[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TENNESSEE]

A Study of Molecular Organic Compounds. V. Parachors of the Phenol-Amines in Solution

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In the last paper[1] of this series it was shown that the parachors of the phenol-amines are not constant, but increase appreciably with a rise in temperature. Such increases have been regarded as being due to dissociation, an explanation which seems plausible in view of the rise in parachor shown among associated substances. To study this phenomenon further the solution method of Hammick and Andrew[2] for the determination of parachors was tried. In order to lessen, if not prevent, any possible dissociation, the mass action effect, in which the solvent was one of the components of the molecular compound, was

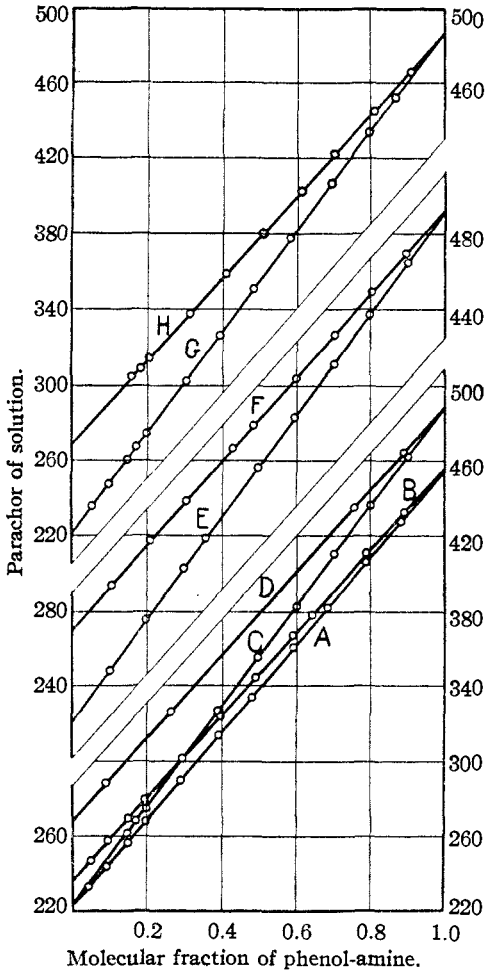

Fig. 1.—Parachor–concentration curves of phenol-amines in components at 40°: A, phenol-aniline in phenol (30°); B, phenol-aniline in aniline; C, phenol-*o*-toluidine in phenol; D, phenol-*o*-toluidine in *o*-toluidine; E, phenol-*m*-toluidine in phenol; F, phenol-*m*-toluidine in *m*-toluidine; G, phenol-*p*-toluidine in phenol; H, phenol-*p*-toluidine in *p*-toluidine.

