sample crystallized from the same solvents in broad colorless needles, m. p. 39–40.5°.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.2; H, 7.9. Found: C, 78.1; H, 7.9.

The β-form obtained from 400 mg. of β-cyclic keto-ester crystallized immediately after evaporative distillation at 120–150° and 0.01 mm.; yield, 275 mg. (86%); m. p. 104–112°. A sample crystallized from 60–75° petroleum ether containing a drop or two of acetone in colorless plates; m. p. 112–113.5°.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.2; H, 7.9. Found: C, 78.2; H, 7.8.

3'-Keto-6-hydroxy-2-methyl-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene (I).—The α-form was obtained by refluxing 400 mg. of pure recrystallized methyl ether in a nitrogen atmosphere with 4 cc. of 48% hydrobromic acid and 4 cc. of glacial acetic acid for forty-five minutes during which time an orange-red color developed. The product which precipitated on dilution with water redissolved completely when excess 10% sodium hydroxide solution was added. The alkaline solution was treated briefly with Norit and filtered into an excess of hydrochloric acid. The hydroxy ketone which precipitated (225 mg.) was filtered off; by extraction of the filtrate with ether–benzene an additional 60 mg. of product was obtained; total yield, 75%; m. p. 154–155.5° with slight previous softening. After sublimation at 135–155° and 0.01 mm. and recrystallization from alcohol–water it formed clusters of colorless needles; m. p. 155–156°.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.7; H, 7.5. Found: C, 77.5; H, 7.4.

The β-form was obtained by refluxing 200 mg. of methyl ether (evaporatively distilled but not recrystallized) in a nitrogen atmosphere with 2 cc. of 48% hydrobromic acid and 2 cc. of glacial acetic acid for forty-five minutes. A green color developed on heating. The product was worked up as described for the α-isomer and sublimed at 130–180° and 0.01 mm.; yield, 100 mg. (53%); m. p. 209–213° (vac.). From benzene it crystallized in almost colorless irregular plates; yield, 70 mg. (37%); m. p. 212–214° (vac.).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.7; H, 7.5. Found: C, 77.6; H, 7.6.

Summary

The *cis* and *trans* forms of 3'-keto-2-methyl-6-hydroxy-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene have been synthesized from 6-methoxy-1-tetralone by the method employed for the synthesis of the sex hormone equilenin. These hormone analogs possess the B, C, and D ring structure of equilenin, but lack the A ring. In addition a hydroxyl group is situated in the aromatic ring. One of the forms is weakly estrogenic when injected into ovariectomized rats.

ANN ARBOR, MICH.   RECEIVED SEPTEMBER 2, 1941

Studies on High Molecular Weight Aliphatic Amines and their Salts. IV. Electrical Conductivities of Aqueous Solutions of the Hydrochlorides and Acetates of Dodecyl- and Octadecylamines[1]

BY A. W. RALSTON, CHARLES W. HOERR AND EVERETT J. HOFFMAN

Our knowledge of the electrical conductivities of solutions of colloidal electrolytes is based chiefly upon studies made with compounds in which the paraffin chain is in the anionic portion of the molecule. In this type of colloidal electrolyte, it has been recently shown by studies upon sodium alkyl sulfates and sodium alkyl sulfonates that when the equivalent conductivity is plotted against concentration the curves show three characteristic slopes.[2] In the first range the equivalent conductivity falls as a linear function of the square root of the concentration similar to the behavior observed in strong electrolytes. An

extremely rapid fall of equivalent conductivity with increased concentration characterizes the second range. In the third range this rapid fall is halted, and the curve shows a definite rise before falling again. These latter two ranges have been explained upon the basis of micelles, the existence of which was first postulated by McBain.[3] In their work upon the conductivity of cetylpyridinium chloride solutions in fields of varying strengths, Malsch and Hartley[4] concluded that their results could only be explained upon the existence of micelles. The present paper reports the electrical conductivities of aqueous solutions of dodecyl- and octadecylamine acetates and the corresponding hydrochlorides, and compares their behavior with that of anionic colloidal electrolytes.

