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Dipole Moments of Silver Perchlorate in Benzene, p-Xylene and Mesitylene

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The dielectric constants and refractions of solutions of benzene, p-xylene and mesitylene containing silver perchlorate have been measured. For very low concentrations in benzene, a dipole moment of 10.7D was confirmed but in more concentrated solutions a value of 4.7D was obtained. For p-xylene and mesitylene only one value was obtained: 2.7D in the case of p-xylene solutions and 4.3D for mesitylene solutions. This behaviour is discussed in terms of ion pair association and donor–acceptor interactions taking place in such systems between the aromatic species and the silver ion.

Introduction

Benzene and a few benzene derivatives have been shown to interact with silver ion (Ag^+) in a type of donor–acceptor, or, more accurately, charge transfer interaction. Andrews and Keefer[1] found from solubility measurements of benzene and benzene derivatives in water solutions containing silver nitrate that a molecular complex is formed between the aromatic species and the silver ion. They also measured the stability of these complexes.

Later on, Mulliken[2] predicted that a charge transfer interaction must take place between aromatic species which are known to be good donors and silver ion which may be a good acceptor. Torre–Mori *et al.*[3] and Murrel *et al.*[4] confirmed Mulliken's prediction by U.V. spectroscopy measurements. On addition of benzene species to aqueous solutions containing silver perchlorate, Murrell found a new absorption band not found in either benzene or silver perchlorate. He attributed this new band to charge transfer. He also suggested a structure for the C.T. complex to accord with his results. In it, the silver ion is positioned above one of the C–C bonds of the aromatic ring. Such a complex would be quite stable and indeed Smith and Rundle[5] succeeded in isolating crystals of the complex $Bz \cdot Ag^+$. They also carried out X-ray studies of the crystals and found an asymmetric structure of the complex, with the silver ion above a C–C bond of the aromatic ring, as deduced above by Murrell.

Crystals of some silver perchlorate complexes with methylbenzenes were prepared and studied with X-rays by Amma *et al.*[6] They succeeded in preparing molecular complexes of the type 2 : 1 ($Ar_2 \cdot Ag^+$) with xylene and 1 : 1 with mesitylene. Avinur and Eliezer later on[7] also prepared and analyzed by UV spectroscopy crystals of silver perchlorate complexes with methylbenzenes in ratios 1 : 1 and 2 : 1 depending on the aromatic species. The solid complex was also studied by nmr,[8] and solutions of benzene in aqueous silver (*I*) salts were investigated by means of chemical shifts in nmr.[9]

It seemed to us that if a charge transfer complex is formed between aromatic species and the silver ion, its effect must be observed in the dipole moments of solutions of the salt in solvents like benzene, *p*-xylene and mesitylene (which are not polar solvents). Dipole moment measurement is a sensitive tool in detecting C.T. complexes. The classic C.T. complex is $Bz \cdot I_2$ for which many investigators measured the dipole moment and from it calculated the percent of charge transferred from the benzene to the iodine molecule (for references, see ref. 10). The dipole moments of other systems have also been studied in terms of charge transfer complexes.[11,12] However, in all these cases the participant molecules are not polar.

The dipole moment of silver perchlorate in benzene was measured quite a while ago by two groups.[13,14] In ref. 13 the measurements were made on more concentrated solutions of silver perchlorate in benzene (10^{-2}–10^{-1} N) and a dipole of 4.7D was obtained while the other measurements[14] were made on very low concentrations of silver perchlorate and a dipole of 10.7D was calculated. Hooper and Kraus[14] suggest that the difference in the dipole moments is due to the fact that in the high concentration range association of solute molecules causes a lowering of dipole moment values. No mention has been made of the values of dipole moments measured in terms of complex formation. Moreover, in ref. 14 it is assumed that the dipole found is the dipole of the silver perchlorate ion pair and, assuming a unit charge on the ions, a value of 2.25 Å was calculated for the distance between the

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silver and perchlorate ions, while the sum of the ionic radii of silver and perchlorate ions is about 2.7 Å[15] (an X-ray study of the crystals in the complex shows[5] that the distance between the silver ion and the closest oxygen of the perchlorate is also about 2.7 Å). It is doubtful that in solution the distance between the ions is less than the sum of their ionic radii.

