727. *Studies in Hydrogen-bond Formation. Part I. Detection of the Interaction of Phenols with Amido- and Azo-groups, etc., by Dielectric-constant Measurement.*

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Hydrogen bonding between organic compounds is readily detected by dielectric-constant measurement of binary solutions in anhydrous solvents. Recent developments in apparatus design enable results to be obtained rapidly with simple equipment.

It is found that phenolic hydroxy-groups have a consistent tendency to bond with other similar groups or with nitrogen atoms in azo-, amino-, and secondary alkyl- and aryl-amido-groups, but not with a keto-group. Cross-linking of azo- and alkylamido-groups by dihydric phenols (resorcinol, quinol) has been detected. Two azo-groups appear to be cross-linked by only one dihydric phenol molecule, whereas two alkylamido-groups appear to be cross-linked by two dihydric phenol molecules in parallel. The amide group seems to react in the enol form and is bifunctional.

THE hydrogen-bonding properties of organic molecules have received considerable attention in recent years, and much information is available on the formation of intra- and inter-molecular bonds by simple molecules, *e.g.*, *o*-nitrophenol, oxalic acid, and polymeric molecules in fibres (for summaries, see, *e.g.*, Pauling, "The Nature of the Chemical Bond," Ithaca, N.Y., Cornell Univ. Press, 2nd edn., 1944; Barrer, *J. Soc. Dyers Col.*, 1941, **57**, 264; Hunter, Price, and Martin, "The Hydrogen Bond," Royal Institute of Chemistry Lectures, Monographs, and Reports, 1950, No. 1). There is, however, little precise knowledge on hydrogen bonding between fibrous substrates and dyes or related materials, although it is believed that such bonding plays an important part in aiding the substantivity of dyes for most types of fibres (see, *e.g.*, Vickerstaff, "The Physical Chemistry of Dyeing," Edinburgh, Oliver and Boyd Ltd., 1950). It is proposed therefore to undertake a study of hydrogen bonding between typical groups found in fibres, dyes, and related reagents, suitable "model" compounds being used.*

It was decided first to examine the use of dielectric-constant measurements of solutions of such "model" compounds in anhydrous solvents, as a means of detecting intermolecular hydrogen bonding, because recent developments in circuit design enable a simple apparatus and technique to be employed. The present paper describes the apparatus and procedure and the results of some preliminary experiments with the method.

The dielectric constant of single organic compounds dissolved in inert, non-polar solvents is, in general, proportional to the concentration (cf., *e.g.*, Clark, "The Fine Structure of Matter," Chapman and Hall Ltd., London, 1938. Part II, Chap. X). In binary solutions of constant total molarity, but having varying proportions of the solutes, proportionality will hold only if no interaction occurs. If a donor compound, $A{=}O$, and an acceptor, $H{-}B$, interact, forming a complex, $A{=}O \rightarrow H{-}B$, the dipole moment of the last will differ from that of either of the components, and a mixed solution will have a dielectric constant differing from the additive value. It can be shown (see Appendix) that the plot of the dielectric constant against molar proportion of solutes should show a change of slope at a point corresponding to the composition of the complex formed.

Previous Work.—Chrétien and Laurent (*Compt. rend.*, 1932, **195**, 792; 1934, **199**, 639), Laurent (*ibid.*, 1934, **199**, 582; 1935, **201**, 554), and Trinh (*ibid.*, 1948, **226**, 403) found distinct kinks in the curves of dielectric constant against relative molar concentration for a number of binary solutions of simple organic compounds in benzene, dioxan, and ether. They interpreted the results as a measure of the ease of salt formation between the

