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## Studies on High Molecular Weight Aliphatic Amines and their Salts. VI. Electrical Conductivities of Aqueous Solutions of the Hydrochlorides of Octyl-, Decyl-, Tetradecyl- and Hexadecylamines

BY A. W. RALSTON AND C. W. HOERR

In a previous paper of this series it was shown that the hydrochlorides and acetates of dodecyl- and octadecylamines are colloidal electrolytes similar in their behavior to compounds in which the paraffin chain is in the anionic portion of the molecule.<sup>1</sup> The present paper is a continuation of this work and presents the electrical conductivities of the hydrochlorides of octyl-, decyl-, tetradecyl- and hexadecylamines with emphasis on their behavior in dilute solutions, together with further studies of the dilute solutions of dodecyl- and octadecylamine hydrochlorides.

### Procedure

The hydrochlorides of octyl-, decyl-, tetradecyl- and hexadecylamines were prepared by the methods which have been previously described for the preparation of the hydrochlorides of dodecyl- and octadecylamines.<sup>2</sup> The amines were prepared by hydrogenation of the appropriate nitrile, and purified by fractional distillation *in vacuo* to separate them from any unchanged nitrile or secondary amine.<sup>3</sup> They were then converted into the hydrochlorides by the addition of equimolar portions of hydrochloric acid. The hydrochlorides of octyl- and decylamines were prepared in the manner of the dodecylamine salt, and those of tetradecyl- and hexadecylamines in the manner of the octadecylamine salt. No melting point could be obtained for these salts since they decompose on heating. Their constants have been reported in a previous paper.<sup>4</sup>

The water used in the conductivity measurements was distilled from an alkaline solution of potassium permanganate in a Pyrex glass still. Its specific conductance was  $0.6 \times 10^{-6}$  mho at 20°,  $0.9 \times 10^{-6}$  at 40° and  $1.2 \times 10^{-6}$  at 60°. The conductivities of the amine salt solutions were corrected by the appropriate amounts for the conductance of the water. The salt solutions were prepared by weighing freshly distilled water directly into previously steamed Pyrex flasks containing known amounts of the amine salt. The molarities of the solutions at the desired temperatures were calculated from the molalities by using the density values presented in this paper (*vide infra*).

The conductivity measurements were made with the equipment and in the manner previously described.<sup>1</sup>

### Experimental Results

The equivalent conductances of solutions of octylamine hydrochloride are listed in Table I.

(1) Ralston, Hoerr and Hoffman, *THIS JOURNAL*, **64**, 97 (1942).  
 (2) Ralston, Hoffman, Hoerr and Selby, *ibid.*, **63**, 1598 (1941).  
 (3) Ralston, Selby, Pool and Potts, *Ind. Eng. Chem.*, **32**, 1093 (1940).

(4) Harwood, Ralston and Selby, *THIS JOURNAL*, **63**, 1916 (1941).

TABLE I

EQUIVALENT CONDUCTANCES OF  $C_8H_{17}NH_2 \cdot HCl$  SOLUTIONS

Temp., °C.	$N_v$	$\Lambda$	$N_v$	$\Lambda$
20.0	0.0007275	93.68	0.1572	66.90
	.003144	91.00	.2620	60.88
	.01353	86.96	.4368	54.92
	.03144	81.70	.7277	48.25
	.07277	75.18	.9348	45.08
	40.0	.0006720	146.2	.1228
.002385		143.6	.2284	97.88
.004785		141.5	.3067	91.22
.009570		137.9	.5740	78.49
.02014		132.6	.7655	71.56
.04580		124.1	.9570	66.42
60.0	.0006370	199.6	.1593	145.5
	.003183	194.0	.3060	126.0
	.006370	190.1	.5100	110.9
	.01223	186.3	.6370	102.5
	.03183	176.0	.9001	94.80
	.06122	165.3		

The equivalent conductances of decylamine hydrochloride solutions are listed in Table II.

