can be seen that although the listed analytical boundary results are only accurate to about 2%, they are as accurate as a reasonably careful Hittorf determination (taking the moving boundary values as correct), and certainly far less tedious and analytically exacting. The accuracy could be improved by a careful purification of materials and by more precise analytical procedures, but is shown to be sufficient for the purposes for which the cell was designed. The substances listed in Table I were run, of course, only for test purposes, since the moving boundary method gives more accurate results just as quickly. In a following paper (with D. J. Salley), an application to colloidal electrolytes will be presented. It is also obvious that the method is applicable to the study of proteins, dyes (where colorimetric analysis may readily be used), and complex systems such as solutions of acid polymerized trimethylol melamine.

Table II

Comparison of Analytical Boundary Results with Other Methods

Solution	Concn.	Cation transference no. Analytical boundary	Moving boundary	Hittorf[a]
$AgNO_3$	0.1	0.473	0.468	0.474
	.01	.469	.465	.474
KBr	.1	.481	.485	...
	.01	.471	.483	.496
NaCl	.05	.399	.390	.396
	.02	.396	.389	.396

[a] These values are at 18°; the temperature correction is small but should tend to *raise* them.

Acknowledgment is due to cyclotron groups at the University of California and at Columbia University for radiotracers. In addition the writer wishes to express his gratitude to Drs. J. K. Dixon and D. J. Salley for advice and criticism, and to thank the Directors of this Laboratory for permission to publish these results.

Summary

1. The design and operation of a cell of simple construction for measuring transference numbers, embodying a combination of the Hittorf and moving boundary techniques, is described. Because of the interchange of the usual roles of the leading and indicator solutions as compared to the moving boundary method, the method is suited for electrolytes containing a colloidal ion.

2. Analytical requirements are much less exacting than in the Hittorf method, permitting a wide choice of methods (*e. g.*, radioactivity counts, conductometric titrations, and colorimetry).

3. In complex systems where the moving boundary results would be difficult or impossible to interpret, radiotracer techniques may be readily applied. Because of the reduced analytical requirements ordinary counting methods may be used.

4. Tests of the cell using solutions of simple electrolytes, employing both analytical and radiotracer methods, indicate an accuracy equivalent to that obtained in reasonably careful determinations by the Hittorf method.

Stamford, Conn. Received March 29, 1947

[Contribution from the Stamford Research Laboratories of the American Cyanamid Company]

The Self-diffusion Coefficients and Transference Numbers of the Small Ions in Colloidal Electrolytes

By A. P. Brady[1a] and D. J. Salley

Introduction

The fraction of small ions associated kinetically with the large aggregates in aqueous solutions of colloidal electrolytes is of general interest for the better understanding of these solutions. The "fraction bound" has been estimated for various colloidal systems from measurement of the thermodynamic properties of the solution, as by freezing point depression[1] or dew point lowering,[2] from the conductivity plus the transference number,[3,4] from e. m. f. measurements,[5,6,7] and from membrane equilibrium.[8] In addition specific methods have been used, such as measuring the *p*H of hexanolamine caprylate solutions containing excess hexanolamine,[9] and the increase of conductivity of lauryl sulfonic acid solutions when potassium nitrate is added.[10] Another general method that suggests itself is self-diffusion, but insofar as the authors are aware it has not yet been applied to this problem.

Any value of the fraction bound derived from experimental data must, of necessity, result from a series of assumptions. Because of this, the values obtained from any one of the above methods may be quite uncertain. This paper compares, under consistent assumptions, the fraction bound as obtained by three methods: self-diffusion, conductivity plus transport, and freezing point lowering.

(1a) Present address: Stanford University, Department of Chemistry, Stanford University, California.

(1b) McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1279 (1919).

(2) McBain and Salmon, This Journal, **42**, 426 (1920).

(3) McBain and Thomas, *J. Phys. Chem.*, **40**, 997 (1936).

(4) Hartley, Collie and Samis, *Trans. Faraday Soc.*, **32**, 785 (1936).

(5) Salmon, *J. Chem. Soc.*, **115**, 530 (1920).

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

(7) McBain and Betz, This Journal, **57**, 1909 (1935).

(8) Northrup and Kunitz, *J. Gen. Physiol.*, **11**, 481 (1928).

(9) Gonick, This Journal, **68**, 177 (1946).

