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SOLUBILITIES OF HIGH MOLECULAR WEIGHT ALIPHATIC COMPOUNDS IN *n*-HEXANE

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Normal hexane is an ideal solvent for comparing the relation of molecular structure to the solubility behavior of the higher aliphatic compounds. It is one of the least complex of the common organic solvents in that it consists of electrically balanced, linearly symmetrical, non-polar molecules of low internal pressure (limited intermolecular attractive forces). Since these molecules possess no active hydrogen atoms and no electron-donor atoms, they are incapable of forming hydrogen bonds, and therefore do not ordinarily enter into molecular association with other compounds. Consequently, by comparing the solubilities of a series of related compounds on an equivalent basis, certain general conclusions can be deduced regarding the effects of various substituent polar groups.

Solubilities in a wide variety of common organic solvents have been reported for several representative high molecular weight normal saturated aliphatic hydrocarbons (1), primary alcohols (2), symmetrical ketones (3), fatty acids (4), nitriles (5), primary amines (6), secondary amines (7), tertiary amines (8), and amides (9). The literature contains no data regarding the solubility of any of these compounds in a normal saturated hydrocarbon. The present paper reports the solubilities of these compounds and those of several 1-haloalkanes and methyl esters in *n*-hexane. By a comparison of the molal solubilities of the compounds containing 16 carbon atoms in the paraffin chain, certain generalizations are deduced regarding the effects of the various polar groups upon the behavior of the paraffin chain.

EXPERIMENTAL

1-Chlorododecane was prepared from vacuum-fractionated 1-dodecanol by reaction with hydrochloric acid (10). The product was distilled under a vacuum through a column packed with glass helices. The fraction used in these experiments had f.p. −9.35°.

1-Iodododecane was prepared from the above alcohol by reaction with iodine and red phosphorus (11). The product was distilled as above, the fraction used having f.p. 2.15°.

1-Bromotetradecane and *1-iodohexadecane* were commercial products which were purified by vacuum fractionation through a column packed with glass helices. The freezing point 5.70° of the 1-bromoalkane exceeds the values reported in the literature, m.p. 5.67° and f.p. 5.5° (12). The freezing point 21.75° of the iodide compares fairly well with the literature values of 21.15° (13), 22.5° (14), and 23.28° (15).

The methyl esters of caprylic, lauric, myristic, palmitic, and stearic acids were prepared by the direct esterification of the highly purified acids with methanol. The products were fractionated under a vacuum through a Stedman-packed column. The fractions used in this study had the following freezing points: methyl caprylate, −33.8°; methyl laurate, 5.08°; methyl myristate, 18.39°; methyl palmitate, 28.90°; and methyl stearate, 37.85°. The latter three values compare favorably with the best values in the literature (16): 18.37°, 29.20°, and 37.85°, respectively.

The other solutes were those used in the previous investigations cited above. Their preparations and freezing points, as well as the experimental procedure used for determining solubilities, have been presented in the appropriate references.

The *hexane* employed was obtained by treating a good grade of commercial hexane with concentrated sulfuric acid and distilling the washed product through a Stedman-packed column. This solvent had b.p. 68.8° (uncorr.) at atmospheric pressure.

RESULTS AND DISCUSSION

The solubilities in *n*-hexane are presented in Tables I–XI and Figures 1–11. These solubility curves approximate, in general, the curves of the respective compounds in other non-polar solvents. With the exception of the hydrocarbons, all the compounds are somewhat less soluble in hexane than in benzene or cyclohexane at any given temperature.

TABLE I

SOLUBILITIES OF NORMAL SATURATED ALIPHATIC HYDROCARBONS IN *n*-HEXANE

TEMP., °C.	GRAMS OF HYDROCARBON PER 100 GRAMS OF HEXANE				
	Octane	Dodecane	Hexadecane	Heptadecane	Dotriacontane
−75.0	61	3.8	—	—	—
−70.0	121	4.1	—	—	—
−65.0	260	4.4	—	—	—
−60.0	835	5.1	—	—	—
−50.0	∞	8.3	—	—	—
−40.0	∞	17.0	0.9	0.5	—
−30.0	∞	61.3	3.9	3.1	—
−20.0	∞	219	11.1	9.9	—
−15.0	∞	515	17.9	15.9	—
−10.0	∞	∞	28.0	25.0	—
0.0	∞	∞	89.4	74.2	—
10.0	∞	∞	320	233	—
15.0	∞	∞	1000	530	0.3
20.0	∞	∞	∞	2750	1.1
30.0	∞	∞	∞	∞	5.9
40.0	∞	∞	∞	∞	25.6
50.0	∞	∞	∞	∞	84.2
60.0	∞	∞	∞	∞	265
68.8	∞	∞	∞	∞	2600

The apparent effects of the various substituent polar groups in governing the solubilities of the aliphatic compounds become evident upon analysis of Table XII. This table lists the hexane solubilities on a molal basis at 15.0° and 30.0° of a series of compounds containing aliphatic chains of 16 carbon atoms ranked in the order of increasing melting points. Dioctylamine, which consists of two 8-carbon chains linked by a secondary amino group, and 8-pentadecanone, which consists of chains of 15 carbon atoms with a carbonyl oxygen atom on the central carbon, have been included for comparison.