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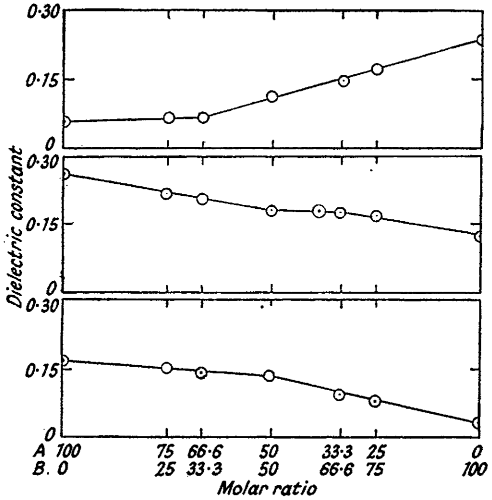
* Since this paper was submitted Flett (*J. Soc. Dyers Col.*, 1952, **68**, 59) has described a quantitative investigation, by infra-red spectrophotometry, of the heats and free energies of formation of hydrogen bonds between 21 pairs of simple organic compounds; none of these pairs is identical with any of those here described.

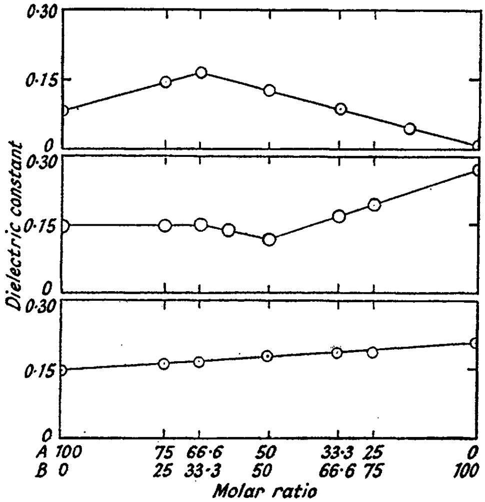
compounds examined and did not consider the possibility of hydrogen bonding. The mixtures they used included a number of mono-, di-, and tri-hydric phenols with nitriles, pyridine, and primary, secondary, and tertiary aliphatic and aromatic amines, and in most cases each phenolic group was found to unite with one nitrogen-containing group. A few exceptions were noted; *e.g.*, no interaction was detected between phenolic groups and dimethylaniline, *p*-phenylenediamine, or " aminophenol " (configuration unspecified). This was attributed to the reduced basicity of these three compounds. *o*-Nitrophenol was the only compound examined for interaction with azobenzene, with which it was found to associate in 2 : 1 ratio. No amides were examined. One hydrocarbon, triphenylmethane, was included; it formed a 1 : 1 complex with pyrrole.

FIG. 1. *Relation between dielectric constant* * *and component ratio in binary solutions.*



Top : A = Azobenzene. B = Aniline;
Middle : A = Aniline; B = Diethylamine.
Bottom : A = *o*-Nitrophenol; B = Diethylamine.

FIG. 2. *Relation between dielectric constant* * *and component ratio in binary solutions.*



Top : A = Phenol; B = Quinol.
Middle : A = Phenol; B = Azobenzene.
Bottom : A = Phenol; B = Benzophenone.

* The ordinates show increments of dielectric constant, on arbitrary base-lines, not absolute values.

Earp and Glasstone (*J.*, 1935, 1709, 1720) measured the dielectric constants of binary mixtures of acetone, dioxan, quinoline, and simple ethers, with chlorinated hydrocarbons, and calculated therefrom the mass-action constants of the complex-formation reactions and the amounts of the complexes present. They made some experiments with binary solutions of the reagents in *cyclo*hexane, but the deviations from additivity of the dielectric constants were too small to be of value in the calculations required. Intermolecular bonding was found to occur between oxygen and hydrogen attached to aliphatic carbon, especially if hydrogen is attached to a negative group, *e.g.*, a phenyl or nitrophenyl group.

Present Work.—The present work covers broadly an examination of the interaction of the phenolic hydroxy-group with the keto-group and with other phenolic hydroxy-groups; with nitrogen-containing groups, *e.g.*, the azo-, alkyl, and aryl-amide groups; with primary, secondary, and tertiary amino-groups; and with the nitro-group. The amides used were (*a*) *N*-*n*-butylpropionamide, chosen for its ease of preparation, suitable physical properties, and similarity to the repeat unit in both Nylon and protein fibre molecules, and (*b*) acetanilide, chosen because it contains the arylamide group, present in many dyes. In order further to study the properties of the two portions of the amide group separately, compounds containing individual keto- and secondary alkylamino-groups, respectively, were also examined. Two compounds likely to demonstrate the effect of an internal chelate link, *o*-nitrophenol and 2 : 3 : 4-trihydroxybenzophenone, were also included in the tests.