TABLE II

EQUIVALENT CONDUCTANCES OF  $C_{10}H_{21}NH_2 \cdot HCl$  SOLUTIONS

Temp., °C.	$N_v$	$\Lambda$	$N_v$	$\Lambda$
20.0	0.0002966	93.72	0.08798	57.90
	.003530	90.25	.1472	46.00
	.01315	86.01	.2350	40.09
	.02411	83.12	.4021	35.20
	.03508	79.30	.5900	33.55
	.05625	68.68	.8270	33.12
40.0	.0003118	145.2	.1262	78.01
	.003118	140.3	.1993	66.98
	.007500	136.3	.2492	64.30
	.01496	131.6	.3742	61.10
	.03118	125.0	.4985	60.15
	.04982	107.2	.6232	59.35
60.0	.07480	95.00	.8890	59.02
	.0003626	193.3	.08741	124.8
	.001764	189.0	.1320	107.7
	.003920	185.1	.1980	94.70
	.01120	178.1	.2746	86.93
	.01980	171.9	.3576	83.56
	.02640	167.5	.4950	80.30
	.03324	163.5	.6600	79.35
	.04258	154.2	.8250	77.68

Due to their limited solubilities, tetradecyl- and hexadecylamine hydrochlorides were studied only

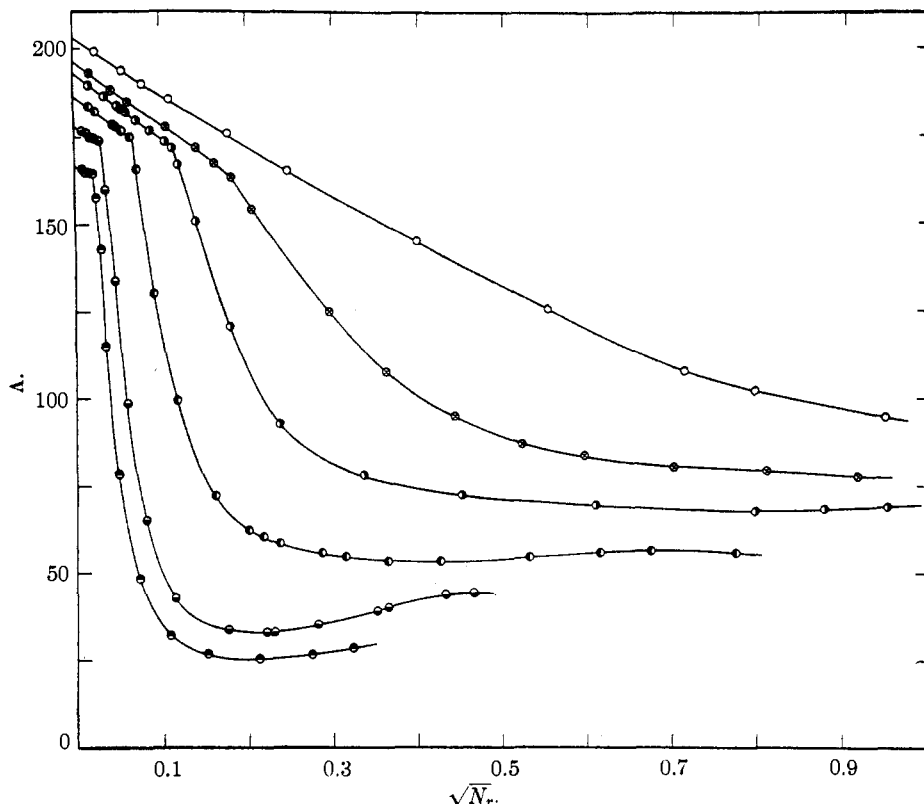


Fig. 1.—Equivalent conductances of amine salt solutions at 60°: O,  $C_8H_{17}NH_2 \cdot HCl$ ; ⊗,  $C_{10}H_{21}NH_2 \cdot HCl$ ; ●,  $C_{12}H_{25}NH_2 \cdot HCl$ ; ○,  $C_{14}H_{29}NH_2 \cdot HCl$ ; ⊙,  $C_{16}H_{33}NH_2 \cdot HCl$ ; ⊕,  $C_{18}H_{37}NH_2 \cdot HCl$ .

at 60°. Table III lists the equivalent conductances of solutions of tetradecylamine hydrochloride and Table IV lists those of hexadecylamine hydrochloride.