(10) Walton, *ibid.*, **68**, 1182 (1946).

The experimental work comprised the determination for two cationic and two anionic agents of the self-diffusion constant and the transference number of the small ion, as well as the solution conductivities. The freezing point data used were taken from the literature.

A feature of the experiments was that radioactive isotopes were employed. In self-diffusion, isotopic tracers are of course required, and they are also of considerable aid in the rapid measurement of transference numbers in complex systems by the "analytical boundary" method described in the foregoing paper.[11] It is worthy of note that the tracer technique obviates errors which may arise if equilibria involving various micelle types are not fast compared to diffusion or electrical transport.

Experimental

Materials

Sodium 2-Ethylhexyl Sulfosuccinate (Aerosol OT).—Commercial "Aerosol OT 100%" (American Cyanamid Company) was used after vacuum drying at 110° for several hours.

Sodium Methyl Amyl Sulfosuccinate (Aerosol MA).—Dried commercial "Aerosol MA 100%" (American Cyanamid Company) was used. At low concentrations faintly hazy solutions were formed presumably because of the presence of a small amount (approximately 1%) of the corresponding maleic ester. Such solutions were cleared by passage through a bacteriological filter, in order to protect the membranes in the diffusion and transport cells. The filtration had no detectable effect upon the conductivity.

N-(Laurylcolaminoformylmethyl)-pyridinium Chloride (E-607).—Material supplied by the Emulsol Corporation was used directly.

Myristamidopropyldimethylbenzylammonium Chloride.—This is hereafter referred to as "Agent M," for purposes of abbreviation. A special preparation made at these Laboratories was employed. The only impurity detected (other than water) was 1.0% of the unbenzylated tertiary amine.

Radiotracers.—The anionic materials were tagged with either Na^{22} or Na^{24}. The former was obtained carrier free as described in the foregoing paper.[11] The latter was usually received as a solution of sodium chloride from Columbia University. In one series of runs, however, Aerosol OT solutions were bombarded directly with neutrons to produce the Na^{24}.

The chloride ion in the cationic agents was followed by Br^{82}, the latter being obtained carrier free from neutron-bombarded ethyl bromide. Radiobromine appears to serve well as a chloride tracer provided the results are corrected for its 3% higher mobility.[11]

Solutions.—The tagging of the various solutions was accomplished by adding the requisite amount of radioactive solution to one aliquot of a stock solution and an equal volume of water to another. The radioactive solutions used for tagging invariably contained extraneous electrolytes, and the amount present was estimated by conductivity or analysis. The specific activities were so high that the total amount of electrolyte introduced in the tagging operation was less than 0.1% of the final concentration. One exception to this is referred to below.

Procedure

Self-diffusion.—The cells used for self-diffusion were the sintered-glass membrane (Pyrex F) type similar to those described by McBain and Dawson.[12] To provide stirring, which is necessary because of lack of density gradients, each compartment contained a 1-cm. length of 1-cm. Pyrex tubing and the cells were rotated end-over-end at 3 r. p. m. A preliminary diffusion period of three to six hours was adopted to establish a steady state in the membrane, after which fresh solutions were substituted and diffusion allowed to proceed until 5 to 10% of the radioactivity had diffused. Determination of the cell constants was carried out with 0.1 N KCl, taking 1.595 sq. cm./day as the diffusion constant.[13] The diffusion results were calculated according to the usual logarithmic formula

$$KD = -\frac{1}{t}\log\left[1 - \frac{(1+F)C}{C_0}\right]$$

where K is the cell constant, D the diffusion constant, F the ratio of the volumes of the diffusate to diffusing compartments, t the duration of the experiment, C the concentration of the diffusate and C_0 the initial concentration of diffusing material. Concentration units cancel, so that radioactivity counts can be substituted directly.

Transference.—Transference numbers were determined by the "analytical boundary" method described in detail in the foregoing paper.[11] The present application involves the measurement of the amount of radioactivity transported electrically across the boundary created by the sintered glass membrane.

Conductivity.—A Leeds and Northrup 60-cycle bridge (Cat. no. 4866) and a dipping electrode were used. Results were good to about ±0.5%, no attempt being made to obtain highly precise data. Diffusion, transference, and conductivity experiments were made at 25 ± 0.01°.