It is clear that it is much more difficult to treat the dipole moments of systems of aromatic species containing silver perchlorate in terms of charge transfer complex formation, than to treat a system like benzene–I_2 or the others mentioned above[11,12] where none of the participant molecules is polar. We felt that a study of the dipole moment of silver perchlorate in other aromatic non-polar solvents like *p*-xylene and mesitylene alongside a re-examination of benzene, would help us to understand more about the interactions taking place in such systems and to compare the conclusions with the above-mentioned solubility, UV and other studies on the Ag^+–aromatic system. We, therefore, repeated the measurements of dielectric constants and refractions in benzene and then measured *p*-xylene and mesitylene solutions of silver perchlorate.

Experimental

Dielectric constants of the solutions were measured using the WTW Dekameter DK06 which is based on the heterodyne beat method. Refractive index measurements were carried out with a Bausch & Lomb precision Abbe refractometer using sodium light. Density measurements were performed with a modification of the Lypkin pycnometer. All the measurements were carried out at a temperature of 30.0 ± 0.2° C. Solutions were prepared and kept under nitrogen. The solvents were analytical grade benzene (Frutarom), *purum* *p*-xylene (Fluka) and *puriss.* mesitylene (Fluka). They were further purified by distillation over sodium. The silver perchlorate used was from B.D.H. For further experimental details see ref. 10.

Results and Calculations

The dipole moments μ were obtained using Debye's method. μ is given by the formula $\mu^2 = 9kT(P_2–R_2)/4\pi N$ where P_2 and R_2 are the molar polarization and refraction of the solute respectively. T is the absolute temperature, N is Avogadro's constant and k is the Boltzmann constant. The molar refractions were calculated from measurement of the refractive index (with sodium light) and the density of solutions and solvents. The values obtained are therefore somewhat higher than the true values, thus compensating, to some extent, for the neglect of atomic polarization for which there is still no good method of evaluation. The molar polarizations were calculated via specific polarizations from the measurements of the dielectric constants and the densities of solutions and solvents. The results are given in Tables I–III. The errors in the values of the dielectric constant, density, index of refraction and weight fraction of the solute were estimated by repeated measurements to be ± 0.0001, 0.0001, 0.00003 and 0.000005 respectively. The values for the pure solvents agree well with literature values.[16–18]

In Table IV the calculated dipole moments for the three systems are given alongside the average molar polarizations and refractions. In solutions of *p*-xylene and mesitylene, no significant change has been observed in molar polarizations and refraction on changing the concentration of salt (Tables II, III) in the range in which measurements could be made. Therefore, the values of P_2 and R_2 in Table IV are average values. For benzene, polarization in the high concentration range does not change on changing concentration (see Table I) and the value of P_2 in Table IV is the average value in that range of concentration. However, in more diluted solutions the polarization increases with dilution (Table V). This agrees with the low concentration measurements in ref. 14. The errors in dipole moment values are standard errors which were calculated according to the equation $\Delta\mu = 2.485 \times 10^{-20}(\Delta P_2{}^2 + \Delta R_2{}^2)^{1/2}/\mu$ (where ΔP_2 and ΔR_2 are again standard errors). μ values were calculated according to the equation $\mu^2 = 4.97 \times 10^{-38}(P_2–R_2)$, where P_2 and R_2 are the values in Table IV.