TABLE III  
EQUIVALENT CONDUCTANCES OF  $C_{14}H_{29}NH_2 \cdot HCl$   
SOLUTIONS AT 60°

$N_v$	$\Lambda$	$N_v$	$\Lambda$
0.0002891	183.6	0.04020	62.18
.0005733	182.5	.04762	60.31
.001840	179.4	.05646	58.50
.002222	178.2	.08245	55.64
.002928	177.4	.09952	54.55
.004100	175.4	.1338	53.33
.005092	166.0	.1828	53.20
.008133	130.3	.2831	54.45
.01377	99.60	.3782	55.92
.02566	72.28	.4574	56.46

The equivalent conductances of these four salt solutions are shown in Fig. 1, together with those of dodecyl- and octadecylamine hydrochlorides<sup>1</sup> at 60°. Several further measurements on the latter two salts have been included in their curves. Figure 2 is an enlarged plot of a portion of Fig. 1 including the theoretical Onsager slope for each curve.

TABLE IV  
EQUIVALENT CONDUCTANCES OF  $C_{16}H_{33}NH_2 \cdot HCl$  SOLUTIONS  
AT 60°

$N_v$	$\Lambda$	$N_v$	$\Lambda$
0.0000627	176.8	0.01272	42.90
.0001730	176.4	.03087	33.83
.0002900	175.6	.04910	33.10
.0005333	175.0	.05302	33.00
.0007830	174.2	.07977	34.89
.001271	160.0	.1240	39.02
.002006	133.9	.1340	40.12
.003454	98.83	.1880	43.78
.006518	65.25		

By extrapolation on an extended scale, the limiting equivalent conductance for octylamine hydrochloride solutions is found to be 95.9 mhos at 20°, 149.2 at 40° and 204.2 at 60°. For decylamine hydrochloride,  $\Lambda_0$  is 95.0 mhos at 20°, 147.4 at 40° and 196.8 at 60°. For tetradecyl- and hexadecylamine hydrochlorides, the values are 186.1 and 178.0 mhos, respectively, at 60°. Using the values of the limiting equivalent conductance of chloride ion at these temperatures,<sup>5</sup> checked against a more recent value<sup>6</sup> at 25°, the following

(5) "International Critical Tables," Vol. VI, 230 (1929).

(6) McInnes, Shedlovsky and Longworth, *THIS JOURNAL*, **54**, 2758 (1932).

TABLE V  
DENSITIES OF AMINE HYDROCHLORIDE SOLUTIONS  
 $d_s = d_w + Am + Bm^2 + Cm^3$

Hydrochloride of	Temp., °C.	Molal range	A	B	C	±
Octylamine	20.0	0-1.0	-0.0078	-0.0158	0.0120	0.0002
	40.0	0-1.0	-.0064	-.0214	.0172	.0001
	60.0	0-1.0	-.0074	-.0183	.0152	.0001
Decylamine	20.0	0-1.0	-.0119	-.0130	.0117	.0001
	40.0	0-1.0	-.0106	-.0178	.0155	.0002
	60.0	0-1.0	-.0103	-.0197	.0172	.0001
Dodecylamine <sup>1</sup>	20.0	0-1.2	-.0157	-.00214	.00267	.0003
	25.0	0-1.2	-.0166	-.00234	.00292	.0003
	30.0	0-1.2	-.0172	-.00250	.00380	.0003
	35.0	0-1.2	-.0215	.0084	-.00318	.0002
	40.0	0-1.2	-.0205	.0054	-.00151	.0004
	45.0	0-1.2	-.0147	-.0106	.0075	.0003
	50.0	0-1.2	-.0157	-.0080	.0064	.0001
	60.0	0-1.0	-.0155	-.0096	.0104	.0001
Tetradecylamine	60.0	0-0.85	-.0171	-.0056	.0052	.0001
Hexadecylamine	60.0	0-0.25	-.0085	-.141	.67	.0001
Octadecylamine <sup>1</sup>	60.0	0-0.12	-.0157	-.00109	.073	.0001

values are obtained for the cations: C<sub>8</sub> 27.6 mhos at 20°, 51.7 at 40° and 71.6 at 60°; C<sub>10</sub> 26.7 at 20°, 49.9 at 40° and 64.2 at 60°; C<sub>14</sub> 53.5 at 60°, and C<sub>16</sub> 45.4 at 60°.