Radioactivity Measurements.—This radioactive solutions were counted in a small glass-jacketed Geiger counter tube with a conventional amplifying and scaling circuit.[11] Sufficient counts were taken to make the probable counting error less than ±1%.

Results

Self-diffusion.—Self-diffusion results for sodium in Aerosol OT and in Aerosol MA, and for bromine in Agent M and in E-607 are given in Table I. Included are the data for the same ions in sodium chloride. The effect of micelle formation in lowering the rate of self-diffusion of the small ions is clearly evident from the data; this will be discussed quantitatively in a later section of this report.

TABLE I

SELF-DIFFUSION COEFFICIENTS OF SODIUM AND OF BROMIDE IONS

Substance	Tagging ion	Concentration N, mole/liter	Self-diffusion constant of tagging ion, D, sq. cm./day a	b	Av.
NaCl	Na^{24}	0.00296	1.20	1.20	1.20
		.0285	1.16	1.17	1.16
Aerosol MA	Na^{22}	.050	0.91	0.88	0.89
		.096	0.97	0.91	0.94
		.186	0.86	0.85	0.86
		.43	0.58	..	0.58
Aerosol OT	Na^{24}	.00293	1.19	1.21	1.20
		.0287	0.82	0.78	0.80
NaCl	Br^{82}	.050	1.63	1.62	1.62
E-607	Br^{82}	.0617	0.53	0.56	0.55
Agent M	Br^{82}	.0194	0.46	0.45	0.46

It may be noted that the self-diffusion coefficient of sodium ion in the dilute solutions of either

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[11] Brady, THIS JOURNAL, **70**, 911 (1948).

[12] McBain and Dawson, *Proc. Roy. Soc.* (*London*), **148A**, 32 (1935).

[13] Gordon, *N. Y. Acad. Sci. Symposium*, Oct. 27-28 (1944).

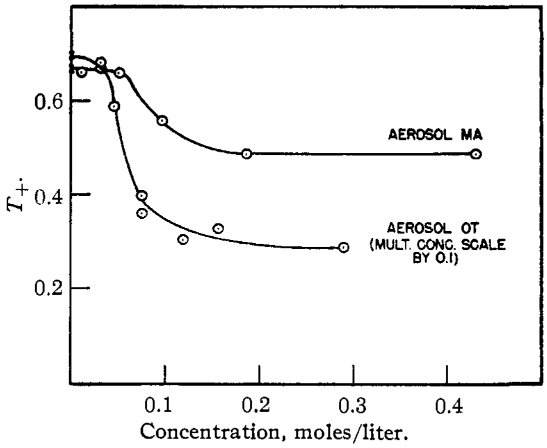

Fig. 1.—Cation transference numbers in Aerosol OT and in Aerosol MA solution.

Aerosol OT or sodium chloride, 1.20 sq. cm./day, is greater than the theoretical limiting value, 1.15 sq. cm./day. This probably arises because the method of calibration of the cells (diffusion of 0.1 *N* KCl into water) leads to density gradients, whereas no such gradients exist in this self-diffusion. Such differences may bring about a 5 to 10% change in the effective thickness of the membrane.[14] Since the self-diffusion will be employed entirely on a comparative basis, a calibration error of this sort will have no appreciable effect upon the conclusions drawn.

Conductivities.—The equivalent conductivities of the two Aerosols are included in Table II; these agree with the data of Haffner, Piccioni and Rosenblum[15] to within 1%. The critical concentrations appear to be about 0.005 *N* and 0.05 *N* for the OT and the MA, respectively. Extrapolation of the usual curves of conductivity *versus* square root of concentration leads to limiting conductivities of 72 and 75, which in turn give 22 and 25 as the limiting conductivities of the two Aerosol anions (using 50.1 for the Na ion).

Transference Numbers.—Table II also gives the mobilities and transference numbers at various concentrations. The specific conductivities are those of the tagged solution, which in most cases do not differ appreciably from those of the untagged. Special mention is required, however, for one series with Aerosol OT, where because of a miscalculation far too much tagging solution was added, and the extra electrolyte so introduced could not be neglected. About the only recourse under these circumstances is to assume that the extra electrolyte did not appreciably affect the mobility of the sodium ion, even though its transference number changed. The observed mobility and the conductivity of the untagged solution may then be employed in order to estimate the transference number in the absence of a foreign electrolyte. Because of the resulting uncertainty, however, a series was also run in which the Aerosol OT solutions were directly bombarded by neutrons to give Na^{24}; this procedure should introduce no foreign electrolyte. As is shown in Table II, results by both methods are in essential agreement.

