

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

The Diffusion of Colloidal Electrolytes; Sodium Oleate

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Soaps afford one whole family of uni-univalent electrolytes to which the hypothesis of complete dissociation is not reasonably applicable.¹ In very dilute solution they are only moderately strong electrolytes and in more concentrated solutions they are colloidal electrolytes. In such cases the high diffusion constant observed² is a composite made up from the various ionic molecular and colloidal species present. The accepted formulas of Nernst³ and Haskell⁴ refer, however, only to infinite dilution and that of Einstein⁵ to uncharged spherical molecules or particles. McBain and Liu,⁶ from a consideration of the principles of interionic attraction as analyzed in the Debye-Hückel-Onsager theory and from experimental data for potassium chloride, sucrose, and potassium laurate, derived four conclusions for dealing with ordinary finite concentrations: (1) that the resistance of ions to motion, all in the same direction, is nearly independent of their concentration; (2) that the change in diffusion coefficient of an electrolyte such as potassium chloride is dependent primarily upon a direct proportion to the observed osmotic pressure rather than to the numerical value of the activity;⁷ (3) for non-electrolytes the diffusion coefficient is not greatly affected by the changes in viscosity with concentration and, therefore, usually diminishes but slowly with increase in concentration; (4) that the total diffusion observed may be arrived at in good first approximation by combining additively (a) the diffusion of known concentrations of molecules and of uncharged colloidal particles, using the Einstein equation, (b) the Nernst equation (for infinite dilution) for the ions of a uni-univalent electrolyte but corrected for decrease in osmotic pressure, and (c) the Haskell formula (for infinite dilution) corrected for change in osmotic pressure for polyvalent electrolytes or charged colloidal particles together with their compensating ions.

(1) McBain, *THIS JOURNAL*, **50**, 1636 (1928).(2) (a) McBain and Liu, *ibid.*, **53**, 59 (1931); (b) see also Hartley and Robinson, *Proc. Roy. Soc.* (London), **A134**, 20 (1931); (c) Svedberg, *Kolloid-Z.*, **36**, Ergänzungsbd., p. 63 (1925), equations 13b and 14.(3) Nernst, *Z. physik. Chem.*, **2**, 613 (1888); "Theoretische Chemie," 10th ed., 1921, pp. 425-431.(4) Haskell, *Phys. Rev.*, [1] **27**, 145 (1908).(5) Einstein, *Z. Elektrochem.*, **14**, 235 (1908).(6) McBain and Liu, *THIS JOURNAL*, **53**, 59 (1931).(7) Compare G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," 1923, p. 362. The approximate proportionality to the observed osmotic pressure was experimentally demonstrated by Öholm [*Z. physik. Chem.*, **50**, 343 (1904)] over the whole range of concentrations of solutions of electrolytes up to several times molar. He showed the advisability of correcting for viscosity, but found a direct proportion an over correction; MacInnes much later proposed $\eta^{0.7}$. Hartley [*Phil. Mag.*, **12**, 485 (1931)] used this and compared the replacement of van't Hoff's i by $d \ln a_{\pm} / d \ln C$ for electrolytes in fairly dilute solution (0.1 N) with an average discrepancy of over 4%. For higher concentrations he writes "... an exact comparison would not, in the present state of the latter, be instructive, even if the method and assumptions of the theory could be considered applicable in the more concentrated solutions."

For the simple case of a highly dissociated uni-univalent electrolyte such as potassium chloride the diffusion coefficient D in sq. cm./day is

$$D = iRT / \left(\frac{1}{U} + \frac{1}{V} \right)$$

where U and V are the mobilities in reciprocal ohms of cation and anion; that is, the denominator is the sum of the resistances to movement and the numerator is the driving force, i being the van't Hoff osmotic coefficient.

Their general equation for such an electrolyte, partially dissociated⁸ (or ions, partially "associated"), α referring to concentrations, is

$$D = \frac{i}{1 + (n - 1)\alpha} RT \left[\alpha \left(\frac{1}{n_+} + \frac{1}{n_-} \right) \left(\frac{1}{U} + \frac{1}{V} \right) + \frac{1 - \alpha}{1/U_m} \right]$$

where n is the number of ions produced by the dissociation of one molecule or particle, n_+ and n_- are the valencies of cation and anion, $1/U$ and $1/V$ are the resistance to movement of one electrochemical equivalent (charge of IF) in each case, whereas $1/U_m$ is the resistance to movement of 1 whole gram molecule (or 60.6×10^{22} "uncharged particles") as defined in the Einstein equation.

$$D = \frac{RT}{N_6\pi\eta r} = \frac{RT}{1/U_m}$$

RT has the value⁹ of 0.02246 at 18° and 0.02300 at 25° if $1/U_m$ is expressed in ohms. The formula is for diffusion into pure solvent. For diffusion into another solution, slightly less concentrated, the gradient of osmotic pressure with concentration would be used.

