[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Hexanolamine Caprylate and Diisopropylamine Caprylate as Colloidal Electrolytes

BY EMANUEL GONICK

The problem of colloidal electrolytes can best be approached by combining several types of physico-chemical measurements. In the following paper, this has been done for a single compound—hexanolamine caprylate—over a wide range of concentrations.

In hexanolamine caprylate the small, spherical, monatomic cation of the alkali soaps hitherto investigated has been replaced by a complex alkyl ammonium ion[1] comparable in size to the *n*-octoate anion, but of sufficiently low molecular weight to be itself non-associating in aqueous solution.[2] Freezing point and conductivity data are presented here showing that in aqueous solution this compound is a colloidal electrolyte. In addition, some comparative data on the similarly constituted diisopropylamine caprylate are included.

The micelles formed in soap solutions, while owing their existence primarily to the fatty acid anion, are known to include as well the ordinarily non-associating ions of opposite charge and to be in thermodynamic equilibrium with them. The fact that hexanolamine caprylate is the salt of a soluble weak base (hexanolamine) suggests a simple method of evaluating the concentration of free cation by measuring the hydroxyl-ion concentration of solutions containing a known excess of hexanolamine and applying the mass law equation. Results of such determinations over a wide range of concentrations are reported here.

A third point of interest involves the relation of hexanolamine caprylate and diisopropylamine caprylate to A. P. Brady's generalized curves for the osmotic behavior of colloidal electrolytes.[3] Brady found that if the osmotic coefficient is plotted against the logarithm of the molality, the resulting curves for all colloidal electrolytes of the same type are parallel *between the critical concentration and that at which the transition to colloid may be considered complete* and may be superimposed by shifting them horizontally by an appropriate amount. Thus, three generalized curves are obtained: one each for straight chain, branched chain, and polycyclic compounds. In all the compounds covered by Brady's generalization one of the ions is monatomic (Na^+, K^+ or Cl^-), the differences in the slopes of the osmotic coefficient–log molality curve thus depending solely on the structure of the colloidogenic ion. The two compounds examined here afford an opportunity to ascertain whether the nature of the non-colloidogenic ion has any influence in this respect, since here we have a straight chain anion and a branched chain cation.

Finally, by correlating the various lines of evidence for hexanolamine caprylate, an attempt has been made to determine the mechanism of micelle formation as the concentration of soap is increased.

Experimental

The hexanolamine caprylate was made by mixing equivalent amounts of Eastman Kodak Co. white label caprylic acid (m. p. 15–16°) and redistilled hexanolamine[4] (b. p. 60.2 at 6 mm.; equiv. wt. 117.3). The resulting solid was twice recrystallized from dry acetone. The salt comes down in white flakes melting at 82–83°. If an acetone solution is allowed to evaporate, long bundles of needle-like crystals are formed. The equivalent weight of the salt was found to be 261.5 (theoretical 261.5) by titrating in carbon tetrachloride solution with aqueous hydrochloric acid to methyl orange end-point. The diisopropylamine caprylate was made in the same way, using Eastman Kodak Co. diisopropylamine, but was not recrystallized. This compound is a white solid melting at approximately 30°. All solutions were made up gravimetrically with conductivity water (specific conductivity about 0.8×10^{-6}).

Freezing point depressions were determined by a modified Beckmann apparatus. The results are expressed in terms of Bjerrum's osmotic coefficient, g, which is essentially the ratio of the observed to the theoretical freezing point depression:

$$g = \theta/2 \times 1.858m \qquad (1)$$

where θ is the observed lowering and m is the concentration in moles per 1000 g. of water. The use of the above approximate formula for the comparatively high concentrations reported here gives somewhat low values of g, but this error is offset by the characteristically high values of θ obtained by the Beckmann method. In any case the qualitative picture is unaffected.

Conductivities were measured at 25 ± 0.005° using a Jones bridge and a Leeds and Northrup vacuum tube sine wave oscillator. Before each determination the conductivity cell was flushed several times with conductivity water and then with the solution to be measured. Each measurement was repeated, and there was agreement to at least four figures in every case.

A Beckman glass electrode *p*H meter was used to determine the *p*H of solutions. The instrument was standardized with *p*H 7 buffer before each measurement, and the electrodes were thoroughly rinsed and wiped with cellulose tissue each time the solution was changed. The temperature was 23–25°. As a check, the *p*H of a solution of hexanolamine caprylate containing an excess of hexanolamine was also measured with the hydrogen electrode, the results obtained by the two methods being identical.

