independent of dielectric, is useful in at least an approximate way to predict solubilities in other media from the known solubility in water, without knowledge of the parameter *a* required for the Born equation. And some of these predictions may be of practical value in analytical and preparative chemistry requiring recrystallizations.

Summary

1. The activity coefficient of a salt in saturated solution has been noted in many cases to be practically constant and independent of the dielectric constant of the medium.

2. This observation leads to an empirical relation between the solubility of a slightly soluble electrolyte and the dielectric constant of the solvent which makes it possible to predict the solubility of a salt in other media from the solubility in water without knowledge of ionic diameters.

3. Calculated and observed solubilities are compared; the agreement is found in general to be satisfactory at least as to the order of magnitude and to be on the whole as good as that obtained by the Born equation where ionic diameters have been estimated.

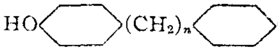
NEW YORK, N. Y. RECEIVED DECEMBER 11, 1939

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

α,ω-Di-*p*-hydroxyphenyl Alkanes

BY EDWIN M. RICHARDSON[1] AND E. EMMET REID

It has been observed that introduction of alkyl groups into phenols increases their bactericidal power and decreases their toxicity. Harden and Reid[2] showed that rather potent bactericides are produced by joining two phenols through a carbon having a side chain of varying length, giving compounds of the type  $HOC_6H_4CH(R)C_6H_4OH$ where R is H or an alkyl group.

This paper reports the preparation of a series of α,ω-di-*p*-hydroxyphenyl alkanes  $HOC_6H_4(CH_2)_nC_6H_4OH$ paralleling the above series.

The solubilities in oil and in water of the compounds are given in Table I along with the partition coefficients calculated from them. The solubilities are plotted in Fig. 1. There is a marked alternation with increasing chain length. The partition coefficients and the maximum killing dilution are plotted in Fig. 2; both increase rapidly with the length of the intervening carbon chain. The two curves show a definite similarity. Unfortunately the low solubility of these compounds made extensive testing impossible. All tests were run in 20% alcohol using 20% alcohol as control. The organism used was *Staphylococcus aureus* strain #209 and the technique was a modified F. D. A. We are greatly indebted to Hynson, Westcott and Dunning for their kindness in carrying out these tests. The α,ω-derivatives here described are much less soluble than the corresponding α,α-derivatives described by Harden and Reid[2]; however, the maximum killing dilu-

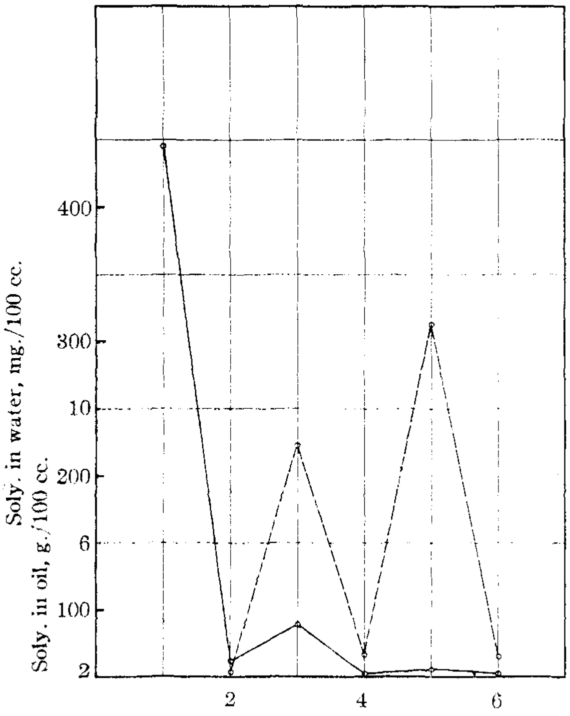


Fig. 1.—Solubility in oil and water: ———, soly. in water; — — —, soly. in oil.

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[1] From a part of a Ph.D. dissertation, Johns Hopkins University, 1938.

