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SOLUBILITIES OF HIGH MOLECULAR WEIGHT 1-HALOALKANES

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The haloalkanes are one of the few major classes of high molecular weight aliphatic compounds whose solubilities have not been investigated extensively. The hexane solubilities of 1-chlorododecane, 1-iodododecane, 1-bromotetradecane, and 1-iodohexadecane have been reported recently (1), but beyond these data, no other quantitative measurements appear in the literature. Since the above compounds are representative of the wide variety of 1-haloalkanes, their solubilities have been determined in benzene, cyclohexane, carbon tetrachloride, chloroform, ethyl acetate, acetone, 95% ethanol, and *n*-butanol, and in addition the solubilities of 1-iodododecane in diethyl ether, butyl acetate, 2-butanone, methanol, 2-propanol, aniline, and acetonitrile. From these data, the solubilities of at least the closely related homologs of these compounds can be estimated with reasonable accuracy.

The preparation of these 1-haloalkanes and their respective freezing points have been reported adequately in the above reference (1). The experimental procedures for determining the solubilities have been described elsewhere (2).

RESULTS AND DISCUSSION

The solubilities of the 1-haloalkanes investigated are presented in Tables I–VII and Figures 1–9.

In general, the solubilities of these compounds markedly resemble those of the corresponding saturated hydrocarbons (3). Beyond increasing the melting points a few degrees above those of the corresponding hydrocarbons and producing a relatively inappreciable polarity in the molecule (dipole moment about 1×10^{18} e.s.u.), the halogen atom apparently does not exert so substantial an influence upon the physical properties as might be expected of such a strongly electronegative atom. This demonstrates the overshadowing influence of paraffin chains containing upwards of 12 carbon atoms.

The chief effect of the halogen atom appears to be its slight solubilizing influence upon the paraffin chain due to the dipole attractive forces between the halogen atom and the polar groups of the solvents. The enhanced solubilities in the halogenated hydrocarbons, carbon tetrachloride and chloroform, and in the moderately polar solvents such as ethyl and butyl acetates, acetone, and 2-butanone, are attributable to this phenomenon. For example, the solubility of 1-iodododecane at −20° is 8.2 g. per 100 g. of acetone, whereas that of dodecane is 3.3 g., although on the basis of the lower melting point of the latter the reverse order of solubilities might be expected. In addition, the haloalkanes are miscible with acetone above their melting points, whereas the systems of the hydrocarbons with this solvent exist as two immiscible liquids over wide ranges above their melting points.

TABLE I

SOLUBILITIES OF 1-HALOALKANES IN CARBON TETRACHLORIDE

	GRAMS OF SOLUTE PER 100 GRAMS OF SOLVENT			
	−20.0°	−10.0°	0.0°	10.0°
1-Chlorododecane	325	9000	∞	∞
1-Iodododecane	101	415	3500	∞
1-Bromotetradecane	44.3	213	970	∞
1-Iodohexadecane	3.7	21.3	85	405

TABLE II

SOLUBILITIES OF 1-HALOALKANES IN CHLOROFORM

	GRAMS OF SOLUTE PER 100 GRAMS OF SOLVENT						
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°
1-Chlorododecane	12.8	33.5	79	225	5450	∞	∞
1-Iodododecane	7.0	19.2	45.1	99	245	1800	∞
1-Bromotetradecane	1.8	7.3	22.5	54	133	515	∞
1-Iodohexadecane	—	0.7	3.1	11.9	32.5	80	212

TABLE III

SOLUBILITIES OF 1-HALOALKANES IN ETHYL ACETATE

	GRAMS OF SOLUTE PER 100 GRAMS OF SOLVENT						
	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°
1-Chlorododecane	11.1	34.6	418	≈ ∞	∞	∞	∞
1-Iodododecane	2.5	6.3	18.1	208	3600	∞	∞
1-Bromotetradecane	0.4	1.7	5.1	30.0	480	∞	∞
1-Iodohexadecane	—	—	—	<0.1	4.2	57	2230

TABLE IV

SOLUBILITIES OF 1-HALOALKANES IN ACETONE

	GRAMS OF SOLUTE PER 100 GRAMS OF SOLVENT						
	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°
1-Chlorododecane	7.9	24.5	52	≈ ∞	∞	∞	∞
1-Iodododecane	0.3	2.0	8.2	65	3500	∞	∞
1-Bromotetradecane	—	0.3	3.0	15.0	610	∞	∞
1-Iodohexadecane	—	—	—	—	<0.1	4.9	1800

