as the dielectric constant is continually lowered.

3. The parameter r always has a reasonable value, but is more a function of the properties of the solvent than of the charge type or chemical properties of the reactants.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Hydrogen Bonds Involving the C–H Link. XIV.[1] Solubility of Donor Solutes in Hydrogen Bonding Solvents

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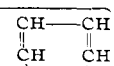
Following the methods previously described[3] we have measured the solubilities of a number of polymeric materials in a variety of hydrogen bonding solvents. The results of the solubility determinations are collected in Table I.

TABLE I

SOLUBILITY OF VARIOUS POLYMERIC SUBSTANCES IN HYDROGEN BONDING SOLVENTS

		Grams of solute per 100 g. of solvent indicated						
	Solute	$C_6H_5C{\equiv}CH$	C_6H_5SH	$CH_3(CH_2)_4C{\equiv}CH$	CH_3NO_2	$(CH_3)_2{-}\overset{OH}{\overset{\vert}{C}}{-}C{\equiv}C{-}H$	$CH_3{-}\overset{O}{\overset{\Vert}{C}}{-}\overset{CH_3}{\overset{\vert}{N}}{-}H$	
1	Polyvinyl acetate	93	85	109	93	71	53	81
2	Polymethyl vinyl ketone	40	24	0.036	35	19	<0.2	25
3	Polymethyl methacrylate	46	33	0.73	19	27	< .3	41
4	Cellulose triacetate	0.018	0.032	.01	0.017	5.4	...	13
5	Polyvinyl chloride	0.085	0.048	.106	.004	0.007	...	0.115
6	"Vinylite" (34.1% Cl)	110	99	.053	2.1	.504	...	86

Discussion of Results

It should be mentioned again that low solubilities could be checked readily to about 10%, whereas the high solubilities are approximated by the scheme previously described.[3] The solvents were commercial or laboratory samples which boiled over a 2° range. The polymers were those used in the earlier work except the "Vinylite" which was a copolymer of vinyl chloride and vinyl acetate containing 34.1% chlorine, and was given to us by Mr. H. B. McClure of Carbide and Carbon Chemicals Corporation.

The high solubilities of the donor type polymer in phenylacetylene and thiophenol agree with predictions based on heats of mixing measurements which have been reported with these solvents.[4,5] Likewise the low solvent power of 1-heptyne agrees with heat of mixing data.[6] Heat of mixing data on nitromethane[5] and hydrogen bonding solvents indicate that it is associated. Yet it has hydrogens sufficiently active to make it a good solvent for donor materials. It is not possible to say whether the acetylenic hydrogen or the alcohol hydrogen in dimethylethylcarbinol is the effective one but it seems logical that it is a combined effect since an aliphatic acetylene is ineffective and a simple alcohol is a much less effective solvent than this acetylene alcohol.

The high solubility of these donor molecules in pyrrole is striking and illustrates the strong tendency for the formation of —N—H ← O bonds. Pyrrole seems to be an exceptionally good solvent for cellulose triacetate. The poor solvent properties of *n*-methylacetamide are apparently due to its very complete association with itself by virtue of strong donor and strong acceptor properties.

The high solubility of polyvinyl acetate in all solvents tried indicates that hydrogen bonding is not playing a very important role in this case.

Summary

Phenylacetylene, thiophenol, nitromethane, dimethylethynylcarbinol and pyrrole have been shown to be good solvents for donor molecules of high molecular weight.

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(1) For the thirteenth paper see THIS JOURNAL, **63**, 254 (1941).

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(3) Marvel, Dietz and Copley, THIS JOURNAL, **62**, 2273 (1940).

(4) Copley and Holley, *ibid.*, **61**, 1599 (1939).

(5) Copley, Marvel and Ginsberg, *ibid.*, **61**, 3161 (1939).

(6) Holley, private communication, has found that mixing 1-heptyne with ethyl ether gives only 113 mole cal. and with acetone no heat effect.