In Table II the densities of the gallium alums calculated from the X-ray data, together with previously reported density data, are tabulated.

It is interesting to compare the structure types and lattice constants of the alums with those of the aluminum and chrome alums.[17] The ammonium and potassium alums of each have the α structure, while the three cesium alums have the β structure. With rubidium the univalent ion, substitution of Cr^{+3} for Al^{+3} results in a change from α to β structure, but with Ga^{+3} the structure is again α. Among the thallous alums all are β except the aluminum alum. On the basis of size alone Ga^{+3} and Cr^{+3} would be expected to act alike in replacing Al^{+3} since they are almost identical in size. Pauling[18] reports for the radii of Ga^{+3}, Cr^{+3} and Al^{+3}, values of 0.62, 0.64 and 0.50 Å., respectively. It is thus evident that the factors determining structure type are rather complex, and sufficient data are not yet available for their description and identification.

The increase in the lattice constant, Δa_0, on substituting Ga^{+3} for Al^{+3} is as follows for the various alums: $NH_4 = 0.029$, $K = 0.065$, $Rb = 0.025$, $Cs = 0.047$, and $Tl = 0.026$ kX. U. Thus Δa_0 for the gallium alums is less constant than for the chrome alums,[17] but its average value is exactly the same, 0.038 kX. U. The variations from the average in both series of alums are without doubt real, since they are much larger than the estimated error ±0.001 kX. U. in determining a_0, and indicate the complexity of the forces involved as compared with the simple ionic lattices where distances are additive and substitution of a larger cation will bring about a corresponding increase in lattice constants.

Summary

1. Lattice constants for a series of gallium alums have been determined at 25 ± 0.1°.

2. The densities of these alums at 25° have been calculated from the X-ray data.

3. The probable structure types of the alums have been determined. All of the gallium alums investigated have the α structure except those of cesium and thallium which possess the β structure.

Minneapolis, Minnesota Received July 26, 1943

[17] Klug, This Journal, **62**, 2992 (1940).

[18] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1st ed., 1939, pp. 326, 330.

[Contribution from the Department of Chemistry of Stanford University]

The Osmotic Activity of Colloidal Electrolytes

By J. W. McBain and A. P. Brady

Introduction

In moderately concentrated solutions of colloidal electrolytes, the lowering of freezing point or of vapor pressure is perhaps a fifth of that expected for an electrolyte, whereas the conductivity may be halved. The existence of colloidal aggregates is necessitated by the low osmotic activity, although the conductivity is at least twice that expected for the osmotically active ion. In 1920, McBain and Salmon[1] interpreted the data then available in terms of the highly conducting ionic micelle and the far less highly charged and conducting lamellar aggregate, unfortunately termed the "neutral micelle." According to the measurements of M. E. Laing McBain,[2] the latter conducts only about seven per cent. as well as an equivalent amount of fully dissociated ions. Its existence and structure have been confirmed by X-ray examination of the solutions of soaps and other detergents.[3-6] The high conductivity of the solution and the comparatively low migration number necessitated the introduction of two types of micelle, the poorly conducting lamellar micelles and the highly conducting small or ionic micelles.

Prior to 1939, only conductivity had been measured in the very dilute solutions where the transition from an ordinary uni-univalent electrolyte to a colloidal electrolyte occurs. The dew-point lowering method employed so successfully by McBain and Salmon at higher concentrations is entirely too inaccurate; even ordinary freezing point technique is not suitable. Recently, however, McBain and Johnston[7] and McBain and Bolduan[8] have studied freezing points in a precise apparatus modelled after that of Scatchard,[9] with which solutions as dilute as 0.001 *m* may be measured with acceptable accuracy. The purpose of the present paper is to supplement these freezing point data, and to collect and to correlate the now fairly extensive experimental material on this subject.

Experimental Method

The Scatchard apparatus was used and calibrated with the standard values given by Scat-

[1] J. W. McBain and C. S. Salmon, This Journal, **42**, 426 (1920).