It follows directly from these equations that if a large particle or a molecule of low mobility such as a protein passes from the isoelectric point to become a polyvalent electrolyte, its diffusion is accelerated almost in proportion to the total number of ions of the polyvalent electrolyte. This was first derived implicitly in 1925 by Svedberg,^{2c} who suggested that diffusion might thus be used for measuring how many charges are carried by a single particle.

It is interesting that the diffusion constant of mercuric chloride, 0.92, which admittedly consists almost entirely of molecules, is very nearly that

(8) Owing to the circumstance that in the special case of potassium chloride $1/U_m = 1/U + 1/V$. McBain and Liu wrote this in the equivalent form, not generally applicable

$$D = \frac{iRT}{\alpha \frac{1}{U} + \alpha \frac{1}{V} + (1 - \alpha) \frac{1}{U_{KCl}}}$$

They committed the algebraic error of recording D as $iRT/(\text{sum of resistances})$, instead of, as in their actual numerical examples, keeping the added fractions separate, the numerators adding to iRT . G. S. Hartley's suggested emendation is obviously erroneous as may be seen if it is considered in connection with a weak electrolyte such as mercuric chloride or succinic acid. He multiplies the diffusion of the neutral molecule by the valencies of the ions into which it would have dissociated had it been dissociated [*Phil. Mag.*, 12, 487 (1931)]. He states at the top of p. 487 that McBain and Liu ignored interionic forces, having overlooked their discussion.

(9) Values calculated from data of "International Critical Tables."

calculated for complete dissociation into independent ions, 0.91. The resistance to movement of the molecule is, therefore, one-third the sum of the three ions. For cadmium iodide, a stronger electrolyte, the diffusion coefficient for completely undissociated molecules is 0.67 as compared with 1.18 for complete dissociation, the resistance for the molecule being 58% of the sum of that of the three ions. From these and other data one might tentatively infer that the more polar the molecule the less differences does dissociation cause in resistance to movement and hence, conversely, the greater the importance of the mere number of molecules and ions present.

The present paper supplements the above analysis of the diffusion of potassium laurate^{2a} with more extended data for sodium oleate. Here it is possible to test the effect of the linking of the primary particles of oleate by showing that diffusion from sodium oleate jelly into water is just as rapid as the diffusion of the oleate sol.

Experimental

The method employed was that previously described,^{2a} in which a Northrop diffusion cell is filled with the soap solution which diffuses through a sintered Jena glass membrane into 0.0015 *N* sodium hydroxide to prevent hydrolysis. As in previous experiments the same values are obtained with each of the four cells used, lower values being found only with a very tight, slow diffusing membrane when studying the higher concentrations of soap. However, the values for dilute solutions, using the same slow cell, lie on the general curve, and it is supposed then that these finer pores became clogged in higher concentrations, either with soap or with fatty acid formed by hydrolysis. Additional tests with cells at 20 and 25° have been carried out and have checked the previous assumptions that different cells yield the same diffusion constants.

The properties of the cells used are given in Table I. The sintered glass membrane was in every case 5 cm. in diameter and 2 mm. thick.

TABLE I
CHARACTERISTICS OF THE DIFFUSION CELLS

Designation Trade	Here	Volume of cell, cc.	Approx. pore radius, Å.	Cell constant
G-4	a	37.08	2.5×10^4	348.2
G-4	b	37.96	2.5×10^4	170.2
G-3	G-3	98.00	$(15-20) \times 10^4$	348.3
G-4	W	106.9	2.5×10^4	253.0
G-4	M	105.3	2.5×10^4	221.8

The diffusion method is accurate to a fifth of one per cent. for electrolytes, but for soaps the error may be increased to several per cent. owing to the extreme difficulty of releasing the air from the soap solutions. Early attempts to find the boiling point of soap solutions¹⁰ failed completely

(10) Compare McBain and Taylor, *Z. physik. Chem.*, **76**, 179 (1911).

because of the air obstinately retained. In many of the diffusion experiments recorded here, however, only a few bubbles were developed if the solutions had previously been thoroughly subjected to suction. The experimental results are calculated by the formula developed by Liu, and displayed in Fig. 1, where data for sucrose and potassium laurate are added for comparison. New values added for 0.05 N_w potassium laurate are $D = 0.510$ and 0.510 .