(1) For previous paper see Ralston, Hoerr and Hoffman, THIS JOURNAL, 63, 2576 (1941).

(2) McBain and Betz, *ibid.*, 57, 1905 (1935); Howell and Robinson, *Trans. Roy. Soc.* (London), A155, 386 (1936); McBain, Dye and Johnston, THIS JOURNAL, 61, 3210 (1939); Wright, Abbott, Sivertz and Tartar, *ibid.*, 61, 549 (1939); Ward, *J. Chem. Soc.*, 522 (1939).

(3) McBain, *Trans. Faraday Soc.*, 9, 99 (1913).

(4) Malsch and Hartley, *Z. physik. Chem.*, 170A, 321 (1934).

Procedure

The preparation of dodecyl- and octadecylamine acetates[1] and their corresponding hydrochlorides[5] has been previously described. The water used in the conductivity measurements was distilled from an alkaline potassium permanganate solution in a Pyrex glass still. Its conductivity was 0.8×10^{-6} mho at 20°.

Conductivity measurements were made with a Jones–Dykes type of bridge equipped with a specially built oscillator and tuned amplifier[6] in conjunction with a Leeds and Northrup resistance box and slide wire. Cell capacitance was balanced by an electrolytic condenser in parallel with a variable air condenser. The three conductivity cells employed had cell constants of 0.1704, 0.5857 and 17.40 at 25°. The constants were determined against 0.01 N potassium chloride, and separate determinations were made at each temperature investigated. Unplatinized electrodes were employed in order to minimize adsorption. The conductivities were determined at frequencies of 1000 cycles, and were checked against frequencies of 3000 cycles. The cells were placed in a water-bath equipped with a mechanical stirrer and a mercury regulated electric heater which maintained the desired temperature with an accuracy of ±0.01°.

The samples were weighed into a glass-stoppered flask and were then placed in the conductivity cells. Separate samples were prepared for each composition investigated, and all flasks and cells were steamed and dried before use.

Experimental Results

The equivalent conductivities of solutions of dodecylamine hydrochloride at various concentrations are shown in Table I.
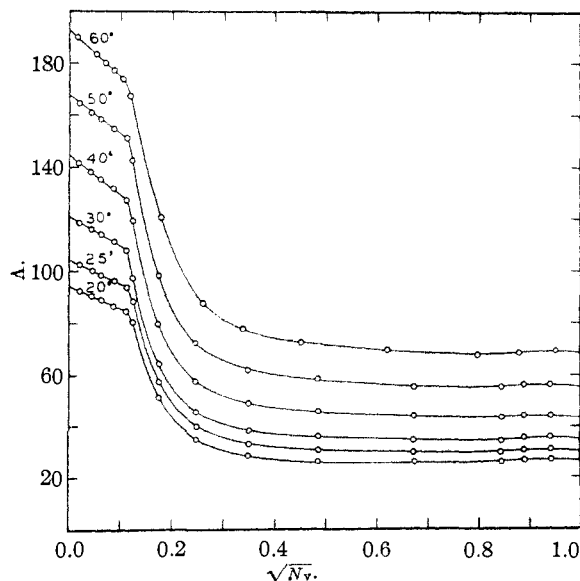

Fig. 1.—Equivalent conductivities of dodecylamine hydrochloride solutions.

(5) Ralston, Hoffman, Hoerr and Selby, This Journal, **63**, 1598 (1941).

(6) The oscillator and amplifier were manufactured by Offner Electronics, Chicago.

