## 433. *Cryoscopy and Association in* p-*Chlorotoluene.*

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THE carboxylic acids are well known to be partly associated to double molecules in the vapour state, and the observed vapour densities can be accounted for quantitatively by assuming that the equilibrium between single and double molecules obeys the classical law of mass action (Drucker and Ullman, *Z. physikal. Chem.*, 1910, **74**, 567; Coolidge, *J. Amer. Chem. Soc.*, 1928, **50**, 2166). Determinations of the apparent molecular weights of carboxylic acids in solution also indicate the presence of double molecules in some solvents, but the experimental data at present available are not sufficiently accurate to decide whether or not the properties of these solutions can be described by a simple mass-law equilibrium.

The only methods of investigation of any value are measurements of elevation of boiling point and lowering of freezing point [those of partition coefficients appear at first sight to offer a convenient approach, and have been largely used for this purpose, but there are difficulties in interpreting the results (cf. Szyszkowski, *Z. physikal. Chem.*, 1928, **131**, 175; Bell, *ibid.*, 1930, **150**, *A*, 20)]. Previous investigations have shown that at convenient concentrations carboxylic acids are in most cases either almost entirely unimolecular (*e.g.*, in ether, acetone, and water) or almost entirely bimolecular (*e.g.*, in benzene and ethylene dibromide). In order to study the postulated equilibrium it is necessary either to use very dilute solutions in the second class of solvent or to find a more suitable solvent. Peterson and Rodebush (*J. Physical Chem.*, 1928, **32**, 709) have measured the freezing points of very dilute solutions of acetic acid in benzene (*ca.* 0·1—0·004*N*), using a very refined technique and covering almost the entire range from 100% single to 100% double molecules. However, if their results are used to calculate a mass-action " constant," this is found to vary by a factor of 5, the variations being equally great with any value between 5·10 and 5·23 for the cryoscopic constant of benzene. Brown and Bury (*ibid.*, 1934, **30**, 694) measured the freezing points of solutions of carboxylic acids in nitrobenzene, which proved to be a much more suitable solvent, but in this case also the results cannot be expressed in terms of a mass-action constant. The matter thus stands in need of further investigation; in particular, it is desirable to find other solvents which give a suitable degree of association at moderate concentrations. It was thought that *p*-chlorotoluene might resemble nitrobenzene in this respect, so it was chosen for the present investigation. Further, the molecular state of carboxylic acids in this solvent is of interest in connexion with previous work on reaction velocities in the very similar solvent chlorobenzene (Bell, *Proc. Roy. Soc.*, 1934, **143**, 377), where it was found that the catalytic power of carboxylic acids varied considerably with their concentrations.

## EXPERIMENTAL.

*Materials.*—*p*-Chlorotoluene, prepared from pure *p*-toludine by the Sandmeyer reaction (see " Organic Syntheses," **3**, p. 33), was washed with concentrated sulphuric acid, sodium hydroxide solution, and water, dried with calcium chloride, and fractionally distilled twice. 900 G. of *p*-toluidine afforded 650 g. of a product boiling within 0·1°, b. p. 162·1°/755 mm. (uncorr.); f. p. 6·86°, unaltered within 0·001° after a further fractionation. Bloch (*Z. physikal. Chem.*, 1913, **82**, 408) gives 6·85°, and Beilstein 7·4—7·5° for samples not specially purified. The refractive index was $n_D^{18°}$ 1·5221, the only previous value being $n_D^{24·35°}$ 1·5193 (Auwers and Frühling, *Annalen*, 1921, **422**, 160).

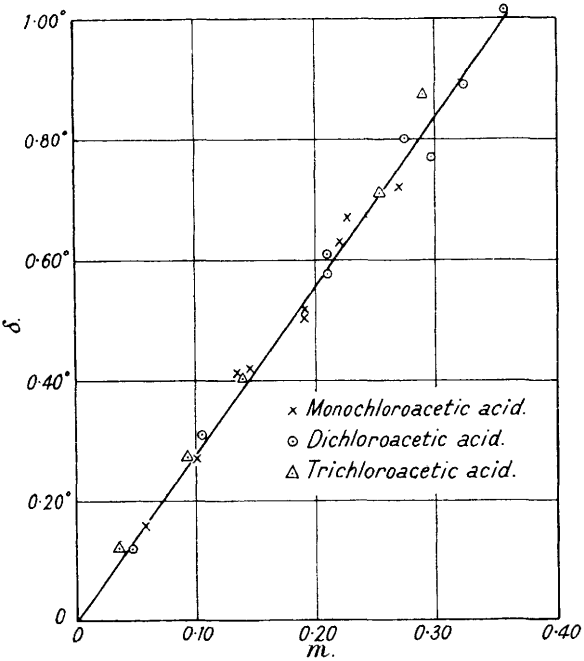
Benzene was a preparation for molecular-weight determinations; m. p. 5·60°, unchanged by partial freezing. Monochloroacetic acid was recrystallised from benzene and dried in a vacuum. Di- and tri-chloroacetic acids were pure commercial products. Bromine was dried over phosphoric oxide and distilled in a vacuum. Ethyl iodide was shaken with sodium thiosulphate solution to remove free iodine, dried with calcium chloride, and fractionally distilled.