[2] Harden and Reid, THIS JOURNAL, **54**, 4325 (1932).

TABLE I

No.	Compd.	Soly., g./100 cc. H2O	Soly., g./100 cc. Oil	Partition coeff.	Max. killing diln.
1	4,4'-$HOC_6H_4CH_2C_6H_4OH$-	0.3950	..	....	300
2	4,4'-$HOC_6H_4(CH_2)_2C_6H_4OH$	.0116	0.10	8.62	1000
3	4,4'-$HOC_6H_4(CH_2)_3C_6H_4OH$	.0381	6.88	180	2000
4	4,4'-$HOC_6H_4(CH_2)_4C_6H_4OH$	.0024	0.67	280	5000
5	4,4'-$HOC_6H_4(CH_2)_5H_6C_4OH$	.0044	10.47	2400	
6	4,4'-$HOC_6H_4(CH_2)_6C_6H_4OH$	insol.	0.62		
7	4,4'-$HOC_6H_4(CH_2)_{10}C_6H_4OH$	insol.	.09		

TABLE II

Compd.	% yield	M. p., °C.	Analyses C Calcd.	Analyses C Found	Analyses H Calcd.	Analyses H Found
4,4'-$CH_3OC_6H_4(CH_2)_2C_6H_4OCH_3$	72	125.5–127				
4,4'-$HOC_6H_4(CH_2)_2C_6H_4OH$	94	198–199				
4,4'-$CH_3OC_6H_4CH{=}CHCOC_6H_4OCH_3$	95	100–101				
4,4'-$CH_3OC_6H_4(CH_2)_3C_6H_4OCH_3$	81	45–46	79.63	79.70	7.86	7.82
4,4'-$HOC_6H_4(CH_2)_3C_6H_4OH$		107–108	78.90	78.67	7.07	7.04
4,4'-$CH_3OC_6H_4(CH_2)_3COOH$	55					
4,4'-$CH_3OC_6H_4(CH_2)_4C_6H_4OCH_3$	53	78–79	79.96	79.66	8.20	8.30
4,4'-$HOC_6H_4(CH_2)_4C_6H_4OH$	62	158–159	79.31	79.30	7.49	7.49
$(4\text{-}CH_3OC_6H_4CH{=}CH)_2CO$	92					
$(4\text{-}CH_3OC_6H_4CH_2CH_2)_2CO$		55–55.2				
4,4'-$CH_3OC_6H_4(CH_2)_5C_6H_4OCH_3$	63					
4,4'-$HOC_6H_4(CH_2)_5C_6H_4OCH_3$	92	104–105				
4,4'-$CH_3OC_6H_4CO(CH_2)_4COC_6H_4OCH_3$	85	145–146	73.60	73.40	6.80	6.75
4,4'-$CH_3OC_6H_4(CH_2)_6C_6H_4OCH_3$	62	70–71	80.49	80.35	8.78	8.74
4,4'-$HOC_6H_4(CH_2)_6C_6H_4OH$	90	144.5–145.5	79.96	79.79	8.20	8.14
4,4'-$CH_3OC_6H_4CO(CH_2)_8COC_6H_4OCH_3$	90	119–119.5	75.36	74.86	7.91	7.85
4,4'-$CH_3OC_6H_4(CH_2)_{10}C_6H_4OCH_3$	58	69–70	81.31	81.11	9.67	9.59
4,4'-$HOC_6H_4(CH_2)_{10}C_6H_4OH$	74	138.5–139.5	80.93	80.89	9.26	9.16

tions are nearly the same, 1000 compared to 1200 for the ethane derivatives, 2000 to 1500 for the propane and 5000 to 3500 for the butane derivatives.