Table I

EQUIVALENT CONDUCTIVITIES OF DODECYLAMINE HYDROCHLORIDE SOLUTIONS

N_v	Λ	N_v	Λ
20.0°		40.0°	
0.000465	92.17	0.000462	141.7
.001976	90.29	.001962	138.0
.003933	88.72	.003909	135.3
.007633	86.54	.007588	131.8
.01310	84.57	.01302	127.5
.01533	80.22	.01524	119.6
.03030	51.16	.03012	79.81
.06058	34.77	.06022	57.57
.1214	28.30	.1206	49.38
.2353	25.92	.2337	45.89
.4520	25.46	.4489	44.05
.7126	25.68	.7071	43.84
.7919	26.39	.7851	44.36
.8876	26.77	.8802	44.15
1.048	26.45	1.037	43.46
25.0°		50.0°	
0.000465	102.2	0.000461	164.7
.001973	100.1	.001955	161.0
.003928	98.22	.003890	158.0
.007626	96.08	.007557	154.8
.01309	93.68	.01298	151.3
.01531	88.22	.01528	142.5
.03027	57.25	.03000	98.19
.06052	39.93	.05998	72.24
.1213	30.03	.1202	61.89
.2350	30.60	.2328	58.45
.4513	29.79	.4470	55.19
.7115	29.76	.7042	55.14
.7900	30.70	.7829	56.21
.8858	30.93	.8768	56.31
1.046	30.36	1.033	55.18
30.0°		60.0°	
0.000464	118.6	0.000306	189.9
.001969	116.1	.002896	183.2
.003920	114.0	.005040	180.0
.007615	111.3	.007525	177.0
.01307	108.3	.01088	173.9
.01529	97.30	.01430	167.2
.03022	64.01	.03245	120.7
.06044	45.37	.06645	87.6
.1211	38.08	.1135	77.8
.2346	35.60	.2040	72.2
.4508	34.53	.3830	69.4
.7104	34.08	.6360	67.8
.7880	35.25	.7721	68.7
.8844	35.32	.9044	69.1
1.042	34.82	1.011	68.5

Figure 1 shows the equivalent conductance of dodecylamine hydrochloride against $\sqrt{N_v}$ for the various temperatures investigated.

Table II shows the equivalent conductivities at various concentrations and temperatures of solutions of dodecylamine acetate.

TABLE II

EQUIVALENT CONDUCTIVITIES OF DODECYLAMINE ACETATE SOLUTIONS

N_v	Λ	N_v	Λ
0.0°		40.0°	
0.0000880	32.11	0.0000873	101.9
.0003232	31.70	.0003207	100.9
.0006928	31.30	.0006874	99.90
.002421	30.20	.002402	96.91
.005133	29.09	.005093	93.50
.008572	28.20	.008505	90.85
.01705	26.35	.01691	81.62
.01927	25.59	.01912	72.07
.02499	23.01	.02477	56.77
.03324	20.03	.03296	47.90
.06606	14.01	.06548	36.56
.1356	12.81	.1342	33.88
.2668	11.89	.2640	33.41
.4989	11.60	.4932	32.41
.8835	9.86	.8723	28.11
1.007	9.32	.9966	26.58
1.218	8.94	1.212	25.38
20.0°		60.0°	
0.0000878	61.82	0.000256	134.8
.0003227	60.83	.000687	132.7
.0006916	60.16	.001851	129.4
.002417	58.45	.003240	126.8
.005124	56.31	.007066	121.7
.008556	54.80	.01011	116.5
.01702	48.78	.01651	102.2
.01923	43.59	.02455	75.41
.02494	36.27	.04000	62.38
.03316	31.18	.08400	51.97
.06589	23.52	.2295	49.34
.1351	21.78	.4295	48.00
.2658	21.34	.8100	45.02
.4965	20.96		
.8784	17.92		
1.003	16.82		
1.216	15.76		

The equivalent conductivity of dodecylamine acetate solutions against $\sqrt{N_v}$ at various temperatures is shown in Fig. 2.

In determining the conductivities of octadecylamine salts measurements could only be made at higher temperatures because of their limited solubilities. The equivalent conductivities of octadecylamine acetate solutions are shown in Table III and of octadecylamine hydrochloride solutions in Table IV.

Figure 3 shows the equivalent conductivities of solutions of octadecylamine acetate against the $\sqrt{N_v}$ at 50 and 60° and of octadecylamine hydrochloride at 60°.