[2] M. E. Laing, *J. Phys. Chem.*, **28**, 673 (1924); M. E. Laing McBain, *Trans. Faraday Soc.*, **31**, 153 (1935); *J. Phys. Chem.*, **47**, (1943).

[3] Hess and Gundermann, *Ber.*, **70B**, 1800 (1937).

[4] Hess, Philippoff and Kiessig, *Kolloid Z.*, **88**, 40 (1939).

[5] Stauff, *ibid.*, **89**, 224 (1939); **96**, 244 (1941); *Naturwissenschaften*, **27**, 213 (1939).

[6] Kiessig and Philippoff, *ibid.*, **27**, 593 (1939).

[7] McBain and Johnston, *Proc. Roy. Soc.* (London), **181A**, 119 (1942).

[8] McBain and Bolduan, *J. Phys. Chem.*, **47**, 94 (1943).

[9] Scatchard, Jones and Prentiss, This Journal, **54**, 2676 (1932).

chard and Prentiss[10] for potassium chloride with results in agreement with those of previous communications.[7,8] The concentration of solutions of colloidal electrolytes was determined by means of a Zeiss interferometer by comparison with standard known solutions of similar concentration, using a four-centimeter cell.

Our results for potassium oleate and potassium laurate were included in previous communications.[7,8] The results are conveniently expressed in terms of Bjerrum's osmotic coefficient, g, which compares the observed freezing point lowering directly with that expected for a fully dissociated ideal uni-univalent electrolyte[11]

$$g = \Theta/(2 \times 1.858m) = 1 - j = i/2$$

where Θ is the observed freezing point lowering, m is the molality, j is the Lewis and Randall function, and i the van't Hoff coefficient. The solute activity, γ, may be derived from the expression

$$-\ln \gamma = (1 - g) + \int_0^m (1 - g)\mathrm{d}\, m/m$$

Experimental Data

N-(Lauryl-colamino-formyl-methyl)-pyridinium Chloride ($C_{12}H_{23}O_2CH_2CH_2NHCOCH_2N$-$(C_5H_5)Cl$) (Commercially known as Catol 607).—Although many cation active soaps are now available, the only published freezing point data are those represented by graphs of Beckmann results on the salts of dodecylamine,[12,13] all of those tested falling on the same curve. We have, therefore, measured a specially purified sample of N-(lauryl-colamino-formyl-methyl)-pyridinium chloride kindly supplied by the Emulsol Corporation. Results are collected in Table I and are shown in Fig. 1. It is seen that the behavior is typically that for a colloidal electrolyte of high molecular weight, with at first a gradual and then a highly pronounced departure from the behavior of an ordinary electrolyte, in that the g value falls to one-sixth of its original value when the molality is still less than 0.1 mole per 1000 g. of water.

TABLE I

FREEZING POINT LOWERING, Θ, AND OSMOTIC COEFFICIENT, g, OF THE CATIONIC ACTIVE DETERGENT, CATOL 607

m	Θ	g	γ
0.001028	0.00370	0.97	0.96
.003235	.01008	.908	.847
.004835	.01513	.843	.737
.00708	.01600	.609	.527
.00956	.01922	.540	.413
.01320	.02060	.420	.310
.01680	.02066	.331	.235
.02521	.02514	.268	.181
.03654	.02943	.217	.126
.0480	.03385	.202	.0993
.0659	.0458	.187	.0738
.0862	.0564	.176	.0598

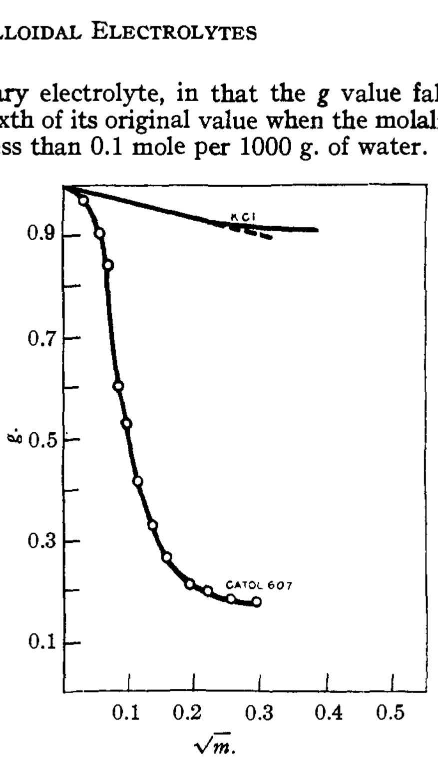

Fig. 1.—Osmotic coefficients of solutions of catol No. 607 compared with those of potassium chloride. The dotted line is the Debye–Hückel slope.

