TABLE I

		Present work		Bell and Roblin
		Mean	Range	
Sulfanilamide	pK_a	10.59	10.45–10.80	10.43
	pK_b	11.90	11.65–12.00	11.64
N^1-Acetylsulfanilamide	pK_a	5.32	5.25– 5.44	5.38
	pK_b	12.60	12.32–12.98	12.22
Sulfadiazine	pK_a	6.25	5.94– 6.71	6.48
	pK_b	11.62	10.93–11.98	12.00

the method outlined for the calculation of pK values may not be as great as that of others. The procedure has, however, proved very valuable in this laboratory in the elucidation of the properties of compounds of unknown structure, compounds of low solubility, and compounds available in limited quantity.

Acknowledgment.—The authors wish to express their appreciation to Mrs. K. H. Lees for her assistance in some of the spectrophotometric measurements.

Summary

1. The details of the changes, with pH, in the ultraviolet absorption spectra of several sulfonamides are described.

2. It is shown that these changes can be used either for the calculation or graphic determination of pK values.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE

The Melting Point and Heat of Fusion of Barium Hydroxide

BY RALPH P. SEWARD

Although it is known that barium hydroxide is easily fused without decomposition, the only values recorded for its melting point are 395° for "impure" barium hydroxide by Balarew[1] and 375–380°, by Hedvall and Heinberger.[2] No value for the heat of fusion of barium hydroxide appears in the literature. The investigation reported here consisted of the determination of the freezing points of barium hydroxide and of solutions of several different salts dissolved in barium hydroxide. From these freezing points the heat of fusion has been calculated. The solutes employed were barium carbonate, sodium hydroxide, barium chloride, and barium bromide.

The latter pair of solutes, barium chloride and barium bromide, were added to see whether they would lower the freezing point of the barium hydroxide twice as much per mole added as the first pair, barium carbonate and sodium hydroxide. This question, which is discussed by Lewis and Randall,[3] has apparently never been thoroughly investigated. The experiment of Goodwin and Kalmus[4] cited by Lewis and Randall in which it was found that the freezing point of lead chloride was lowered about 70% more by lead bromide than the calculated lowering for a non-dissociated solute, has no quantitative significance since it has been shown that lead bromide forms solid solutions with lead chloride.

Experimental

Materials.—To prepare pure anhydrous barium hydroxide a technical grade of barium hydroxide containing considerable carbonate was dissolved in hot water, filtered and twice recrystallized in Corning alkali resistant glassware, precautions being taken to prevent any contact with air containing carbon dioxide. To dehydrate the crystallized octahydrate without fusion most of the hydrate water was removed at room temperature with a vacuum pump. The material was then brought to 100° and the pumping continued for two days. The barium hydroxide prepared by this treatment is a free flowing powder. Gravimetric analysis as barium sulfate corresponded to 99.5% barium hydroxide. Titration with standard hydrochloric acid indicated a barium hydroxide content of 99.3%. This hydroxide dissolved in water to an almost perfectly clear solution, showing that very little carbonate was present. From the nature of the cooling curve at the freezing point it was calculated that there was less than 0.3 mole per cent. of liquid soluble–solid insoluble impurity present. The solute materials were of ordinary C. P. quality.

Experimental Method.—A known weight, about 20 g., of barium hydroxide was fused in a nickel crucible 80 mm. high and 18 mm. diameter. The crucible fitted into a small electric furnace by means of which the rate of cooling could be regulated. Cooling curves were taken, the temperature being measured by means of a chromel–alumel thermocouple which was placed with no protection in the molten hydroxide. No corrosion or change in the temperature–e. m. f. characteristics of the couple was observed. Several cooling curves were taken with each sample, successive additions of weighed amounts of solute being added. The thermocouple was calibrated at the melting points of cadmium and zinc. Although the freezing points are recorded to tenths of a degree it is not contended that they are that accurate. Individual freezing points are probably not in error by more than 1°.

Results

The m. p. of barium hydroxide was found to be 408 ± 1°. With the solutes barium carbonate and barium bromide the eutectic halt was detected with the smallest solute concentration used. For this reason it was concluded that the solid phase was pure barium hydroxide. With barium carbonate the eutectic temperature was 374° and the composition 89 mole % barium hydroxide, with barium bromide 345° and 88 mole %.

When sodium hydroxide is added to barium hydroxide the cooling curves show an initial break at temperatures which decrease with increased

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[1] Balarew, *Z. anorg. allgem. Chem.*, **134**, 121 (1924).

[2] Hedvall and Heinberger, *ibid.*, **140**, 250 (1924).

[3] Lewis and Randall, "Thermodynamics," McGraw-Hill, New York, N. Y., 1923, p. 219.

[4] Goodwin and Kalmus, *Phys. Rev.*, **28**, 19 (1909).

sodium hydroxide content, and a second break at about 309° for concentrations of sodium hydroxide up to 33%. On further addition of sodium hydroxide the initial break occurs at lower temperatures and a new halt appears at 280°. The halt at 309° cannot, therefore, be a eutectic. However, this behavior is consistent with the formation of a compound which is decomposed at 309° with the solid phase above this temperature being barium hydroxide.