Relative viscosities were measured with an Ostwald capillary viscometer.

Results

The osmotic coefficients, g, and equivalent conductivities, Λ, of solutions of hexanolamine caprylate are summarized in Table I. Relative

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[1] The formula of the hexanolamine was $CH_3—CHOH—CH_2—C(CH_3)_2—NH_2$.

[2] The freezing point depression of $1.025N_w$ hexanolamine hydrochloride was found to be 3.873° (theoretical 3.809°); that of $1.902N_w$ hexanolamine was 3.673° (theoretical 3.625°). Therefore, neither the free amine nor the ion shows any tendency to form colloid over the range of concentrations concerned.

[3] McBain and Brady, THIS JOURNAL, **65**, 2072 (1943).

[4] Kindly supplied by the Shell Development Co., Emeryville, California.

viscosities, η, are given in Table II, the values listed in Table I being graphically interpolated. In contrast to other soaps, the conductivity was found to be markedly affected by the viscosity of the solution. At the higher concentrations, even the specific conductivity diminishes with concentration. Therefore, in an attempt to place these data on a comparable basis with those of other soaps, the experimental values have been multiplied by the $^2/_3$ power of the viscosity, the corrected values being tabulated under the heading "$\Lambda_{\text{corr.}}$" The values of the "Arrhenius" coefficient, $\alpha = \Lambda/\Lambda_0$ are based on the corrected conductivities.

TABLE I

THE RELATIVE VISCOSITY, η, EQUIVALENT CONDUCTIVITY AT 25° AND OSMOTIC COEFFICIENT OF AQUEOUS SOLUTIONS OF HEXANOLAMINE CAPRYLATE

N_w	N_v	η^a	$\Lambda_{\text{obs.}}$	$\Lambda_{\text{corr.}} = \Lambda_{\text{obs.}} \times \eta^{2/3}$	α	g
0.005352	0.005335	1.01	48.87	49.2	0.91	..
.1567	.01555	1.02	45.78	46.4	.86	..
.03545	.03504	1.04	42.47	43.6	.81	0.99
.06480	.06406	1.07	39.06	40.9	.76	.96
.1160	.1123	1.13	35.05	37.9	.70	.96
.2656	.2472	1.31	26.44	31.7	.59	.93
.4254	.3817	1.58	19.98	27.1	.50	.82
.5440	.4749	1.82	17.26	25.7	.48	.69
.6859	.5796	2.17	15.05	25.2	.47	.59
.8846	.7162	2.74	12.82	25.1	.46	.48
1.409	1.024	5.05	9.412	27.7	.51	.38
1.842	1.245	7.20	7.621	28.4	.53	.36
2.703	1.568	12.59	5.288	28.6	.53	.36

[a] Interpolated values from experimental curve.

TABLE II

RELATIVE VISCOSITIES OF SOLUTIONS OF HEXANOLAMINE CAPRYLATE

N_w	η	N_w	η
0.07311	1.079	0.7602	2.370
.1244	1.146	.9867	3.074
.1792	1.216	1.297	4.519
.2322	1.275	1.543	5.727
.3164	1.401	2.017	8.668
.4284	1.591	2.545	12.52
.5660	1.875	2.703	12.59

The limiting conductivity, Λ_0, of hexanolamine caprylate was found to be 54.08 mhos by means of Shedlovsky's[5] empirical equation

$$(\Lambda + \beta\sqrt{C})/(1 - \alpha\sqrt{C}) = \Lambda_0 + BC \qquad (2)$$

in which α and β are the constants 0.2274 and 59.79, respectively, of the Onsager equation for 1–1 electrolytes at 25° and B is an empirical constant. When the left-hand term is plotted against the concentration, this equation is linear with slope B and intercept Λ_0. Shedlovsky has shown that it is applicable to strong, non-associating, 1–1 electrolytes up to 0.1 N. It fitted the data for hexanolamine caprylate, using corrected conductivities, at the three lowest concentrations: 0.005336, 0.01556 and 0.03503 N_v. This compound can therefore be regarded as non-associated up to 0.03503 N_v.

Tables III and IV summarize the data for diisopropylamine caprylate.