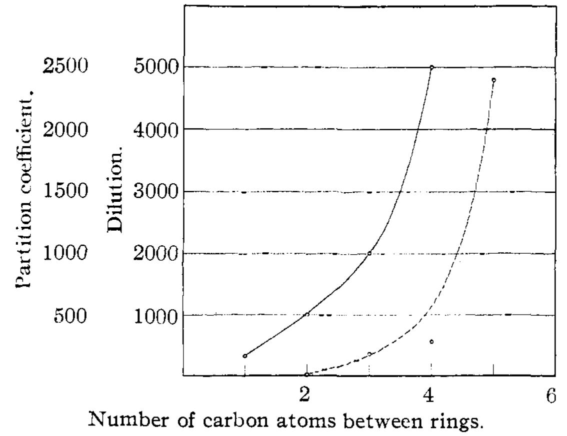

Fig. 2.—Maximum killing dilution ——— and partition coefficient — — —.

The melting points of the phenols and their methyl ethers are plotted in Fig. 3. The two curves are remarkably similar and both show marked alternation.

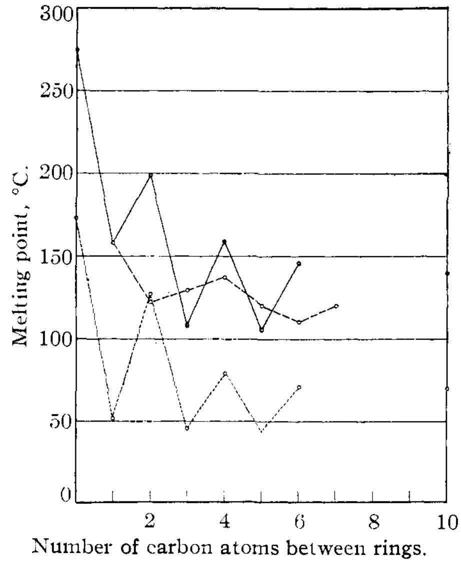

Fig. 3.—Melting points of α,ω-di-*p*-hydroxyalkanes ———, α,ω-di-*p*-methoxyalkanes, - - - - - -, α,α-di-*p*-hydroxyalkanes — — —.

Experimental

Hydrogenation of ethylenic double bonds was carried out using the Adams[3] PtO_2 catalyst. Ketones were re-

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[3] Adams, Voorhees and Shriner, *Org. Syntheses*, Vol. VIII, 1928, p. 92.

duced in all cases by the Clemmensen reduction or Martin's[4] modification of it. Demethylation was accomplished in all cases by refluxing 0.1 mole with a mixture of 130 g. of glacial acetic acid and 50 g. of constant boiling hydrobromic acid.

1,2-Di-*p*-hydroxyphenylethane.—Anisoin was reduced by the Martin modification of the Clemmensen reduction giving 1,2-dianisylethane which on demethylation gave 1,2-di-*p*-hydroxyphenylethane.

1,3-Di-*p*-hydroxyphenylpropane.—*p*-Acetylanisole prepared according to Baranger[5] was condensed with anisaldehyde to give 1-anisyl-2-anisoylethylene. This on reduction and demethylation gave 1,3-di-*p*-hydroxyphenylpropane.

1,4-Di-*p*-hydroxyphenylbutane.—γ-Anisylbutyric acid was prepared by reduction of the *p*-anisoylpropionic acid obtained by condensing succinic anhydride and anisole according to Rosenmund and Shapiro.[6] The acid chloride prepared using thionyl chloride was condensed with anisole and the crude ketone obtained was reduced and demethylated to give 1,4-di-*p*-hydroxyphenylbutane.

1,5-Di-*p*-hydroxyphenylpentane.—Dianisalacetone prepared from anisaldehyde and acetone by the method of Conard and Dolliver[7] was reduced and demethylated to give 1,5-di-*p*-hydroxyphenylpentane, previously prepared by Borsche.[8]

1,6-Di-*p*-hydroxyphenylhexane.—One mole of adipoyl chloride was condensed with two moles of anisole using 2.25 moles of anhydrous aluminum chloride in 500 cc. of carbon disulfide. The diketone was reduced and demethylated to give 1,6-di-*p*-hydroxyphenylhexane. Oxidation of the diketone with alkaline potassium permanganate gave *p*-anisic acid, showing that condensation took place *para* to the methoxyl group.