TABLE II

TRANSFERENCE NUMBERS OF SODIUM AND OF CHLORIDE IONS

Substance	Tagging ion	Concentration, *N*, mole/liter	Sp. cond. mho/cm. × 10^3	W, sq. cm./volt, sec. × 10^4	*T*	Λ^c
Aerosol MA	Na^{22}	0.0100	0.69	4.75	0.65	69
	Na^{22}	.0300	1.93	4.70	.68	64
	Na^{22}	.0498	3.04	4.18	.66	61
	Na^{22}	.0960	4.89	2.97	.56	51
	Na^{22}	.1863	7.81	2.12	.49	42
	Na^{22}	.430	16.83	1.98	.49	39
Aerosol OT	Na^{24a}	.00295	0.205	4.57	.66	69
	Na^{24b}	.00298	.231	4.73	.67	..
	Na^{24b}	.00447	.333	4.14	.59	68
	Na^{24a}	.00738	.485	2.47	.36	65
	Na^{24b}	.00745	.513	2.69	.40	..
	Na^{24a}	.0118	.731	1.97	.31	62
	Na^{22}	.0147	.873	1.99	.32	60
	Na^{22}	.0289	1.54	1.59	.29	53
E-607	Br^{82}	.0617	2.75	1.360	.30	..
Agent M	Br^{82}	.0194	0.727	0.0	.0	..

[a] Activity produced directly by neutron bombardment of the solutions. [b] Excess electrolyte, see text. [c] Derived from measurements on the untagged solutions.

The transference numbers of Aerosols MA and OT are plotted against concentration in Fig. 1. There is a sharp change in transference number in the neighborhood of the critical concentration.

Calculation of the Fraction of Small Ions Bound to the Micelles.—In order to utilize the foregoing data for calculating the fraction of small ions bound, a general model for the association is necessary. We shall assume that below the critical concentration the long chain ions have a concentration equal to the stoichiometric concentration of the solution; above the critical, large aggregates are formed by these ions, including varying amounts of small ions. The free monomeric ions will be assumed to behave roughly as they would in a univalent salt solution at the same total concentration. This is in accord with earlier data of others[7,16] obtained on similar systems.

Since the aggregate is assumed large, as a first approximation the concentration of monomeric long chain ions may be taken to change little with total concentration above the critical, in the range considered in this paper. Actually, since more long chain ions than small ions are included in the micelle, mass law predicts that at concentrations above the critical the concentration of monomeric long chain ions will decrease with increasing

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(14) Moquin and Cathcart, This Journal, **57**, 1791 (1935).

(15) Haffner, Piccioni and Rosenblum, *J. Phys. Chem.*, **46**, 662 (1942).

(16) McBain and Searles, *J. Phys. Chem.*, **40**, 493 (1936).

total concentration. However, calculation of the rate of decrease on a reasonable model indicates that, in the concentration region where the influence of the single long chain ions is important in the equations to be developed, the inaccuracy of the above simple assumption is small compared to other uncertainties.

In the following equations the colloidal electrolyte will be considered to be anion active; for a cation active agent the signs of the subscripts are simply interchanged. Because of lack of detailed knowledge concerning the colloidal particles, all species must, of necessity, be lumped together and thought of as an "average" micelle. This effectively assumes that the mobility of the average bound small ion is the same as that of the average aggregate, which is, of course, not necessarily true.

Self-diffusion.—Denoting the diffusion constant of the average micelle by D_m, that of the free cations by D_+^0, and the measured net diffusion constant of the cations by D_+

$$D_+C = D_+^0C_+^0 + D_mC_+^B \qquad (1)$$

where C, C_+^0 and C_+^B are the total, free cation, and bound cation concentrations, respectively. Noting that $C_+^B + C_+^0 = C$, equation (1) transforms to

$$C_+^B/C = \frac{D_+^0 - D_+}{D_+^0 - D_m} \qquad (2)$$

Transference.—Letting W be the mobility in sq. cm./volt second, with subscripts and superscripts having the same meaning as before, the flux of the positive and negative ions across one square centimeter at a field strength of one volt/cm. is given by

$$\begin{aligned} CW_+ &= C_+^0W_+^0 - C_+^BW_m \\ CW_- &= C_-^0W_-^0 + C_-^BW_m \end{aligned} \qquad (3)$$