To carry out the examination of their bonding properties, the pairs of solutes for test are each separately dissolved in the same solvent at the same molar concentration. The required series of binary solutions is then readily prepared by mixing small volumes of the solutions, in the required ratios, measured from microburettes, and the mixtures are then stored in ground-glass stoppered test-tubes until required. The dielectric constants of the solutions are determined as described below and the values are plotted against the molar ratios. The curves are linear in almost every case, usually showing one distinct change of slope, and sometimes two. These changes always occur exactly at the simple molar ratios 1 : 1 or 1 : 2. In a few cases a single straight line is obtained, attributed to the absence of a complex, and in some cases the presence or absence of change of slope is uncertain. Some typical curves are shown in Figs. 1 and 2 and the conclusions drawn from the whole series of results are summarised in Table 1.

TABLE 1.

Solutes		Solution		
a	*b*	Solvent *	Total mol. concn.	Mol. ratio of complex (*a* : *b*) †
Acetanilide	Aniline	D	0·2	(1 : 1)
	Azobenzene	D	0·2	(1 : 1)
	Phenol	D	0·2	1 : 2
	Triethylamine	D	0·2	1 : 1
Azobenzene	Aniline	B	0·3	2 : 1
	Phenol	B	0·3	1 : 1; 1 : 2
	Catechol	E	0·3	1 : 1
	Resorcinol	E	0·3	2 : 1
	Quinol	E	0·15	2 : 1
N-*n*-Butylpropionamide	Phenol	B	0·3	1 : 2
	Catechol	E	0·3	(2 : 1)
	Resorcinol	E	0·3	1 : 1
	Quinol	E	0·15	1 : 1
	2 : 3 : 4-Trihydroxybenzophenone	E	0·3	2 : 1
	o-Nitrophenol	B	0·3	1 : 1
	p-Nitrophenol	E	0·3	2 : 1
	Azobenzene	B	0·3	1 : 1
Di*iso*butyl ketone	Aniline	B	0·3	‡
	Phenol	B	0·2	‡
	Catechol	E	0·3	(‡)
	Quinol	E	0·15	(‡)
	Azobenzene	B	0·2	‡
Diethylamine	Aniline	B	0·3	1 : 1; 2 : 1
	Phenol	B	0·2	1 : 1
	Catechol	E	0·3	1 : 1; 2 : 1
	Resorcinol	E	0·3	1 : 1; [1 : 2(?) (solid complex §)]
	Quinol	E	0·15	2 : 1; (1 : 1)
	o-Nitrophenol	B	0·3	1 : 1
	p-Nitrophenol	E	0·3	[2 : 1(?) (solid complex §§)]
	Azobenzene	B	0·2	1 : 1
Phenol	Benzophenone	B	0·25	‡
	Catechol	E	0·2	2 : 1
	Quinol	E	0·15	2 : 1
	Quinoline	B	0·2	1 : 1
	Triethylamine	B	0·2	1 : 1

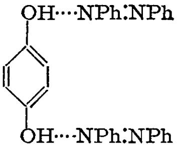
* Solvents : B = benzene; D = dioxan; E = diethyl ether.
† Data in parentheses denote uncertain indications.
‡ No evidence of complex formation.
§ Colourless needles, m. p. 118°.
§§ Yellow needles, m. p. 88°.

Crystalline complexes separated from the solutions of diethylamine with resorcinol (on storage) and with *p*-nitrophenol (when first mixed). These crystals were collected and analysed. Their empirical compositions did not exactly correspond to simple ratios of the components, though they approximated to the ratios shown in Table 1. This is probably accounted for by selective removal of one of the components when the precipitate is washed with fresh solvent.

