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SOLUBILITIES OF SOME NORMAL ALIPHATIC AMIDES, ANILIDES, AND N,N-DIPHENYLAMIDES

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The relatively high melting points of the saturated aliphatic amides combined with the fact that, unlike other aliphatic compounds, the amides do not exhibit the gradation in physical properties in the solid state characteristic of most homologous series has long been attributed to some form of molecular association. This is further evidenced by the high dielectric constants of these compounds. X-ray examination (1) has indicated that the amides are probably associated in their crystalline state, since their crystals consist of bimolecular layers with the polar groups adjacent. Cryoscopic and ebullioscopic investigations (2-7) of amides in various non-polar solvents have indicated that these compounds form large polymers, while the anilides are moderately associated, probably as dimers, and N, N-disubstitution appears to inhibit association.

The actual structure of the amides and their derivatives is controversial. Early preparations of imido ethers (8) and preparation of amides from sodamides (9) suggested the existence of the enol tautomer. Tautomerism of the amides is further demonstrated by measurements of their dielectric constants and dipole moments (10, 11), infrared absorption spectra (12, 13), and ultraviolet absorption spectra (14). Calculations from thermochemical data (15) show that the amides consist of resonating molecules. These investigations and those on the solubilities of halogen substituted hydrocarbons in amides (16, 17) suggest that the association of the amides and anilides is effected through hydrogen bonding. Thus, it has been shown that acetamide forms polymers of indefinite molecular weight, and the solubility of chloroform in N-ethylacetamide could be accounted for by assuming that the pure liquid consists largely of dimers (12, 16).

Several structures have been postulated for the amidic polymers. Linear polymers are probably eliminated, for they do not usually lead to excessively high melting points; it has been shown (16) that the large linear polymers formed by hydrogen bonding of the alcohols have relatively low melting points. Furthermore, it has been proved (12) that enolization in the amides would of necessity involve a molecular rearrangement equivalent to ionization of a hydrogen atom. Such an occurrence would be improbable in a non-polar solvent. A cyclical structure has been suggested, for example, one resulting from a fusion of dimers by hydrogen bonding (16). The high dielectric constants of these compounds appear to offer an objection to a symmetrical cyclic structure, since such a structure should involve neutralization of the dipole moments. The high dielectric constants observed may be due to the presence of a high percentage of monomeric molecules (16). No investigation has yet suggested that the large amidic polymers may exist as asymmetrical cyclic structures.

All previous studies have been made upon amides containing less than six carbon atoms. This paper is a report of the preliminary investigation of the be-

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havior of the higher amides and presents the solubilities of caprylamide, capramide, capranile, N,N-diphenylcapramide, lauramide, lauranilide, N,N-diphenyllauramide, myristamide, palmitamide, palmitanilide, N,N-diphenylpalmitamide, stearamide, stearamilide, and N,N-diphenylstearamide in benzene, cyclohexane, tetrachloromethane, ethyl and butyl acetates, acetone, 2-butanone, methanol, 95% ethanol, isopropanol, *n*-butanol, nitroethane, and acetonitrile.

AMIDE	no. of C atoms	F.P., °C.	ref. (м.р., °С)
Caprylamide	8	105.9	$\begin{array}{c} 104 \ (19) \\ 105.5 \ (20) \\ 106 \ (21) \\ 105 \ (22) \\ 106 \ (23) \end{array}$
Capramide	10	98.5	98 (19, 24, 25) 101.1 (20) 99 (22) 98-99 (23)
Lauramide	12	102.4	98–99 (19) 100 (22) 102 (26)
Myristamide	14	105.1	103 (22) 103.0 (setting pt.) (27) 102 (28) 102-103 (29)
Palmitamide	16	107.0	106 (22) 106-107 (25) 103-104 (29) 105.3 (30) 104-105 (31)
Stearamide	18	109.7	105-106 (19) 109 (22) 108.5-109 (26) 108.4 (30)

TABLE I FREEZING POINTS OF PURIFIED AMIDES

EXPERIMENTAL

The amides and their derivatives used in this investigation were prepared from fatty acids¹ which had been highly purified by previously described methods (18). Ammonia was passed through the acids at 190-210° for 10-14 hours to obtain the amides. The crude product was poured into water while still hot to remove excess ammonia and any ammonium soap which was formed. The product was then dissolved in tetrachloromethane, washed free of fatty acid with alcoholic potassium hydroxide, and recrystallized from acetone until a constant freezing point was obtained. The freezing points of the amides are listed in Table I.