Equations (3) may be combined with the well known equations $W_i = \Lambda_i/F$, $T_+ + T_- = 1$, and $T_i = \Lambda_i/\Lambda$ (where Λ is the observed equivalent conductivity) and the material balance $C = C_+^0 + C_+^B = C_-^0 + C_-^B$. It follows that

$$C_+^B/C = 1 - \frac{\Lambda - (C_-/C)(T_+\Lambda + \Lambda_-^0)}{\Lambda_+^0 + (1 - T_+)\Lambda - (C_-^0/C)\Lambda^0} \qquad (4)$$

where $\Lambda^0 = (\Lambda_+^0 + \Lambda_-^0)$ is the hypothetical conductivity the solution would have if there were no micelle formation. Now, according to the assumption made above for the model, $C_-^0 \cong C_c$ at concentrations above the critical; consequently in applying equation (4) in subsequent calculations, this approximation will be used. It may be noted that at concentrations far above the critical, where $C_c/C \ll 1$, the above equation reduces to that derived and discussed by Molliet, Collie and Hartley.[17]

Freezing Point Depression.—Since it is supposed that the micelles are of sufficient size so that their contribution to the freezing point depression is negligible, the osmotic coefficient, g (the ratio of the observed to the theoretical freezing point lowering), may be considered to be the sum of two terms, the first arising from the free long chain ions, the second from free small ions

$$g = \frac{C_-^0 + C_+^0}{2C}$$

Again using the approximation that $C_-^0 \cong C_c$, along with the equation for the material balance

$$C_+^B/C = 1 - 2g + C_c/C \qquad (5)$$

Calculations.—The non-experimental quantities in equations (2), (4) and (5) are D_+^0, D_m, Λ_+^0 and Λ^0. Accordingly, the model must be used for their estimation.

The self-diffusion constants for the sodium ions, D_+^0, may be taken directly from the experiments on sodium chloride recorded in Table I, except in the case of Aerosol MA, which was studied in a higher concentration range. Since Jehle[18] has found that the self-diffusion coefficient of Na^+ in NaCl in the concentration region 0.05–0.5 N is nearly constant and about 8% lower than at infinite dilution, D_+^0 may be taken as 1.10 sq. cm./day throughout the range studied for the Aerosol MA.

There is no very good way to estimate the self-diffusion coefficient of the micelles, D_m. It is hoped to measure this in the near future for the sulfosuccinates using radiosulfur. One logical assumption is that the micelles binding small ions are so large that their diffusion constant can be neglected. Another, which is that employed here, is to extend the observation of Hartley and Runnicles[19] that the diffusion coefficients of some cationic agents swamped with salt roughly correspond to those of spheres with a radius equal to the length of the molecule. This leads to a D_m of 0.16 and 0.14 sq. cm./day for the micelles of Aerosols MA and OT, respectively, corresponding to lengths of 13 Å. and 15 Å. Those for E-607 and Agent M will be taken as 0.073 and 0.070, corresponding to 29 and 30 Å.

The electrical conductivities of the free monomeric ions, Λ_+^0 and Λ_-^0, will, according to the model, vary with concentration in the same proportion as the conductivity of sodium chloride solutions.

No correction will be applied to D_+^0, D_m, Λ_+^0 or Λ_-^0 for the viscosity increase of the solution. Such a viscosity correction would not greatly influence results for Aerosol OT and the cationic agents, but if applied to the results for Aerosol MA the self-diffusion of the sodium ion not only falls out of line with the other salts but becomes unreasonably high at the higher concentrations. This lack

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[17] Molliet, Collie and Hartley, *Trans. Faraday Soc.*, **31**, 120 (1935).

[18] Jehle, Ph.D. Thesis, University of California, 1938.

[19] Hartley and Runnicles, *Proc. Roy. Soc.* (*London*), **168A**, 420 (1938).

of influence of solution viscosity on the mobility of the small ions is in harmony with McBain's observations on the conductivity of solutions of colloidal electrolytes.[20]

The critical concentration for micelles is also needed for utilization of the equations for the fraction of small ions bound. Table III lists this quantity for the surface active agents considered here, as determined by transference (Fig. 1), conductivity (Table II and Ref. 16), freezing point,[21,22] and surface tension.[23] The present self-diffusion data are too meager to be useful in this connection.