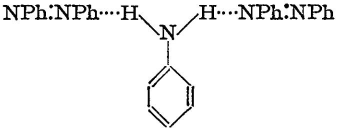
Discussion.—In the present work, only the *ratio* in which the solutes combine is strictly determined, but in most cases a consideration of the bonding tendencies of the individual groups, which is disclosed by the results as a whole, and, in some cases the use of scale-model molecules, enables the formula of the actual complex(es) formed to be given with some confidence.

There is a consistent tendency for each phenolic hydroxy-group to bond with one other similar group or with nitrogen atoms of the azo-, alkylamido-, and amino-groups. In the nitrophenols one oxygen of the nitro-group appears to form a bond with a hydrogen atom in the second solute; the internal chelate bond in the *o*-compound prevents the hydroxy-group from taking part in any such intermolecular bond, but in the *p*-isomer it can do so and as a result *p*- nitrophenol can cross-bond two alkylamido-groups. 2 : 3 : 4-Trihydroxybenzophenone reacts in the same ratio with the alkylamide group as does catechol, confirming the presence of a chelate linkage between the keto-group and the adjacent hydroxy-group.

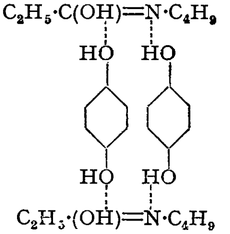
Two phenol molecules can unite simultaneously with the two nitrogen atoms of azobenzene.* The two active hydrogen atoms in quinol, resorcinol, and aniline must form cross-linkages with two azobenzene molecules † because this seems to be the most reasonable interpretation of the 2 : 1-ratio complexes detected [*e.g.*, as in (I) and (II)]. Examination of models shows that steric hindrance prevents two of the cross-linking molecules from combining in parallel with the azo-groups.



(I) With quinol.



(II) With aniline.



(III)

Catechol appears to be able to form complexes by means of either one or two of its hydroxy-groups. The 1 : 1-ratio complex observed with catechol–azobenzene solutions might therefore be interpreted either as evidence of a single hydrogen bond between one hydroxy-group and one azo-nitrogen atom, or of a complex in which each azo-nitrogen atom is attached to one of the hydroxy-groups of the catechol molecule. Although it can be shown, with scale models, that such a structure is possible with azobenzene in the normal *trans*-form, it seems less likely because it involves an eight-membered ring.

A study of models gives no evidence of steric hindrance to such double cross-bonding of alkylamido-groups and it does indeed appear to occur with *N*-*n*-butylpropionamide and resorcinol or with quinol, where complexes only of 1 : 1-ratio are detected. The only structural configuration which seems to satisfy this ratio is that shown in (III), it being borne in mind (*a*) that both hydroxy-groups in the aromatic compound appear to be equally reactive, and (*b*) that a polymer with a very long chain of cross-bonded groups (the only other possible configuration), would probably be insoluble.

There is no evidence that the phenolic hydroxy-group forms a stable bond ‡ with the keto-group in simple ketones, yet the •CO•NH• group in both *N*-*n*-butylpropionamide and acetanilide appears to be bifunctional in forming hydrogen-bond complexes. This group may thus be reacting in the enol form, •C(OH)⁚N•, which could be considered bifunctional, because it is clear from Table 1 that both tertiary nitrogen atoms and hydroxy-groups can form bonds.

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* Azobenzene itself thus differs from its *oo'*-dihydroxy-derivatives, in which only one hydroxy-group appears to be chelated with the azo-group (Schetty, *Textil-Rundschau*, 1950, **5**, 399).

† Similar cross-linking of azobenzene derivatives by quinol has been observed in monolayers on water (Giles and Neustädter, following paper).

‡ Some of the curves of solutions containing a ketone are not quite linear, though no kinks are present. This may indicate the formation of unstable complexes.

EXPERIMENTAL

(Microanalyses were by Drs. Weiler and Strauss, Oxford.)

