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Apparent Dipole Moments and Dielectric Relaxation Times of 1,4-Benzoquinone and Its Derivatives in Solutions

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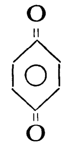
Atom polarisations, apparent dipole moments and dielectric relaxation times of 1,4-benzoquinone in various solvents were determined together with those of some of its derivatives in benzene solution. Solvent effects on the apparent dipole moments of 1,4-benzoquinone and its derivatives were examined in comparison with the absorption spectra in the submillimetre region.

In spite of the observation that 1,4-benzoquinone has a centre of symmetry[1)] it has been shown to exhibit an apparent permanent dipole moment of appreciable magnitude, 0.67 D, in solution.[2)] The observed large dipole moment could be due solely to an exceptionally large atom polarisation[3)] if there were no solute-solvent interaction.[4)] The observations of polarisation in the vapour phase[3)] show that the latter is not a major cause of the apparent moment.

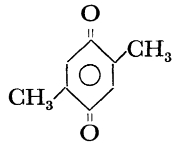
First, in the present work a new determination of the atom polarisation was made for 1,4-benzoquinone by dielectric measurements at an extremely high frequency (96.52 GHz, 3.219 cm^{-1}). The experimental atom polarisation thus obtained was compared with the values calculated by Waddington *et al.*[5)] from its absorption spectrum over the whole infrared range.

Secondly, the nature of solute-solvent interaction was investigated by measuring apparent dipole moments and relaxation times of 1,4-benzoquinone in a variety of solvents.

Thirdly, not only 1,4-benzoquinone (A), but also its derivatives, 2,5-dimethyl-1,4-benzoquinone (B), 2,5-dichloro-1,4-benzoquinone (C) and 2,5-di-*tert*-butyl-1,4-benzoquinone (D) were studied using the same procedure.



(A)



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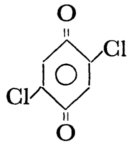

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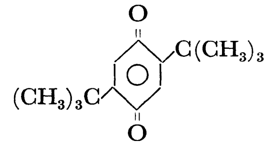

(D)

Experimental

By use of the apparatus and techniques described previously[6)] dielectric and optical measurements were carried out at the frequencies 1 MHz, 96.52 GHz and that the Na–D line. The real and unreal dielectric constants ε' and ε'' of the dilute solutions measured at 96.52 GHz are assumed to be linear with the concentration (weight fraction w_2) of the solute.

$$\begin{aligned} \varepsilon' &= \varepsilon_1' + a'w_2 \\ \varepsilon'' &= \varepsilon_1'' + a''w_2 \end{aligned} \tag{1}$$

in which subscripts 1 and 2 refer to the pure solvent and to the solute, respectively. Similarly the dielectric constant at any frequency (including the static one, ε_0, and the high frequency limiting value, ε_∞), the squares of refractive indices n_D^2 and the specific volumes v are also assumed to be linear with the concentration.†

$$\begin{aligned} \varepsilon_0 &= \varepsilon_{10} + a_0 w_2, & \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty w_2 \\ n_D^2 &= n_{1D}^2 + a_D w_2, & v &= v_1 + b w_2 \end{aligned} \tag{2}$$

The total, *i.e.*, low frequency molecular polarisation of the solute at infinite dilution was obtained from the Halverstadt-Kumler equation.[7)]

$$P_2 = M_2 \left\{ \frac{3a_0 v_1}{(\varepsilon_{10}+2)^2} + (v_1+b)\frac{\varepsilon_{10}-1}{\varepsilon_{10}+2} \right\} \tag{3}$$

in which M_2 is the molecular weight of the solute. The distortion polarisation P_E+P_A is, in principle, obtainable using a_∞ and $\varepsilon_{1\infty}$ instead of a_0 and ε_{10} in Eq. (3), respectively.[8)] The difference $\varepsilon_1'-\varepsilon_{1\infty}$ expresses the effect of dispersion in the microwave region.

$$P_A + P_E = M_2 \left\{ \frac{3a_\infty v_1}{(\varepsilon_{1\infty}+2)^2} + (v_1+b)\frac{\varepsilon_{1\infty}-1}{\varepsilon_{1\infty}+2} \right\} \tag{4}$$