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¹ The freezing points of these acids were 16.26° for caprylic, 30.62° for capric, 43.77° for lauric, 54.15° for myristic, 62.30° for palmitic, and 69.28° for stearic acid.

During the course of this investigation it was decided to prepare an amide by another method as a check on the compounds prepared by the above method. Highly purified caprinitrile (10 g.) was poured into concentrated sulfuric acid (200 ml.) and left for 24 hours. The addition product thus formed was then hydrolyzed by pouring the mixture over a large excess of ice, and the amide which precipitated was filtered and recrystallized from acetone. The freezing point of this capramide was identical with that prepared by the reaction of ammonia with caproic acid, and the solubilities of the two compounds were identical. A small quantity of myristamide was obtained by Mr. E. F. Binkerd as a secondary reaction product in the course of the preparation of myristonitrile. This amide, upon purification, was identical with the myristamide prepared previously.

COMPOUND	NO. OF C* ATOMS	F.P., °C.	REF. (M.P., °C.)
Capranilide	10 <i>φ</i>	69.5	67-8 (19) 70 (22)
Lauranilide	12ϕ	77.2	75 (19, 32) 78 (22)
Palmitanilide	16 <i>φ</i>	90.2	89 (22) 90.6 (30) 87 (32) 88–90.5 (33) 87.5 (34) 88.5 (35) 90.5 (36)
Stearanilide	18 φ	94.9	94 (22, 33) 95.05 (30) 88 (35) 93.6 (37)
N, N-Diphenylcapramide	10 φφ	47.5	
N, N-Diphenyllauramide	$12 \phi \phi$	57.0	
N, N-Diphenylpalmitamide	16 <i>φ</i> φ	69.5	
N, N-Diphenylstearamide	18 φφ	72.3	

TABLE II FREEZING POINTS OF PURIFIED SUBSTITUTED AMIDES

* The numbers shown refer only to the number of carbon atoms in the aliphatic chain; $\phi = C_6 H_5$ in all tables and figures.

Capranilide, lauranilide, and palmitanilide were obtained by heating the appropriate fatty acids with redistilled aniline (added dropwise) for 2-3 hours at 150-170°. After washing by the treatment used for the amides, the anilides were recrystallized alternately from petroleum ether, b.p. 60-71°, (Skellysolve B) and from acetone-water mixtures until constant freezing points were obtained.

For stearanilide and the N, N-diphenylamides the corresponding acid chlorides were first prepared by the action of phosphorus trichloride upon the acids. After removal of the solvent (tetrachloromethane) and excess PCl_a, stearanilide was prepared by adding aniline (dropwise) to stearoyl chloride, maintaining the temperature of the reaction mixture below about 50°. The stearanilide was washed as above and crystallized from acetone to a constant freezing point.

The diphenylamides were prepared by heating the appropriate acid chlorides with diphenylamine for 2-4 hours at 135-145°. After washing, the compounds were crystallized from petroleum ether (Skellysolve B) to constant freezing points. The freezing points of the substituted amides are listed in Table II. Nitrogen analyses were obtained for all of the compounds to check their identities, and cooling curves were run to verify their purity. It can be seen from Tables I and II that a number of the compounds had higher freezing points than some of the melting points previously reported.

The solubilities of the amides and their derivatives were determined in sealed tubes by the method and with the apparatus previously described (38, 39). The solvents which were employed were those used in previous solubility studies (40). Temperatures were measured with an accurately calibrated thermometer which was graduated in 0.1° intervals. Solution temperatures of the amides and their derivatives were reproducible to $\pm 0.1^{\circ}$, and are, in general, considered accurate to at least $\pm 0.2^{\circ}$.