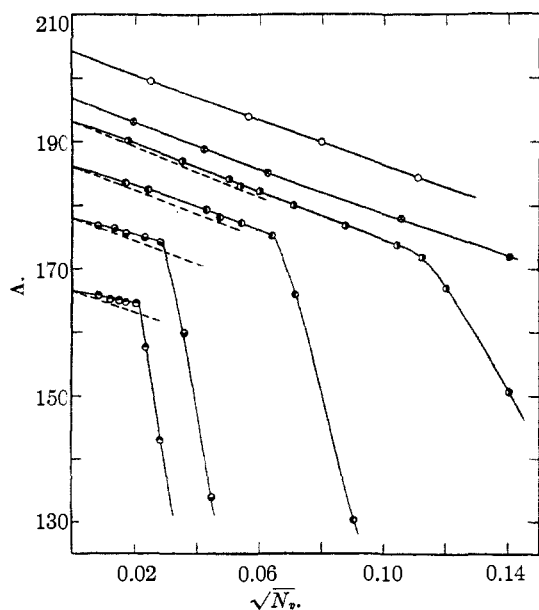


Fig. 2.—Equivalent conductances of amine salt solutions: O, C<sub>6</sub>H<sub>17</sub>NH<sub>2</sub>·HCl; ⊗, C<sub>10</sub>H<sub>21</sub>NH<sub>2</sub>·HCl; ●, C<sub>12</sub>H<sub>25</sub>NH<sub>2</sub>·HCl; ⊙, C<sub>14</sub>H<sub>29</sub>NH<sub>2</sub>·HCl; ⊖, C<sub>16</sub>H<sub>33</sub>NH<sub>2</sub>·HCl; ⊕, C<sub>18</sub>H<sub>37</sub>NH<sub>2</sub>·HCl. The broken lines indicate the Onsager values for each salt.

The densities of these amine salt solutions were determined with a Geissler pycnometer at the temperatures of the conductivity measurements. The densities, when plotted against molal concentration, in all cases are expressed by the

general equation

$$d_s = d_w + Am + Bm^2 + Cm^3$$

where  $d_s$  is the density of the solution,  $d_w$  the density of water at the given temperature,  $m$  the molal concentration of amine salt, and  $A$ ,  $B$  and  $C$  are arbitrary constants which were calculated from the data and are presented in Table V.

### Discussion

The equivalent conductance curves (Fig. 1) of the salts of this series from decylamine hydrochloride upwards show the three characteristic ranges of conductivity previously reported.<sup>1</sup> The behavior of octylamine hydrochloride appears to be similar to that of ordinary strong electrolytes throughout the concentration range investigated.

In Fig. 2 the actual slopes for the octyl- and decylamine salts coincide with the theoretical Onsager slopes. The upward deviation from the theoretical slope which is evidenced by the higher members of the series has been observed in numerous studies of the colloidal electrolytes.<sup>7,8,9</sup> The rise of conductance in dilute solutions of this type of electrolyte has been attributed to the presence of small, highly conducting micelles.<sup>9</sup> However, since it is typical for the curves of ordinary strong electrolytes to have an upward curvature above the theoretical Onsager slope, the several cases which have been reported for the col-

(7) Hartley, "Aqueous Solutions of Paraffin Chain Salts," Hermann et Cie., Paris, 1936.

(8) Wright, Abbott, Sivertz and Tartar, THIS JOURNAL, **61**, 549 (1939).

(9) McBain, Dye and Johnston, *ibid.*, **61**, 3210 (1939).

loidal electrolytes cannot be accepted *per se* as proof of the presence of micelles in dilute solution. The Onsager equation has been modified by the addition of arbitrary parameters so that it will fit the data for any salt.<sup>10</sup>

The sharp break in these curves, and the abrupt decrease of conductance after the break, distinguishes colloidal electrolytes from ordinary strong electrolytes. Recent investigations<sup>11</sup> indicate that it is at the concentration where the break occurs that micellar agglomeration takes place. In the case of the amine salts, this transition occurs at the following concentrations:  $C_{10}$  0.04  $N_v$ ,  $C_{12}$  0.013  $N_v$ ,  $C_{14}$  0.004  $N_v$ ,  $C_{16}$  0.0008  $N_v$  and  $C_{18}$  0.0003  $N_v$ . These values are of approximately the same magnitude as are those reported for the alkyl sulfonates containing corresponding paraffin chains.<sup>9</sup>