Discussion

From Table IV we can see a decrease in dipole moment on going from benzene to *p*-xylene, but the dipole value increases again on going from *p*-xylene to mesitylene, so that a minimum obtains for *p*-xylene. Assuming that these are the ion pair dipoles, their values are too small to explain a dipole of an ion pair with a unit charge on both ions. In other words, if we assume a unit charge on both ions only an unreasonably short distance between the ions can explain these low dipole values. For a completely ionized ion pair with a distance of 2.7 Å between the ions the dipole moment should be about 13 D. Therefore, only some type of interaction between the solvent molecules and the solute or among the solute molecules themselves can explain these low dipole moments. Moreover, the change of the dipole values of the solute on going from benzene through *p*-xylene to mesitylene, shows that the strength of interaction depends on the structure of the solvent molecules.

As mentioned above, it has been shown[2–5] that in the systems under discussion there are charge transfer interactions between the aromatic species as a donor

TABLE I. Molar Polarizations and Molar Refractions of $AgClO_4$ in Benzene.[a]

x_2	w_2	n	d	ε	r_{12}	R_{12}	r_2	R_2	p_{12}	P_{12}	p_2	P_2
0	0	1.4941	0.8672	2.265	0.3358	26.23	–	–	0.3420	26.71	–	–
0.003086	0.008149	1.4949	0.8741	2.374	0.3336	26.19	0.07	15	0.3594	28.22	2.48	514
0.003205	0.008463	1.4948	0.8738	2.365	0.3336	26.20	0.08	17	0.3579	28.10	2.22	460
0.003261	0.008608	1.4948	0.8741	2.383	0.3335	26.19	0.07	15	0.3610	28.35	2.55	529
0.003803	0.010031	1.4951	0.8732	2.387	0.3340	26.25	0.16	33	0.3621	28.46	2.34	485
0.005144	0.013537	1.4953	0.8776	2.400	0.3325	26.19	0.10	21	0.3625	28.56	1.85	384
0.01342	0.034843	1.4970	0.8952	2.723	0.3269	26.10	0.08	17	0.4075	32.54	2.22	460
0.02072	0.053178	1.4987	0.9106	2.991	0.3223	26.04	0.092	19	0.4381	35.39	2.15	446

[a] x_2, mole fraction of solute; w_2, weight fraction of solute; n, index of refraction; d, density (g/cm^3); ε, dielectric constant; r, specific refraction (cm^3/g); R, molar refraction (cm^3/mol); p, specific polarization (cm^3/g); P, molar polarization (cm^3/mol). Indexes 12 and 2 refer to the mixture and solute respectively.

TABLE II. Molar Polarizations and Molar Refractions of $AgClO_4$ in *p*-Xylene.

x_2	w_2	n	d	ε	r_{12}	R_{12}	r_2	R_2	p_{12}	P_{12}	p_2	P_2
0	0	1.4896	0.8511	2.248	0.3395	36.04	–	–	0.3452	36.65	–	–
0.000622	0.001213	1.4906	0.8530	2.260	0.3393	36.05	0.1	20	0.3468	36.84	1.0	210[a]
0.003027	0.005893	1.4902	0.8557	2.265	0.3380	35.99	0.09	19	0.3466	36.91	0.59	122
0.006247	0.012126	1.4905	0.8604	2.306	0.3363	35.92	0.08	17	0.3525	34.65	0.95	197
0.009118	0.017652	1.4910	0.8646	2.328	0.3350	35.88	0.09	19	0.3550	38.02	0.91	189
0.015227	0.029309	1.4918	0.8736	2.379	0.3320	35.76	0.08	17	0.3604	38.82	0.864	179

[a] This solution was prepared from a solvent sample with n = 1.4905, d = 0.8522 and ε = 2.254.