Table III

Critical Concentration of the Surface Active Agents

Substance	Critical concn., N	Method
Aerosol MA	0.055	*a, b, c*
Aerosol OT	.0035	*a, c, d*
	.0055	*b*
Agent M	.0009	*d*
E-607	.005	*c*

[a] Transference numbers. [b] Conductivity. [c] Freezing point lowering. [d] Surface tension.

Table IV gives a comparison of the application of equations (2), (4), and (5) in estimating the fraction of small ions bound to the micelle. The osmotic coefficients for the Aerosols were taken from McBain and Bolduan,[21] that for E-607 from McBain and Brady.[22] The data of the table show that there is fair concordance among the three methods of measurement up to concentrations three to four times greater than the critical. This lends support not only to the model, but to the general validity of the self-diffusion or the transport approach to systems where the freezing point method is not applicable. (An exception to the general agreement is the self-diffusion run at the lowest concentration of Aerosol MA; this value is included because nothing could be found wrong with the experiment, but it can be seen even in Table I that it falls out of line.)

Table IV

Comparison of Percentage of Small Ions Bound as Calculated from Self-Diffusion, Transport, and Freezing Point

Substance	Concn., N	% Small ion bound		
		Self-diff.	Trans.	F. P.
Aerosol MA	0.050	22 (?)	0	0
	.096	17	12	14
	.186	25	37	39
	.430	50	30	55
Aerosol OT	.0029	0	0	0
	.0045	..	15	11
	.0074	..	22	19
	.0118	..	29	30
	.0289	36	35	52[a]
Agent M	.0194	75	65	..
E-607	.0617	69	54	70

[a] Calculated from an extrapolated value of *g* obtained from a generalized curve for this compound.[22]

The results of the calculation according to equation (2) are relatively insensitive to values chosen for the self-diffusion coefficient of the micelles, D_{m}, since under any reasonable assumption, D_{m} should be small compared with D_0^+. If, for instance, zero had been assumed instead of 0.16 for D_{m}, then at 0.430 N Aerosol MA, the calculated per cent. bound would be 47 rather than 50. Results from Equation (4) are still less sensitive to variations in Λ_0^-, the equivalent conductivity of the monomeric long chain ions.

At the higher concentrations, the agreement in the calculated "fraction bound" becomes less satisfactory, especially between freezing point and transport results (at still higher concentrations than those studied here it is known[4] that such disparity becomes even greater). The disagreement could arise from a true difference in this quantity when the three different measurements are involved; thus surface conductivity on lamellar micelles of high surface area would give a lower "fraction bound" for diffusional or electrical transport processes than that derived from osmotic measurements. Another cause for disagreement lies in the assumption of an "average" micelle, since the presence of some "ionic" micelles, proposed by McBain a number of years ago,[2] would lead to an apparently lower "fraction bound" from the transport than from the diffusion and freezing point methods.

The inclusion of small ions in the colloidal particle is a logical consequence of the electrostatic effects of aggregation. The juxtaposition of the like charges of the end groups at the water-micelle interface would disrupt the micelle unless a large number of small ions of opposite charge are drawn in to neutralize partially what would otherwise be an excessive electrostatic potential. In the interior of the lamellar micelles indicated by X-ray diffraction studies,[24] this effect will be even more pronounced, so that there should be virtually no osmotically active small ions arising from this region. Because of the masking effect of the small ions, osmotic data from freezing points consequently give no direct idea of the size of the micelle, except in that it is fairly large.

A further consideration of the question of bound ion, however, offers an opportunity for indirect comparison between certain colloidal electrolytes. The values for the fraction bound given in Table IV are based on total long chain ion, micellar plus monomeric. In order to determine the amount bound per mole of micellar ion, use can be made of the probability that in the range considered the concentration of monomeric long

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(20) Laing and McBain, *Trans. Faraday Soc.*, **117**, 1506 (1920).

(21) McBain and Bolduan, *J. Phys. Chem.*, **47**, 94 (1943).

(22) McBain and Brady, This Journal, **65**, 2072 (1943).

(23) Unpublished work in this Laboratory.