Figure 1 illustrates the usual observation that the osmotic coefficient of a colloidal electrolyte in very dilute solution commonly lies below the Debye–Hückel slope and increasingly departs from it with increasing concentration. In contrast, the conductivity curve of most colloidal electrolytes in great dilution lies above the Debye–Hückel–Onsager slope and then crosses it somewhat abruptly to fall to low values. This may be interpreted in agreement with the suggestion of various authors[14,15] that in very dilute solution there are present a few small micelles or ionic micelles, of enhanced conductivity as compared with the simple ions. In higher concentrations the lamellar micelles of lower conductivity and low osmotic activity predominate. It has been demonstrated repeatedly[16,17] that solubilization of dyes, which is a test for the presence of colloidal particles, becomes appreciably noticeable below the so-called critical concentration for the initial formation of micelles. Possibly, however, exposure to the dye may help to promote formation of micelles capable of associating with dye.

Ammonium Aerosol OT.—The osmotic coefficients of a number of "Aerosols" have been published previously,[8] and show a great divergence depending upon molecular weight. The Aerosols are salts of sulfosuccinic esters; Aerosol OT the dioctyl (2-ethyl-1-hexanol) ester; MA the di-

---

[10] Scatchard and Prentiss, THIS JOURNAL, **55**, 4355 (1933).

[11] E. A. Guggenheim, "Modern Thermodynamics by the Methods of Willard Gibbs," Methuen and Company, Ltd., London, 1933.

[12] Ralston, Hoerr and Hoffman, THIS JOURNAL, **63**, 2576 (1941).

[13] Hoerr and Ralston, *ibid.*, **64**, 2824 (1942).

[14] McBain, Dye and Johnston, THIS JOURNAL, **61**, 3210 (1939).

[15] Hoerr and Ralston, *ibid.*, **65**, 976 (1943).

[16] McBain, Merrill and Vinograd, *ibid.*, **63**, 670 (1941).

[17] McBain and Merrill, *Ind. Eng. Chem.*, **34**, 915 (1942).

hexyl (methyl amyl) ester; AY the diamyl (mixture of 2-methyl-1-butanol and 3-methyl-1-butanol) ester; and IB the diisobutyl ester. When the metallic ion is not specified the sodium salt is understood. Sodium Aerosol OT is fully colloidal in very dilute solution, with a critical concentration for the initial formation of micelles at about $m = 0.004$. The following approximate data show that this is likewise true for the ammonium salt of the di-octyl ester of sulfosuccinic acid.

m	0.0042	0.0057	0.0081	0.0113	0.0137	0.0170
Θ	.0150	.0188	.0219	.0263	.0283	.0326
g	.97	.89	.74	.63	.56	.52

Colloidal Electrolytes in Presence of Added Electrolytes.—Previous work on osmotic coefficients of colloidal electrolytes with added electrolytes, by Quick,[18] and by McBain and Searles,[19] was confined to regions of concentration in which micelle formation is already complete. In this case, it was found that the total freezing point depression of the mixture was very slightly greater than that of the sum of the pure constituents taken separately. Although it is known that added salt promotes micelle formation, no data on osmotic effects in the transition region of concentration have been published. Hence two series of experiments were made with (a) potassium laurate and potassium chloride in an equimolar mixture, and (b) potassium laurate plus potassium sulfate in equivalent concentrations, both series being run at varying total molalities.