*Cryoscopic Constant of* p-*Chlorotoluene.*—The only previous values for this constant are those of Auwers (*Z. physikal. Chem.*, 1902, **42**, 513), who obtained values ranging from 5·54 to 5·81 by the Beckmann method. Preliminary experiments using the same method (with naphthalene and camphor as solutes) gave very variable results ranging from 5·7 to 6·2. Each series of readings gave concordant values, but an alteration in the vessel or other experimental conditions led to large changes in the value of the constant. This behaviour appears to be a characteristic of the Beckmann method : for instance, the values given in International Critical Tables for the cryoscopic constant of benzene range from 5·09 to 5·23, and it is significant that the latter value, which depends on the very accurate work of Jones and Bury (J., 1925, **127**, 1947) on the Beckmann method, is in poor agreement with the value of 5·12 derived from the most accurate measurements of the latent heat of fusion (Huffman, Parks, and Daniels, *J. Amer. Chem. Soc.*, 1930, **52**, 1547).

The present work was therefore carried out by using an equilibrium method, *i.e.*, the solution in equilibrium with solid at a known temperature was analysed. As a check on the method, the cryoscopic constant of benzene was also determined. Bromine and ethyl iodide were chosen as solutes, since they may both be expected to behave normally, and they can be determined accurately by chemical means. Bromine was determined by titrating the iodine liberated from potassium iodide, and ethyl iodide by Viebock and Schweppach's method (*Ber.*, 1930, **63**, 2818), in which it is oxidised to iodic acid by bromine in the presence of acetic acid, sodium acetate, and water ($C_2H_5I + 3Br_2 + 3H_2O \longrightarrow C_2H_5Br + 5HBr + HIO_3$), excess bromine being destroyed with formic acid, and the iodic acid titrated in the usual way. This method was tested with solutions of known amounts of ethyl iodide in benzene and *p*-chlorotoluene, and found to give satisfactory results; *e.g.*, in *p*-chlorotoluene, 0·0252, 0·0278, 0·0441, and 0·0712 g. of ethyl iodide gave on analysis 0·0251, 0·0276, 0·0439, and 0·0720 g. respectively.

The thiosulphate solution used in both titrations was standardised with pure iodine and with potassium iodate.

The freezing-point determinations were carried out in a 250 c.c. vacuum flask closed by a cork, through which passed a Beckmann thermometer and a glass stirrer. A third hole served for the addition and withdrawal of solution. About 100 c.c. of pure solvent were half frozen, and the mush of liquid and fine crystals transferred to the flask. After the f. p. of the pure solvent had been taken, 2 c.c. of a solution of bromine or ethyl iodide were added. (The concentration of these solutions was chosen so that the addition of 2 c.c. produced a f.-p. depression of 0·2—0·4°. Independent tests showed that bromine did not react appreciably with either solvent under the conditions of the experiments.) With gentle stirring, a constant temperature was rapidly attained, and although it rose slightly on standing (presumably by heat conduction down the thermometer), yet on renewed stirring the same reading was obtained over a period of at least ½ hour. When a constant reading had been obtained, about 2 c.c. of the solution were removed with a pipette and transferred to a weighed, glass-stoppered flask, after which it was analysed as described above. The pipette terminated in a capillary fine enough to prevent the entry of any particles of solid solvent. The same procedure was then repeated with further additions of solution.



The results obtained for the cryoscopic constants of the two solvents are given in Table I, where δ = f.-p. depression, $m$ = concentration of solute (mols. per 1000 g. of solvent), and $K = \delta/m$ = cryoscopic constant.

TABLE I.