TABLE V

SOLUBILITIES OF 1-HALOALKANES IN 95% ETHANOL

	GRAMS OF SOLUTE PER 100 GRAMS OF SOLVENT							
	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°	40.0°
1-Chlorododecane*	2.2	5.1	8.7	10.5	12.9	16.5	25.0	∞
1-Iodododecane†	—	0.3	1.7	6.0	6.8	7.6	9.0	11.9
1-Bromotetradecane	—	—	<0.1	1.4	4.1	4.9	6.0	7.3
1-Iodohexadecane	—	—	—	—	0.1	1.9	2.9	3.9

* Miscible above 38.5°.

† Miscible above 58.6°.

TABLE VI

SOLUBILITIES OF 1-HALOALKANES IN *n*-BUTANOL

	GRAMS OF SOLUTE PER 100 GRAMS OF SOLVENT					
	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°
1-Chlorododecane	16.2	65	≈ ∞	∞	∞	∞
1-Iodododecane	1.0	6.0	27.5	1960	∞	∞
1-Bromotetradecane	—	—	3.5	51	∞	∞
1-Iodohexadecane	—	—	—	<0.1	6.6	720

TABLE VII

SOLUBILITIES OF 1-IODODODECANE IN VARIOUS ORGANIC SOLVENTS

SOLVENT	GRAMS OF 1-IODODODECANE PER 100 GRAMS OF SOLVENT						
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°
Diethyl ether	1.2	11.1	39.8	121	470	5000	∞
Butyl acetate	1.5	3.9	9.1	28.4	267	3950	∞
2-Butanone	0.2	0.8	2.8	10.3	149	3600	∞
Methanol	—	—	—	—	0.4	4.3	4.9
2-Propanol	—	—	0.1	2.3	14.3	1830	∞
Aniline	—	—	—	—	—	3150	∞
Acetonitrile	—	—	—	—	<0.1	2.4	3.3

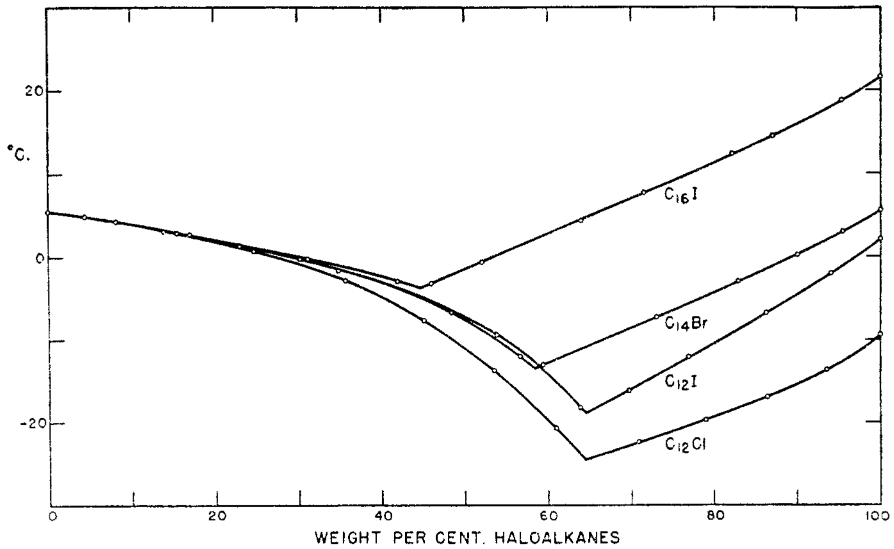

FIG. 1. LIQUIDUS CURVES OF SOME HIGHER HALOALKANES IN BENZENE. In this and the following diagrams, the symbols on the curves refer to the following: $C_{12}Cl$, 1-chlorododecane: $C_{12}I$, 1-iodododecane; $C_{14}Br$, 1-bromotetradecane; $C_{16}I$, 1-iodohexadecane.

