	Temp.	Solubility moles hydrocarbon/mole silver	Aromatic hydrocarbon vapour pressure (atm.)
Benzene	5°	0·640	
Benzene	20	0·570	0·0991
m-Xylene	0	0·013	
m-Xylene	20	0·013	0·0088

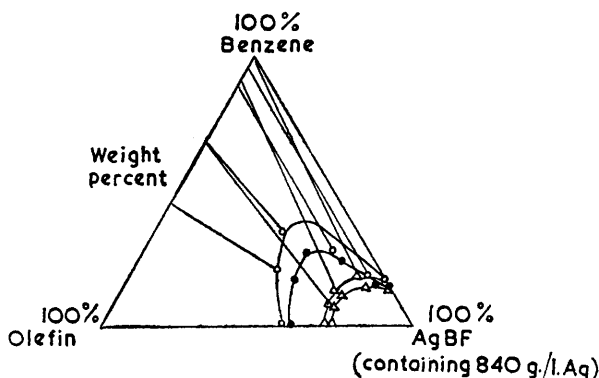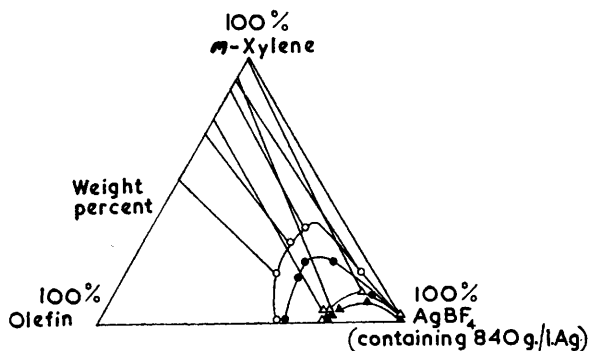The silver fluoroborate solution contained 840 g./l. Ag.

FIG. 3. Ternary systems: oct-1-ene–benzene–AgBF$_4$, ○ 5°, ● 20°; pent-1-ene–benzene–AgBF$_4$, △ 5°, ▲ 20°.

FIG. 4. Ternary systems: oct-1-ene–*m*-xylene–AgBF$_4$, ○ 0°, ● 20°; pent-1-ene–*m*-xylene–AgBF$_4$, △ 0°, ▲ 20°.

observed in each of the systems in the region of maximum solubility of aromatic hydrocarbon. The three phases were not studied separately during this investigation and, in considering the results, the bottom two phases were regarded as the aqueous phase. Clearly, the solubility of aromatic hydrocarbons in aqueous silver fluoroborate is considerably increased by addition of an olefin. Lowering the temperature enhances the effect. It is also clear from the results that different olefins enhance the solubility of aromatic hydrocarbons to different extents. Thus, the solubility of benzene and *m*-xylene in aqueous silver fluoroborate is increased by the addition of olefins in the order:

oct-1-ene > pent-1-ene > styrene
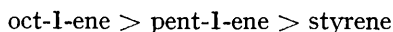
The greater effect of oct-1-ene led us to study the contribution made by carbon chain length of the olefin (see Table 4). Increasing the chain length of straight chain α-olefins

results in enhanced solubility of benzene in aqueous silver fluoroborate. Contact of tetradec-1-ene with the aqueous solution produced a solid white complex; although this

TABLE 4.

The effect of carbon chain length of the olefin on the solubility of benzene in aqueous silver fluoroborate.

	Raffinate composition, % w/w		Aqueous phase composition, % w/w		
Olefin	Olefin	Benzene	Olefin	Benzene	AgBF$_4$ aq.
Pent-1-ene	14	86	19	10	61
Oct-1-ene..........................	14	86	9	23	68
Dec-1-ene..........................	14	86	9	28	63
Tetradec-1-ene	White solid formed between olefin and AgBF$_4$ aq.				

Temperature: 20°. The silver fluoroborate solution contained 840 g./l. Ag.

olefin was not studied further in the present investigation, it is probable that it could be used to enhance the solubility of aromatic hydrocarbons if more dilute silver salt solutions were used.

The molar compositions at maximum aromatic solubility with reference to silver as unity were calculated from the curves in Figs. 3 and 4, and are given in Table 5. These

TABLE 5.

Molar compositions at maximum aromatic solubility in olefin–aromatic hydrocarbon–silver fluoroborate systems.