Similarly, by use of n_{1D}^2 and a_D the molar refraction for the D-line is given by

$$R_D = M_2 \left\{ \frac{3a_D v_1}{(n_{1D}^2+2)^2} + (v_1+b)\frac{n_{1D}^2-1}{n_{1D}^2+2} \right\} \tag{5}$$

If the system under consideration is characterized by a single Debye dispersion, then the relaxation time will be obtained from either of the following two equations[9)]

$$\tau = \frac{1}{\omega}\frac{a''}{a'-a_\infty} \equiv \tau(1) \tag{6}$$

$$\tau = \frac{1}{\omega}\frac{a_0-a'}{a''} \equiv \tau(2) \tag{7}$$

where ω is the frequency of observation. The limiting value a_∞ is obtainable from Eqs. (6) and (7).

$$a_\infty = a' - \frac{(a'')^2}{a_0-a'} \equiv a_G \tag{8}$$

It is impossible to determine a_∞ experimentally on the basis of Eq. (8) because of other extra dispersions; however, we shall assume tentatively that a_G evaluated from the a' and a'' at a very high frequency (96.52 GHz) would approximate to a_∞. On the basis of the above assumption Eq. (4) can be

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† The parameter a_∞ in Eq. (2) will be discussed later (see Eq. (8)).

Table 1. Experimental results at 25 °C

Solute	Solvent	a_0	a'	a''	a_D	a_G	b	P_2[a)] (cm^3)	$(P_E+P_A)_G$ (cm^3)	R_D[a)] (cm^3)
(A)	[Bz]	0.523	0.490	0.031	0.081	0.462	−0.302	37.8	36.6	28.4
(A)	[Xy]	0.546	0.493	0.036	0.101	0.468	−0.331	38.1	36.5	28.4
(A)	[M]	0.563	0.512	0.033	0.103	0.490	−0.336	38.4	36.8	28.3
(A)	[Dx]	0.691	0.661	0.035	0.296	0.620	−0.131	38.4	37.2	28.8
(A)	[CCl$_4$]	1.052	0.962	0.064	0.331	0.917	0.214	38.6	37.1	28.9
(A)	[Hx]	0.450	—	—	0.208	—	−0.631	36.0	—	28.3
(A)	[Hp]	0.469	—	—	0.194	—	−0.602	36.5	—	28.0
(A)	[CHx]	0.462	—	—	0.143	—	−0.384	36.8	—	28.7
(B)	[Bz]	0.453	0.347	0.021	0.054	0.342	−0.230	48.7	46.0	37.9
(C)	[Bz]	0.460	0.386	0.023	0.162	0.379	−0.509	48.8	46.2	38.4
(D)	[Bz]	0.261	0.183	0.037	−0.016	0.166	−0.115	78.4	74.6	66.9

Solute: (A) 1,4-benzoquinone, (B) 2,5-dimethyl-1,4-benzoquinone, (C) 2,5-dichloro-1,4-benzoquinone and (D) 2,5-di-*tert*-butyl-1,4-benzoquinone.

Solvent: [Bz] benzene, [Xy] *p*-xylene, [M] mesitylene, [Dx] dioxan, [CCl$_4$] carbon tetrachloride, [Hx] *n*-hexane, [Hp] *n*-heptane and [CHx] cyclohexane.

a) The errors in P_2 and R_D are all about ±0.2 cm^3.

rewritten by using a_G and ε_1' instead of a_∞ and $\varepsilon_{1\infty}$, respectively.[8]

$$(P_E+P_A)_G = M_2\left\{\frac{3a_Gv_1}{(\varepsilon_1'+2)^2} + (v_1+b)\frac{\varepsilon_1'-1}{\varepsilon_1'+2}\right\} \qquad (9)$$

All the compounds used in this study were obtained from commercial sources. Purchased materials of the best grade were purified by repeated recrystallization from benzene. The melting points of the purified samples were: 1,4-benzoquinone 113 °C, 2,5-dimethyl-1,4-benzoquinone 123 °C 2,5-dichloro-1,4-benzoquinone 160 °C, and 2,5-di-*tert*-butyl-1,4-benzoquinone 150 °C. Solvents: benzene, *p*-xylene, mesitylene, dioxan, carbon tetrachloride, *n*-hexane, *n*-heptane, and cyclohexane of the best grade were carefully purified by distillation before the dielectric measurements.