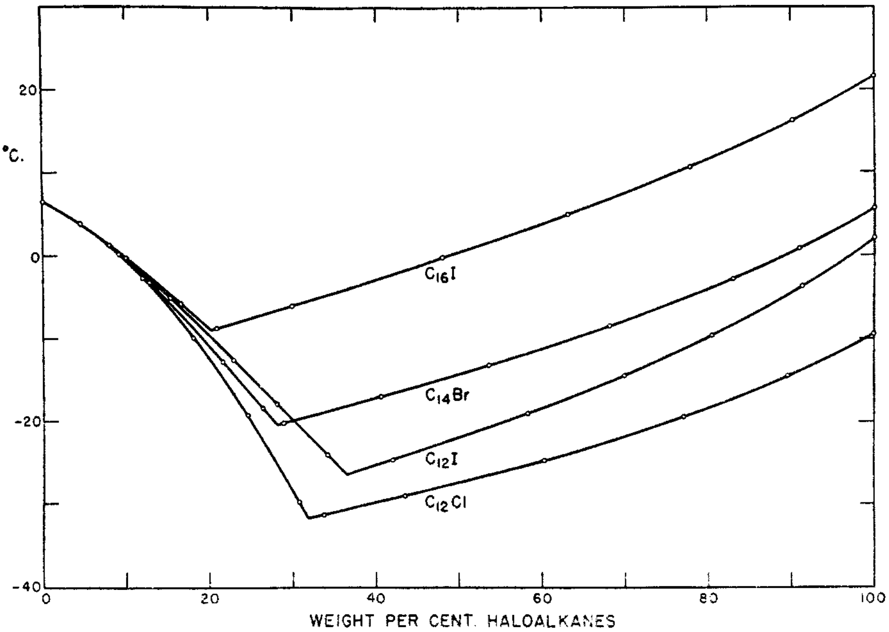

FIG. 2. LIQUIDUS CURVES OF SOME HIGHER HALOALKANES IN CYCLOHEXANE

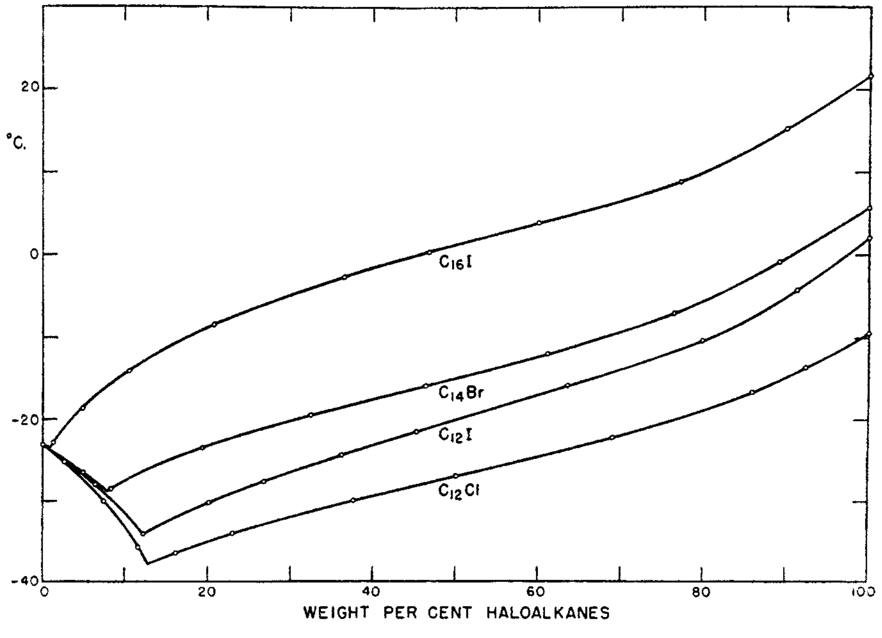

FIG. 3. LIQUIDUS CURVES OF SOME HIGHER HALOALKANES IN CARBON TETRACHLORIDE