TABLE III

THE OSMOTIC COEFFICIENTS, g, OF AQUEOUS SOLUTIONS OF DIISOPROPYLAMINE CAPRYLATE

N_w	N_v	g
0.5282	0.4587	0.89
.6602	.5621	.75
.8295	.7227	.62
1.149	.8330	.54
1.511	1.083	.50
2.171	1.385	.50

TABLE IV

EQUIVALENT CONDUCTIVITIES AND RELATIVE VISCOSITIES OF DIISOPROPYLAMINE CAPRYLATE

N_w	N_v	η	$\Lambda_{\text{obs.}}$	$\Lambda_{\text{cor.}}$	$\alpha_{\text{cor.}}$
0.5427	0.4744	1.838	19.80	29.7	0.550
.674	.5727	2.174	17.61	29.5	.546
.8309	.6818	2.650	15.68	29.6	.547
.8925	.7227	2.762	...	..	...
1.019	.8038	3.347	13.92	34.5	.639
1.149	.8330	3.775	...	..	...
1.351	.9966	...	11.62	..	...
2.171	1.385	...	7.955	..	...

The concentration of free cation in solutions of hexanolamine caprylate are given in the last column of Table V, expressed as the ratio of free cation to total soap, C_+/C. The cationic concentrations were obtained from the hydroxyl ion concentration of solutions, to which a quantity of free amine approximately equal to the soap concentration was added, by applying the mass law expression

$$(\text{RNH}_3^+) = K_b \frac{(\text{RNH}_3\text{OH})}{(\text{OH}^-)} \qquad (3)$$

where $K_b = 3.16 \times 10^{-4}$. In a solution of hexanolamine caprylate, the principal equilibrium is that between the simple ions, micelles, and other association products, which may be present, such as neutral ion pairs

$$x\text{RNH}_3^+ + y\text{Cap}^- \rightleftharpoons \text{micelles} + \cdots \qquad (\text{I})$$

Secondary equilibria involve the hydrolysis of the free ions, the solution being somewhat alkaline (pH = *ca.* 8.4), as the dissociation constant for caprylic acid is smaller than that of hexanolamine. If now a quantity of free hexanolamine be added to the solution, a new equilibrium between the amine, the free base, and hydroxyl ion will be set up. The presence of RNH_3^+ from equation (I) represses the dissociation of the amine, so that the increase in cationic concentration is slight and the equilibrium between cation and colloid is but slightly disturbed. In solving equation (3), the concentration of amine (RNH_3OH) may be taken as equal to that of the amine added less the hy-

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(5) Shedlovsky, THIS JOURNAL, 54, 1405 (1932).

droxyl ion concentration. Experiments show that the amine is not appreciably sorbed by the colloid. The concentration of cation calculated by equation (3) should be to a first approximation that existing in a solution of the caprylate alone. As a further approximation, the calculated concentrations have been reduced by an amount equal to the hydroxyl ion concentration. It should be noted that activity coefficients were assumed to be unity, and the results approximate more nearly activities, true concentrations probably being somewhat higher.

The value of K_b in equation (2) represents the average of three values calculated from conductivity data for hexanolamine solutions at concentrations of 0.002626, 0.001392 and 0.0008094 N, by means of the equation of Ives and Sames[6]:

$$K_b = (2C \times 10^{-2A\sqrt{C_i}})/(\Lambda_0 - a\sqrt{C_i})(\Lambda_0 - a\sqrt{C_i} - \Lambda)$$

in which C_i is the concentration of either ion, C is the concentration of the solution, $A = 0.5065$ and $a = 59.79 + 0.2274\ \Lambda_0$. The value of Λ_0 (= 229.5) was obtained by adding the mobility of OH^- (= 198) to that of the hexanolammonium ion (= 31.5). The latter value was obtained by extrapolation to zero concentration of the conductivities of dilute solutions of hexanolamine hydrochloride containing a slight excess of free amine.[7]

An independent determination of K_b based on the pH of a half neutralized solution of the amine likewise yielded the value 3.16×10^{-4}.

Discussion

The osmotic coefficients of hexanolamine caprylate and diisopropylamine caprylate together with the α and C_+/C values for hexanolamine caprylate have all been brought together in Fig. 1 to facilitate comparison. The g curve for potassium chloride is also included for comparison. The equivalent conductivities, both observed and corrected, are shown in Fig. 2. The g-curves are seen to be typical for colloidal electrolytes, that for the hexanolamine salt paralleling the potassium chloride curve at low concentrations, then falling off abruptly with increasing concentration as transition from ordinary electrolyte to colloid becomes prominent, and finally leveling off.