RESULTS AND DISCUSSION

The solubilities of the amides, anilides, and N, N-diphenylamides in the solvents investigated are listed in Tables III-XV.

CO1/20/20/20	G. PER 100 G. BENZENE								
COMPOUND	10.0°	30.0°	50.0°	60.0°	70.0°	80.1°			
8	0.5	0.6	4.1	13.8	52	153			
10	0.6	0.8	3.2	11.4	57	195			
12	0.6	1.0	6.7	26.6	83	238			
14	0.3	0.4	1.5	5.2	27.4	95			
16	0.3	0.4	2.0	7.6	41.2	145			
18	0.3	0.4	1.6	5.2	25.0	89			
10 <i>φ</i>	10.1(13.7)	67(110)	283	720	∞	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			
12ϕ	1.5	14.7(56)	155	340	1000	∞			
16ϕ	1.0	2.2	30.5	97	222	640			
18ϕ	0.7	1.5	14.1	56	145	555			
10 φ φ	100	329	~	∞	∞	∞			
$12 \phi \phi$	56	179	915	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	∞	∞			
16 φφ	18.8	81	283	720	~	∞			
$18 \phi \phi$	11.0	65	230	520	3500	~ ~			

TABLE III Solubilities in Benzene

 $*\phi = C_6H_{\delta}.$

The absence of a homologous influence in the amide series is striking, since there appears to be no orderly arrangement of the solubility curves of these compounds in the less polar solvents. For example, in benzene, ethyl acetate, 2-butanone, and others, lauramide is, in general, more soluble than capramide, and palmitamide more soluble than myristamide, while in cyclohexane, the latter is less soluble than stearamide, and caprylamide is the least soluble compound investigated. However, in the three highly polar solvents, nitroethane, methanol, and acetonitrile, the solubilities decrease with increased molecular weight, although the intervals between the curves are not regular. All of the N-substituted derivatives, on the other hand, appear in orderly sequence in all solvents. This behavior is illustrated by the solubility curves of these compounds in several representative solvents of various polarities: benzene, Fig. 1; cyclohexane, Fig. 2; butyl acetate, Fig. 3; *n*-butanol, Fig. 4; 2-butanone, Fig. 5; 95% ethanol, Fig. 6; nitroethane, Fig. 7; and acetonitrile, Fig. 8. In the course of examination of the anilides it was observed that the lower members of the series, capranilide and lauranilide, form an unstable modification which has a relatively greater solubility in a number of solvents than the stable

COMPOTIND*		G. PER 100 G. CYCLOHEXANE								
	10.0°	30.0°	50.0°	60.0°	70.0°	81.4°				
8		0.1	0.2	0.3	1.2	53				
10		0.4	0.5	0.6	3.3	150				
12	_	0.5	0.6	1.3	23.9	163				
14	_	0.2	0.3	0.4	1.7	61				
16		0.3	0.4	0.8	8.8	122				
18		0.3	0.4	0.6	3.3	88				
10 <i>φ</i>	3.3(3.6)	29.9(78)	273	680	×	×				
12ϕ	0.6	0.9(2.8)	105	265	785	∞				
16ϕ	0.4	0.6	2.4	61	173	535				
18ϕ	0.3	0.4	1.1	17.7	105	308				
$10 \phi \phi$	64	255	∞	∞	∞	×				
$12 \phi \phi$	27.2	119	800	~	∞	∞				
$16 \phi \phi$	9.2	38.5	232	660	~	∞				
$18 \phi \phi$	6.0	25.0	172	460	2850	∞				