The densities used in the calculation of N_v are given in Tables V, VI and VII. These were determined by use of a Giessler pycnometer.
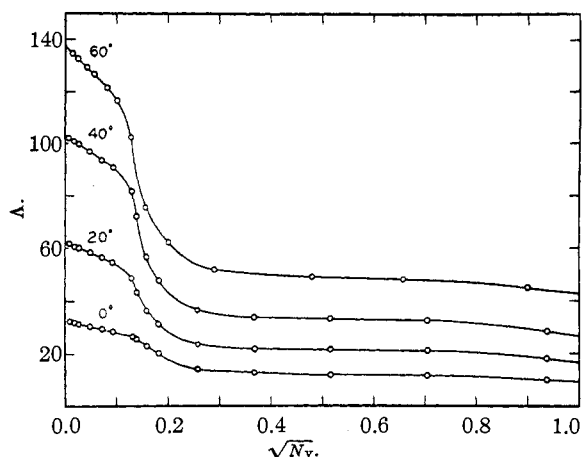

Fig. 2.—Equivalent conductivities of dodecylamine acetate solutions.

TABLE III

EQUIVALENT CONDUCTIVITIES OF OCTADECYLAMINE ACETATE SOLUTIONS

N_v	Λ	N_v	Λ
50.0°		55.0°	
0.0000449	77.0	0.004587	30.72
.0001270	74.5	.01055	19.58
.0003022	70.8	.02083	15.23
.0006120	60.4	.04170	15.13
.001324	47.78	.07082	15.12
.002610	37.08	60.0°	
.004600	27.05		
.01058	17.32	0.0000447	91.9
.02089	12.99	.0001263	88.1
.04180	13.00	.0003007	84.0
.07102	12.99	.0006088	73.0
		.001317	56.12
55.0°		.002593	43.03
0.0000448	84.8	.004569	32.35
.0001267	82.8	.01052	21.92
.0003016	79.0	.02078	17.15
.0006105	66.0	.04163	16.96
.001321	47.93	.07050	16.92
.002608	40.00		

TABLE IV

EQUIVALENT CONDUCTIVITIES OF OCTADECYLAMINE HYDROCHLORIDE SOLUTIONS

N_v	Λ
60.0°	
0.0000710	165.8
.0001417	165.1
.0002780	164.8
.0005522	157.6
.0008060	143.1
.001147	115.2
.002368	78.64
.005260	48.38
.01137	32.23
.02272	26.90
.04495	25.08
.07540	26.41

TABLE V

DENSITIES OF DODECYLAMINE ACETATE SOLUTIONS

| Molality | _____Temp., °C._____ | | | | | | | | | | |
	0.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0	60.0
0.0250	0.9999	0.9994	0.9988	0.9979	0.9967	0.9953	0.9937	0.9918	0.9898	0.9877	0.9829
.0500	.9999	.9993	.9985	.9974	.9962	.9948	.9932	.9913	.9893	.9872	.9824
.0998	.9998	.9991	.9979	.9967	.9954	.9939	.9923	.9904	.9884	.9863	.9815
.1498	.9994	.9986	.9972	.9958	.9945	.9931	.9915	.9896	.9876	.9854	.9807
.2495	.9984	.9973	.9959	.9943	.9928	.9914	.9898	.9878	.9858	.9837	.9789
.4001	.9962	.9950	.9937	.9918	.9903	.9888	.9873	.9853	.9833	.9811	.9763
.5980	.9932	.9919	.9906	.9884	.9870	.9855	.9838	.9819	.9798	.9777	.9729
.9995	.9873	.9858	.9839	.9818	.9802	.9787	.9770	.9750	.9730	.9709	.9663

TABLE VI

DENSITIES OF DODECYLAMINE HYDROCHLORIDE SOLUTIONS

| Molality | _____Temp., °C._____ | | | | | | | |
	20.0	25.0	30.0	35.0	40.0	45.0	50.0	60.0
0.05004	0.9973	0.9963	0.9950	0.9932	0.9915	0.9897	0.9875	0.9825
.1601	.9956	.9945	.9930	.9908	.9891	.9873	.9857	.9806
.3497	.9924	.9911	.9897	.9874	.9856	.9836	.9819	.9770
.5499	.9892	.9877	.9854	.9843	.9824	.9803	.9781	.9733
.8002	.9856	.9841	.9827	.9804	.9782	.9759	.9740	.9691
1.200	.9808	.9788	.9771	.9748	.9726	.9704	.9688	...