The conductivity curve for hexanolamine caprylate follows the Onsager slope at very low concentrations. At somewhat higher concentrations the conductivity departs upward from the Onsager slope, but the values fall *below* those which would be expected from Shedlovsky's equation for non-associated electrolytes. The usual sharp drop at the "critical concentration" is marked here by a barely perceptible change in slope. The corrected conductivity curves pass through the characteristic minimum, though the uncorrected curves continue to fall indefinitely owing to viscosity effects.

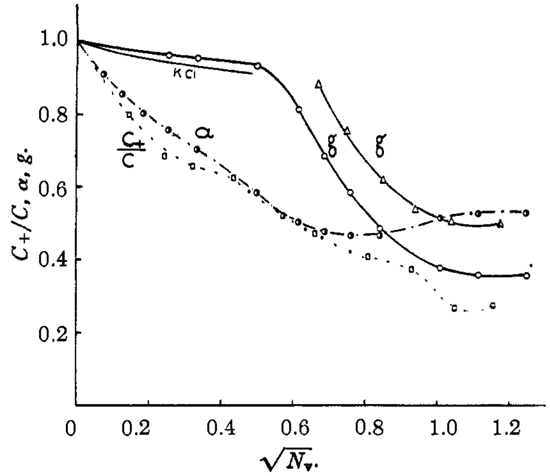

Fig. 1.—The osmotic coefficient (g), the "Arrhenius" conductivity rates (α), and the ratio of cationic concentration to total concentration (C_+/C) of solutions of hexanolamine oleate; and the osmotic coefficient of solutions of diisopropylamine caprylate, all plotted against the square root of volume normality, N_v. Δ refers to diisopropylamine caprylate; all other points refer to hexanolamine caprylate. The g-curve for potassium chloride is given for reference.

The most striking feature of Fig. 1 is the close agreement of the C_+/C curve for hexanolamine caprylate with the α-curve and its complete nonconformity with the g-curve, although at the highest concentration it appears to be tending toward the latter.

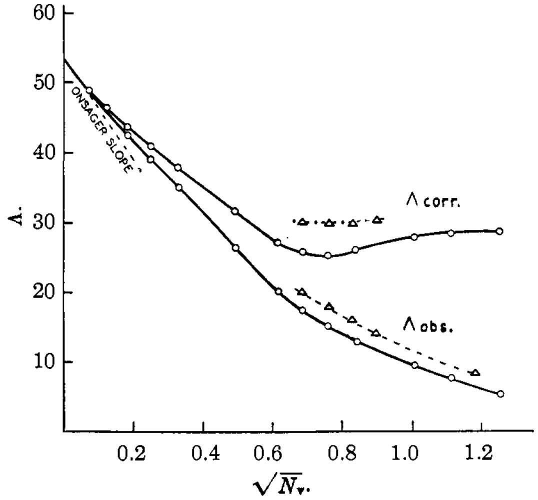

Fig. 2.—The equivalent conductivity, Λ, of solutions of hexanolamine caprylate and of diisopropylamine caprylate plotted against the square root of volume normality, N_v: ○, hexanolamine caprylate; Δ, diisopropylamine caprylate.

In Table V values of the osmotic coefficient, g, have been calculated from the data in the last column on the basis of three different assump-

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[6] Ives and Sames, *J. Chem. Soc.*, 511 (1943).

[7] In a forthcoming paper, a method of calculating ionic conductances where experimental data are lacking is developed. The calculated value for the hexanolammonium ion agrees closely with the experimental value.

TABLE V

FREE HEXANOLAMMONIUM ION CONCENTRATIONS IN SOLUTIONS OF HEXANOLAMINE CAPRYLATE, AND VALUES OF THE OSMOTIC COEFFICIENT CALCULATED THEREFROM COMPARED WITH THE OBSERVED OSMOTIC COEFFICIENT, g, AND THE CONDUCTIVITY RATIO, α

N_w	N_v	pH	$g_{calc.}$[a]	$g_{calc.}$[b]	$g_{obs.}$[d]	α	C_+/C[c]
0.03072	0.03033	10.62	0.90	0.40	0.98	0.84	0.81
.06296	.06131	10.69	.84	.34	.96	.78	.69
.1140	.1088	10.70	.84	.34	.96	.71	.67
.2067	.1908	10.73	.81	.31	.95	.63	.63
.3746	.3260	10.81	.76	.26	.92	.54	.52
.5344	.4412	10.85	.74	.24	.73	.49	.48
.8846	.6560	10.90	.70	.20	.52	.48	.41
1.138	.8685	10.91	.68	.18	.42	.49	.37
1.546	1.099	11.07	.63	.13	.37	.53	.26
2.035	1.335	11.06	.63	.13	.35	.55	.27