In the case of barium chloride solid solutions are formed and the eutectic halt could not be detected with the first two additions of solute. To obtain the composition of the solid phase in this case the time of eutectic halt was plotted against composition, extrapolation to zero time indicating a composition of 92 mole % barium hydroxide for the composition of the solid phase at the eutectic temperature 344°. On a temperature–composition plot a straight line was drawn from this point to the freezing point of pure barium hydroxide and the solid phase compositions read off this line at the freezing points of the solutions. Since this procedure is probably not very reliable due to the difficulty of maintaining equilibrium with a solid of changing composition, the results with barium chloride are included only because this treatment brings them into agreement with the effects of barium bromide.

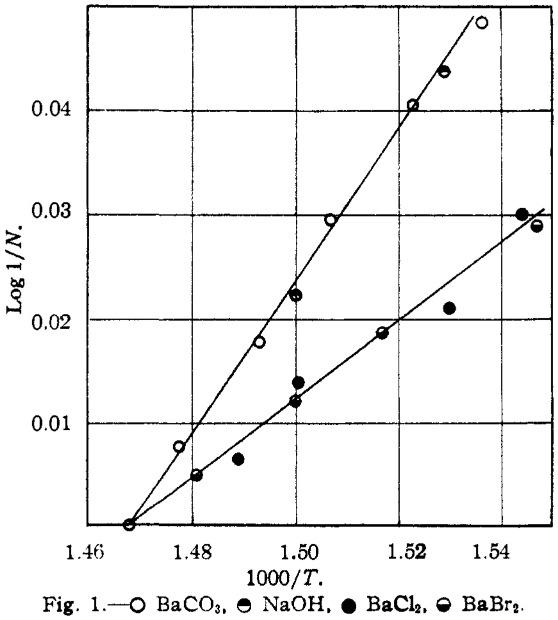

Fig. 1.—○ $BaCO_3$, ◓ NaOH, ● $BaCl_2$, ⊖ $BaBr_2$.

The observed freezing points of the solutions are shown in Table I where t designates the temperature in °C. at which a liquid of N mole fraction barium hydroxide is in equilibrium with solid barium hydroxide or, with barium chloride as the solute, in equilibrium with a solid of N' mole fraction barium hydroxide.

TABLE I

FREEZING POINTS OF SOLUTIONS

	Solute barium carbonate					
t	408.0	403.7	397.6	390.3	383.3	377.7
N	1.000	0.982	0.960	0.934	0.911	0.894
	Solute sodium hydroxide					
t	393.8	380.8	370.0	327.0		
N	0.950	0.904	0.842	0.730		
	Solute barium chloride					
t	399.7	391.0	380.4	374.8	365.3	354.7
N	0.972	0.946	0.917	0.894	0.862	0.833
N'	0.988	0.978	0.965	0.958	0.946	0.933
	Solute barium bromide					
t	401.9	393.7	386.2	373.3		
N	0.988	0.972	0.958	0.935		

To calculate the heat of fusion the conventional plot of log $1/N$ (log N'/N for barium chloride as solute[5]) against $1/T$ was made as shown in Fig. 1. The figure shows that points for the solutes barium carbonate and sodium hydroxide lie close to a straight line having a slope of 743 while for the solutes barium bromide and barium chloride the points are close to a line with a slope slightly more than half as great. On multiplying the slope 743 by $2.3R$, a value of 3400 ± 100 cal. per mole is obtained for the heat of fusion.

The behavior observed with these solutions is, within the limits of experimental error, in agreement with that expected for complete dissociation to ions whose activities are proportional to their mole fraction. The behavior of solutions of barium carbonate and sodium hydroxide in barium hydroxide should be essentially the same whether dissociated or not, since d ln $a_{Ba(OH)_2}$ differs but little from d ln $N_{Ba(OH)_2}$ in the concentration range covered. Such is not the case with barium bromide and chloride, however. In one mole of a mixture of barium hydroxide and barium bromide of mole fraction N in barium hydroxide, complete dissociation yields 1 mole Ba^{++}, $2N$ moles OH^- and $2(1 - N)$ moles Br^-. The total is 3, the mole fraction of Ba^{++} is $^1/_3$ and the mole fraction of OH^- is $2N/3$. If the ion activities are assumed equal to their mole fractions

$$a_{Ba(OH)_2} = a_{Ba^{++}} a^2_{OH^-} = 4/27\ N^2 \tag{1}$$

and[6]

$$\frac{d \ln a_{Ba(OH)_2}}{d(1/T)} = \frac{2\ d \ln N}{(d\ (1/T))} = \frac{-\Delta H_f}{R} \tag{2}$$

If ΔH_f does not vary appreciably over the temperature range, a straight line results when log $1/N$ is plotted against $1/T$. $\Delta H_f/2.3\ R$ is then equal to twice the slope of this line. This treatment brings the results for all four solutes into agreement. It is clear that a heat of fusion calculated as above is dependent on an assumption as to the molecular species present. The value chosen is that which seems most consistent with the experimental data. Whether it is cor-

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(5) Kelly, U. S. Bureau of Mines, Bulletin 393 (1936).