TABLE VII

DENSITIES OF SOLUTIONS OF OCTADECYLAMINE ACETATE
AND OF OCTADECYLAMINE HYDROCHLORIDE

| | $C_{18}H_{37}NH_2 \cdot CH_3COOH$ | | | $C_{18}H_{37}NH_2 \cdot$ HCl |
| Molality | _____Temp., °C._____ | | | 60 |
	50	55	60	
0.01060				0.9830
.01495	0.9878	0.9854	0.9829	
.02478				.9828
.03253	.9875	.9851	.9826	
.05001	.9872	.9848	.9824	.9825
.07502	.9867	.9844	.9820	
.07910				.9822

Fig. 3.—Equivalent conductivities of solutions of octa-decylamine acetate and octadecylamine hydrochloride: ◑, octadecylamine acetate at 50° and ◐, at 60°; O, octa-decylamine hydrochloride at 60°.

Discussion

The curves in every instance show three distinct slopes characteristic of colloidal electrolytes. The equivalent conductance at infinite dilution was determined by extrapolation on an extended scale. For dodecylamine hydrochloride solution Λ_0 is 94.0 mhos at 20°, 104.1 mhos at 25°, 121.1 mhos at 30°, 144.7 mhos at 40°, 168.0 mhos at 50° and 192.8 mhos at 60°. Using the values of l_a for the chloride ion from the "International Critical Tables," the following values of l_c were calculated: 25.7 at 20°, 28.6 at 25°, 39.0 at 30°, 47.2 at 40°, 52.0 at 50° and 60.2 at 60°.

Dodecylamine acetate solutions have the following values for Λ_0: 32.5 mhos at 0°, 62.4 mhos at 20°, 103.0 mhos at 40° and 137.6 mhos at 60°. The calculated values for l_c are: 25.6 at 20°, 47.2 at 40° and 59.6 at 60°. These values are in good agreement with those calculated for l_c from dodecylamine hydrochloride.

The values for Λ_0 in the case of octadecylamine acetate are 80.9 mhos at 50° and 97.4 mhos at 60°, and Λ_0 for octadecylamine hydrochloride is 167.0 at 60°. The values of l_c are 14.1 at 50° and 19.4 at 60° for octadecylamine acetate and 34.4 at 60°, for octadecylamine hydrochloride. The discrepancy between the values of l_c obtained from the acetate and hydrochloride conductivities may be due to hydrolysis of the former in dilute solution.