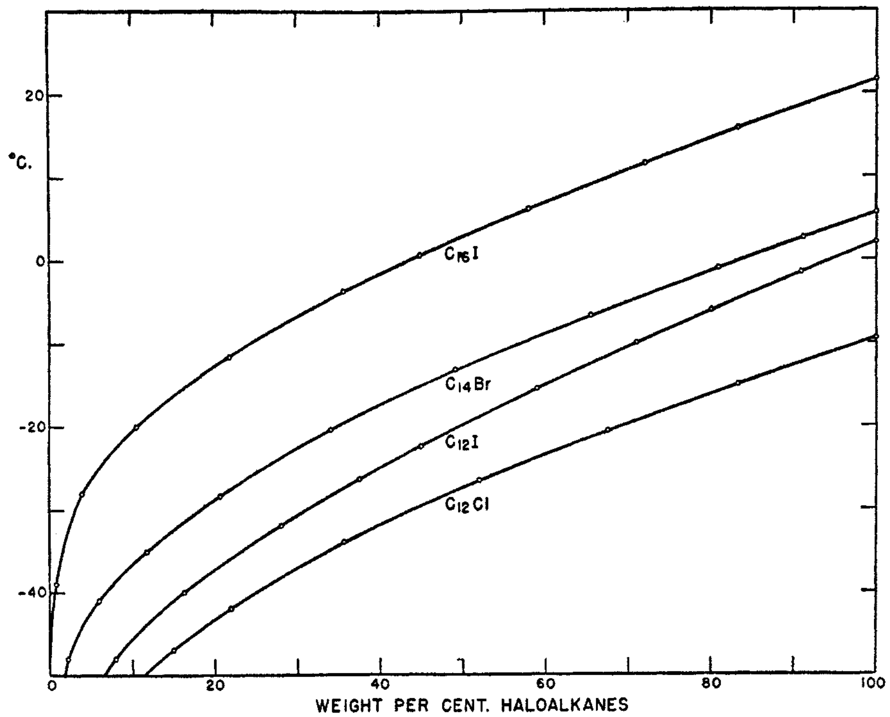

FIG. 4. SOLUBILITIES OF SOME HIGHER HALOALKANES IN CHLOROFORM

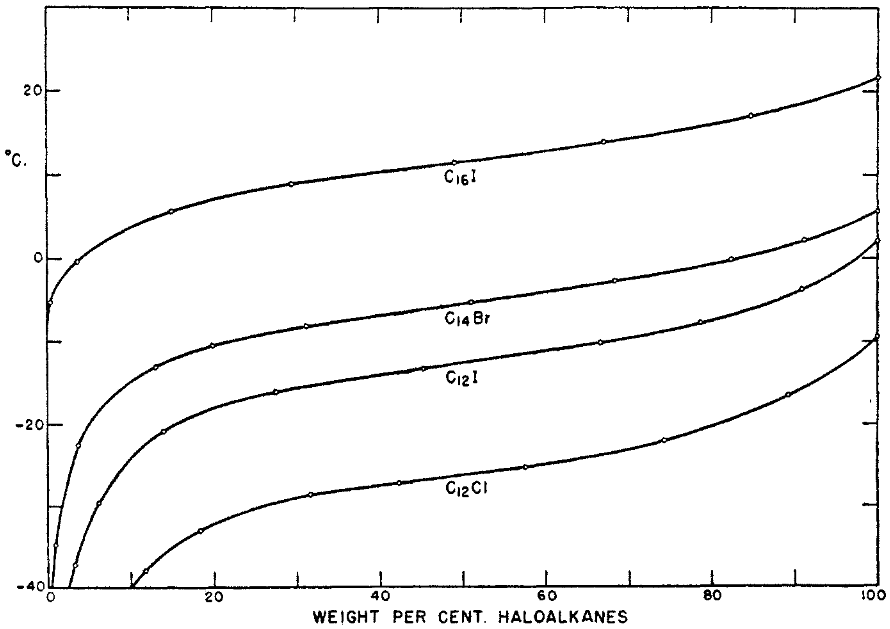

FIG. 5. SOLUBILITIES OF SOME HIGHER HALOALKANES IN ETHYL ACETATE

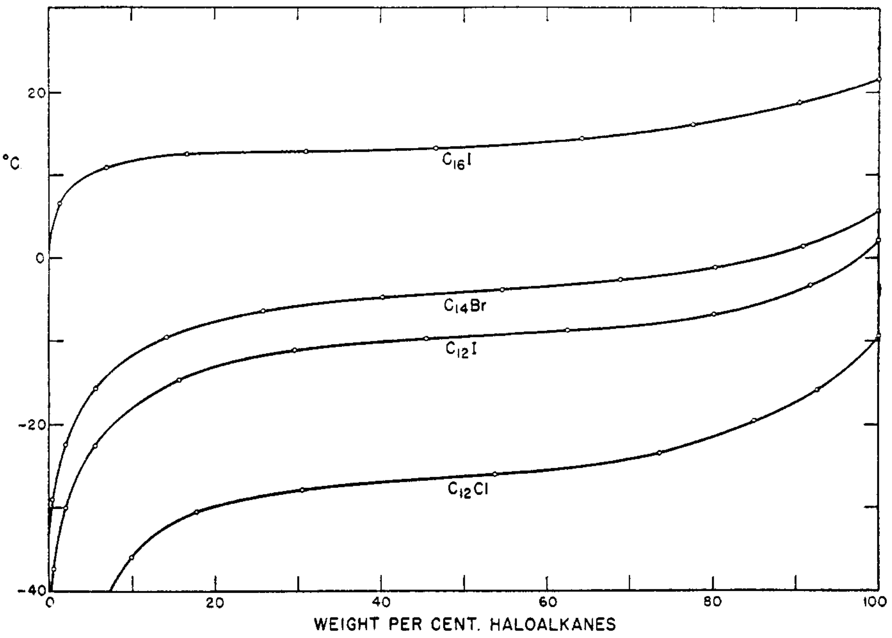