TABLE IV Solubilities in Cyclohexane

 $*\phi = C_6 H_5.$

TABLE V Solubilities in Tetrachloromethane

6010000 0 0		g. per 100 g. tetrachloromethane								
COMPOUND	10.0°	30.0°	50.0°	60.0°	70.0°	76.0°				
8	_	0.4	0.7	3.7	18.2	42.5				
10		0.2	0.5	2.6	23.6	59				
12		0.4	1.5	9.9	40.8	72				
14	-	<0.1	0.2	1.4	10.1	27.6				
16	-	0.1	0.3	3.5	19.8	46.5				
18		<0.1	0.3	1.6	10.5	28.4				
10ϕ	34.2	52(110)	275	880	∞	∞				
12ϕ	8.5	14.0(43)	134	375	1375	almost ∞				
16ϕ	1.0	1.2	20.2	86	235	408				
18ϕ	0.4	0.5	7.0	43.3	167	300				
$10 \phi \phi$	72	310	∞	~	~~~~	∞				
$12 \phi \phi$	37.9	147	1065	∞	∞	8				
$16 \phi \phi$	16.0	44.7	240	820	~	~				
18 φφ	10.5	30.1	166	485	3800	~				

 $\phi = C_6 H_5.$

modification. This phenomenon was observed by rapidly chilling tubes containing solutions of the anilides and then placing the tubes in a water-bath at temperatures below those at which the stable form of the compounds was soluble. If the samples are held at the lower temperatures for a short time they transform

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into the stable modification. This transformation occurs more rapidly as the concentration of anilide is increased. This behavior appears to occur only in solvents with relatively low dielectric constants, *viz.*, benzene, cyclohexane,

COMPOTENT*	G. PER 100 G. ETHYL ACETATE							
/	10.0°	30.0°	50.0°	60.0°	70.0°	77.2°		
8	2.2	5.7	18.9	35.4	69	115		
10	0.5	2.2	10.2	23.9	59	123		
12	0.5	2.5	12.9	29.4	68	133		
14	0.3	1.0	3.3	7.8	22.1	55		
16	0.2	0.6	2.9	8.5	27.7	65		
18	0.1	0.3	2.0	5.4	16.6	41.		
10 φ	17.1	53(72)	248	750	~	∞		
12ϕ	6.8	17.2(23)	107	286	1250	∞		
16 ø	0.7	3.0	17.2	52	159	410		
18 φ	0.4	1.8	8.8	22.7	93	266		
10 φφ	68	302	∞	∞	∞	∞		
$12 \phi \phi$	25.5	125	1075	∞	∞	∞		
16 φφ	7.7	24.7	182	610	∞	∞		
$18 \phi \phi$	3.9	13.6	124	378	3125	∞		

TABLE VI Solubilities in Ethyl Acetate

 $*\phi = C_6H_5.$

COMBOTIND*	G. PER 100 G. BUTYL ACETATE							
COMPOUND	10.0°	30.0°	50.0°	70.0°	90.0°	100.0		
8	2.6	6.0	17.0	48.1	205	740		
10	0.9	2.9	9.6	39.5	505	×		
12	0.4	3.0	12.4	52	330	2550		
14	0.3	1.2	5.0	22.4	165	700		
16	0.2	0.8	4.6	25.0	205	670		
18	0.1	0.5	2.9	17.0	135	463		
10ϕ	18.3	42.6(62)	198	∞		~		
12ϕ	10.5	21.1(25)	86	730	80	~		
16ϕ	1.0	4.3	18.9	116	almost ∞	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		
18ϕ	0.4	1.8	8.7	68	930	æ		
10 φφ	54	221	∞	∞	8	~		
$12 \phi \phi$	24.4	92	750	~	∞	8		
$16 \phi \phi$	8.2	24.8	158	~~~	8	8		
18 φφ	5.6	16.8	110	2350	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~		

TABLE VII Solubilities in Butyl Acetate

 $^{\ast}\phi=\mathrm{C}_{6}\mathrm{H}_{5}.$

tetrachloromethane, ethyl and butyl acetates, and *n*-butanol; in addition, this behavior occurs in isopropanol in spite of the fact that the dielectric constant of this solvent is higher than those of acetone, 2-butanone, and 95% ethanol,

in which the metastable compound formation does not appear. In Figs. 1–4 the solubilities of the unstable form are shown by broken lines, and in Tables III-VII, XII and XIII these solubilities are listed in parentheses.