[a] Here g is calculated as if for a half strong electrolyte, $g_{calc.} = 0.5(1 + C_+/C)$. [b] If there were only RNH_3^+ ions and negatively charged colloid $g_{calc.} = 0.5\ C_+/C$. [c] If there were only RNH_3^+ and Cap^- ions and neutral colloid formed by association of neutral ion pairs, $g_{calc.} = C_+/C$ as in the last column. [d] Interpolated from the data of Table I for solutions of the caprylate alone.

tions: (a) that hexanolamine caprylate is an ordinary half strong electrolyte associating only into ion pairs, *i. e.*, $g = 0.5\ (1 + C_+/C)$; (b) that the solution contains only RNH_3^+ ions and negatively charged colloid, the contribution of the latter to g being negligible, *i. e.*, $g = 0.5\ C_+/C$; and (c) that the solution contains only RNH_3^+ and Cap^- ions in approximately equal numbers and neutral colloid, *i. e.*, $g = C_+/C$. The values listed under "$g_{obs.}$" and α were obtained by graphical interpolation of the values listed in Table I. None of the calculated values agrees with the observed g values, but those based on assumption (a) agree best up to 0.4412 N_v, while above this concentration better agreement is shown by the values based on assumption (c).

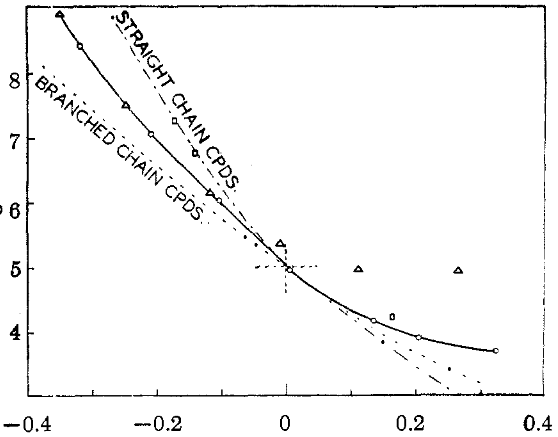

Fig. 3.—The osmotic behavior of solutions of hexanolamine caprylate and of diisopropylamine caprylate in relation to A. P. Brady's generalized curves for straight and branched chain colloidal electrolytes; ○, hexanolamine caprylate; △, diisopropylamine caprylate; □, potassium caprylate.

The conclusion therefore appears justified that a primary association into ion pairs occurs, followed by a secondary association into colloid. That the colloid cannot be entirely neutral is shown by the rise in conductivity at high concentration. In considering the discrepancy between the calculated and observed g values it should be borne in mind that the values of C_+ on which the calculations are based are approximately activities rather than true concentrations and therefore give low values of $g_{calc.}$.

Fig. 3 shows Brady's generalized curves for straight chain and branched chain colloidal electrolytes and the experimental curves for hexanolamine caprylate and diisopropylamine caprylate. The curves for these two compounds are seen to coincide and to fall midway between the other two curves over the range of concentration for which Brady's curves are applicable, *i. e.*, from the critical concentration to that at which the transition to colloid may be considered complete. Brady's practice of shifting the plots by an amount equal to log $m_{g\,=\,0.5}$ in order to make them coincide has been followed here with hexanolamine caprylate. In the case of diisopropylamine caprylate, however, $m_{g\,=\,0.5}$ falls outside the range of applicability. A shift of log 1.170 along the abscissa brought the curve for this compound into coincidence. The value 1.170 may be considered as the molality at which g would have been 0.5, if the transition to colloid had not been virtually completed before g fell to this value.

Points for potassium caprylate have been included for comparison. As is seen, these fall on the straight chain curve, as expected.