FIG. 6. SOLUBILITIES OF SOME HIGHER HALOALKANES IN ACETONE

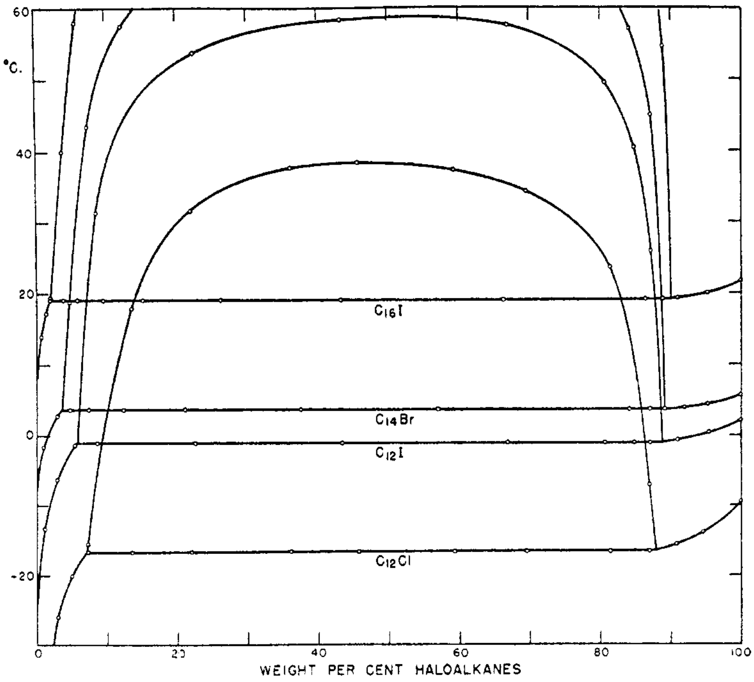

FIG. 7. THE SYSTEMS OF SOME HIGHER HALOALKANES IN 95% ETHANOL. The area above the isotherms represents two-phase regions of two immiscible liquids.