CONDOTINT *		G. PER 10	00 g. acetone	
CORFOUND	10.0°	30.0°	50.0°	56.5°
8	3.4	7.8	31.4	48.4
10	2.0	3.8	15.4	23.9
12	1.3	3.4	18.3	30.5
14	0.4	1.0	3.7	6.4
16	0.3	0.8	3.9	6.9
18	0.2	0.5	2.0	3.7
10 φ	39.1	93	490	870
12ϕ	6.3	12.5	210	352
16ϕ	1.1	3.3	22.1	52.9
18ϕ	0.7	2.0	13.0	28.5
10 φφ	96	735	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	∞
$12 \phi \phi$	46.8	192	1350	almost ∞
16 φφ	12.0	45.5	298	630
18 φφ	5.0	10.6	185	390

TABLE VIII Solubilities in Acetone

 $\phi = C_{5}H_{5}$.

covromp!		G. PER 100 G. 2-BUTANONE								
	10.0°	30.0°	50.0°	60.0°	70.0°	79.6°				
8	3.4	8.3	27.9	50.8	89	163				
10	2.2	3.8	13.3	30.8	79	189				
12	1.2	3.8	17.6	41.6	93	194				
14	0.6	1.2	4.7	11.1	32.8	100				
16	0.4	1.0	4.8	12.7	39.1	118				
18	0.3	0.7	2.9	8.2	23.6	79				
10ϕ	25.5	81	289	800	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	∞				
12ϕ	10.7	34.8	152	358	1350	∞				
16ϕ	2.7	6.6	35.5	89	208	600				
18ϕ	0.8	2.2	14.0	47.0	121	327				
$10 \phi \phi$	78	337	∞	∞	∞	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
$12 \phi \phi$	41.5	162	1250	∞	∞	~~~				
$16 \phi \phi$	13.1	52	268	800	∞	∞				
$18 \phi \phi$	5.6	23.9	147	432	3450	8				

TABLE IX Solubilities in 2-Butanone

 $\phi = C_6 H_5.$

The solubility curves for the N, N-diphenylamides in benzene are characteristic of compounds which are not associated in solution, in that the concentration is practically a linear function of the temperature. The amides and anilides, on

the other hand, exhibit the marked deviation from linearity which is typical of the solubility curves of long-chain compounds which are associated in solution,

COMPOUND*		G. PER 100 G. METHANOL							
COLICORD	10.0°	30.0°	50.0°	60.0°	64.7°				
8	22.1	53.0	130	206	263				
16	6.8	15.2	67	125	170				
12	4.2	12.4	77	164	206				
14	1.0	2.7	14.3	36.8	56				
16	0.7	1.2	10.0	32.0	51				
18	0.4	0.7	3.5	12.7	23.3				
10ϕ	18.3	70.1	400	1050	2250				
12ϕ	2.9	11.1	187	430	645				
16ϕ	0.5	0.8	6.3	25.4	68				
18ϕ	0.1	0.2	1.0	6.7	16.1				
10 φφ	32.6	200	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	∞	∞				
$12 \phi \phi$	9.0	81	965	~	∞				
$16 \phi \phi$	1.7	5.6	102	525	1400				
$18 \phi \phi$	1.1	3.9	37.2	300	600				

TABLE X Solubilities in Methanol

 $*\phi = C_{\delta}H_{\delta}.$

TABLE XI Solubilities in 95.0% Ethanol

	G. PER 100 G. 95% ETHANOL								
CORPOUND	10.0°	30.0°	50.0°	60.0°	70.0°	78.5°			
8	13.4	32.8	76	120	193	303			
10	4.3	12.0	43.7	88	174	350			
12	2.9	11.4	54	102	193	370			
14	1.2	3.8	15.1	33.5	81	180			
16	0.4	1.5	10.6	29.4	89	216			
18	0.2	0.8	5.7	15.6	50	124			
10 φ	33.6	81	365	1125	∞	80			
12ϕ	10.7	22.3	128	365	1450	∞			
16ϕ	0.6	2.2	14.2	49.5	205	720			
18 ø	0.3	1.2	7.7	21.6	77	124			
10 φφ	48.4	275	~	~	∞	~			
$12\phi\phi$	14.7	53	900	~~~	∞	~			
16 \$ \$	1.1	5.0	100	565	∞	8			
$18 \phi \phi$	0.8	2.6	52	310	3350	80			