The almost direct relationship of solubility to the melting points of the solutes is to be noted. This phenomenon has been discussed with reference to the solu-

TABLE II

SOLUBILITIES OF HALOALKANES IN *n*-HEXANE

HALOALKANE	GRAMS OF HALOALKANE PER 100 GRAMS OF HEXANE						
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°
1-Chlorododecane	4.8	14.7	49.7	288	*ca.* ∞	∞	∞
1-Iodododecane	3.5	11.1	32.6	86	289	2500	∞
1-Bromotetradecane	1.6	3.8	8.1	23.3	73	465	∞
1-Iodohexadecane	0.1	0.5	2.3	6.1	16.8	45.1	141

TABLE III

SOLUBILITIES OF PRIMARY ALIPHATIC ALCOHOLS IN *n*-HEXANE

ALCOHOL	GRAMS OF ALCOHOL PER 100 GRAMS OF HEXANE							
	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°	40.0°	50.0°
Decanol	3.0	40.5	310	∞	∞	∞	∞	∞
Dodecanol	—	0.5	9.3	96	725	∞	∞	∞
Tetradecanol	—	—	0.1	3.7	46.0	300	∞	∞
Hexadecanol	—	—	—	—	2.7	42.2	270	∞
Octadecanol	—	—	—	—	—	4.7	65	385

TABLE IV

SOLUBILITIES OF ALIPHATIC KETONES IN *n*-HEXANE

KETONE	GRAMS OF KETONE PER 100 GRAMS OF HEXANE						
	10.0°	20.0°	30.0°	40.0°	50.0°	60.0°	68.8°
10-Nonadecanone (Caprinone)	3.9	11.9	38.1	109	440	∞	∞
12-Tricosanone (Laurone)	1.0	2.9	8.2	26.6	93	320	4660
16-Hentriacontanone (Palmitone)	—	—	0.7	3.2	12.0	63	136
18-Pentatriacontanone (Stearone)	—	—	—	0.6	5.8	23.6	77

TABLE V

SOLUBILITIES OF NORMAL SATURATED FATTY ACIDS IN *n*-HEXANE

ACID	GRAMS OF ACID PER 100 GRAMS OF HEXANE								
	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°	40.0°	50.0°	60.0°
Caprylic	14.7	42.5	136	2600	∞	∞	∞	∞	∞
Nonylic	25.2	74.7	249	640	∞	∞	∞	∞	∞
Capric	2.1	6.7	23.8	81.2	290	5150	∞	∞	∞
Lauric	0.2	1.5	4.9	14.7	47.7	193	1440	∞	∞
Myristic	—	0.1	1.2	4.1	11.9	41.8	198	1650	∞
Pentadecylic	—	—	0.5	2.9	14.0	60.2	289	2950	∞
Palmitic	—	—	—	0.5	3.1	14.5	62.4	239	2280
Heptadecylic	—	—	—	0.2	2.9	17.4	73.0	300	7600
Stearic	—	—	—	—	0.5	4.3	19.0	79.2	303

TABLE VI

SOLUBILITIES OF METHYL ESTERS IN n-HEXANE

METHYL ESTER	GRAMS OF ESTER PER 100 GRAMS OF HEXANE								
	−50.0°	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Caprylate	44.3	274	∞	∞	∞	∞	∞	∞	∞
Laurate	0.5	2.4	7.6	20.8	73.9	415	∞	∞	∞
Myristate	—	—	0.6	3.5	14.2	53.6	238	∞	∞
Palmitate	—	—	—	—	2.2	14.2	55.8	229	∞
Stearate	—	—	—	—	—	2.2	15.9	68	286

TABLE VII

SOLUBILITIES OF ALIPHATIC NITRILES IN n-HEXANE

NITRILE	GRAMS OF NITRILE PER 100 GRAMS OF HEXANE							
	−40.0°	−30.0°	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°
Caprinitrile	8.3	31.7	327	∞	∞	∞	∞	∞
Lauronitrile	—	0.6	5.8	50.2	640	∞	∞	∞
Myristonitrile	—	—	0.6	4.4	23.9	172	∞	∞
Palmitonitrile	—	—	—	0.7	4.5	21.7	137	2650
Stearonitrile	—	—	—	—	0.3	4.8	27.3	166

