[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Adsorption of Barium Salts on Barium Sulfate from Solutions in 50% Ethanol

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In work previously reported in this Journal,[1] it was mentioned that a considerable adsorption of barium nitrate on barium sulfate was found from a medium containing approximately 50 volume per cent. ethanol, whereas the adsorption from aqueous medium was negligibly small. This medium effect upon the adsorption of electrolytes on ionic lattices has not been studied in the literature. The results of the investigation described in this paper constitute a first approach to the problem. Moreover, they allow us to test the quantitative relation between the adsorption of potential determining ions and the concentration of the latter under equilibrium conditions, and the relation between adsorbability and solubility (Paneth-Fajans rule).

Materials Used

Barium Sulfate.—The preliminary experiments were carried out with a fine product of barium sulfate used in previous work,[1a] the average particle size of which was about 0.14 micron. A large amount of a product prepared in a similar way was used in the determination of the adsorption isotherm of various barium salts.

Solvent.—A mixture of equal volumes of 95% undenatured ethanol and conductivity water was used as a solvent, and designated as 50% ethanol, although the alcohol content is slightly less.

Barium Nitrate.—A C. P. product was twice recrystallized from water, dried at 110° and stored over anhydrous calcium chloride.

Barium Chloride and Barium Bromate.—C. P. products were twice recrystallized from water, dehydrated and rehydrated over deliquescent sodium bromide. They were weighed as dihydrate and monohydrate, respectively, and dehydrated at 150° before dissolving in 50% ethanol. In the solubility experiments the anhydrous salts were used.

Barium Perchlorate.—This salt was prepared by neutralizing barium hydroxide with perchloric acid, and recrystallizing the salt from water. The monohydrate was dried at 150° before dissolving in 50% ethanol. In the solubility experiments Baker's "Dessicchlora" was used.

Barium Iodide.—A C.P. product was used without further purification.

Barium Bromide and Barium Thiocyanate.—C. P. products were recrystallized three times from water and dried over fused sodium hydroxide.

Barium Formate.—This salt was prepared by neutralizing formic acid with barium hydroxide. The product was recrystallized three times and dehydrated over fused sodium hydroxide.

Calcium Bromate.—To a suspension of barium bromate in water an equivalent amount of sulfuric acid was added and the mixture shaken until the transformation was complete (seventy-two hours). After shaking for five more days the barium sulfate was filtered off and the bromic acid in the filtrate neutralized with a calcium hydroxide suspension. The crystals separating out upon evaporation showed pronounced triboluminescence, either when dry or suspended in the mother liquor. The salt was recrystallized three times from water and dried at 120°

Potassium Bromate.—A C. P. product was used.

Analytical.—The *barium* concentration was determined before and after adsorption by evaporating measured portions to a small volume and adding an excess of 0.1 molar potassium chromate to the hot solutions. The mixture was made alkaline with ammonia, digested for an hour and cooled. The barium chromate was filtered, washed, dissolved in 6 *N* hydrochloric acid and the chromate determined iodometrically after diluting with water.

Bromate was determined iodometrically. In order to get accurate results it was necessary to remove the alcohol by evaporation. The solution was made slightly alkaline with sodium hydroxide to prevent reduction of bromate by the alcohol and evaporated to dryness. The residue was taken up in water and the bromate determined iodometrically by the standard procedure.

Nitrate was determined by reduction to ammonia with Devarda's alloy.[2] The ammonia was distilled into an excess of dilute hydrochloric acid and determined iodometrically by the hypochlorite-bromide method.[3] Calcium was determined after removal of the alcohol by precipitation as calcium oxalate and titrating the precipitate with permanganate.

Experimental Results

Solubility Determinations in 50% Ethanol

An excess of the anhydrous salt was shaken at room temperature (25 ± 1°) in the 50% ethanol for forty-eight hours. The solution was filtered and 25 ml. of the filtrate evaporated in a weighed platinum dish. The residue was weighed after drying to constant weight at 150°. The results are given in Table I.

TABLE I

SOLUBILITY OF BARIUM SALTS IN 50% ETHANOL

Barium salt	Bromate	Nitrate	Formate	Chloride
Solubility in mols per liter	1.72×10^{-3}	5.71×10^{-2}	0.14	0.384
	Bromide	Iodide	Perchlorate	Thiocyanate
Solubility in mols per liter	1.46	2.53	2.77	2.89

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(1) I. M. Kolthoff and Wm. M. MacNevin (a) THIS JOURNAL, **58**, 499 (1936); (b) **58**, 725 (1936).

(2) *Cf.* W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., 1929, p. 639.

(3) I. M. Kolthoff and V. A. Stenger, *Ind. Eng. Chem., Anal. Ed.*, **7**, 79 (1935).

The solubility of potassium bromate was found to be 0.051 molar and that of calcium bromate 1.05 molar.