A comparison of the calculated and actual values obtained over the first range for the On-sager slope shows that in most instances these salts behave as simple uni-univalent electrolytes. The
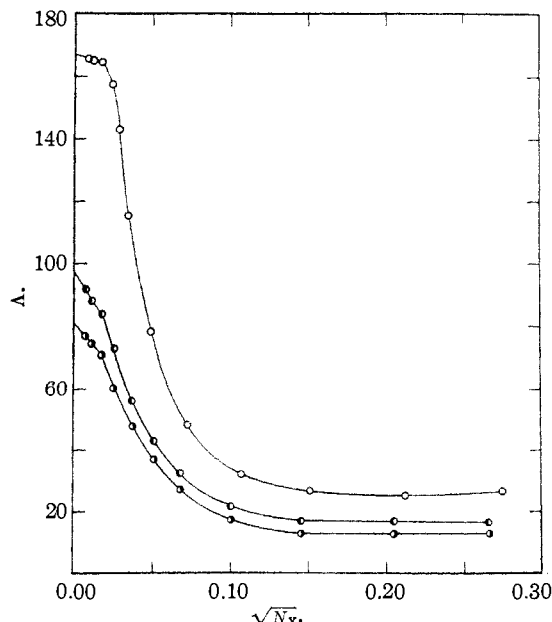
following values were obtained for dodecylamine hydrochloride at 20, 25, 30, 40, 50 and 60°: calcd., 74.20, 83.67, 95.02, 116.7, 139.6 and 164.3; found, 74, 83, 94, 115 137 and 160. The values found are approximately those calculated, which is in agreement with the work of others upon colloidal electrolytes.[2] The values for dodecylamine acetate at 0, 20, 40 and 60° are as follows: calcd., 36.61, 67.10, 107.0 and 150.6; found, 45, 84, 130 and 180. Octadecylamine hydrochloride shows a calculated value of 157.9 and an actual value of 156 at 60°. The calculated values for octadecylamine acetate differ materially from the actual values. At 50° the calculated value is 118.7 and the actual value 530, while at 60° the calculated value is 140.8 and the actual value 825.

The slope of the second and third ranges is undoubtedly due to the formation of micelles. Micelle formation begins at approximately 0.013 molar for the dodecylamine salts and at approximately 0.0003 molar for the octadecylamine salts, and in both cases micelle formation begins at a slightly lower concentration as the temperature is increased. Both of the hydrochlorides show a slight increase in equivalent conductance with concentration over a portion of the third range.

Dodecylamine acetate–water systems show a gel area beyond 0.90 molar. It will be noted that there is no noticeable change in the slope of the curve (Fig. 2) as the system goes from a solution to a gel.

Calculations of l_c/Λ_0 give the following values of n_c for dodecylamine hydrochloride at infinite dilutions: 0.273 at 20°, 0.275 at 25°, 0.322 at 30°, 0.325 at 40°, 0.309 at 50° and 0.312 at 60°. Values of n_c for dodecylamine acetate are 0.410 at 20°, 0.459 at 40° and 0.434 at 60°. It will be noted that in both cases n_c reaches a maximum at approximately 40°. Determinations of the transference numbers over the entire range of concentration for the salts reported in this paper are now in progress.

Summary

1. Conductivities and densities of aqueous solutions of dodecyl- and octadecylamine acetates and the corresponding hydrochlorides have been determined.

2. The conductivity curves show three ranges characteristic of colloidal electrolytes.

3. These salts appear as simple strong electrolytes in dilute solution as shown by the fact that in several cases the actual slopes are found to be almost exactly the values calculated from the Onsager equation.

4. Values for Λ_0, l_c and n_c at infinite dilution have been calculated from the data obtained.

A Nephelometric Method for Determination of Solubilities of Extremely Low Order

BY W. W. DAVIS AND T. V. PARKE, JR.

In an investigation[1] of the reactions of carcinogenic and related polycyclic hydrocarbons, the need arose, for reasons set forth in detail in the following paper, to determine the solubilities of these substances in water, in aqueous media containing various solubilizing agents, and in natural biological fluids. The development of a method for this purpose was governed by two principal considerations. First, the method must be extremely sensitive, capable of measuring solubilities down to less than 1 microgram of solute per liter of solvent (i. e., 0.001 part per million). Secondly, it must be sufficiently general in principle to be applicable to a variety of complex solvents.

On the basis of preliminary experiments with various potential methods for measuring the amount of a given hydrocarbon held in solution, ultraviolet absorption spectrometry was rejected because of insufficient sensitivity and the possibility of interference by components of the solvent media, such as proteins. The fluorometric method, though applicable in a few cases, was found to be unsuitable as a general method because of insufficient sensitivity, and because of the possibility of errors due to quenching of hydrocarbon fluorescence by the solvent. The possibility of estimating the amount of hydrocarbon

(1) W. W. Davis, M. E. Krahl and G. H. A. Clowes, THIS JOURNAL, 62. 3080 (1940).