error in the vapor-pressure measurements, all the values of $h/m^{1/2}$ being slightly high, but from the nature of the function the relative amount will be larger the more dilute the solution. The uncertainty in log γ due to the difference of limits corresponds to about 0.2% in the activity coefficient.

We give in Table I the activity coefficient calculated from the curve of Fig. 1. The first row gives the molality, moles per 1000 g. of water, and the second the values of the activity coefficient at 20° from vapor-pressure data. Below 0.1 M, the values of the activity coefficient at 0° calculated from this same curve are in agreement with those calculated by Scatchard[11] by another method.

TABLE I

THE ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE AT 20°

m	0.1	0.2	0.5	1.0	2.0
γ	.772	.715	.651	0.601	0.570

Summary

We have extended the application of the divergence function h of Lewis and Randall to the calculation of the activity coefficient of electrolytes, and have shown the application of this method in the case of potassium chloride.

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THE ACTIVITY COEFFICIENT OF SOAP SOLUTIONS

BY MERLE RANDALL, JAMES W. MCBAIN AND A. MCLAREN WHITE

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The work of McBain and others has shown that we may consider dilute aqueous soap solutions as typical electrolytes and that in the more concentrated solutions such properties as the conductance, viscosity, etc., are explainable if we assume the existence of micelles.[1]

McBain and Salmon[2] have determined the vapor-pressure lowering of the sodium and potassium soaps from the acetate to the behenate by measuring the change in dew point at 90°. McBain, Laing and Titley[3]

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[11] Scatchard, THIS JOURNAL, 47, 648 (1925).

[1] For references see McBain, "The Study of Soap Solutions and Its Bearing upon Colloid Chemistry." Union Internationale de la Chimie Pure et Appliquée, Cambridge, June, 1923; J. Soc. Chem. Ind., 42, 615 (1923); Chimie et Industrie, 11, 3 (1924); Am. Dyestuff Rep., 12, 822 (1923). Bogue, "Colloidal Behavior," McGraw-Hill Book Co., New York, 1924, vol. I, p. 427.

[2] McBain and Salmon, THIS JOURNAL, 42, 426 (1920); Proc. Roy. Soc., 97A, 49 (1920).

[3] McBain, Laing and Titley, J. Chem. Soc., 115, 1289 (1919).

measured the freezing-point lowering. Their experiments, however, did not include the heavier soaps, as these soaps are too insoluble at $0°$.

These measurements give us the activity of the water. The experimental difficulties and the slight hydrolysis precluded measurements below 0.1 M. But if we assume that these substances in dilute solution behave as typical strong electrolytes, we may combine these results with others and obtain values for the activity coefficient. It will be seen that the results obtained are satisfactorily explained if we assume the micellar theory.

For the purpose of making these computations we will utilize the methods outlined by Randall[4] and by Randall and White.[5] From the data in the papers mentioned above we have calculated the values of the functions[6] $h/m^{1/2}$ and $j/m^{1/2}$. In the case of the sodium and potassium acetates the curve of $h/m^{1/2}$ against $m^{1/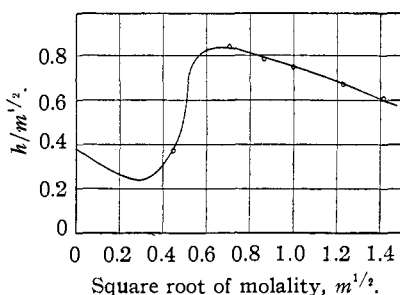2}$ is as would be expected similar to the curves for typical uni-univalent electrolytes. As an example of the data for the heavier soaps we present in Fig. 1 the experimental points of the function $h/m^{1/2}$ plotted against the square root of the molality for potassium palmitate at $90°$. If we were not fairly certain that the value of $h/m^{1/2}$ at infinite dilution is approximately[7] 0.39 as was shown by Randall, we might have neglected the point at $m^{1/2} = 0.45$;

Fig. 1.—Potassium palmitate (C_{16}) at $90°$.

but from an inspection of the curves of all the soaps and of the similar $j/m^{1/2}$ curves we are confident that this point is approximately correct and that the curve really has a shape somewhat as shown in the figure. The maximum in the case of the hexoate and octoate is not pronounced. In making the

[4] Randall, THIS JOURNAL, **48**, 2512 (1926).