TABLE VIII

SOLUBILITIES OF ALIPHATIC PRIMARY AMINES IN n-HEXANE

AMINE	GRAMS OF AMINE PER 100 GRAMS OF HEXANE							
	−20.0°	−10.0°	0.0°	10.0°	20.0°	30.0°	40.0°	50.0°
Decylamine	5.4	14.4	50.2	279	∞	∞	∞	∞
Dodecylamine	0.1	1.9	11.6	43.7	196	∞	∞	∞
Tetradecylamine	—	—	1.8	12.5	50.8	216	∞	∞
Hexadecylamine	—	—	—	2.6	18.3	64.8	288	∞
Octadecylamine	—	—	—	—	5.4	27.9	105	760

TABLE IX

SOLUBILITIES OF ALIPHATIC SECONDARY AMINES IN n-HEXANE

TEMP., °C.	GRAMS OF AMINE PER 100 GRAMS OF HEXANE				
	Dioctylamine		Didodecylamine	Ditetradecylamine	Dioctadecylamine
	α	β			
−20.0	6.3	1.8	—	—	—
−10.0	20.8	5.5	—	—	—
0.0	93.5	19.6	—	—	—
10.0	615	79.2	0.2	—	—
20.0	∞	390	5.6	—	—
30.0	∞	∞	27.5	4.5	—
40.0	∞	∞	136	30.7	2.1
50.0	∞	∞	1750	160	19.2
60.0	∞	∞	∞	6150	105

TABLE X

Solubilities of Aliphatic Tertiary Amines in *n*-Hexane

TEMP., °C.	GRAMS OF AMINE PER 100 GRAMS OF HEXANE		
	Trioctylamine	Tridodecylamine	Trioctadecylamine
−60.0	58.7	—	—
−50.0	156	—	—
−40.0	635	—	—
−30.0	∞	1.0	—
−20.0	∞	8.7	—
−10.0	∞	35.0	—
0.0	∞	107	—
10.0	∞	482	0.1
20.0	∞	∞	5.4
30.0	∞	∞	36.4
40.0	∞	∞	134
50.0	∞	∞	720
60.0	∞	∞	∞

TABLE XI

Solubilities of Aliphatic Amines in *n*-Hexane

AMIDE	GRAMS OF AMIDE PER 100 GRAMS OF HEXANE			
	40.0°	50.0°	60.0°	68.8°
Capramide	—	0.08	0.33	1.00
Lauramide	0.04	.20	.61	1.84
Myristamide	—	.03	.20	0.64
Palmitamide	—	.06	.29	1.03
Stearamide	—	.05	.28	0.84

TABLE XII

Solubilities in *n*-Hexane of Compounds Containing Aliphatic Chains of 16 Carbon Atoms

COMPOUND	M.P., °C.	MOLES PER 1000 GRAMS OF HEXANE	
		15.0°	30.0°
Hexadecane	18.2	44.4	∞
1-Iodohexadecane	21.7	10.0	∞
Dioctylamine	26.7	6.75	∞
Methyl palmitate	28.8	4.07	∞
Palmitonitrile	31.4	2.49	110
8-Pentadecanone	41	2.0*	95*
Hexadecylamine	46.8	0.34	2.68
1-Hexadecanol	49.6	0.01	1.75
Palmitic acid	62.8	0.05	0.57
Palmitamide	107.0	<0.0001	<0.0001

* Estimated by interpolation from Figure 4.