The decrease of conductance in the second range is ascribed by McBain to the formation of large micelles of low conductivity, "neutral colloid," which are formed so rapidly that they overshadow the effects of the small, highly conducting micelles. Lottermoser and Puschel<sup>12</sup> concur with this interpretation. Hartley,<sup>7</sup> on the other hand, holds that the fall of conductivity is due to the attraction of the oppositely charged ions to the highly conductive micelles so that their effective conductance is decreased. A somewhat similar interpretation is made by Tartar.<sup>8</sup>

The amine salts show no definite point of transition between the second and third ranges of conductance. The minima in the curves are very broad in contrast to the sharp minima of some of the soap solutions. The rise of conductivity of the amine salt solution is not so great in the third range as that of some of the soaps and alkyl sulfonates, although for hexadecylamine hydrochloride the rise is approximately 35% above the minimum.

The increased conductivity in the third range is explained by McBain as being due to the effects of steadily increasing numbers of highly conductive micelles, while Hartley ascribes this effect to a loss of the oppositely charged ions by the micelles.

The viscosities of dodecylamine hydrochloride solutions were measured at 30° with an Ostwald viscometer to determine whether the viscosity had any marked effect on the conductivity. Due

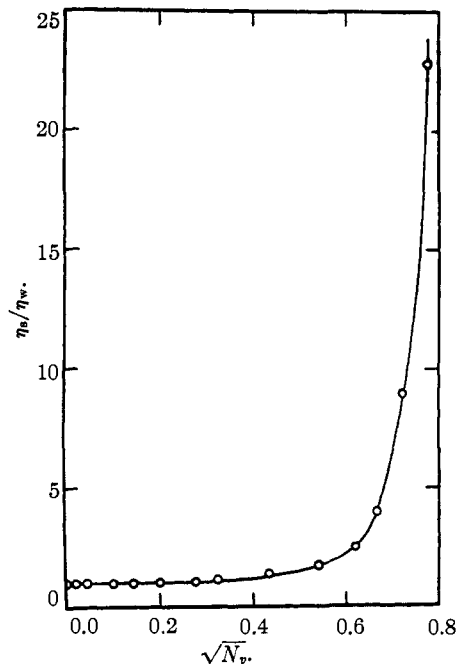


Fig. 3.—Relative viscosities of  $C_{12}H_{25}NH_2 \cdot HCl$  solutions at 30°.

to the highly surface-active nature of these solutions, measurements made in this manner are accurate only to approximately  $\pm 3\%$ . Their results are plotted in Fig. 3 as the relative viscosity against the square root of the molarity. These values are averages of 15 to 25 measurements at each concentration shown. In the neighborhood of 0.7 molar the relative viscosity exceeds a value of 65. This study shows that there is no sharp change in the equivalent conductance in the concentration range where the viscosity increases abruptly (from about 0.5 molar upward). If it were not for the increased viscosity, the rise of equivalent conductance would probably be even greater.

Further discussion of the behavior of the amine salts in aqueous solution can be presented when the studies on the transference numbers of these salts are completed.

### Summary

1. Conductivities and densities of aqueous solutions of the hydrochlorides of octyl-, decyl-, tetradecyl- and hexadecylamines have been determined.

2. The first member of the series behaves as a simple strong electrolyte, while the higher homologs exhibit behavior typical of colloidal electrolytes.

3. The equivalent conductance of these salts has been discussed with reference to the modern theories of colloidal electrolytes.

(10) Jones and Dole, *THIS JOURNAL*, **52**, 2245 (1930); Shedlovsky, *ibid.*, **54**, 1405 (1932).

(11) Tartar and Wright, *ibid.*, **61**, 539 (1939); Wright and Tartar, *ibid.*, **61**, 544 (1939).

(12) Lottermoser and Puschel, *Kolloid-Z.*, **63**, 175 (1933).

4. In the case of dodecylamine hydrochloride the conductivity rises in the third range in spite of greatly increased viscosity.