N-n-*Butylpropionamide*.—Propionyl chloride (37 g.) was added dropwise to *n*-butylamine (58·4 g.) under a reflux condenser, in a flask cooled in a bath of ethanol and solid carbon dioxide. When addition was complete the mixture was heated to 80°, kept thereat for 15 minutes, and allowed to cool overnight. The liquor was then shaken with an equal volume of water, and the oily layer separated and retained. The aqueous layer was then shaken with ether and the ether extract added to the oil, which was then twice distilled, and the *amide* collected; yield: 45 c.c. of a colourless liquid, b. p. 236°/760 mm. (Found: C, 64·9; H, 11·6; N, 10·7. $C_7H_{15}ON$ requires C, 65·1; H, 11·6; N, 10·85%).

2 : 3 : 4-*Trihydroxybenzophenone* (Alizarin-yellow A, Colour Index, No. 1014).—Benzotrichloride (40 g.) was added slowly to pyrogallol (20 g.) in boiling 90% ethanol (40 g.), and the mixture poured into cold water; the product formed yellow needles, m. p. 139—140°, from water (Found: C, 67·7; H, 4·4. Calc. for $C_{13}H_{10}O_4$: C, 67·8; H, 4·35%).

Specially dried solvents of analytical reagent quality were used.

Measurement of Dielectric Constant.—Determination of dielectric constants depends on accurate capacitance measurement. Three procedures have been commonly used for this purpose: (*a*) the capacity bridge, (*b*) the heterodyne beat method, and (*c*) the resonance method.* Chrétien and Laurent used (*a*) (cf. Chrétien, *Compt. rend.*, 1931, **192**, 1385), and Earp and Glasstone used (*b*). In the present work, advantage has been taken of recent developments which enable the resonance method to be used with simple apparatus of high sensitivity. The instrument incorporates a tuned-anode, quartz crystal-controlled grid oscillator, based on the principle first employed for dielectric-constant measurement by Henriquez (Reilly and Rae, " Physico-Chemical Methods," Methuen and Co. Ltd., London, 3rd edn., 1940, Vol. II, pp. 509, 510). Energy is transferred between a tuned oscillatory circuit and the quartz crystal through the anode-grid capacitance of a triode valve, the condition of resonance being reached when the natural frequency of the tuned circuit approaches that of the quartz crystal and oscillation sets in. At the resonant frequency, the circuit offers maximum impedance to the direct current through it, and the change in anode current thus produced may be employed as a means of determining the oscillation point. A dielectric cell or condenser is placed in parallel with a calibrated tuning condenser in the anode oscillatory circuit, and the system tuned to resonance. Introduction into the cell of the dielectric medium to be tested, by altering the capacitance of the anode circuit, causes the circuit to go out of oscillation. The oscillation point is restored by re-tuning the variable condenser, the difference between the two readings of which gives a measure of the required dielectric constant.

A milliammeter was formerly employed for recording the change in anode current, but Alexander (*Electronics*, 1945, **18**, No. 4, 116) first employed an electron ray (" magic eye ") tube to serve as a combined oscillator and tuning indicator of improved sensitivity.

Design of Instrument.—The instrument (Fig. 3) used in the present work incorporates a Y 63 electron-ray (" magic eye ") tuning indicator and is based on the circuits used by Alexander (*loc. cit.*), Bender (*J. Chem. Educ.*, 1946, **23**, 179), and Fischer (*Anal. Chem.*, 1947, **19**, 835). The triode portion of the indicator is used as the oscillator, and the target electrode as the resonance detector. The target, coated with fluorescent material, is positive with respect to the cathode. The resulting electron stream from cathode to target is influenced by a control electrode grid (internally connected with the triode anode), which, when it is made negative with respect to the target, deflects the electron stream, producing a shadow on the target, the normal " open eye." The angle of this shadow is reduced by making the control electrode more positive. In the non-oscillating position the anode current produces a large potential difference across the anode resistor R_2, which holds the anode and control electrode potentials at a low value with respect to the target; the " eye " is then open. When the anode and grid circuits are brought to resonance, the anode current decreases and therefore the potential difference across R_2 drops. Consequently, the potential of the control electrode with respect to the cathode, rises—it becomes less negative with respect to the target and the " eye " closes. The most convenient reference point for making measurements is the critical off-resonance capacity setting when the " eye " just flicks open or shut with increase or decrease of capacity, respectively.