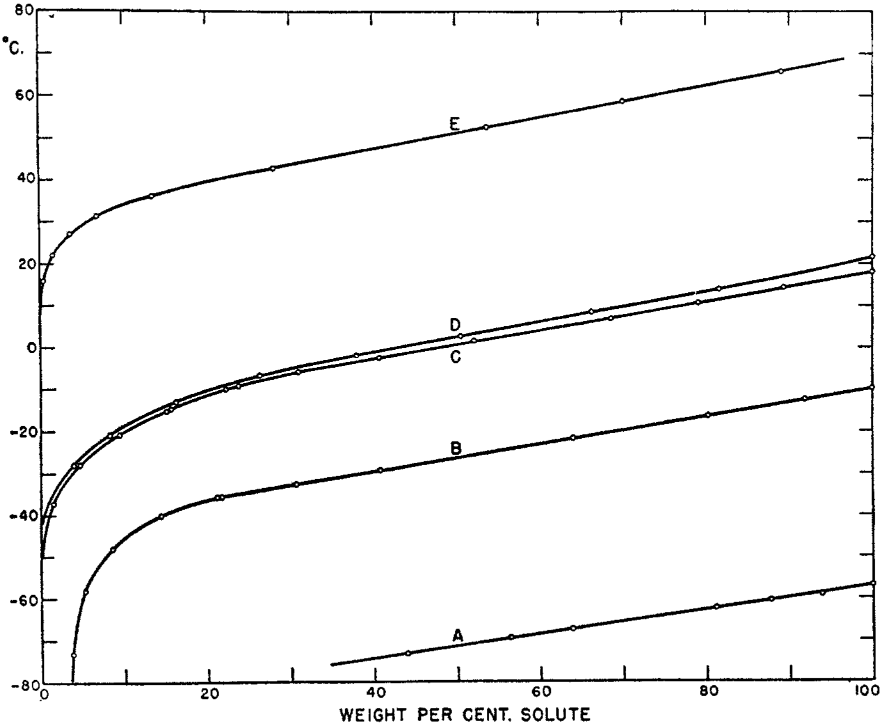

FIG. 1. SOLUBILITIES OF SOME HIGHER HYDROCARBONS IN *n*-HEXANE: A, octane; B, dodecane; C, hexadecane; D, heptadecane; E, dotriacontane.

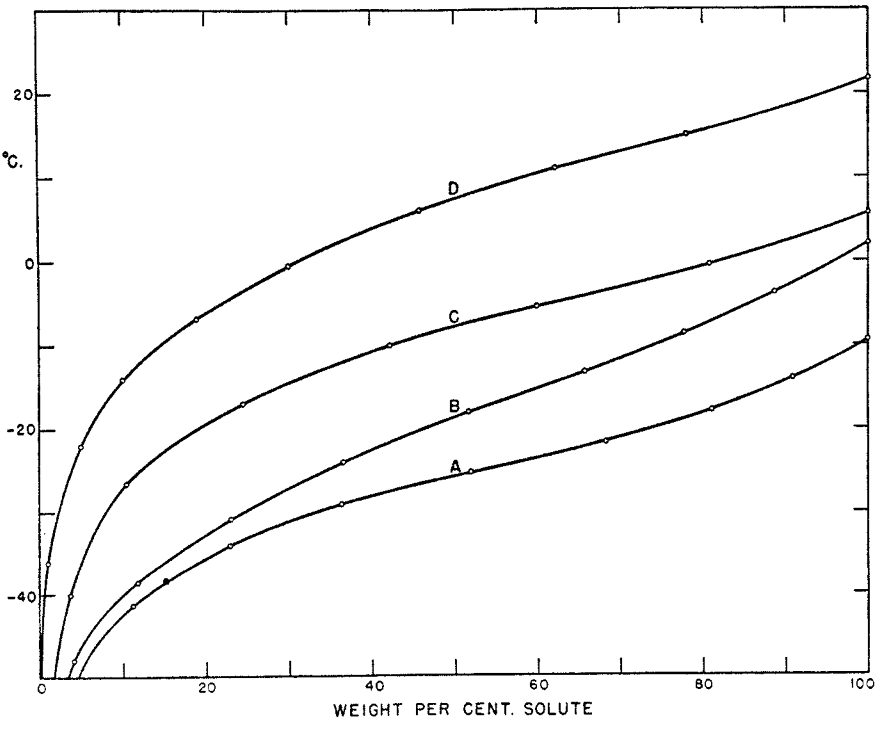

FIG. 2. SOLUBILITIES OF SOME HIGHER HALOALKANES IN *n*-HEXANE: A, 1-chlorododecane; B, 1-iodododecane; C, 1-bromotetradecane; D, 1-iodohexadecane.

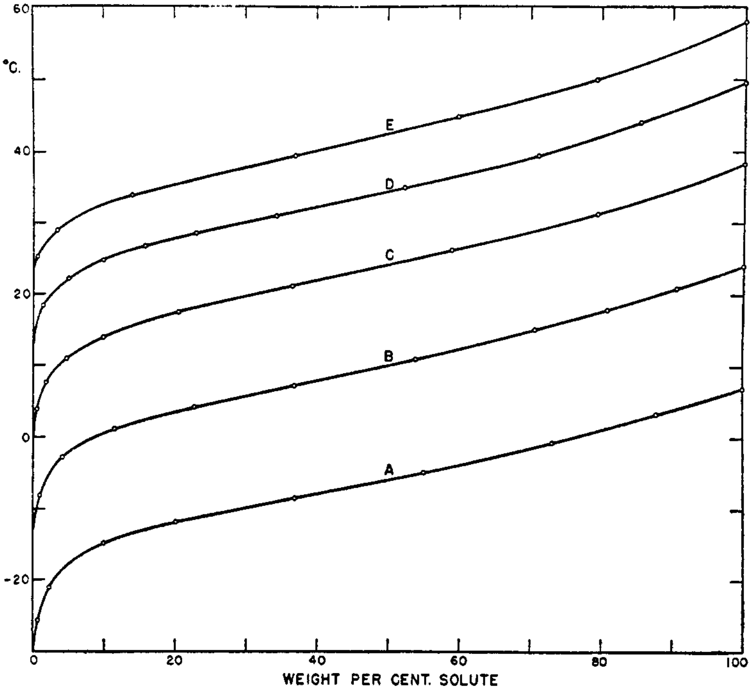

FIG. 3. SOLUBILITIES OF SOME HIGHER ALCOHOLS IN n-HEXANE: A, 1-decanol; B, 1-dodecanol; C, 1-tetradecanol; D, 1-hexadecanol; E, 1-octadecanol.