TABLE III. Molar Polarizations and Molar Refractions of $AgClO_4$ in Mesitylene.

x_2	w_2	n	d	ε	r_{12}	R_{12}	r_2	R_2	p_{12}	P_{12}	p_2	P_2
0	0	1.4943	0.8568	2.261	0.3400	40.87	–	–	0.3453	41.51	–	–
0.000514	0.000886	1.4943	0.8573	2.267	0.3398	40.86	0.1	20	0.3464	41.65	1.6	330
0.000732	0.001262	1.4943	0.8575	2.278	0.3398	40.87	0.1	20	0.3484	41.90	2.2	456[a]
0.000798	0.001375	1.4944	0.8578	2.273	0.3396	40.84	0.05	10	0.3472	41.76	1.7	352
0.001177	0.002028	1.4944	0.8583	2.283	0.3394	40.83	0.04	8	0.3491	42.00	2.3	477
0.001375	0.002370	1.4945	0.8585	2.285	0.3394	40.84	0.09	19	0.3494	42.04	2.1	435
0.001753	0.003019	1.4945	0.8590	2.285	0.3392	40.82	0.08	17	0.3492	42.03	1.6	332

[a] This solution was prepared from a solvent sample with n = 1.4944, d = 0.8566 and ε = 2.264.

TABLE IV. Polarization, Refraction and Dipole Moments of Silver Perchlorate in Benzene, *p*-Xylene and Mesitylene.

Solvent	P_2	R_2	μ (D)
Benzene	468 ± 18	19.6 ± 2.4	4.7 ± 0.1
Xylene	179 ± 15	18.4 ± 0.6	2.8 ± 0.1
Mesitylene	397 ± 27	15.7 ± 2.2	4.3 ± 0.2

and the silver ion as an acceptor. Such an interaction can explain the small dipole moments of the solute measured in our systems and also the trend of the dipole values on going from benzene to mesitylene.

A charge transfer interaction between the aromatic species and the silver ion involves a transfer of negative charge from the aromatic molecule to the positive silver ion and thus causes, in part, a neutralization of the effective charges on the silver and perchlorate ions, a fact which will lead to lowering the dipole moment of the solute molecules. This is actually observed in our systems. Moreover, the more the charge transfer is effective, or the more the molecular complex is stabilized, a greater negative charge would be transferred from the aromatic ring to the positive silver ion, and thus the silver and perchlorate ions would be more neutralized and the dipole moment of the ion pair would be even lower. *p*-Xylene differs from benzene

TABLE V. Molar Polarizations and Molar Refractions of $AgClO_4$ in Benzene at Low Concentrations.[a]

x_2	w_2	n	d	ε	r_{12}	R_{12}	r_2	R_2	p_{12}	P_{12}	p_2	P_2
0	0	1.4941	0.8672	2.265	0.3358	26.23	–	–	0.3420	26.71	–	–
0.000151	0.000401	1.4942	0.8674	2.281	0.3357	26.21	0.1	20	0.3450	26.96	7.8	1600
0.000416	0.001103	1.4943	0.8681	2.291	0.3355	26.22	0.1	20	0.3466	27.09	4.5	930
0.000453	0.001202	1.4944	0.8683	2.285	0.3355	26.22	0.1	20	0.3454	27.00	3.1	640

[a] See also ref. 14.

only in the two methyl groups on the ring. Methyl groups stabilize the charge transfer complex[1,3] and therefore one can expect a decrease in dipole moment on going from benzene to *p*-xylene. In mesitylene, with three methyl groups on the aromatic ring, a steric hindrance may cause a destabilizing of the complex especially as in these systems the silver ion is positioned above the C–C bond in the ring and not on the six-fold axis.[4,5,6] Therefore, one can expect a complex between mesitylene and silver ion which is less strong than the complex between *p*-xylene and the silver ion. This explains the low dipole moment of silver perchlorate in xylene and the higher value for the dipole in mesitylene.

A similar trend is observed in the stability constants of the complex. Andrews and Keefer[1] found from solubility measurements that the stability constants of the 1 : 1 complexes with Ag^+ in aqueous are 2.4, 2.6–3.0 and 1.8M^{-1} for benzene, xylene and mesitylene complexes respectively. Torre–Mori *et al.*[3] found from UV spectroscopy that the stability constants K_c in methanol medium are 1.66, 6.07 and 0.51 for benzene, *m*-xylene and mesitylene respectively. In both sets of data a maximum in stability constant is observed in xylene, in agreement with our observation from dipole moment measurements.