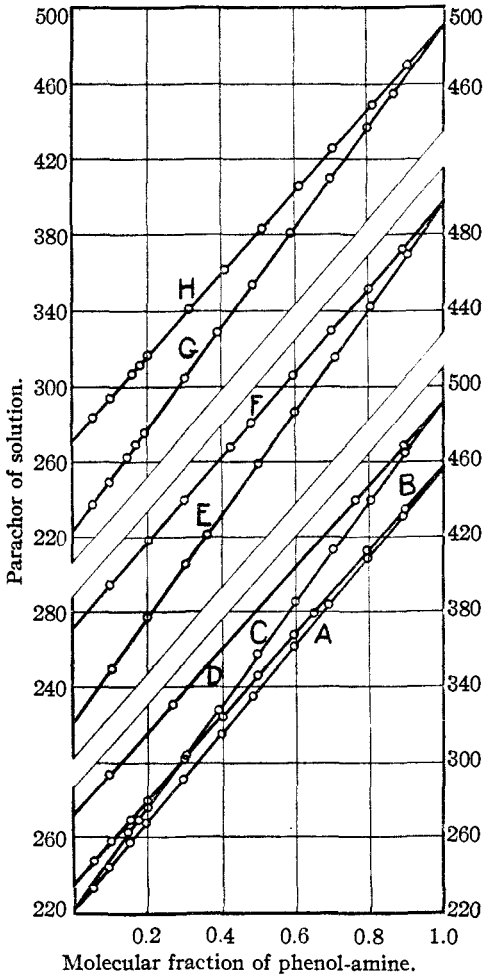

Fig. 2.—Parachor–concentration curves of phenol-amines in components at 75°: A, phenol-aniline in phenol; B, phenol-aniline in aniline; C, phenol-*o*-toluidine in phenol; D, phenol-*o*-toluidine in *o*-toluidine; E, phenol-*m*-toluidine in phenol; F, phenol-*m*-toluidine in *m*-toluidine; G, phenol-*p*-toluidine in phenol; H, phenol-*p*-toluidine in *p*-toluidine.

(1) Buehler, Wood, Hull and Erwin, THIS JOURNAL, **54**, 2398 (1932).

(2) Hammick and Andrew, *J. Chem. Soc.*, 754 (1929).

employed. With this plan the difference in surface tensions of the solute and solvent was not great enough to interfere with the reliability of the method.

By plotting the parachors of the solutions examined against the molecular fractions the straight lines as shown in Figs. 1 and 2 were obtained. Extrapolation of these lines gave at zero the parachor of the solvent, and at one molecular fraction the parachor of the pure solute.

The extrapolated values, obtained by plotting carefully the determined solution parachors on a large scale, are found in Table I. These agree, in the main, with the values previously obtained on the pure phenol-amines, and they may be regarded as being constant in either component as solvent at the same temperature. However, with an increase in temperature an unexpected rise in the parachor follows much in the same way as in the determinations on the pure compounds. In fact, the temperature coefficient over like ranges in both cases appears to be the same (about 0.07 per degree). The molecular weight determinations in phenol (Table I) indicate that, with the possible exception of the *m*-toluidine compound, the molecular compounds, at least at lower temperatures, exist in an undissociated state in this component. Some dissociation might be expected at higher temperatures, but certainly not to a like extent both in the absence and presence of one of the components. It seems unlikely, too, that the phenomenon should be affected so decidedly by a temperature change, and not at all by a change in concentration. For these reasons it appears to be justifiable to question whether such parachor rises among the phenol-amines indicate dissociation. In fact, an examination of parachor values shows that small rises[3] occur occasionally with temperature elevation among non-associated substances. Since this effect appears to have been largely disregarded, it is proposed to study it more systematically.

TABLE I

MOLECULAR WEIGHTS AND PARACHORS OF PHENOL-AMINES

Compound	Mol. wt. (1:1) Calcd.	Found	Parachors 40° in phenol	in amine	Parachors 75° in phenol	in amine	Parachors pure[b] 50°
Phenol-aniline	187.1	189.7	453.5	453.0[a]	455.4	455.7	454.9
Phenol-*o*-toluidine	201.1	205.0	489.4	489.5	491.5	491.7	492.2
Phenol-*m*-toluidine	201.1	178.7	491.6	491.4	494.5	494.4	490.6
Phenol-*p*-toluidine	201.1	192.7	488.2	488.1	490.4	490.7	489.1

[a] Temperature 30°. [b] Buehler, Wood, Hull and Erwin, Ref. 2, p. 2402.

Experimental

The phenol-amines were prepared by freezing them out three or four times from an original equimolecular mixture of freshly distilled C. P. components. The freezing points of the products used were

Phenol-aniline	30.4° (corr.)
Phenol-*o*-toluidine	34.7° (corr.)
Phenol-*m*-toluidine	−3.5 ± 0.5°
Phenol-*p*-toluidine	28.8° (corr.)

The purification of the solvents, with the exception of phenol, which was fractionally distilled twice, and the surface tension and density methods have been described previously. Molecular weight determinations were by the freezing point method.

Summary

The parachors of the phenol-amines in a solution of either of the components are constant at a constant temperature, but with an increase in temperature a rise in the parachor occurs.

Evidence has been presented to show that this increase with temperature does not indicate dissociation.

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(3) Sugden, *J. Chem. Soc.*, **127**, 2517 (1925).