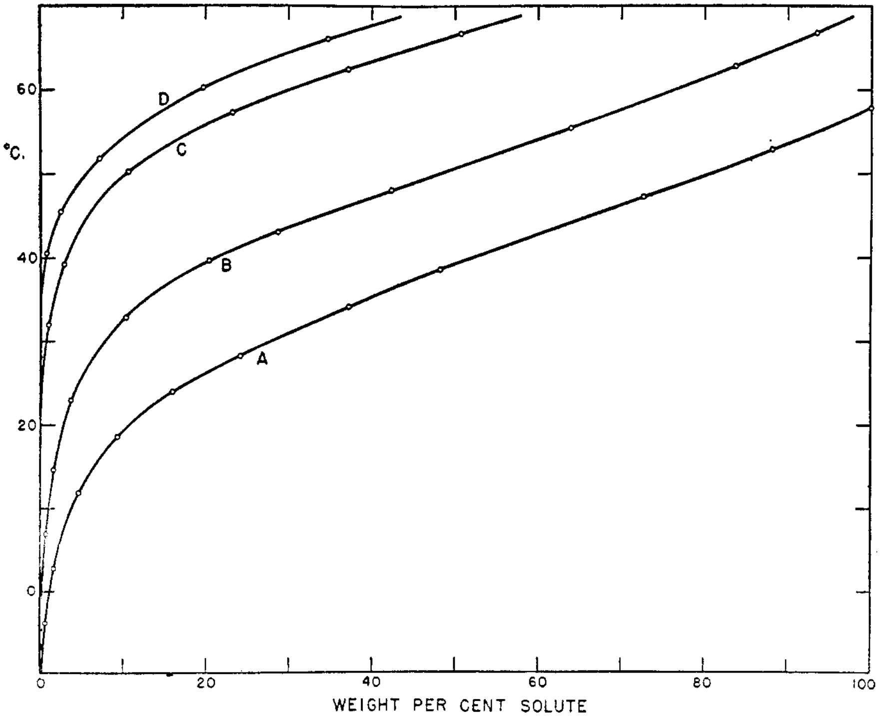

FIG. 4. SOLUBILITIES OF SOME HIGHER KETONES IN n-HEXANE: A, 10-nonadecanone; B, 12-tricosanone; C, 16-hentriacontanone; D, 18-pentatriacontanone.

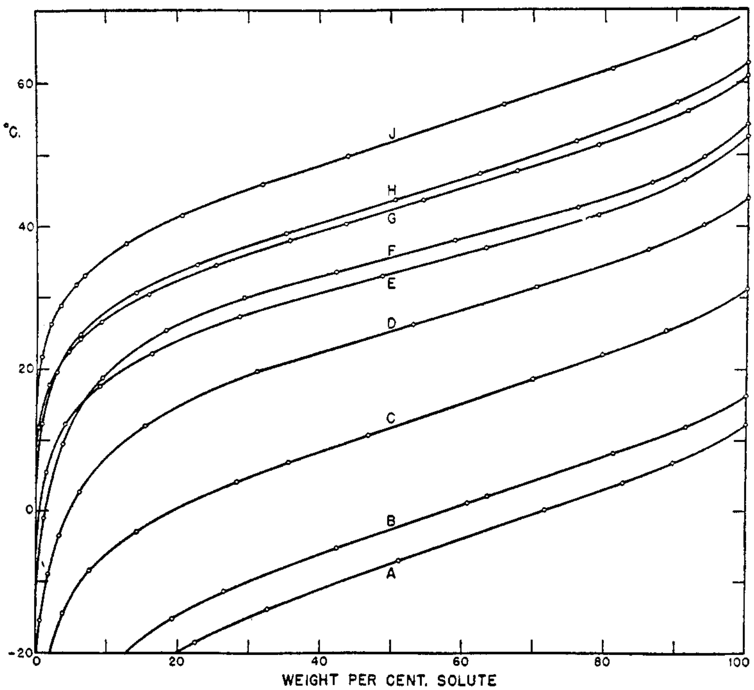

FIG. 5. SOLUBILITIES OF SOME HIGHER FATTY ACIDS IN *n*-HEXANE: A, caprylic acid; B, pelargonic acid; C, capric acid: D, lauric acid; E, myristic acid; F, pentadecylic acid; G, palmitic acid; H, heptadecylic acid; J, stearic acid.