[5] Randall and White, *ibid.*, **48**, 2514 (1926).

[6] For a discussion of these functions see (a) Refs. 4 and 5; (b) Lewis and Randall, "Thermodynamics and The Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, pp. 273–275, 285–290, 345–348.

[7] The theoretical limit at $90°$ would be about 0.44 instead of 0.39 because of the change in the product of dielectric constant by absolute temperature. The heat of dilution of the soaps is unknown, but the sign of that of potassium acetate is opposite to that of potassium chloride. The curves, therefore, for temperatures above $0°$ will lie above the $0°$ curve all the way, and not cross as in the case of the chloride in Fig. 1 of the previous paper. They will, however, lie closer to the $0°$ curve at moderate concentrations than at the limit or in more concentrated solutions. The error in making the curves approach amounts to only a few tenths of a per cent. as we have done is constant in the more concentrated solutions. If the soaps have a small "ionic diameter" in the sense of Debye and Hückel, then Bjerrum [*Det. Kgl. Danske Videnskab. Selskab Math.-fys. Medd.*, **7**, No. 9 (1926)] has shown that we must consider the soaps not fully dissociated, which will have the effect of raising the curve of $h/m^{1/2}$ in the dilute solution, but the limit will be the same as for strong salts.

extrapolations to infinite dilution we have assumed a shape of the curve similar to that of Fig. 1, and an approach to the curve of typical strong electrolytes in the most dilute solutions. All the available thermodynamic evidence seems to show that the slope of the curve in dilute solutions is dependent upon the particular ions present in the solution.[8] We have, however, merely as an expedient, made these curves asymptotic with that of potassium acetate.

In order that the behavior of these soaps may be better understood, we have reproduced in Fig. 2 the family of curves for the potassium soaps and for sodium behenate at 90°. These curves are the average curves as finally taken, due consideration being given to the value of the experimental points

Fig. 2.—Average curve for soaps at 90°.

not only at 90° but also to the values taken from the freezing-point data. It must be remembered that the experimental data are not always in complete agreement, and that the curves as given are necessarily somewhat

Fig. 3.—Potassium laurate (C_{12}).

approximate, especially since the number of experimental points in the range of rapid change of $h/m^{1/2}$ is small.

It is obvious that the soaps of low molecular weight (if we are to call potassium acetate a soap) are essentially typical strong electrolytes and that in the case of the higher soaps two opposing factors are involved. The effect of hydration will be to lower the value of $h/m^{1/2}$ (increase the activity coefficient) while the effect of association of ions into ionic micelles and into un-ionized micelles will be to increase the value of $h/m^{1/2}$. This is strikingly shown in the curves, for with increasing molecular weight we find increasingly sharp rise in the value of $h/m^{1/2}$ at the concentrations where micelle has been assumed to appear.

Before discussing this subject further we present in Fig. 3 the curve for

[8] In addition, the conductivity ratio for dilute solutions of the higher soaps is less than that for typical uni-univalent electrolytes.
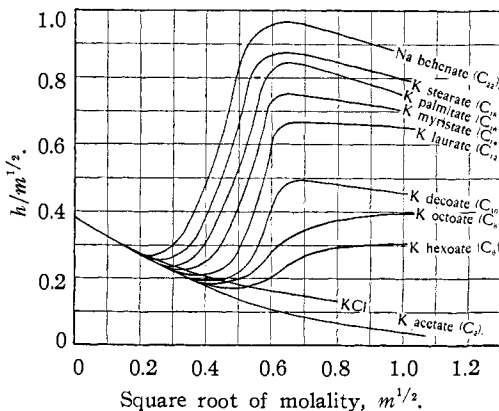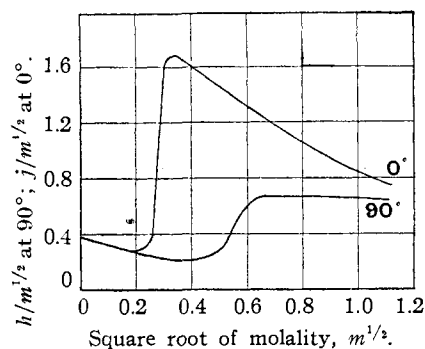
potassium laurate at $0°$ and at $90°$. It will be noted that the rise in the curve at $0°$ occurs at a much lower concentration and that the values are much higher. This again is in accordance with the view that micellar formation is much greater at lower temperatures.