Results and Discussion

Atom Polarisation. In Table 1 are given several observed basic parameters and the polarisations derived therefrom. Five parameters are slopes a_0(static), a', a'' (96.52 GHz), a_D(optical) and b(volume) obtained from three to four dilute solutions for each solute by use of Eqs. (1) and (2) and the remaining a_G is evaluated from a', a'' and a_0 using Eq. (8). Three polarisations P_2, $(P_E+P_A)_G$ and R_D are calculated from a_0 and Eq. (3), from a_G and Eq. (9) and from a_D and Eq. (5), respectively.

In Table 2 are given three atom polarisations. P_A(exp) is obtained as $(P_E+P_A)_G-R_D$. This procedure for evaluating P_A(exp) has two sources of error. One is that $(P_E+P_A)_G$ is not necessarily equal to P_E+P_A. This is because a_G and ε_1' would differ from a_∞ and $\varepsilon_{1\infty}$, respectively. We may safely assume $\varepsilon_1'\simeq\varepsilon_{1\infty}$ for non-polar solvents; but sometimes a_G appears to be slightly larger than the probable a_∞ values. For instance, $(P_E+P_A)_G$ would be larger than the true distortion polarisation, if it included some of the effects of dipole relaxation, *e.g.*, alkyl acetates.[10]

The other source of error is that R_D is not equal to the electron polarisation P_E at 96.52 GHz which we really want to have. Again R_D is usually slightly larger than P_E at zero frequency, *e.g.*, 1.1—1.4 cm^3 for halobenzenes.[11] However, $(P_E+P_A)_G-R_D$ is probably a good estimate of P_A. P_A(exp) compares well with P_A(calc) calculated from the absorption spectra by Waddington *et al.*[5]

The radio-visible polarisation difference P_2–R_D is found to be larger than P_A(exp) since P_2 represents a total polarisation, *i.e.*, the sum of any orientation polarisation plus the distortion polarisation.

Molar Polarisation P_2 in Various Media. The $(P_E+P_A)_G$ values recorded in Table 1 for 1,4-benzoquinone are almost equal to the P_2 value observed in the vapour phase by Coop and Sutton.[3] This indicates that the $(P_E+P_A)_G$ values are not appreciably affected by solute-solvent interactions.

$(P_E+P_A)_G$ values could not be observed for the relatively dilute solutions which were all that could be obtained in *n*-hexane, *n*-heptane and cyclohexane; but for these the P_2 values (36.0 to 36.8 cm^3) observed at radio frequencies are also equal to the vapour phase value of P_2 (36.55 cm^3) within the limit of experimental error.[††] Consequently the dipole moments of 1,4-benzoquinone in these solvents may be taken to be zero.

In solutions of 1,4-benzoquinone in the aromatic solvents, in carbon tetrachloride and in 1,4-dioxan, P_2 is 1—2 cm^3 greater than $(P_E+P_A)_G$. Moreover, a_0 is greater than a_G and a Cole-Cole dispersion seems to exist (Fig. 1). These facts suggest that 1,4-benzoquinone becomes slightly polar in benzene and possibly

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[††] Recently John Haigh[12] obtained P_2=36.99±0.5 cm^3 at 29.7 cm^{-1} in benzene which is slightly larger than $(P_E+P_A)_G$ =36.6±0.5 cm^3 deduced at 3.22 cm^{-1} (96.52 Hz). From the observed absorption peak at 110 cm^{-1} of 1,4-benzoquinone in CCl$_4$ the fall of polarisation from its maximum situated at about 96 cm^{-1} is expected to occur on both sides of the frequency. Using the Kramers-Kronig relation we calculated the polarisation for the submillimetre region. The results corrected to Haigh's value at 29.7 cm^{-1} are the following: P(cm^3)/$\bar{\nu}$(cm^{-1}) 36.5/0; 36.99/29.7; 37.2/50; 40.8/90; 41.8/96; 41.1/100; 25.4/112; 14.2/120; 21.1/150; 25.2/200.