1,10-Di-*p*-hydroxyphenyldecane.—Sebacoyl chlorideand anisole were condensed as in the case of adipoyl chloride, and the diketone reduced and demethylated to give 1,10-di-*p*-hydroxyphenyldecane.

The solubilities in water were determined by the usual method. Solubilities in olive oil were determined by the method of Dunning, Dunning and Reid.[9]

Summary

1. A series of α,ω-di-*p*-hydroxyphenyl alkanes has been prepared having 2, 3, 4, 5, 6 and 10 methylene groups between the benzene rings.

2. The lower members of the series have decided bactericidal properties but are too insoluble in water to prove useful as antiseptics.

BALTIMORE, MD.

RECEIVED DECEMBER 1, 1939

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[4] Martin, THIS JOURNAL, **58**, 1438 (1936).

[5] Baranger, *Bull. soc. chim.*, [4] **49**, 213–222 (1931).

[6] Rosenmund and Shapiro, *Arch. Pharm.*, **272**, 313–323 (1934).

[7] Conard and Dolliver, *Org. Syntheses*, Vol. XII, 1932, p. 22.

[8] Borsche, *Ber.*, **52**, 2079 (1919).

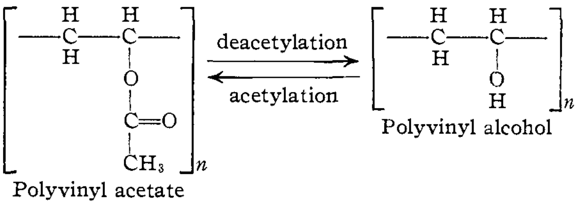
[9] Dunning, Dunning and Reid, THIS JOURNAL, **58**, 1565 (1936).

[COMMUNICATION NO. 741 FROM THE KODAK RESEARCH LABORATORIES]

Some Relationships between Polyvinyl Acetates and Polyvinyl Alcohols*

BY W. H. MCDOWELL AND W. O. KENYON

By analogy to the simple organic esters such as ethyl acetate, polyvinyl acetate would be expected to yield the corresponding polyvinyl alcohol by deacetylation and, conversely, polyvinyl acetate would be expected from the acetylation of polyvinyl alcohol as indicated in the formulas:



$$\left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\substack{| \\ O \\ | \\ C=O \\ | \\ CH_3}}{C}}-\right]_n \underset{\text{acetylation}}{\overset{\text{deacetylation}}{\rightleftarrows}} \left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\substack{| \\ O \\ H}}{C}}-\right]_n$$

These reactions have been described by Staudinger and his co-workers,[1,2] by Herrmann and Haehnel[3] and by others.

The present investigations were undertaken to determine whether polyvinyl acetates could be transformed into polyvinyl alcohols and whether the alcohols could be reacetylated to produce polyvinyl acetates which are similar to the original acetates. Because of the polymeric nature of the polyvinyl alcohols and acetates, comparisons are made on the basis of the degree of polymerization as determined by viscosity measurements.

Experimental

Two different series of polyvinyl acetates of various viscosities were used. One series, composed of commercial samples, was used without further purification. The second series was prepared by the following method.

Monomeric vinyl acetate (practical grade) was distilled in an all-glass apparatus and the fraction boiling between 72.2 and 72.8° used for polymerization. Samples of the monomer were placed in all-glass reflux apparatus with the amounts of benzoyl peroxide catalyst (Eastman grade) shown in Table I and heated overnight on steam-baths.

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* Presented before the Paint and Varnish Division of the American Chemical Society at the Boston Meeting, September 11–15, 1939.

[1] Staudinger, *Ber.*, **59**, 3019 (1926).

[2] Staudinger and Schwalbach, *Ann.*, **488**, 8–56 (1931).

[3] Herrmann and Haehnel, *Ber.*, **60**, 1658–1663 (1927).