5. The values of  $\Lambda_0$  and  $l_c$  have been determined from the experimental data.

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## Effects of Heat, Solvents and Hydrogen-bonding Agents on the Crystallinity of Cellulose Esters

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Recent investigations<sup>1-4</sup> have sought to elucidate the nature of the solid state of cellulose and its derivatives. X-Ray studies have shown the presence of crystalline components, and the existence of "amorphous" or disorganized inter-crystalline matter has been inferred. The importance to physical properties of the balance between the crystalline and non-crystalline phases in these polymers is increasingly evident. However, relatively little progress has been made in determining the configurations of amorphous or disordered states or the circumstances causing them. The present work aims to indicate an important type of disorder which can be produced in cellulose esters by heat treatment, and to investigate with X-ray diffraction the crystallizing effects of various agents on these disordered systems.

The behavior of the synthetic linear polyamides previously noted<sup>5</sup> is strictly parallel to that of the cellulose polymers. The concepts of coexisting crystalline and disordered states and of kinetic mobility of chain segments in solid polymers appear to have general application.

### Experimental

**Materials.**—The cellulose triacetate<sup>5a</sup> had a solution viscosity of  $(\eta_{sp}/c)_{c \rightarrow 0} = 0.564$ , at 25.0° in chloroform. (Viscosity values are from extrapolation to  $c = 0$  of the linear concentration dependence of  $\eta_{sp}/c$ .) The cellulose tributyrates<sup>5a</sup> was of  $(\eta_{sp}/c)_{c \rightarrow 0} = 0.757$ , 25.0°, in chloroform, and the cellulose acetate-butyrates,  $(\eta_{sp}/c)_{c \rightarrow 0} = 1.929$ , 25.0°, in acetone. The cellulose esters were obtained from the Eastman Kodak Company and all were white, pure finely-divided flakes.

(1) W. A. Sisson, *Ind. Eng. Chem.*, **30**, 530 (1938); *Chem. Rev.*, **26**, 187 (1940).

(2) H. Mark, *Chem. Rev.*, **26**, 169 (1940).

(3) P. H. Hermans, *J. Phys. Chem.*, **45**, 27 (1941).

(4) K. Hess and C. Trogus, *Z. physik. Chem.*, **B15**, 157 (1932).

(5) C. S. Fuller, W. O. Baker and N. R. Pape, *THIS JOURNAL*, **62**, 3275 (1940).

(5a) The designation "triesters" means that technical class of esters, and does not imply stoichiometrically complete esterification. Tests indicate, however, that the acyl value was within 1% of complete esterification.

**Heat Treatment.**—Samples allowed to solidify near their melting points were formed to uniform cross-section by extruding ribbons under slight pressure into a small steel mold open at one end and maintained a few degrees below the melt temperature. Since the molten polymer occupied nearly the total volume of the system, no appreciable oxidation occurred by air exposure. The samples were dried and maintained so during the whole treatment. The triacetate was fused at 240° under slightly elevated pressure, the tributyrates at 180° and the acetate-butyrates at 210°. These may be regarded as about the normal melting points of the compounds. Melts for the quenching experiments were maintained at about 250° for the triacetate and acetate-butyrates, and about 190° for the tributyrates. Samples were quenched from their melts at both 20° and -75°, with apparently equivalent results. The quenched samples discussed below were prepared by rapid transfer of molten pellets to a heavy brass plate of high heat capacity maintained at -75° with dry-ice. A second plate, likewise cooled, was immediately applied above the sample and was separated from the lower plate by shims yielding samples of 0.069 cm. thickness except that this thickness was increased to 0.086 cm. for the crystallization rate measurements on the tributyrates.

For the annealing experiments, the dry quenched samples were mounted rigidly on the X-ray collimating insert, photographed with filtered copper X-radiation for a given constant period, at constant voltage in the tube, and were then inserted in a Pyrex tube in a thermostated electric furnace, at selected temperatures below their softening or deforming points. The tube contained aluminum granules, on which the metal insert was placed, so that the high heat capacity and conductivity of its environment warmed the small cellulose ester strip quickly. This was important for short annealing times at high temperatures. Likewise, the position of the strip with respect to the incident beam was kept constant for successive exposures during the annealing, as required for the intensity comparisons. The annealing was always in a reduced, dry hydrogen atmosphere, and the prolonged heating times noted for some of the esters produced no sign of decomposition. Samples were cooled to room temperature before exposure and were stored in desiccators when not mounted in the camera.

**Solvent Treatment.**—Quenched ribbons of standard, equal thickness were suspended at 25° in a vapor concentration of representative solvents produced by their equilibrium vapor pressure at the given temperature. Treatment times were insufficient to cause noticeable