 $*\phi = C_6H_5.$

the fatty acids (41), ketones (40), and amine salts (39). It is to be noted that only in benzene are the solubilities of all of the N, N-diphenylamides linear with temperature; in all of the other solvents the curves of the higher members of the series deviate from linearity, and in the most polar solvents even the lower members of the series give irregular solubility curves.

COMPOINT *	G. PER 100 G. ISOPROPANOL									
CONFOUND	10.0°	30.0°	50.0°	60.0°	70.0°	82.3°				
8	15.7	26.3	66	102	157	288				
10	6.0	10.9	37.2	72	140	380				
12	3.7	11.4	47.5	86	154	357				
14	1.2	3.2	15.5	34.2	76	208				
16	0.4	1.8	12.1	29.9	79	229				
18	0.2	1.0	6.9	20.0	56	172				
10 φ	19.0	46.4(67)	220	665	∞	∞				
12 φ	6.7	16.6(25)	102	254	930	~~~				
16ϕ	0.6	2.4	14.2	39.5	147	1050				
18 φ	0.3	1.3	8.4	25.8	91	570				
10 φφ	51	224	8	∞	∞	∞				
$12 \phi \phi$	21.5	77	990	×	∞	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~				
$16 \phi \phi$	6.6	13.4	90	452	∞	∞				
18 φφ	4.3	10.9	41.6	232	2525	∞				

TABLE XII Solubilities in Isopropanol

 $\phi = C_{6}H_{5}$.

TABLE XIII Solubilities in *n*-Butanol

COMPOUND*	G. PER 100 G. n-BUTANOL						
	10.0°	30.0°	50.0°	70.0°	90.0°	100.0°	
8	17.1	25.8	51	132	420	1300	
10	3.5	9.1	30.9	118	690	8	
12	2.2	10.1	38.1	126	580	3550	
14	0.8	3.8	13.7	58	276	1150	
16	0.3	1.9	11.2	67	353	1050	
18	0.1	1.1	7.3	44	204	590	
10 φ	25.3	55(100)	221	×	8	80	
12ϕ	13.2	26.1(37)	108	890	∞	80	
16ϕ	1.8	5.5	21.6	152	almost ∞	∞	
18ϕ	0.6	3.2	11.2	85	1450	~	
$10 \phi \phi$	57	226	8	∞	∞	8	
$12 \phi \phi$	25.8	84	760	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	∞	~	
$16 \phi \phi$	7.5	19.0	108	œ	∞	~	
18 φφ	4.9	13.7	68	2500	×	~	

 $*\phi = C_6H_5.$

There appears to be no general correlation between the solubilities of the amides and the polarities of the solvents. In general, the solubilities of a given compound at a given temperature are relatively the same in non-polar solvents as in the most polar solvents investigated, while the solubilities are relatively much greater in the solvents of intermediate polarity, being the greatest in the

COMPOUND*	G. PER 100 G. NITROETHANE						
	10.0°	30.0°	50.0°	70.0°	90.0°	100.0°	
8	1.0	2.1	7.5	37.5	307	1600	
10	0.8	1.1	4.2	25.2	850	∞	
12	0.8	1.1	3.9	24.2	495	5100	
14	0.3	0.5	2.0	7.5	142	1500	
16	0.2	0.3	0.9	7.5	208	1075	
18	0.1	0.2	0.5	5.2	93	61	
10ϕ	14.0	21.8	133	∞	×	∞	
12ϕ	6.0	8.5	22.3	720	~	∞	
16ϕ	0.5	0.8	3.4	41.8	almost ∞	~	
18 φ	0.4	0.6	2.0	14.7	1060	∞	
$10 \phi \phi$	57	310	~	8	~	∞	
$12\phi\phi$	29.0	118	1100	œ	~	∞	
$16 \phi \phi$	16.1	29.0	179	∞	~	∞	
$18 \phi \phi$	10.9	17.8	92	3100	∞	~	