Assuming a charge transfer interaction and with our values for the dipole moments we can evaluate the amount of charge transfer (in electron charge units) from the aromatic ring to the silver ion. A short calculations shows that the charge which should be transferred from the ring to the silver ion in order to reduce the dipoles to the experimental values seems somewhat high, if 1 : 1 complex formation is assumed. However, as was mentioned above, crystals of complexes of xylene with silver ion were shown to be of the type 2 : 1 ($Ar_2 \cdot Ag^+$).[6] With benzene and mesitylene, crystals of the form 1 : 1 were prepared[5,8] but we believe that in solution a complex of the type 2 : 1 may also be stable (high solvent to solute ratio). If we take the values of 4.7, 2.8, 4.3 for benzene, *p*-xylene and mesitylene solutions respectively, assume these values are caused by 2 : 1 complex formation, and take a distance of 2.7 Å between the silver ion and the perchlorate ion (see introduction) we get for δ (the fraction of electron charge transferred from the aromatic ring to the silver ion) the values $\delta = 0.31$, 0.39 and 0.33 for benzene, *p*-xylene and mesitylene respectively. These are upper limits for the fractions of charge transferred, as in the calculation we assume a unit charge on silver and perchlorate if CT complexes were not formed. Actually, the solute is probably not completely ionized and therefore the δ values should be lower than the above calculated values.

The above values of δ are comparable to those in charge transfer complexes studied previously. For example, for dioxane–$HgCl_2$ a transfer of 0.12 electron charge units and for benzene–$HgBr_2$ a transfer of 0.1 electron charge units have been calculated[10] while for some sulfur donors with iodine as an acceptor[12] values of about 0.23 were calculated from dipole moment measurements. It would seem that for positive ions like silver ion as acceptor, the values of δ we obtain are reasonable. From these values we observe that in *p*-xylene solutions the percent of C.T. contribution to the ground state of the complexes is the highest, which is in agreement with the higher stability constant found for this complex as mentioned above.[1,3] From the δ values, we also see that in mesitylene the degree of C.T. is slightly greater than in benzene ($\delta = 0.33$ for mesitylene and 0.31 for benzene) and from these, one can conclude that the complex with mesitylene is somewhat stronger than with benzene. However, from the equilibrium constants mentioned above an opposite conclusion seems called for. The reason for this disagreement is not so clear, although it may be that the 2 : 1 complex with mesitylene is stronger than with benzene, while the equilibrium constants mentioned above are for the 1 : 1 complex.

Of the two values for the dipole moment of benzene, the one in the higher concentration range, 4.7 D, was discussed above in terms of 2 : 1 complex formation. The second, 10.7 D, obtained in very low solute concentrations, which was calculated in ref. 14 (and rechecked by us), could be explained by the assumption that at very low concentrations the dipole moment measured is that of the silver perchlorate ion pair forming a 1 : 1 complex with the solvent (which would give us $\delta = 0.17$) or perhaps even just that of the ion pair itself (which would mean that silver perchlorate in benzene is 17% covalent). However, it is unlikely that the proportion of 2 : 1 to 1 : 1 complexes will vary with silver perchlorate concentration in the range used since the activity of benzene probably remains relatively constant. This leads us to the possibility, mentioned in ref. 14, that the low dipole value in the high concentration range in benzene solutions is due to association between the ion pairs. Such behaviour can be assumed also in the *p*-xylene and mesitylene systems and thus explain the low dipole values. However, we do not observe any change in polarization in the range of concentration which is measurable in *p*-xylene and mesitylene. Also, it may be argued that as more stabilized complexes are formed in *p*-xylene and, possibly, mesitylene, association should be less effective in these solutions than in benzene.

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