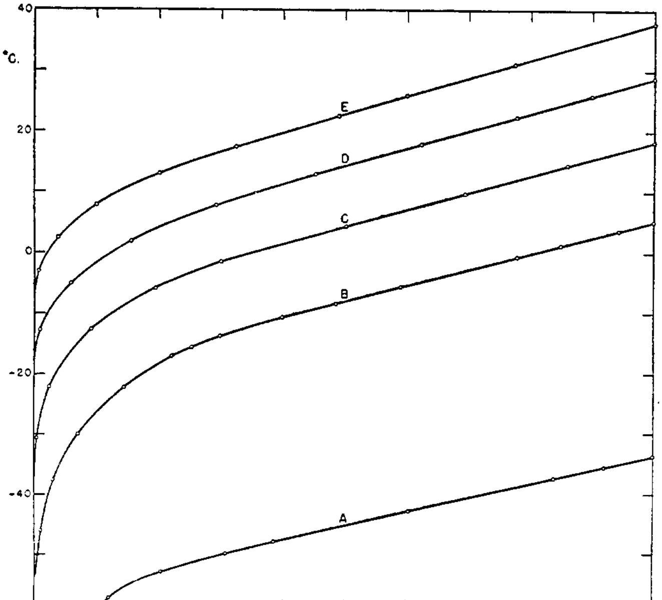

FIG. 6. SOLUBILITIES OF SOME METHYL ESTERS OF THE HIGHER FATTY ACIDS: A, methyl caprylate; B, methyl laurate; C, methyl myristate; D, methyl palmitate; E, methyl stearate.

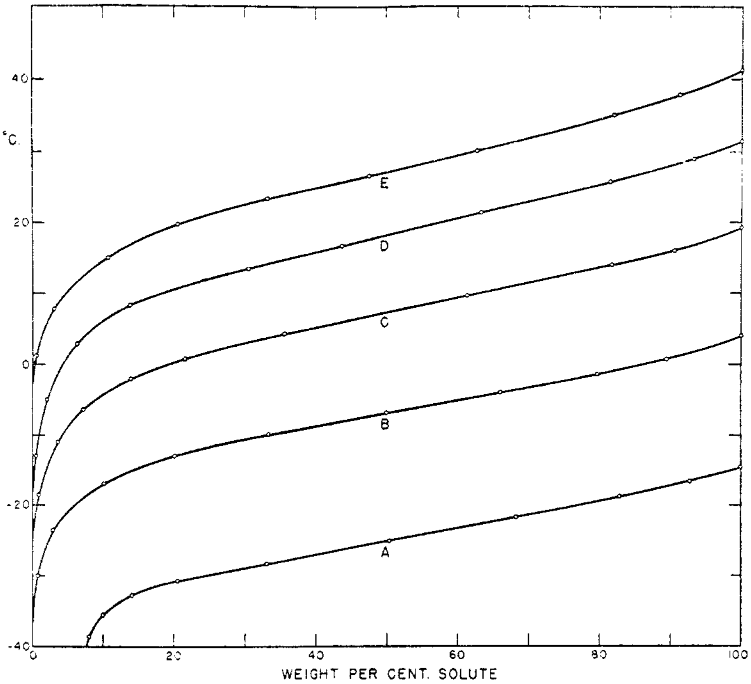

FIG. 7. SOLUBILITIES OF SOME HIGHER NITRILES IN *n*-HEXANE: A, caprinitrile; B, lauronitrile; C, myristonitrile; D, palmitonitrile; E, stearonitrile.