TABLE II
DIFFUSION OF ORDINARY ISOTROPIC SOLUTIONS OF SODIUM OLEATE AT 25°

Concn. N_w	Cell	Time in hours	Concn. change in g. equivalents	D
0			(Predicted)	0.731
0.0250	a	56.00	0.001668	.461
.0250	W	23.33	.000798	.463
.0253	(b)	90.00	.001883	.496
.0456	(a)	47.65	.003138	.388
	G-3	47.42	.003088	.387
	(a)	47.66	.003170	.392
.0490	G-3	48.00	.003212	.365
.0503	G-3	17.74	.001282	(.368) ^b
.098	M	40.81	.003303	.322
	W	40.85	.003753	.322
.150 ^c	(a)	41.00	.006260	.265
	(a)	24.33	.004027	.281
	G-3	22.00	.003567	.280
.300	(a)	19.00	.004922	.217
	G-3	17.50	.004458	.215
	(a)	17.63	.004856	(.233)
.376	W	22.00	.005320	.214
	G-3	22.00	.006905	.214
.500	G-3	26.00	.01172	.229
	G-3	23.75	.01235	.224

^a Mean of cells M and W. ^b From residue (0.328), from diffusate (0.407). ^c At 20°.

Discussion of Results

We may compare the observed results (a) with the predictions of the Nernst and Haskell equations and (b) with values for other substances (see Fig. 1). Taking the mobilities of potassium and sodium from the data of "International Critical Tables" and that of a simple fatty ion as 23.2 and assuming the equivalent conductivity of the ionic micelle to be equal to that of the potassium ions, we calculate from the Nernst equation for complete dissociation into simple ions $D = 0.813$ for potassium laurate and $D = 0.731$ for sodium oleate. Again the Haskell formula for hypothetical complete dissociation into a decavalent ionic micelle and 10 alkali ions yields $D = 0.936$ for the ionic micelle (plus potassium ions) of potassium laurate and $D = 0.759$ for that of sodium oleate. It is noteworthy that

these numbers show a distinctly higher rate of diffusion for the colloid form as compared with the simple ions, assuming infinite dilution in both cases.

However, for colloidal soap this is offset by the much lower diffusion velocity of the undissociated colloid or neutral micelle which is present in even larger quantity than this ionic micelle and for which the driving force per colloid particle is only one-eleventh that on the ionic micelle with its ten compensating ions. Thus in Fig. 1 the observed diffusion values are much lower than those calculated above because of the incomplete dissociation both of the simple molecules in dilute solution and of the colloidal electrolyte in more concentrated solution. Once the colloidal electrolyte is fully formed, as in 0.3 N_w solution upward, its diffusion, like its apparent degree of dissociation, changes very little with concentration.¹¹ As a matter of fact, the observed diffusion rate is an approximately linear function of the proportion of total colloid.

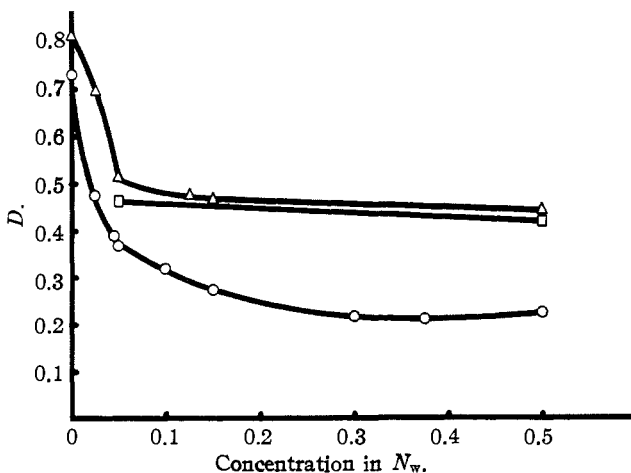


Fig. 1.—The diffusion coefficients D in sq. cm./day of potassium laurate, sucrose, and sodium oleate, at 25°; Δ , potassium laurate; \square , sucrose; \circ , sodium oleate.

A 0.025 N_w sodium oleate solution contains only 1.5% of colloid, accounting for 0.011 of the observed diffusion, 0.462, leaving 0.451 for simple ions and molecules. The composition diagram of these solutions was published by McBain, Laing and Titley,¹² but the Arrhenius conductivity ratio was not then corrected for interionic attraction, so that the 25% Arrhenius dissociation (left after allowing for products of hydrolysis) really means about 26.3% true dissociation. This correction, however, is partly offset by the lowering of osmotic pressure. 26% of 0.731 is 0.190 which

(11) This is a further confirmation of the point made by McBain that for the ionic micelles of soap the charges are so widely spaced that the ionic strength of the solution is only that of a uni-univalent salt [THIS JOURNAL, 50, 1636 (1928)].

(12) McBain, Laing and Titley, *Trans. Chem. Soc.*, 115, 1279 (1919).

when subtracted from 0.451 leaves 0.268 due to the diffusion of simple molecules which comprised 61% of the total soap. Their diffusion constant $D_m = 0.261/0.61 = 0.428$, and their mobility from the Einstein formula 18.6. This is somewhat less than the mobility of the oleate ion (23.2), and the resistance to movement of this more strongly polar molecule is 85% of the sum of its two ions in accordance with the tentative rule on a previous page.