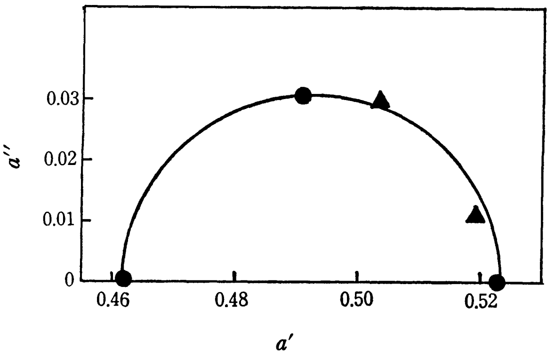

Fig. 1. Cole-Cole plot of 1,4-benzoquinone in benzene solution at 25°C.

●: Present work. ▲: C, W, N. Cumper and R. F. Rossiter, *J. Phys. Chem.*, **76**, 525 (1972).

Table 2. Atom polarisations

Compound	P_A(exp) (cm^3)	P_A(calc) (cm^3)	P_2-R_D (cm^3)
(A) in [Bz]	8.2±1.0	8.1±2.1	9.4±0.2
[Xy]	8.1±1.0	—	9.7±0.2
[M]	8.5±1.0	8.2±2.2	10.1±0.2
[Dx]	8.4±1.3	8.5±2.6	9.6±0.3
[CCl$_4$]	8.2±1.5	9.6±2.2	9.7±0.3
(B) in Bz	8.1±1.5	8.4±2.1	10.8±0.2
(C) in Bz	7.8±1.8	—	10.4±0.2
(D) in Bz	7.7±2.0	—	11.5±0.2

See Table 1 regarding the codes (A), (B), (C), (D) for the solutes and [Bz], *etc.*, for the solvents.

in other solvents of this group.

Dipole Moments and Relaxation Times. In Table 3 dipole moments and relaxation times for 1,4-benzoquinone and its derivatives in solutions are collected. In this table dipole moments μ were obtained from the following equation,

$$\mu(\mathrm{D}) = 0.0128\sqrt{\{P_2-(P_E+P_A)_G\}T} \qquad (10)$$

where T is the absolute temperature; and the relaxation time $\tau(2)$ is obtained from a' and a'' for $\omega=2\pi(9.652)\times 10^{10}$ and a_0(static) on the basis of Eq. (7). All the $\tau(2)$ values are much smaller than would be expected for the rotation of a dipolar molecule the size of 1,4-benzoquinone. According to Crump and Price,[4] following Anderson and Smyth,[13] the polarity arises from complex formation between molecules of 1,4-benzoquinone (electron acceptor) and solvent (electron donor); and $\tau(2)$ is controlled by the lifetime of the complex, not by the time of rotation of a long-lived dipole. The accuracy of measurement of the moments of the complexes hardly warrants any attempt to correlate them with the base strengths of the solvents; and much the same applies to the relaxation times $\tau(2)$.

Far Infrared Absorption. The effects of solvents upon the submillimetre wave absorption of 1,4-benzoquinone, previously shown by Waddington *et al.*[5] to be a bending mode, are very striking. Two features are immediately apparent. Shifts occur to higher frequencies (so-called blue shifts) and are large. An attempt was made to study the dependence of absorption frequencies upon solvents on the basis of the simple electrostatic treatment given by Kirkwood[14] and by Bauer and Magat.[15] Their model imagines a polar oscillating molecule placed at the centre of a spherical cavity in a continuous dielectric medium of refractive index n. Charges are set up on the walls of the cavity and produce an electric field which reduces the effective force constant of the molecule. The model leads to the equation;

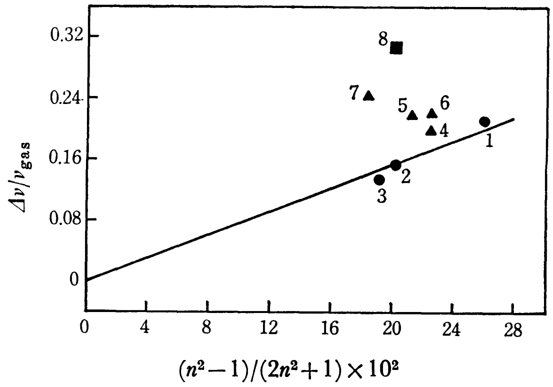

Fig. 2. Solvent dependence of the far-infrared absorption band of 1,4-benzoquinone.