A comparison of the g curves in Fig. 1 discloses that hexanolamine caprylate begins to form an appreciable amount of colloid at lower concentrations and becomes more completely colloidal with rising concentration than does diisopropylamine caprylate. This difference in nature may be provisionally ascribed to the lesser degree of branching of hexanolamine, together with the presence of the hydroxyl group with its possible

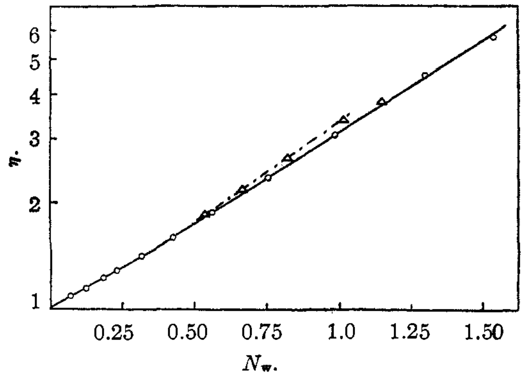

Fig. 4.—Plot of the logarithm of relative viscosity (η) *versus* weight normality, N_w: ○, hexanolamine caprylate; △, diisopropylamine caprylate.

hydrogen bonding, both of which would facilitate packing in the micelle.

The relative viscosities, η, of the solutions of the two compounds discussed here are represented in Fig. 4. Log η is seen to be linear with weight normality, N_w, over most of the range with a sharp change of slope occurring at approximately 0.35 N_w in the case of hexanolamine caprylate. At higher concentrations not shown in the graph, the viscosity falls below the extrapolated curve.

Acknowledgment.—The author wishes to thank Professor J. W. McBain for his interest in this work.

Summary

1. The osmotic behavior, conductivity and relative viscosity of solutions of hexanolamine caprylate and diisopropylamine caprylate have been investigated. The concentration of free cation in solutions of hexanolamine caprylate have also been determined. The results are correlated and discussed.

2. From a comparison of the ratio of free cation to total concentration with the osmotic coefficients and a modified "Arrhenius" conductivity ratio, it is concluded that hexanolamine caprylate associates first to neutral ion pairs followed by secondary association to colloid.

3. The presence of a branched chain cation combined with a straight chain colloidogenic anion causes the osmotic behavior to fall midway between Brady's generalized curves for straight and branched chain compounds, although the cation is of itself non-associating.

4. The logarithms of the relative viscosities of solutions of hexanolamine caprylate and diisopropylamine caprylate are linear with weight normality, and in the case of the former compound exhibit a change of slope at approximately the "critical concentration."

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[CONTRIBUTION FROM BAKER LABORATORY, CORNELL UNIVERSITY]

The Fractionation of Proteins by Electrophoresis-Convection

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Introduction

A new method for the fractionation of proteins in solution was suggested several years ago.[1a] The method depends upon the superposition of differential horizontal transport of the components by electrophoresis upon vertical convective transport of the solution as a whole in a narrow channel connecting two storage reservoirs. The theory of the method was developed under the assumption that the vertical convective transport could be controlled by a horizontal temperature gradient maintained between the channel walls. However, preliminary experiments demonstrated that with solutions not inconveniently dilute, the convection was controlled by horizontal density gradients produced by the electrophoretic transport of the proteins across the channel. This effect dominates that of temperature gradients of convenient magnitude and produces a much greater transport and separation than had been expected. However, when complicated by the effect of electrophoretic transport on density, the differential equations describing the process become rather unmanageable. It therefore seemed most expedient to us to carry out an exploratory experimental investigation to determine in a systematic manner the influence of the various factors affecting transport upon the degree of separation in representative protein mixtures.

The fractionation unit consists schematically of a narrow vertical channel connecting upper and lower reservoirs. In batch operation, the reservoirs and channel are filled with the protein mixture in solution, and a horizontal electric field is applied across the channel walls. Differential transport of all proteins from the top to the bottom reservoir takes place, resulting in a separation. At the end of the operation, the solutions in the two reservoirs are removed and collected for a further stage of fractionation. For a unit of specified geometry, the significant variables affecting transport and separation are (1) dimensions; length, width and wall separation of the channel; (2) temperature and the initial composition of the protein solution; (3) electrophoretic mobilities of the components, determined principally by *p*H; (4) strength of the applied electric field; (5) duration of the operation. The influence of these variables on the transport of several proteins in an experimental fractionation unit and upon the fractionation of representative mixtures of these proteins has been investigated and is the subject of this report.

The results of the exploratory investigation suggest that the method may be of practical value in protein fractionation. It permits operation on a larger scale than in the Tiselius electrophoresis apparatus, and promises to have advantages over solubility methods of fractionation in certain cases.

Experimental

The apparatus used in this investigation is shown in Fig. 1. The channel for the protein solution was formed

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[1] Present address: Research Laboratory, Monsanto Chemical Company, Springfield, Massachusetts.

[1a] I. G. Kirkwood, *J. Chem. Phys.*, **9**, 878 (1941).