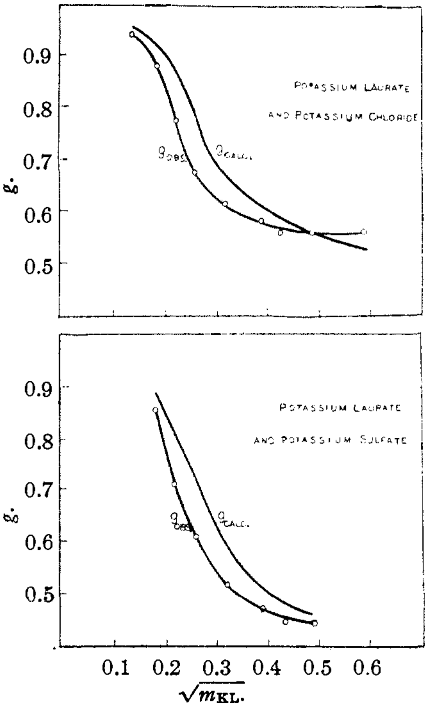

Fig. 2.—Osmotic coefficients, g, for solutions, each containing one equivalent of potassium laurate and one equivalent of potassium chloride or sulfate at a total molality, m, to show that in the dilute range the salts promote the formation of micelles, making the total value of $g_{observed}$ less than the sum of those for the two substances taken separately.

Since the published values for the g *vs.* m curves for potassium sulfate exhibit discrepancies[20,21] of as much as 5%, it was felt advisable first to establish values for potassium sulfate itself with some certainty in the concentration range of interest, in order to interpret the results from mixtures of this salt with potassium laurate. The results of a series of runs with the Scatchard apparatus are given in Table II. The data agree well with those cited by Landolt–Börnstein.[21a]

Table II

Osmotic Coefficients of Potassium Sulfate from Freezing Point Lowering

m	Θ	g
0.0313	0.1369	0.838
.0401	.1921	.825
.0657	.2858	.789
.0907	.392	.781
.112	.481	.759

Table III

Freezing Point Lowering of Mixtures of Potassium Laurate and Potassium Chloride; Mole Ratio 1:1

m_1 (KL)	m_2 (KCl)	g_1	g_2	$\Theta_{calcd.}$	$\Theta_{obs.}$	$g_{calcd.}$	$g_{obs.}$
0.01923	0.02015	0.951	0.960	0.1398	0.1375	0.957	0.945
.03465	.0354	.912	.948	.2320	.2305	.932	.887
.04902	.0500	.795	.939	.320	.286	.869	.778
.0660	.0674	.620	.935	.389	.337	.783	.680
.0990	.1010	.410	.927	.499	.460	.671	.618
.1493	.1522	.292	.917	.682	.654	.608	.584
.1801	.1835	.255	.913	.782	.757	.587	.561
.2372	.2420	.212	.907	1.003	.996	.564	.560
.3426	.3478	.183	.898	1.390	1.444	.543	.563

Table IV

Freezing Point Lowering of Mixtures of Potassium Laurate and Potassium Sulfate; Mole Ratio 2:1

m_1 (KL)	m_2 (K_2SO_4)	g_1	g_2	$\Theta_{calcd.}$	$\Theta_{obs.}$	$g_{calcd.}$	$g_{obs.}$
0.0324	0.0164	0.935	0.876	0.1898	0.1840	0.890	0.863
.0466	.0236	.813	.857	.250	.2185	.817	.713
.0679	.0345	.600	.834	.314	.2685	.715	.612
.1027	.0521	.395	.811	.392	.348	.580	.515
.1510	.0768	.288	.788	.506	.470	.510	.473
.1867	.0949	.246	.777	.582	.544	.482	.443
.2364	.1201	.212	.757	.706	.681	.454	.438

Tables III and IV and Fig. 2 give the results of the experiments with the mixtures. The calculated value of the freezing point lowering, $\Theta_{calcd.}$, as well as the calculated value of the osmotic coefficient, $g_{calcd.}$, are based on the assumption that the colloidal electrolyte and the electrolyte are without influence on each other, the freezing point lowerings being merely additive. Thus $\Theta_{calcd.}$ for a solution of concentration m_1 in potas-

---

[18] Quick, *J. Chem. Soc.*, **127**, 1401 (1925).