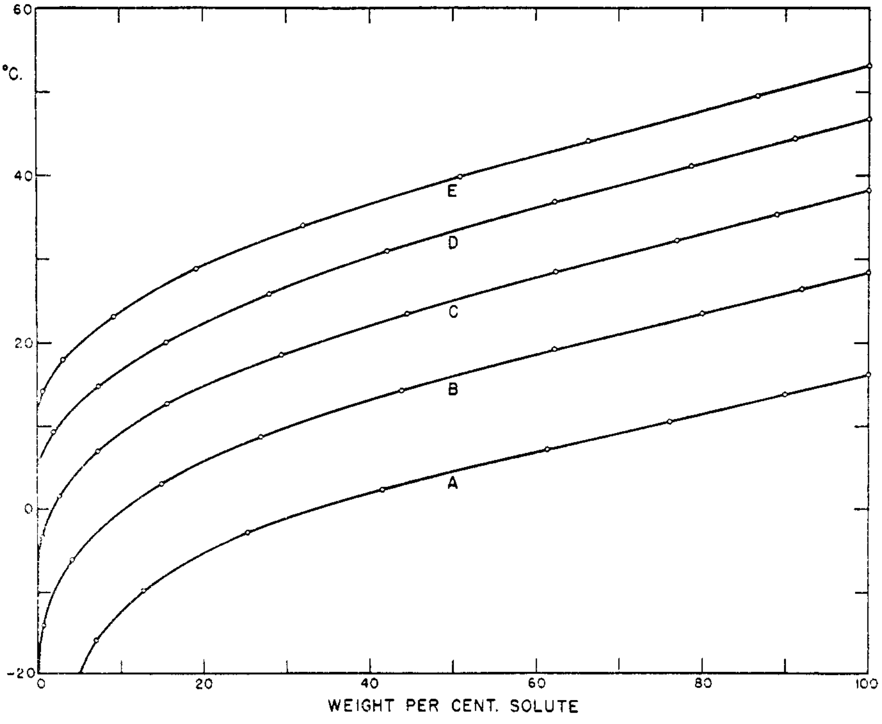

FIG. 8. SOLUBILITIES OF SOME HIGHER PRIMARY AMINES IN *n*-HEXANE: A, decylamine; B, dodecylamine; C, tetradecylamine; D, hexadecylamine; E, octadecylamine.

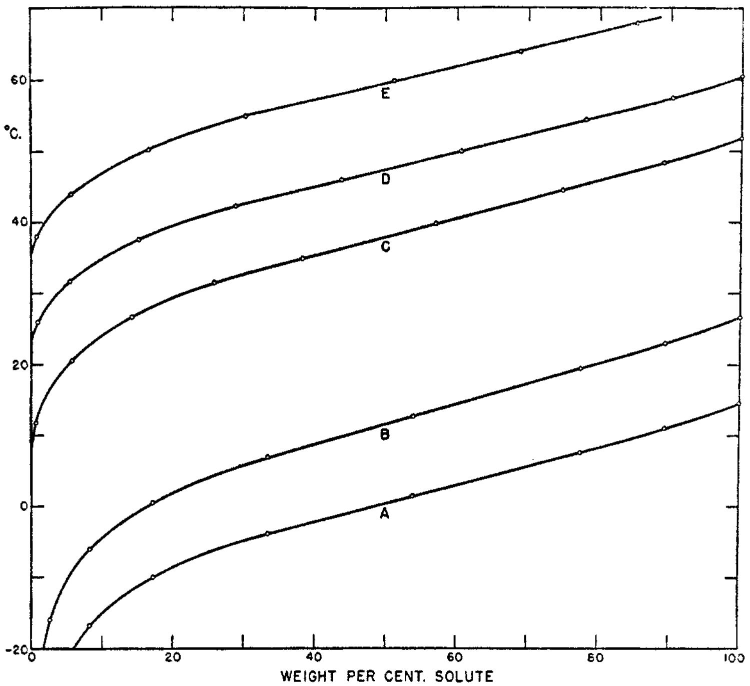

FIG. 9. SOLUBILITIES OF SOME HIGHER SECONDARY AMINES IN *n*-HEXANE: A, lower-melting form of dioctylamine; B, higher-melting form of dioctylamine; C, didodecylamine; D, ditetradecylamine; E, dioctadecylamine.

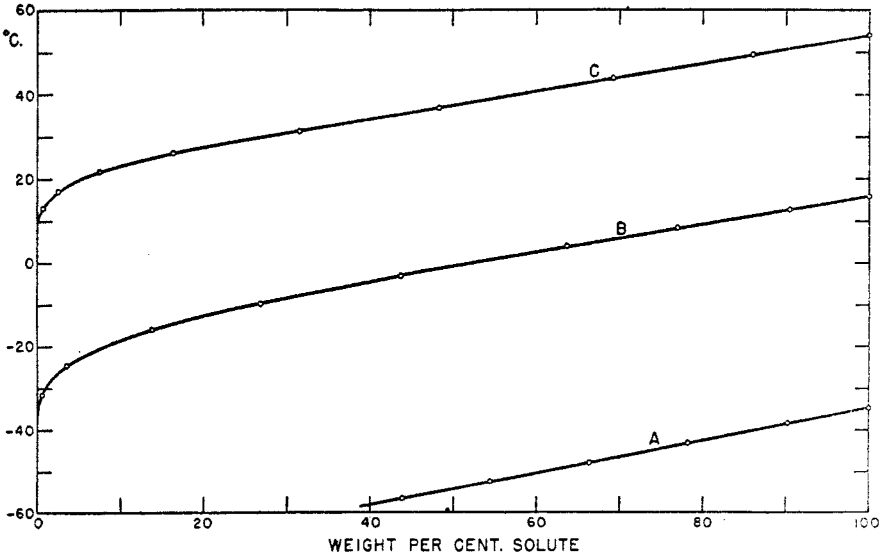

FIG. 10. SOLUBILITIES OF SOME HIGHER TERTIARY AMINES IN *n*-HEXANE: A, trioctylamine; B, tridodecylamine; C, trioctadecylamine.

bility of mixtures of fatty acids (17) where it was clearly demonstrated that the solubility of stearic-palmitic acid mixtures varied directly with the melting point. This relationship of solubility to melting point can be more readily understood if solubilization is considered to be a process of melting of the solute in the presence of a saturated solution. Such consideration is in accord with interpretation of Raoult's law, which can be expressed thermodynamically in terms of solubility as a function of the latent heat of fusion (18). In any series of aliphatic compounds, the latter value varies directly with the length of the paraffin chain, with the polarity of the substituent groups on the chain, and with the degree of intermolecular association of the compounds. The heat of fusion, in conjunction with the melting point, determines the theoretical slope of the solubility curve for each given compound. Deviations from this theoretical slope are a direct reflection of the influence of the various characteristics of the solvents employed, and of modification of the molecular structure of the solute in a given solvent.