From the curves thus drawn we have calculated the values of the activity coefficient shown in Table I. In obtaining the values for the acetate, hexoate and octoate we have averaged the points at $90°$ and at $0°$, and hence obtain an approximate mean activity coefficient for the temperature range $0°$ to $90°$. The values for the activity coefficients are given to three decimal places but the last place probably has no significance.

TABLE I

ACTIVITY COEFFICIENT OF SOAPS

Molality	Na acetate C_2	K acetate C_2	K hexoate C_6	Na octoate C_8	K octoate C_8	K decoate C_{10}, 90°	Na and K laurate C_{12}, 90°	Na myristate C_{14}, 90°
0.01	0.903	0.902	0.902	0.903	0.902	0.902	0.902	0.902
.02	.872	.871	.871	.872	.871	.871	.871	.872
.05	.823	.821	.820	.821	.820	.820	.820	.820
.1	.780	.778	.778	.779	.778	.778	.776	.773
.2	.738	.734	.733	.730	.728	.723	.703	.683
.3	..	..	..	..	..	.651	.592	.565
.4	..	..	..	..	..	.525	.446	.400
.5	.709	.696	.601	.545	.542	.466	.383	.344
.8	..	..	..	..	..	.362	.265	.235
1.0	.735	.699	.451	.380	.374	.317	.217	.195

Molality	K myristate C_{14}, 90°	Na and K palmitate C_{16}, 90°	Na stearate C_{18}, 90°	K stearate C_{18}, 90°	Na behenate C_{22}, 90°	K decoate 0°	K laurate 0°	K oleate 0°
0.01	0.902	0.902	0.902	0.902	0.902	0.901	0.900	0.903
.02	.871	.871	.873	.871	.871	.867	.866	.844
.05	.879	.819	.820	.818	.817	.809	.801	.367
.1	.772	.769	.765	.760	.744	.752	.472	.203
.2	.681	.641	.612	.606	.557	.673	.255	.116
.3	.562	.474	.425	.419	.377	.576	.177	.081
.4	.397	.356	.336	.329	.290	.398	.136	.062
.5	.337	.296	.281	.274	.235	.318	.111	.049
.8	.228	.196	.181	.175	.145	.212	.073	.028
1.0	.185	.159	.146	.139	..	.176	.060	.020

As is the case with strong electrolytes, the temperature coefficient of the activity coefficient is practically zero in the region in which the soap is acting as a strong electrolyte. Therefore, the heat of dilution of the soap in this region is zero or very small. In the case of potassium laurate, illustrated in Fig. 3, it is noted that there is a very large positive temperature coefficient which would indicate that the heat of dilution is much larger at $0°$ than at $90°$. The temperature coefficient is greater for the soaps of higher molecular weight. For example, at $1\ M$ the decoate (C_{10}) has approximately the same activity coefficient at $0°$ as has the myristate

(C$_{14}$) at 90°, and at this same concentration the activity coefficient of the decoate is about doubled on heating from 0° to 90°.

McBain and Salmon found anomalous dew-point lowerings at concentrations greater than 1 M for the soaps laurate to behenate. Systems containing about 1.5 moles of these soaps and 1000 g. of water form two phases at these temperatures. We have not attempted, therefore, to consider solutions more concentrated than 1 M. Such extrapolations of the curves of Fig. 2 as might be made would probably refer to supersaturated aqueous soap.