Solvents: 1 carbon disulphide, 2 cyclohexane, 3 *n*-heptane, 4 benzene, 5 carbon tetrachloride, 6 mesitylene, 7 hexafluorobenzene and 8 dioxan.

$$\frac{\tilde{\nu}_{\mathrm{vap}}-\tilde{\nu}}{\tilde{\nu}_{\mathrm{vap}}} = C\frac{(n^2-1)}{(2n^2+1)} \qquad (11)$$

in which C is a positive constant and so allows only the prediction of "red" shifts and cannot explain the observations reported here. If, however, the above equation can be used even when C is negative then a plot of $(\tilde{\nu}_{\mathrm{vap}}-\tilde{\nu})/\tilde{\nu}_{\mathrm{vap}}$ against $(n^2-1)/(2n^2+1)$ allows us to classify the observations into three groups(Fig. 2). The explanation of the observed frequency increases probably is that the solvent molecules enclathrate and hem in the vibrating solute molecules thus making it more difficult for the quinone molecule to bend. The effectiveness of this process would be expected to increase with increasing solvent-solute attraction. It is hence not unreasonable to suppose that deviation from a linear relationship between the relative shift in the bending frequency $(\tilde{\nu}_{\mathrm{vap}}-\tilde{\nu})/\tilde{\nu}_{\mathrm{vap}}$ and a function of the dielectric constant of the solvent such as $(n^2-1)/(2n^2+1)$ would indicate the presence of special solvent-solute attractions. These attractions are likely to be due to the solvents behaving as weak electron donors to the 1,4-benzoquinone. The results may be classified into three groups. The *first* group consists of carbon disulphide, cyclohexane, and *n*-heptane the points for which lie on a straight line passing through the gas phase point. This may indicate an interaction due to polarisation of the solvent by the double dipole field of the solute. Deviations from this straight line are observed in the *second* group; benzene, carbon tetrachloride, mesitylene and hexafluorobenzene; and especially in the *third* group; dioxan. These may indicate specific hyperpolarisation which is much the same as donor-acceptor interaction. Hexafluoroben-

Table 3. Dipole moments and relaxation times at 25° C

Solute	Solvent	μ(D)	τ(2) (ps)
(A)	Benzene	0.24	1.76
	p-Xylene	0.28	2.37
	Mesitylene	0.29	2.50
	Dioxan	0.25	1.39
	CCl_4	0.27	2.33
(B)	Benzene	0.36	8.26
(C)	Benzene	0.36	5.25
(D)	Benzene	0.43	3.49

zene is not normally regarded as an electron donor but rather as an electron acceptor. However, it seems possible that the carbonyl groups in 1,4-benzoquinone can act as electron donors to strong electron acceptors.

From an examination of the dielectric data no significant difference was noticed between the *second* and *third* groups and small but finite dipole moments of 0.24—0.29D are observed in these cases (Table 3) whilst the molecules belonging to the *first* group have no dipole moment. This would imply that no interaction of the donor-acceptor type occurs with the molecules of the *first* group.

Concluding Remarks

The following conclusions are reached from the present investigation.

1) 1,4-Benzoquinone is non-polar in the free state.

2) Polarity is produced when 1,4-benzoquinone is transferred from the gaseous phase into solutions in certain solvents such as benzene, dioxan, and carbon tetrachloride.

3) From dipole moments and dielectric relaxation times the above polarity is considered as due not to a conventional permanent dipole moment, but rather as due to some other cause such as the production of short-lived donor-acceptor complexes.

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