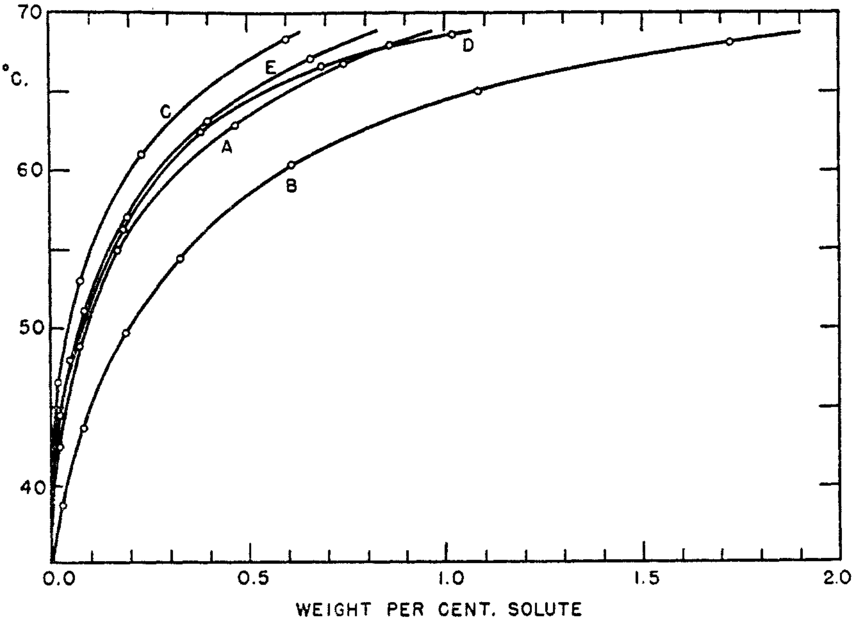

FIG. 11. SOLUBILITIES OF SOME HIGHER AMIDES IN *n*-HEXANE: A, capramide; B, lauramide; C, myristamide; D, palmitamide; E, stearamide.

With reference to Table XII, certain conclusions can be deduced regarding the influence of the substituent groups in this series. Although the polarities of many of the higher aliphatic compounds are not known and their values must be estimated on the basis of those of their lower homologs, it can be observed that the decreasing solubilities of the 16-carbon compounds follow almost exactly the increasing polarities of the solutes in the order tabulated. The only major exception is the solubility of the nitrile, which is somewhat greater than would be predicted on this basis alone, since its dipole moment is presumed to be appreciably higher than that of the corresponding alcohol and acid.

The excessively diminished solubilities of the amine, alcohol, acid, and amide in comparison with those of the other compounds in this series cannot be explained simply as due to their relatively greater polarities. These limited solubilities demonstrate the influence of intermolecular association of these compounds. By virtue of their hydrogen bonding capabilities, these compounds form polymeric molecules, thereby markedly reducing their solubilities in non-polar solvents. The relative solubilities of the amine, alcohol, and acid are of interest in view of the fact that their dipole moments are of about the same magnitude (1.4, 1.6, and 1.5×10^{18} e.s.u., respectively). The appreciably greater solubility of the amine over that of the alcohol and acid at 15° indicates that the latter are associated to a greater extent, the association of the alcohol possibly slightly exceeding that of the acid. The alcohols form linear polymers by hydrogen bonding, and it is not improbable that such a molecular structure would be more effective in decreasing the solubility in hexane than that of the acids which form cyclic dimers. This effect is less pronounced in the case of the lower homologs (compare Tables III and V) and disappears at higher temperatures as shown by the solubilities at 30° in Table XII. Additional factors, such as tautomerism and fusion of dimers, are probably responsible for the exceedingly limited solubilities of the amides (19).

The authors wish to acknowledge the assistance of Dr. R. G. Brault in the preparation of 1-chlorododecane.

SUMMARY

The solubilities of some representative high molecular weight normal saturated aliphatic hydrocarbons, 1-haloalkanes, primary alcohols, symmetrical ketones, fatty acids, nitriles, primary amines, secondary amines, tertiary amines, and amides have been determined in *n*-hexane. Some influences attributable to their molecular structure have been discussed.

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