[19] McBain and Searles, *J. Phys. Chem.*, **40**, 493 (1936).

[20] Noyes and Falk, This Journal, **32**, 1011 (1910).

[21] Landolt-Börnstein, Ed. V, (a) p. 1448 and Supplement I (b) p. 795.

sium laurate and m_2 in salt is the sum of the freezing point lowerings of the soap and salt in pure water and concentrations m_1 and m_2, respectively. In analogy to two component systems $g_{\text{calcd.}} = \Theta_{\text{calcd.}}/\Theta_{\text{ideal}}$, and $\Theta_{\text{ideal}} = \nu_1\lambda m_1 + \nu_2\lambda m_2$; where ν_1 and ν_2 are the number of ions into which (ideally) the soap and salt, respectively, dissociate, and λ is the ideal molal freezing point lowering (1.858°).

From an inspection of the data it can be seen that the expected promotion of micelle formation by the salt does occur in the transition region, displacing the g *vs.* $\sqrt{m}$ curve to the left; the effect of the added equivalent of the chloride or of the sulfate is nearly identical in this respect. In contrast to the behavior in this concentration range, after the formation of micelles is complete the osmotic activity of the mixture rises above that calculated, an effect in accord with previous experimenters. This enhanced activity must be at least in part due to hydration; some water is immobilized by the micelle and does not act as solvent,[22] hence the effective molality of the added salt is greater than that calculated.

It is not at all necessary to ascribe the results observed with added electrolyte to interionic attraction, because mass action is fully adequate to produce this effect. If it were Debye–Hückel effects, the phenomenon would mean that the added salt is of greatly reduced activity in the dilute region but not in the less dilute range where the conducting micelles are fully formed and are present in much higher absolute concentration. Mass action law, on the other hand, predicts that more micelles must be formed in the dilute region, until that reaction is complete. This is because potassium ions are included in the micelles. Convincing evidence that added salt forms more micelles through common ion effect may be adduced, for example, from the experiments by Hartley,[23] and in this Laboratory,[17] on the solubilizing action of cetyl pyridinium chloride and other colloidal electrolytes on dye in the presence of sodium chloride. Further confirmatory evidence is the similarity of the effect of potassium chloride and sulfate noted above.

A Generalized Curve for each Type of Colloidal Electrolyte.—The chief point of the present paper is that one of us (A. P. B.) has found that all the existing data for osmotic coefficients for colloidal electrolytes whose freezing points have been measured in any laboratory may be represented on a single simple diagram (Fig. 5)—quite contrary to the impression given by the separate individual diagrams.

There is a limit to the steepness with which the osmotic coefficient can fall off with increased concentration, for the reason that in any continuous phase the activity of the solvent must decrease with increased concentration of the solute; hence $d\Theta/dm$ is greater than 0. The limiting case $d\Theta/dm = 0$, the dashed line in Figure 5, would correspond to separation of the solution into two layers. If we define a quantity Y as being equal to $d(gm)/dm = g + dg/d \ln m$, then $Y > 0$. Also $Y = -d \ln a_0/dm = \nu(1 + d \ln a_s/d \ln m)$. Incidentally, the driving force used in the expressions for differential diffusion coefficients suggested by Onsager and Fuoss and by Gordon, is $Y\, dm/dx$ rather than dm/dx.

Suppose that two solutes obey the same dilution law, then for the respective concentrations m and m' at which their osmotic coefficients are equal $g = g'$ and $Y = Y'$, hence $dg/d \ln m = dg'/d \ln m'$. This is mathematically equivalent to the result of the following consideration which suggests a method to determine whether the two series of dissociation and association reactions are strictly analogous but with different values of the equilibrium constants.