McBain has concluded that the potassium soaps contain more ionic micelle than the sodium soaps, but approximately the same amount of neutral micelle. In this sense the potassium soaps are better soaps than the sodium. From the table we see that in general the potassium soaps have slightly lower activity coefficients than the sodium soaps. This is also the case with the ordinary electrolytes in moderate concentrations.

In making the activity-coefficient curves of a soap identical in the most dilute solutions with that of potassium chloride we are considering a soap which is unhydrolyzed. Actually, there is some hydrolysis but the measurements have all been made in solutions that were concentrated enough that the error due to hydrolysis could be neglected. Therefore, the activity coefficients given are for that ideal soap which is unhydrolyzed. In dealing with a soap in very dilute solution, it will be necessary to consider the solution as a mixture and to take the activity coefficient in accordance with the principle of the ionic strength.

It may be interesting to speculate regarding the effect of electrolytes upon the activity coefficient of soaps. If we think of the ionic micelle as a single aggregate with, say, ten negative charges, then the contribution of a single micelle to the ionic strength, μ, will be 100 times that of chloride ion. The mean activity coefficient of a solution containing only potassium ions and decavalent micelles would be given by the formula[9] K$_{10}$ Micelle; log $\gamma = -5 \sqrt{\mu}$ from which it is seen that doubling the ionic strength would result in a very considerable decrease in the activity coefficient of the micelle. However, in the region where there is considerable micelle formation, about 40% of the soap is in the form of ionic micelle, and hence even a large amount of added salt will not greatly increase the ionic strength, and therefore will not largely affect the activity coefficient of the ionic micelle. This leaves out all consideration of hydration, which amounts to an appreciable fraction of the total water and which would normally be expected to increase the activity coefficient. We may expect the principle of the ionic strength to be approximately true only at low concentrations. There is some experimental evidence that indicates that

[9] Calculated from the simple form of the Debye and Hückel theory.

the percentage of ionic micelle is not greatly affected by the addition of electrolytes.[10]

Summary

1.   We have calculated the activity coefficients of the various soaps.

2.   The activity coefficient so calculated offers evidence in favor of the micellar theory.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE VAPOR PRESSURES AND THERMAL PROPERTIES OF POTASSIUM AND SOME ALKALI HALIDES

BY ERNEST F. FIOCK[1] AND WORTH H. RODEBUSH

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The physicists within the last few years have made a large number of measurements of energy changes in atoms and molecules by ionization and spectroscopic methods and have postulated various electron displacements and dissociations as accompanying these changes. It is desirable to obtain direct thermal data for these postulated reactions for purposes of checking against the calculations of the physicists and verifying their postulates. Thus, if the reaction Na + Cl ⟶ NaCl in the vapor state consists simply of the transfer of an electron from the sodium to the chlorine, the heat of this reaction should be calculable from the ionization potential of sodium and the electron affinity of chlorine. The comparison of this calculated heat with the more directly determined quantity should decide whether the mechanism of the reaction is the simple one postulated above.

It is true that the physicists have not been able to agree upon a value for the electron affinity of chlorine but it seems probable that a satisfactory value will be established in the near future. On the other hand, the classical calculation of this sort made by Foote and Mohler[2] for gaseous hydrogen chloride now appears to be in fortuitous agreement only with thermal data since Barker and Duffendack[3] have shown that the hydrogen chloride molecule does not dissociate on ionization as they supposed. In fact, it seems likely that no chemical reaction is so simple as the elementary process that the physicist brings about in his measurement. Thus the

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

[1] This communication is an abstract of a thesis submitted by Ernest F. Fiock in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Foote and Mohler, "The Origin of Spectra," Chemical Catalog Co., New York, 1922, p. 185.

[3] Barker and Duffendack, *Phys. Rev.*, **26**, 339 (1925).