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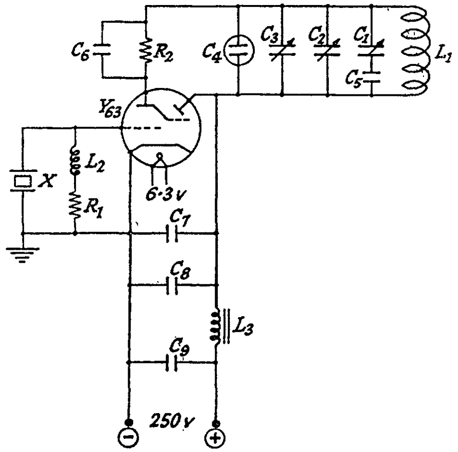
[*] For a full discussion of the relative merits of (*a*), (*b*), and (*c*), see Smith, " Dielectric Constant and Molecular Structure," The Chemical Catalog Co. Inc., New York, 1931, Chap. 3.

The following are the values of the components used: C_1, 350 μμF; C_2, 12·5 μμF; C_3, 25 μμF; (C_4 is the dielectric cell); C_5, C_7, 0·01 μF; C_6, 0·001 μF; C_8, C_9, 2 μF; R_1, 1 megohm; R_2, 42,000 ohms; X, 4·55 Mc./s. quartz crystal; L_1, 11 turns of 20 S.W.G. enamelled copper wire close-wound on a 1-in. former; L_2, small R.F. choke; L_3, 7-Henry 50-mA choke. The condensers C_1 and C_2 are fitted with low-geared vernier dials. The dielectric cell (C_4) is constructed from a 12-μμF variable condenser, with silvered plates, by stripping all but one plate from the stator and all but two plates from the rotor. A brass stop is fitted so that the plates cannot be opened more than about half the maximum extent. The cell unit is connected to the main circuit by a short, screened cable. For use, the condenser plate assembly is submerged in about 20 c.c. of the liquid under test, contained in a small glass beaker.

Calibration of Instrument.—The instrument is switched on 15 minutes before use. It is first necessary to determine the values of the scale readings of the fine tuning condenser (C_2) against the main condenser (C_1). This procedure is repeated several times with a series of settings of C_1, the corresponding values of C_1 and C_2 being noted. In use, when the resonance position is reached, the reading of C_2, corrected to its value on C_1, is added to that of C_1.

FIG. 3.



The instrument is then calibrated, first with air and then with a series of pure liquids of known dielectric constant, as follows. With the plates of the measuring cell condenser open, in air, the anode and grid circuits are brought to resonance (the "eye" just flicks shut at this point), by tuning first with C_1 and then with C_2. The measuring cell plates are now closed, and C_1 and C_2 again adjusted to resonance. The difference between the two readings of C_1, each corrected by addition of the respective readings of C_2, gives the maximum capacitance increment in the measuring cell with air dielectric. The procedure is then repeated with the measuring cell filled with each liquid in turn. The dielectric constant of any liquid is given by the ratio of the maximum capacitance increments of the cell filled with that liquid and with air. (This method of measurement by using capacitance increments eliminates errors due to stray capacities between the cell, leads, and chassis.) The typical series of calibration readings in Table 2 shows that the plot of dial readings (*i.e.*, values of C_1, corrected as described above) against dielectric constant is virtually linear over a wide range. In the present work, where only the relative values of dielectric constant of a series of liquids are required, a simpler procedure may be followed: readings are taken only with the condenser plates closed, and they may then be plotted directly against the molar ratios of the solutes in the solutions used.