(6) Ref. 3, p. 282.

rect can be established only by calorimetric measurement. It should be noted that Hildebrand and Ruhle[7] mention that W. C. Bray has suggested an alternative to complete dissociation which would equally well explain the observed effects.

Summary

The melting points of barium hydroxide and of solutions of barium carbonate, barium chloride, barium bromide and sodium hydroxide in fused barium hydroxide have been measured by the cooling curve method.

The observed m. p. of barium hydroxide was 408 ± 1°, and its heat of fusion calculated as 3400 ± 100 cal. per mole.

The observed freezing point lowerings are consistent with complete dissociation with ion activities proportional to their mole fractions.

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[7] Hildebrand and Ruhle, THIS JOURNAL, 49, 728 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

An Equation for the Conductance of Colloidal Electrolytes in the Region of the Minimum

BY EMANUEL GONICK

The equivalent conductivity curves of uni-univalent colloidal electrolytes typically pass through three regions: (1) the very dilute region in which the conductivity decreases with increasing concentration at a rate similar to that of ordinary strong uni-univalent electrolytes, (2) a region at intermediate concentration in which the conductivity drops abruptly, as the simple ions aggregate to colloidal particles, and (3) a region in which the conductivity definitely increases with concentration. It is with the portion of the conductivity curve about the minimum between regions (2) and (3) that this paper is concerned.

This minimum suggests a relation of the form: $\Lambda = A/f(\mathrm{C}) + Bg(\mathrm{C})$, where A and B are constants and $f(\mathrm{C})$ and $g(\mathrm{C})$ represent functions of concentration. It is now found, in fact, that nearly all colloidal electrolytes for which data are available obey the equation

$$\Lambda = A/\sqrt{C} + B\sqrt{C} \qquad (1)$$

in the region under discussion. The only exceptions so far found are the long chain substituted ammonium acetates (Fig. 2).

Multiplication of equation (1) by $\sqrt{C}$ gives

$$\Lambda\sqrt{C} = A + BC \qquad (2)$$

A plot of $\Lambda\sqrt{C}$ *vs.* C should be linear with slope B and intercept A, if equation (1) holds. Figure 1 shows such plots for a number of sodium and potassium salts. Figure 2 shows similar plots for several long-chain substituted ammonium chlorides. Undecyl, lauryl, and myristyl sulfonic acids at 25° are shown in Fig. 3. Some of the conductivities published for these acids appear to be definitely in error, as they cannot be fitted to the same conductivity *vs.* concentration curve with the other data. These points have been designated by ● on Fig. 3, but have been ignored in drawing the curves. The short bars drawn across the plots at right angles indicate the concentration, $C_{\mathrm{min.}}$, at which the conductivity minimum occurs. It should be emphasized that equation (1) applies only to the concentration range about the minimum, where the colloidal

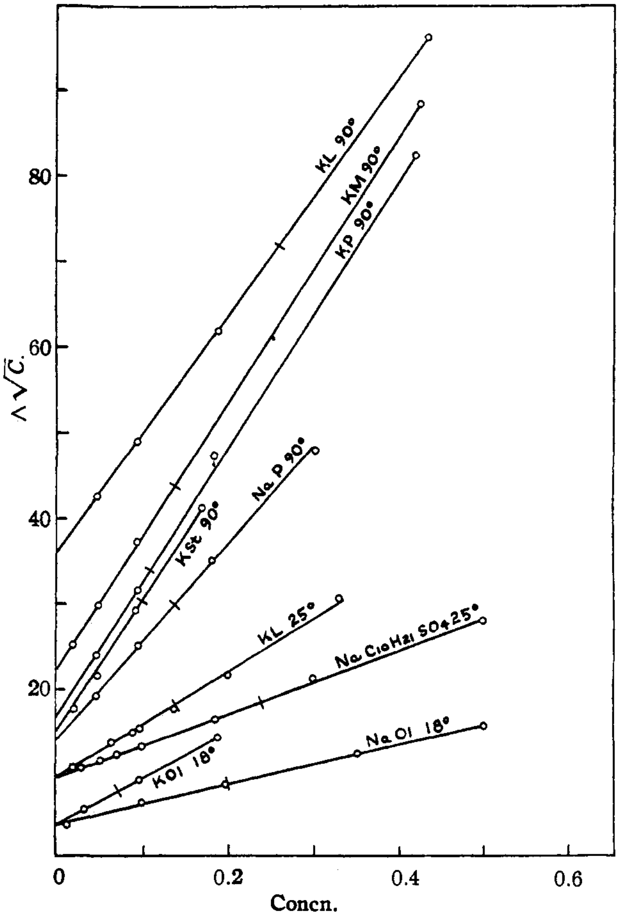

Fig. 1.—Plot of equation (2) for sodium and potassium salts of long-chain fatty acids.