Temp.	Moles aromatic hydrocarbon/ mole silver (in absence of olefin)	Moles olefin/ mole silver (in absence of aromatic hydrocarbon)	Molar composition at maximum aromatic solubility			Total moles organic/ mole silver
			Aromatic hydrocarbon	Olefin	Silver	
			Benzene	Oct-1-ene		
5° *	0·64	1·72	2·93	0·76	1	3·7
20 *	0·57	1·52	1·65	0·66	1	2·3
			Benzene	Pent-1-ene		
5	0·64	1·36	0·89	0·46	1	1·4
20	0·57	1·33	0·65	0·32	1	1·0
			m-Xylene	Oct-1-ene		
0 *	0·13	1·80	1·82	0·37	1	2·2
20 *	0·13	1·52	1·27	0·61	1	1·9
			m-Xylene	Pent-1-ene		
0	0·13	1·50	0·37	0·44	1	0·8
20	0·13	1·33	0·25	0·48	1	0·7

Density of silver fluoroborate solution containing 840 g./l. Ag = 2·14.

* 3-Phase systems formed; molar compositions quoted calculated on assumption that bottom two layers are the aqueous phase.

show a greater percentage increase in solubility with m-xylene than with benzene, and a more marked synergistic effect on addition of oct-1-ene compared with pent-1-ene. The final column in Table 5 shows that there is a considerable variation in the total moles of organic material per mole of silver. This was taken to indicate that the systems contain a number of different complexes, and that other effects such as physical solution must be allowed for when considering the species present in the aqueous phase.

In silver fluoroborate–olefin systems, in which the silver concentration is $\geqslant 5$N, we consider that the following species are likely to be present,

$$(\text{Ag olefin})^+, (\text{Ag olefin}_2)^+, (\text{olefin H})^+\text{BF}_4^-$$
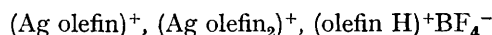
In addition, physical solution of the olefin must be considered.

Addition of a small amount of aromatic hydrocarbon to this system could lead to the formation of a protonated aromatic complex, (aromatic H)$^+$BF$_4^-$, at the expense of the

protonated olefin complex. The observation that the solubility of aromatic hydrocarbons increases with increasing chain length of the added olefin is consistent with protonation of aromatic hydrocarbons. Thus, the longer the carbon chain of the olefin in the (Ag olefin)$^+$ complex the more effectively will the fluoroborate ion be separated from the silver ion, and hence the greater the tendency to form the protonated aromatic hydrocarbon complex. The greater percentage increase in solubility of *m*-xylene compared with benzene is consistent with the protonation effect being greater with the more basic *m*-xylene.[4] Increasing the chain length of the olefin would also tend to modify the nature of the solution by making it less polar, and thus raise the solubility of the aromatic hydrocarbon by favouring physical solution.

In the region of maximum solubility of the aromatic hydrocarbon, it is suggested that the following species are present in the aqueous phase,

$$(\text{Ag olefin})^+, \ (\text{Ag olefin, aromatic})^+, \ (\text{Ag aromatic})^+, \ (\text{aromatic H})^+\text{BF}_4^-$$
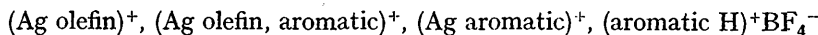
Physical solution would also be expected to make a fairly large contribution to the solubility of the aromatic hydrocarbon in this region.

The presence of n-heptane in the aqueous phase on extracting benzene–n-heptane mixtures with aqueous silver fluoroborate–oct-1-ene mixture (Table 6) shows that physical solution can be appreciable.

TABLE 6.

Extraction of benzene–n-heptane mixtures with a AgBF$_4$–oct-1-ene mixture.

Organic mixture before extraction, % w/w		Ratio Ag solution : organic mixture (v/v)	Composition of aqueous phase after extraction, % w/w			
Benzene	n-Heptane		Benzene	n-Heptane	Oct-1-ene	AgBF$_4$ aq.
30	70	1 : 1	5·1	4·3	17·8	72·8
50	50	1 : 1	8·4	2·6	16·3	72·7
60	40	1 : 1	11·2	2·0	14·2	72·6
60	40	2 : 1	9·5	3·2	21·2	66·1
60	40	4 : 1	6·1	2·5	26·8	64·6

Extraction temperature: 20°.
Extractant: Aqueous silver fluoroborate–38% w/w oct-1-ene.
The silver fluoroborate solution contained, before addition of olefin, 840 g./l. Ag.

With a further rise in the aromatic hydrocarbon content of the organic mixture the concentration of (Ag olefin)$^+$ and (Ag olefin aromatic)$^+$ will decline. Consequently, the concentration of the complex formed by protonation of the aromatic hydrocarbon will also decrease, as will the amount in physical solution. Finally, in the absence of olefin, the silver–aromatic hydrocarbon complex would be present in the aqueous phase.

IMPERIAL CHEMICAL INDUSTRIES LTD., HEAVY ORGANIC CHEMICALS DIVISION,
    RESEARCH DEPARTMENT, BILLINGHAM, CO. DURHAM.   [*Received, January 20th,* 1964.]

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