TABLE 2. *Calibration of instrument.*

Dielectric	Air	Benzene	Ethyl ether	Chloroform	Ethyl acetate	Quinoline	Pyridine	Acetone
Dielectric constant	1·00	2·88	4·33	4·95	6·10	8·90	12·50	21·30
Max. capacitance increment of cell (dial reading)	96·04	92·64	86·84	85·80	81·77	74·20	62·22	32·00

The solutions of the two solutes to be examined were prepared and stored until required in ground-glass-stoppered tubes, then measured quickly in succession in the instrument at room temperature. After each solution had been measured, the plates were carefully washed with successive changes of pure dry ether and finally well dried in an air stream. The additional complication of thermostatic temperature control of the test liquid was considered unnecessary because the complete series of readings to detect complex formation between two solutes can be made in 30 minutes or less and any slight temperature variation between different series of experiments does not affect the position on the curves at which the changes of slope occur.

In an attempt to avoid the need for immersing the variable condenser plates in the test liquid, a method also used by Fischer (*loc. cit.*) and based on that proposed by Jensen and Parrack (*Ind. Eng. Chem. Anal.*, 1946, **18**, 585) for conductiometric analysis, was examined. A circuit embodying the electron-ray indicator was employed and the oscillator was loaded by placing the test liquid in a glass tube, on which the coil of the anode oscillatory circuit was wound. The use of the method was not pursued, because with the available equipment the instrument proved less sensitive than the one described above and the calibration curve was not quite linear.

The results have been checked where necessary by examination of scale-model molecules.

APPENDIX

To demonstrate that the dielectric constant–concentration curve may be expected to show a break at the ratio of components corresponding to a complex, consider the special case of a binary solution, originally containing A molecules of a substance X and B molecules of a substance Y, in which z molecules of a complex Z, of formula XY have been formed. By the law of mass action $(A - z)(B - z)/z = 1/K$, where K is the equilibrium constant. Solving this for z, we have

$$z = \tfrac{1}{2}[(A + B + 1/K) \pm \sqrt{(A + B + 1/K)^2 - 4AB}]$$

Only the smaller root is a solution of this equation, since the larger one is greater than the larger of A and B and hence is impossible. It has a simple solution only if $1/K$ may be neglected in comparison with $A + B$, *i.e.*, if the compound is stable relative to X and Y, when $z = A$ or B, whichever is the smaller.

If we now measure any physical property of the binary solution (in this case the dielectric constant), which depends linearly upon the concentration of any of the three components of the solution considered separately, its value $\varepsilon_{\text{obs.}}$ is given by the expression

$$C\varepsilon_{\text{obs.}} = \varepsilon_{\text{X}}(A - z) + \varepsilon_{\text{Y}}(B - z) + \varepsilon_{\text{Z}}z$$

where $C = A + B$ and ε_{X}, ε_{Y}, ε_{Z} are respectively the physical constants (here, the dielectric constants) of the individual substances X and Y and the complex XY.

If the ratio $A : B$ is varied, $A + B$ remaining constant, then over the range $A < B$, we have $z = A$ and therefore

$$C\varepsilon_{\text{obs.}} = \varepsilon_{\text{Y}}(B - A) + \varepsilon_{\text{Z}}A = B(2\varepsilon_{\text{Y}} - \varepsilon_{\text{Z}}) - C\varepsilon_{\text{Y}} + C\varepsilon_{\text{Z}}$$

i.e., $\varepsilon_{\text{obs.}}$ varies linearly with B, the gradient being $(2\varepsilon_{\text{Y}} - \varepsilon_{\text{Z}})/C$. Over the range $A > B$, $z = B$ and therefore $C\varepsilon_{\text{obs.}} = B(-2\varepsilon_{\text{X}} + \varepsilon_{\text{Z}}) + \varepsilon_{\text{X}}C$, $\varepsilon_{\text{obs.}}$ again varying linearly with B, and the gradient being $(-2\varepsilon_{\text{X}} + \varepsilon_{\text{Z}})/C$. The two lines will intersect where $A = B = \tfrac{1}{2}C$, and at the intersection $\varepsilon_{\text{obs.}} = \tfrac{1}{2}\varepsilon_{\text{Z}}$.

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