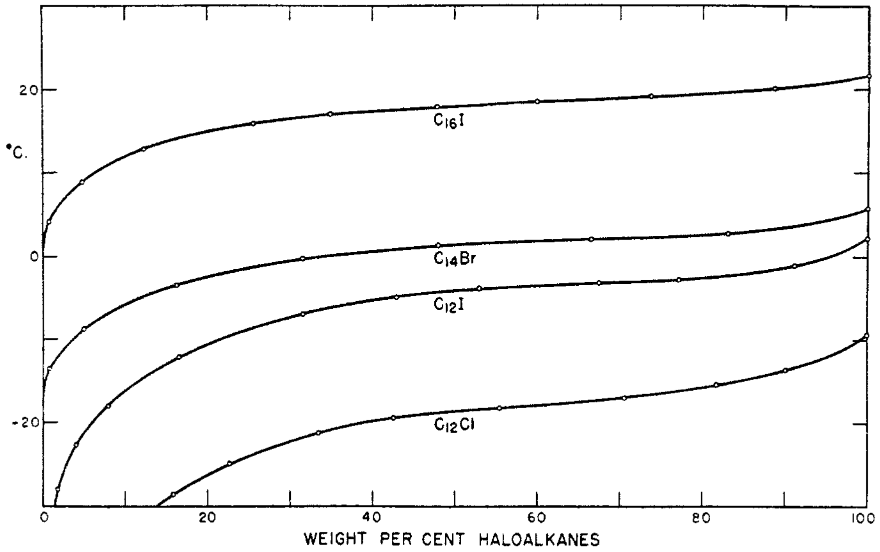

FIG. 8. SOLUBILITIES OF SOME HIGHER HALOALKANES IN *n*-BUTANOL

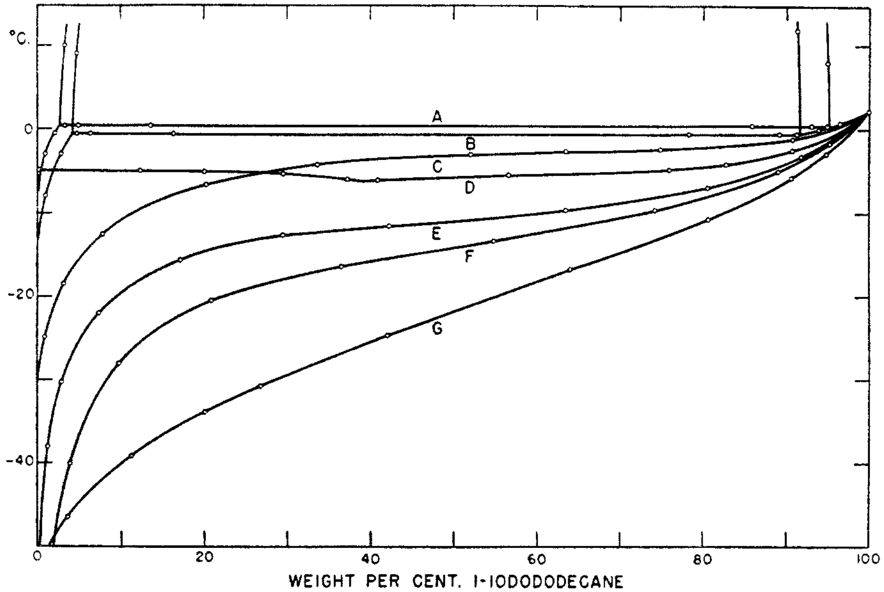

FIG. 9. SOLUBILITIES OF 1-IODODODECANE IN VARIOUS ADDITIONAL SOLVENTS. The letters on the curves refer to the following systems: A, acetonitrile; B, methanol; C, 2-propanol; D, aniline; E, 2-butanone; F, butyl acetate; G, diethyl ether.

The 1-haloalkanes resemble the hydrocarbons in possessing very limited solubilities in the highly polar "associated" solvents such as methanol, ethanol, and acetonitrile. In view of the above discussion, however, particularly with regard to the behavior in acetone, further investigation is required to explain the paradoxical solubilities in 2-propanol and *n*-butanol. In these alcohols the 1-haloalkanes are considerably less soluble than the corresponding hydrocarbons, although the opposite effect should be expected because of the polarity of the halogenated derivatives. In this connection it should be noted that no hydrogen bonding phenomena are evident in the solubilities of the higher 1-haloalkanes. Chloroform and some of the 1-haloethanes exhibit marked hydrogen bonding activity in the presence of electron-acceptor atoms, such as the oxygen atom of an alcohol. The limited solubilities of the higher 1-haloalkanes in the alcohols indicate that the hydrogen atoms on their halogenated terminal carbon atoms are not sufficiently activated to break the existing bonds in the strongly associated solvents.

SUMMARY

The solubilities of 1-chlorododecane, 1-iodododecane, 1-bromotetradecane, and 1-iodohexadecane have been determined in benzene, cyclohexane, carbon tetrachloride, chloroform, ethyl acetate, acetone, 95% ethanol, and *n*-butanol. Additional solubilities of 1-iodododecane have been determined in diethyl ether, butyl acetate, 2-butanone, methanol, 2-propanol, aniline, and acetonitrile. The solubility behavior of these 1-haloalkanes has been compared with that of the corresponding hydrocarbons.

CHICAGO, ILLINOIS

REFERENCES

(1) HOERR AND HARWOOD, *J. Org. Chem.*, **16**, preceding article.
(2) HOERR, BINKERD, POOL, AND RALSTON, *J. Org. Chem.*, **9**, 68 (1944).
(3) RALSTON, HOERR, AND CREWS, *J. Org. Chem.*, **9**, 319 (1944).