In 0.5 *N* solution of sodium oleate the only constituents present are ionic micelle and its sodium ions and the neutral colloid. The Arrhenius conductivity ratio was 20%, which as a first approximation may be corrected by comparing it with the Arrhenius ratios for decinormal solutions,¹³ thus indicating a true degree of dissociation of about 23.5%. This again from the standpoint of diffusion is partly offset by the lowering of osmotic pressure due to interionic attraction.¹⁴ Approximately, then, the diffusion due to the ionic micelle and its ions may be taken as 22% of 0.759 (see above) = 0.167. This subtracted from the observed value of 0.226 leaves 0.059 for the 76.5% of neutral micelle, whose diffusion coefficient is, therefore, 0.077 and mobility U_m is 3.35. From this, Einstein's equation for a spherical uncharged particle would give a diameter of only 55 Å.

The size of the primary particle of neutral colloid is, therefore, only a little greater for sodium oleate than for potassium laurate^{2a} (48 Å.). In both cases the ionic micelle, from the mobility assumed, has an effective diameter of 25 Å. The small size of the primary particles of soap solutions is confirmed by measurements on light scattering to be reported elsewhere. It thus appears that the great difference experimentally observed between potassium laurate and sodium oleate is not essentially due to difference in size of the primary particles but to the fact that in the sodium oleate there is a great tendency for the formation of loose secondary aggregates. The light scattering does not change when sodium oleate sol sets to a clear jelly.¹⁵ Potassium laurate, on the contrary, does not show the slightest tendency to gelatinize even in the presence of salts; and it passes through fine ultrafilters.

Diffusion of Sodium Oleate Jelly.—Having found that the relatively high viscosity and ready ultrafilterability must be ascribed to loose aggregation of the neutral colloidal particles, it becomes of great interest to note that this has interfered to only a very minor extent with the diffusion coefficient of the sol. This may be pictured as a comparison between the diffusibility of a number of particles loosely strung together, as in a flexible necklace, with their diffusibility when completely separated. McBain and Liu^{2a} pointed out the remarkable fact that with sucrose a manifold increase of viscosity caused by diffusing molecules themselves only slightly

(13) Compare Kraus, "Properties of Electrically Conducting Systems," 1922, p. 35, Table 4.

(14) Ref. 13, pp. 233, 234.

(15) McBain and McBain, *Nature*, **125**, 125 (1930).

affects the rate of their diffusion. Upon the same principle, the necklace would be expected to diffuse almost as fast as the component beads.¹⁶

The following experiments were carried out to ascertain how fast sodium oleate diffuses from the completely jellied form into water (with 0.0015 *N* sodium hydroxide). Comparative experiments were likewise made with other portions of the same specimen of solution which had been allowed to crystallize out far enough to form a hard white curd and with two intermediate samples in which only a small amount of curd fibers had separated.

TABLE III

DIFFUSION FROM DIFFERENT SAMPLES OF THE SAME 0.5 *N_w* SODIUM OLEATE SOLUTION
IN DIFFERENT PHYSICAL STATES

State of soap	Temp., °C.	<i>D</i> in sq. cm./day	
Clear sol	25	0.221	0.221
Clear jelly	25	.232	.228
Cloudy gel	25	.186	.194
Translucent cloudy gel	23-25	.187	.189
Hard white curd	22-23	.135	.149

It is really quite remarkable to find that soap can diffuse as fast when its colloidal particles are fixed as when they are fluid and free to move and that the diffusing power is only lessened when the amount of material present decreases by crystallizing out as it does in curding, which removes soap from solution. This finding would exclude loose aggregation as a noticeable cause of lessened diffusibility of colloids.

Summary

1. General equations for diffusion are given to comply with the experimental fact that diffusion is proportional to osmotic pressure and not to activity.
2. It is suggested that the resistance to movement of an undissociated molecule is dependent upon its degree of polarity.
3. Colloidal electrolytes such as soaps exhibit high diffusion coefficients, which are analyzed. Primary particles of sodium oleate are not much larger than those of potassium laurate. The viscosity and gelatinizing power of sodium oleate is due to loose linking of primary particles and this does not appreciably affect the rate of diffusion.

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RECEIVED AUGUST 8, 1932
PUBLISHED FEBRUARY 9, 1933

(16) Svedberg and Chirnoaga [THIS JOURNAL, 50, 1399 (1928)] have adopted an exactly opposite point of view to explain the discrepancy observed with hemoeyanin between diffusion and sedimentation velocity which, however, must become identical for sedimentation equilibrium at all concentrations.