Consider reactions of the type $a\text{A} + b\text{B} = \text{A}_a\text{B}_b$ for different substances at molalities m and m' and m'', etc., such that α, the fraction of total A in the complex, has the same value for all. Then g likewise will be the same provided that the equilibrium constants are functionally the same even if in general numerically different, that is, if a and b are the same for all the substances. It then follows that the ratios between m, m' and m'', etc., for equal values of α are not a function of g or of m. Hence if the reactions are directly comparable, curves of g *vs.* log m will be parallel. Then multiplication of all the molalities of each substance by a given constant k for that substance will make all curves coincide. Furthermore, the ratio of the k's to each other is fixed. We therefore define the reciprocal of each k as the concentration at which $g = 0.5$, denoted by $m_{g = 0.5}$. Although all curves must then pass through the point $1 = m/m_{g = 0.5}$ at $g = 0.5$, only those belonging to one type or family can then coincide at any other value of g. The experimental test of this relation is given in Figs. 3 and 4 for all the best data for g for straight chain salts and for branched chain salts, respectively. The inclusion of potassium oleate in the latter class may be ascribed to the kink in the chain due to the double bond.

It is a remarkable fact that all the published data fit upon these curves within the experimental error for values of g between 0.9 and 0.2.

Higher and lower values of g were not included because the interfering Debye–Hückel effects at high values, and hydration effects at low values, are not completely submerged by the mass action effect which is the main feature of the association of colloidal electrolytes.

Figure 5 includes, in addition to the curves from Figs. 3 and 4, the dashed line representing the absolute limit of slope for any solution to remain homogeneous without breaking into separate

---

(22) McBain, Kawakami and Lucas, THIS JOURNAL, **55**, 2762 (1933).

(23) As replotted by McBain from Hartley's data, "Advances in Colloid Science," Interscience publishers, 1942, p. 129.

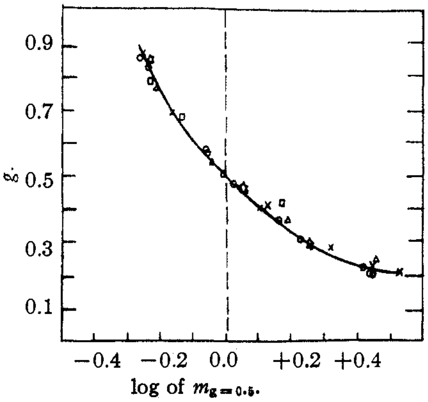

Fig. 3.—Osmotic coefficients of five straight chain colloidal electrolytes brought to coincidence throughout the curve by dividing the concentration for each by $m_{g=0.5}$, the molality at which $g = 0.5$.

Legend	Substance	Ref.	$m_{g=0.5}$
□	Potassium caprylate	8	1.37
△	Potassium caprate	8	0.33
×	Potassium laurate	8	.0735
○	Lauryl sulfonic acid	7	.0206
☆	Dodecylamine acetate	12	.042

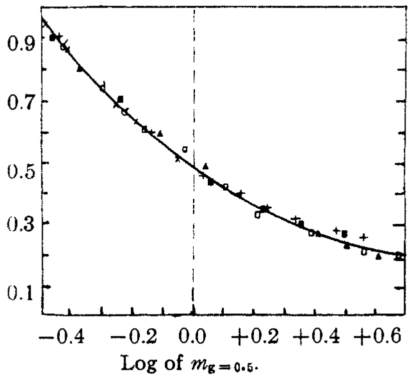

Fig. 4.—Osmotic coefficients of five branched chain colloidal electrolytes brought to coincidence throughout the curve by dividing the concentrations for each by $m_{g=0.5}$, the molality at which $g = 0.5$.

Legend	Substance	Ref.	$m_{g=0.5}$
▲	Potassium oleate	7	0.00281
σ	Aerosol 1B	8	.83
+	Aerosol AY	8	.28
■	Aerosol MA	8	.177
×	Aerosol OT	8	.0118
□	Catol 607	Here	.0102

layers, and also a curve of far less slope for the single example of a colloidal electrolyte with rigid polycyclic structure, the bile salt, sodium desoxycholate.[7]

From inspection of Figs. 3, 4 and 5 it becomes evident that straight chain compounds associate, or pack, with equal readiness, to form the lamellar micelles revealed by X-ray examination of these solutions. Branched chains pack less readily, but the X-ray examination again shows them to form