(24) Harkins, Mattoon and Corrin, This Journal, **68**, 220 (1946), and references therein.

chain ions changes little with total concentration above the critical. The desired quantity is then dC_+^B/dC, the number of small ions bound per mole of colloidal electrolyte added to an infinite amount of solution. From equation (5)

$$\frac{dC_+^B}{dC} = 1 - 2\frac{d(gC)}{dC} \qquad (6)$$

Figure 2 shows a plot of gC *vs.* C for Aerosols MA and OT, and, for comparison potassium laurate.[21,25] It can be seen that slightly above the critical concentration straight lines result, the slopes of which provide values for d(gC)/dC in equation (6). The slopes for the Aerosol-type agents are about 0.16; hence, dC_+^B/dC = 0.68, and consequently for each hundred moles of Aerosol added 68 moles of sodium are included in the micelles. For potassium laurate, on the other hand, dC_+^B/dC = 0.86. Since nearly all of the potassium is included, this suggests much larger micelles for this substance, although possibly the structure of the micelles may also play a role. This general difference exists between the branched chain salts, to which class most of the efficient wetting agents belong, and the straight chain salts, among which are found the more efficient solubilizing and emulsifying agents.

Acknowledgment.—The authors wish to thank the cyclotron groups at Columbia University and the University of California for the supply of radiotracers. Also, we wish to express our indebtedness to Dr. J. K. Dixon for valuable advice and criticism, and to the Directors of these Laboratories for permission to publish these results.

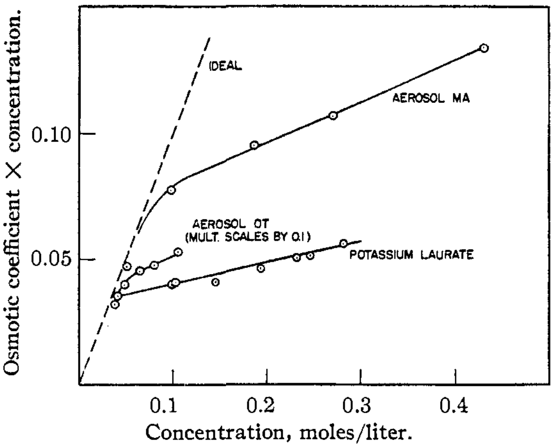

Fig. 2.—Osmotic coefficient times concentration *vs.* concentration for some colloidal electrolytes.

Summary

1. The transference numbers and self-diffusion coefficients for two anionic and two cationic surface active agents were determined using radiotracer techniques.

2. Utilizing the present results and freezing point data extant in the literature, the fraction of the small ions bound to the colloidal aggregates was calculated under consistent assumptions. The values calculated from the three types of measurements agreed well with one another up to several times the critical concentration for micelles. Possible causes for disagreement among the three types of measurements at higher concentrations were discussed.

3. The relationship of the extent of binding to the structure and size of the micelles was briefly considered.

STAMFORD, CONN. RECEIVED MARCH 29, 1947

(25) Brady, Thesis, Stanford University, 1944, and unpublished work.

[CONTRIBUTION FROM U. S. NAVAL RESEARCH LABORATORY]

Liquid Immiscibility in the System H_2O–Na_2O–SiO_2

BY O. F. TUTTLE[1] AND I. I. FRIEDMAN

Introduction

The dwindling supply of natural quartz for piezoelectric uses, together with the remarkable success attained in growing other crystals for a variety of uses, has stimulated interest on the part of the Armed Forces in the production of synthetic quartz. This work on phase equilibria in a portion of the ternary system H_2O–Na_2O–SiO_2 is a result of efforts to find a commercially feasible method for growing quartz crystals.

The data presented here are incomplete, but publication at this time seems advisable because of the theoretical and practical value of the information. Liquid immiscibility has been observed and investigated in the region $Na_2Si_2O_5$–SiO_2–H_2O. The 250, 300 and 350° isotherms have been worked out at the vapor pressures of the compositions investigated.

Preparation of Materials

All mixtures used in this work were made from a stock solution of sodium hydroxide and quartz or silica glass. The solution was prepared by saturating distilled water with reagent grade sodium hydroxide at 80°. The sodium carbonate precipitated was allowed to settle and the solution decanted through glass wool. The saturated solution was then diluted to approximately 20 N and stored in a wax-lined bottle. The composition was determined by titrating a weighed volume against a standard solution of sulfuric acid. The resulting solution contained 388 g. of sodium oxide per 1000 g. and had a specific gravity

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