TABLE XIV Solubilities in Nitroethane

 $\phi = C_6 H_{\delta}.$

TABLE XV

COMPOUND*	G. PER 100 G. ACETONITRILE						
	10.0°	30.0°	50.0°	60.0°	70.0°	82.0°	
8	1.1	5.4	16.4	31.6	73	200	
10	0.5	1.4	6.0	13.4	44.5	178	
12	0.3	0.9	5.1	12.1	39.8	175	
14	0.2	0.6	1.1	2.9	7.8	43.3	
16	0.2	0.3	0.7	1.6	5.9	34.8	
18	0.1	0.2	0.4	0.9	2.6	16.8	
10 φ	9.3	18.0	297	825	×	∞	
12ϕ	0.8	3.0	24.1	308	1100	∞	
16ϕ	0.3	0.7	2.2	5.5	32.5	733	
18ϕ	0.2	0.5	1.4	3.3	13.8	480	
10 φφ	39.3	252	∞	×	~	∞	
$12 \phi \phi$	12.6	75	1075	∞	~	∞	
$16 \phi \phi$	1.5	5.8	75	635	æ	∞	
$18 \phi \phi$	0.6	2.4	23.3	359	3350	8	

SOLUBILITIES IN ACETONITRILE

 $\phi = C_6 H_{\delta}.$

alcohols. Even in solvents of the same polarity, such as benzene and cyclohexane, there is, at 70° for instance, as much as 25- to 50-fold difference in the solubilities of a given amide. In general, the substituted amides behave simi-



FIG. 1. SOLUBILITIES OF AMIDES AND SUBSTITUTED AMIDES IN BENZENE The broken lines represent the solubilities of the metastable compounds



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larly to the amides with respect to the polarities of the solvents, except that the solubilities of the N, N-diphenylamides decrease markedly with increased polarity of the solvent. In this respect, the behavior of the latter compounds is similar to that of the high molecular weight ketones (40).

The results of this investigation show that none of the structures yet proposed for the amides and their derivatives can adequately explain the anomalous



FIG. 3. SOLUBILITIES OF AMIDES AND SUBSTITUTED AMIDES IN BUTYL ACETATE

behavior of these compounds. All of the proposed theories imply a semblance of homology. The assumption of polymer formation does not *per se* explain, for instance, the anomalous solubilities of caprylamide and myristamide. The fact that the phenyl substituent of the anilides precludes the formation of polymers larger than dimers by hydrogen bonding does not explain why the slopes of the anilide solubility curves are less steep and break more sharply in dilute solutions than do those of the corresponding amides. There is no present ex-



FIG. 4. SOLUBILITIES OF AMIDES AND SUBSTITUTED AMIDES IN n-BUTANOL





Fig. 7. Solubilities of Amides and Substituted Amides in Nitroethane

planation for the deviation from linearity of the solubility curves of the N,Ndiphenylamides if one assumes that N,N-disubstitution prevents association by hydrogen bonding.

Further investigations are being carried out in this laboratory in an attempt to establish the structure of the higher amides.

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FIG. 8. SOLUBILITIES OF AMIDES AND SUBSTITUTED AMIDES IN ACETONITRILE

SUMMARY

The solubilities of the amides containing 8, 10, 12, 14, 16, and 18 carbon atoms, and the anilides and N, N-diphenylamides containing 10, 12, 16, and 18 carbon atoms in the hydrocarbon chain have been determined in benzene, cyclohexane, tetrachloromethane, ethyl and butyl acetates, acetone, 2-butanone, methanol, 95% ethanol, isopropanol, *n*-butanol, nitroethane, and acetonitrile.

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