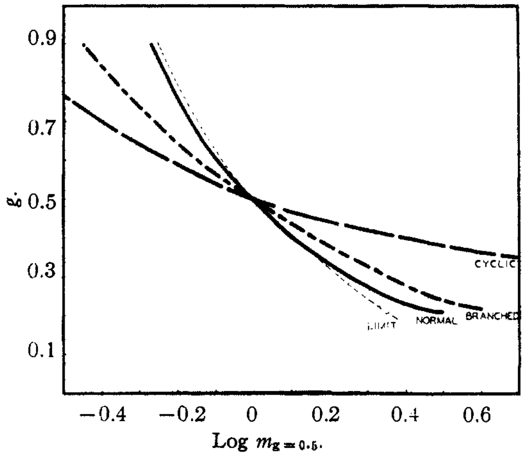

Fig. 5.—Osmotic coefficients of all colloidal electrolytes brought to coincidence on one or other of three curves depending on whether they are straight chain, branched chain or polycyclic, by dividing the concentrations for each by $m_{g=0.5}$, the molality at which $g = 0.5$. The dashed line represents the limiting slope at which the solution would fall into separate layers.

lamellar micelles. The change in packing is apparently quite insensitive to all but the first branching, as is evident by the occurrence of the kinked potassium oleate in the same class as the highly branched Aerosols or Tergitols. Finally, the polycyclic colloidal electrolyte packs least readily and requires the largest range of concentration to be fully associated.

Within each family, the effect of molecular weight and the exact chemical composition is reflected only in the scale of concentration over which the same effects occur. These scales differ for individual members by as much as one hundred fold and yet they all coincide in Fig. 5.

Activity Coefficients of Colloidal Electrolytes from a Single Freezing Point.—The activity coefficient of a straight or branched chain colloidal electrolyte, in the region where the osmotic coefficient lies between 0.2 and 0.9, may be derived from a single freezing point measurement with fair accuracy from Fig. 5 by making use of the fact that the g *vs.* m curves of these compounds rapidly approach that for potassium chloride as the concentration is reduced.[8]

From the value of g determined at a given molality, m, the value of $m_{g=0.5}$ may be readily obtained from Fig. 5. A plot of $(1 - g)/m$ *vs.* m can then be made to pass into the well-known curve for potassium chloride.[10] If we denote by m^* the molality at which this junction of the two curves occurs, and m^{**} the molality at which g should be 0.90, as determined from Fig. 5 and the freezing point determination, we have

$$-\log \gamma = (1 - g)/2.303 + \int_0^{m^*} (1 - g)\,\mathrm{d} \log m + \int_{m^*}^{m^{**}} (1 - g)\,\mathrm{d} \log m + \int_{m^{**}}^{m} (1 - g)\,\mathrm{d} \log m =$$

$$(-\log \gamma^*_{\text{KCl}} - (1 - g^*_{\text{KCl}})/2.303) + ((1 - g)/2.303 + \int_{m^{**}}^{m} (1 - g)\, \text{d} \log m) + \int_{m^*}^{m^{**}} (1 - g)\, \text{d} \log m$$

where γ^*_{KCl} is the activity of potassium chloride and g^*_{KCl} its osmotic coefficient, both at m^*. These values are readily obtained from the literature.[10] The quantity in the second parenthesis is independent of $m_{g\,=\,0.5}$, and is given in Fig. 6 as a function of g. The last integral can be easily estimated with sufficient accuracy from the curve by which m^* was determined.

Summary

1. It is shown that all data for osmotic coefficients of colloidal electrolytes are brought into coincidence on one of three curves, by merely changing the scale of concentration. There is one curve for straight chain compounds, one for branched and one for polycyclic colloidal electrolytes.

2. The osmotic and conductivity data indicate the presence of a small proportion of highly conducting micelles in very dilute solutions, a conclusion which is supported by previously published migration data.

3. The addition of potassium chloride or of potassium sulfate to very dilute solutions of potassium laurate promotes the formation of colloid, so that the result is distinctly less than additive; in higher concentrations, where the colloid is already fully formed, the effect on freezing point lowering is slightly more than additive. There is no marked indication of high ionic strength in solutions of colloidal electrolytes.