*Benzene.*

| Bromine. | | | | | | Ethyl iodide. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| δ. | *m.* | *K.* | δ. | *m.* | *K.* | δ. | *m.* | *K.* | δ. | *m.* | *K.* |
| 0·450° | 0·0879 | 5·12° | 0·450° | 0·0879 | 5·12° | 0·340° | 0·0685 | 4·96° | 0·730° | 0·1425 | 5·12° |
| 0·901 | 0·1799 | 5·07 | 0·701 | 0·1370 | 5·10 | 0·505 | 0·0974 | 5·18 | 0·945 | 0·1826 | 5·17 |
| 1·121 | 0·2208 | 5·08 | 0·901 | 0·1739 | 5·16 | 0·670 | 0·1286 | 5·21 | 1·081 | 0·2085 | 5·18 |
| 1·395 | 0·2699 | 5·17 | 1·096 | 0·2690 | 5·12 | | | | | Mean | 5·15 |
| | Mean | 5·11 | 2·001 | 0·3909 | 5·11 | | | | | | |
| | | | | Mean | 5·12 | | | | | | |
| p-*Chlorotoluene.* | | | | | | | | | | | |
| 0·550 | 0·1019 | 5·40 | 1·342 | 0·2421 | 5·54 | 0·263 | 0·0468 | 5·62 | 0·880 | 0·1577 | 5·58 |
| 0·821 | 0·1491 | 5·51 | 1·621 | 0·2822 | 5·74 | 0·487 | 0·0875 | 5·55 | 1·066 | 0·1943 | 5·49 |
| 1·121 | 0·2002 | 5·60 | 1·850 | 0·3363 | 5·50 | 0·708 | 0·1283 | 5·52 | 1·262 | 0·2270 | 5·56 |
| | | | | Mean | 5·54 | | | | | Mean | 5·52 |

Mean for both solutes, 5·53.

The mean value of the cryoscopic constant for benzene, 5·13, agrees well with Huffman, Parks, and Daniels' value 5·12 (*loc. cit.*), and also with that of Bury and Jenkins (this vol., p. 688), obtained by a much more accurate equilibrium method using six different solutes. The method described here can therefore be considered to be reliable.

*The Association of Carboxylic Acids in* p-*Chlorotoluene.*—The f.-p. measurements with carboxylic acids were carried out in exactly the same way, the acid concentration being determined by titration with baryta. The results are given in Table II, and shown graphically in the fig., in which the straight line is the theoretical line for complete association into double molecules, with the value 5·53 for the cryoscopic constant. It is seen that the experimental points show no systematic deviation from the line, so that all three acids must be present almost exclusively in the bimolecular form over the concentration range 0·05—0·35*M*. *p*-Chlorotoluene is therefore not a suitable solvent for a study of the equilibrium between single and double molecules.

TABLE II.

*Acids in* p-*chlorotoluene.*

| Monochloroacetic. | | | | Dichloroacetic. | | | | Trichloroacetic. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| δ. | *m.* | δ. | *m.* | δ. | *m.* | δ. | *m.* | δ. | *m.* | δ. | *m.* |
| 0·16° | 0·057 | 0·52° | 0·191 | 0·12° | 0·046 | 0·61° | 0·212 | 0·12° | 0·034 | 0·76° | 0·255 |
| 0·27 | 0·097 | 0·62 | 0·220 | 0·23 | 0·075 | 0·77 | 0·298 | 0·37 | 0·097 | 0·87 | 0·291 |
| 0·41 | 0·136 | 0·67 | 0·226 | 0·31 | 0·105 | 0·80 | 0·357 | 0·41 | 0·139 | | |
| 0·42 | 0·144 | 0·72 | 0·271 | 0·58 | 0·209 | 0·87 | 0·302 | | | | |
| 0·51 | 0·190 | | | | | | | | | | |

The fact that the molecular state of these acids does not vary with concentration should lead to a similar constancy of other physical properties. This was confirmed by measurements of the refractive indices of similar solutions at 18°, using a water-jacketed Pulfrich refractometer. It was found that the molar refractivity of each acid remained constant within the experimental error. It should, however, be pointed out that this constancy does not extend to the catalytic powers of the same acids in the very similar solvent chlorobenzene (Bell, *Proc. Roy. Soc., loc. cit.*); *e.g.*, the catalytic power of trichloroacetic acid varies from 3·5 to 2·0 over the range 0·05—0·35*M*. The cryoscopic results in *p*-chlorotoluene make it very improbable that the extrapolated catalytic constants in chlorobenzene refer (as previously supposed) to the single carboxylic acid molecules. This point is being further investigated.

## SUMMARY.

(1) The cryoscopic constant of purified *p*-chlorotoluene has been determined by an equilibrium method, giving the value 5·53 per mol. of solute per 1000 g. of solvent.

(2) Mono-, di-, and tri-chloroacetic acids were found cryoscopically to be entirely bimolecular in *p*-chlorotoluene over the concentration range 0·05—0·35 mol. per 1000 g.

(3) The molar refractivity of these acids was found to be constant over the same concentration range.

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