4. Owing to the remarkable regularity noted in item 1 of this summary it is possible to obtain the value of the activity coefficient with fair accuracy from a single freezing point determination.

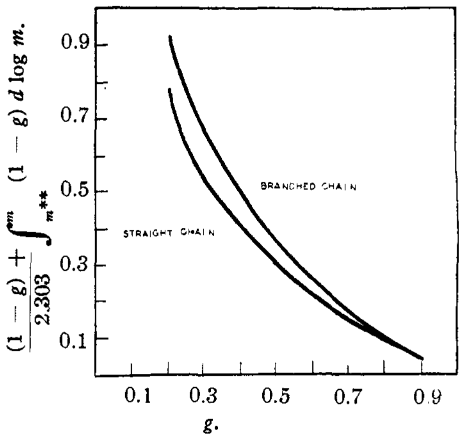

Fig. 6.—Graph for use in calculating activity coefficients of colloidal electrolytes from a single freezing point measurement.

STANFORD UNIVERSITY, CALIF. RECEIVED JUNE 7, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Chemical Studies on Crystalline Barium Acid Heparinate[1]

BY M. L. WOLFROM, D. I. WEISBLAT,[2] J. V. KARABINOS,[3] W. H. MCNEELY[2] AND JAY MCLEAN

McLean,[4] working in Howell's laboratory, isolated a blood anticoagulant from dog liver and beef heart. This substance was further studied by Howell[5] and the name heparin was given to it. Jorpes[6] considers that the active material is a mucoitinsulfuric acid containing much more ester sulfate than the normal type of mucoitinsulfuric acid.

Charles and Scott[7] isolated from beef lung a crystalline barium salt possessing heparin activity and having the following recorded analysis: C, 18; H, 3.9; N, 1.68; S, 9.3; ash, 33.6; Ba, 19.8; amino-N (Van Slyke), 0.4. These analyses were apparently made on material that was not anhydrous.[8] Charles and Scott considered that glycuronic acid was absent in the substance and demonstrated that the biological activity was destroyed by nitrous acid or formaldehyde. A sample of the crystalline barium salt received from Dr. Charles was analyzed by Meyer and Smyth[9] with the following results: N, 2.36; amino sugar, 16.3; uronic acid, 20.1; acetyl, 2.2; sulfur, 9.8; ash, 33.3. Meyer stated that the substance was an acid salt and recorded an equivalent weight of 749. Reinert and Winterstein[10] reported an analysis of a neutral sodium salt regenerated from the crystalline barium salt and stated that this preparation contained 10% (dry basis) acetyl. Charles and Todd[8] considered that the crystalline barium salt prepared from beef liver was identical with that prepared from beef lung. They con-

---

(1) A preliminary notice of this work has appeared in *Science*, **97**, 450 (1943). The original version of this manuscript was received May 12, 1943, and then withdrawn by the authors for certain minor additions and alterations.—*The Editor.*

(2) Hoffmann-La Roche Postdoctoral Fellow of The Ohio State University Research Foundation.

(3) Hoffmann-La Roche Fellow of The Ohio State University Research Foundation.

(4) J. McLean, *Am. J. Physiol.*, **41**, 250 (1916).

(5) W. H. Howell and E. Holt, *ibid.*, **47**, 328 (1918); W. H. Howell, *ibid.*, **63**, 434 (1923); **71**, 553 (1925).

(6a) E. Jorpes, "Heparin," Oxford University Press, London, 1939; (b) E. Jorpes, *Biochem. J.*, 203 (1942).

(7) A. F. Charles and D. A. Scott, *ibid.*, **30**, 1927 (1936).

(8) *Cf.* A. F. Charles and A. R. Todd, *Biochem. J.*, 112 (1940).

(9) K. Meyer and Elizabeth M. Smyth, *Cold Springs Harbor Symposia Quant. Biol.*, **6**, 97 (1938).

(10) M. Reinert and A. Winterstein, *Arch. intern. pharmacodynamie*, **62**, 47 (1939).