Adsorption Experiments

Experiments were made in which samples of barium sulfate were shaken for half an hour, one hour and twenty-four hours with solutions of the barium salts in 50% ethanol. It was found that after a period of one hour of shaking the amount of salt adsorbed remained constant. A shaking period of one hour was adopted in the final experiments. Working with the fine product of barium sulfate used in previous work[1] it was ascertained first that an equivalent adsorption of barium ions and anions occurred. Experiments were carried out with barium nitrate and bromate at various concentrations and the amounts of barium and anion adsorbed determined separately (for details see doctor's thesis of junior author). Within the experimental error an equivalent adsorption of barium and anion was found. Thus, after shaking 0.6 g. of barium sulfate with 50 ml. of 0.0002 molar barium bromate in 50% ethanol, 24.8% of barium and 24.0% of bromate were found to be adsorbed. In the case of barium nitrate 28.0 (±1)% of nitrate and 26.6(±1)% of barium were found to be adsorbed from the 0.0002 molar solution. From the 0.001 molar solution 13.0% of nitrate and 12.4% of barium had disappeared.

The determination of the amount of salt adsorbed was attempted in a direct way by making use of the washing process described and applied by Miss de Brouckère.[4] This method did not yield useful results in our hands. After shaking, the suspensions were centrifuged, the supernatant liquid decanted and the precipitate shaken for one minute with 10 ml. of a saturated solution of barium sulfate in 50% ethanol. The mixture was centrifuged and the process repeated. After three such washings, 88% of the total amount of barium bromate originally adsorbed in a certain case was removed from the surface.

After the above results were obtained, it was decided to determine the amounts adsorbed in the following way. A given amount of the new sample of finely divided barium sulfate was shaken with 50 ml. of the barium salt solution in 50% ethanol for one hour, the suspension centrifuged and the barium or anion concentration determined in 25 ml. of the clear centrifugate.

The results are given in the following tables. It was found that within the range of concentrations studied, the adsorption was given quantitatively by the expression

$$x/m = ac^{1/n} \qquad (1)$$

in which x is the amount adsorbed expressed in moles, m the amount of adsorbent used in grams, c the final concentration in the solution, and a and $1/n$ constants.[5] The values of the latter, computed from the experimental results, and the values of x/m calculated with the aid of the above equation are reported in the tables.

Table II

Adsorption of Barium Bromate

1 g. of $BaSO_4$; 50 ml. of solution; BrO_3^- determined; $a = 1.80 \times 10^{-4}$; $1/n = 0.40$

Init. concen., molar × 10^3	Final concen., molar × 10^3	Absorbed in, %	$x \times 10^5$ Found	$x \times 10^5$ Calcd.
1.527	1.287	15.7	1.20	1.26
1.000	0.795	20.5	1.02	1.04
0.500	.348	30.4	0.76	0.76
.250	.146	41.7	.52	.52
.100	.039	61.2	.31	.32

Table III

Adsorption of Barium Nitrate

5 g. of $BaSO_4$; 50 ml. of solution; Ba determined; $a = 0.69 \times 10^{-4}$; $1/n = 0.32$

Init. concn., molar × 10^3	9.48	3.79	1.90	0.948[a]
Final concn., molar × 10^3	8.01	2.74	1.14	.68
Adsorbed in %	15.4	27.8	40.0	28.3
$x/m \times 10^5$ found	1.46	1.05	0.76	0.67
$x/m \times 10^5$ calcd.	1.50	1.12	.79	.68

[a] Barium sulfate used, 2 g.

The adsorption of barium nitrate increases upon addition of alkali nitrate to the solution. The first experiment in Table III was repeated, the solution also containing 0.1 mole of sodium nitrate per liter. In the latter case 21.6% of the barium nitrate was adsorbed, as compared with 15.4% in the absence of sodium nitrate.

Table IV

Adsorption of Barium Perchlorate

10 g. of $BaSO_4$; 50 ml. of solution; Ba determined; $a = 0.59 \times 10^{-4}$; $1/n = 0.40$

Init. concn., molar × 10^3	9.77	4.89	0.98[a]
Final concn., molar × 10^3	8.04	3.67	.65
Adsorbed in %	17.7	25.0	33.6
$x/m \times 10^5$ found	0.86	0.61	0.33
$x/m \times 10^5$ calcd.	.85	.63	.31

[a] Barium sulfate used, 2 g.

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[4] L. de Brouckère, *Ann. chim.*, [X] **19**, 92 (1933).

[5] In some preliminary work, P. P. von Weimarn, *Repts. Imp. Ind. Research Institute*, Osaka, Japan, **12**, 153 (1931), arrived at a similar conclusion.

TABLE V

ADSORPTION OF BARIUM CHLORIDE

5 g. of $BaSO_4$; 50 ml. of solution; Ba determined; $a = 0.54 \times 10^{-4}$; $1/n = 0.38$

Init. concn., molar $\times 10^3$	10.1	5.05	1.01	0.505
Final concn., molar $\times 10^3$	9.25	4.39	0.678	.260
Adsorbed in %	8.4	13.0	33.4	48.5
$x/m \times 10^5$ found	0.85	0.66	0.34	0.24
$x/m \times 10^5$ calcd.	.91	.68	.34	.23

The adsorption of the other salts was determined at one concentration only. The results are found in Table VI.

TABLE VI

ADSORPTION OF VARIOUS BARIUM SALTS

50 ml. of solution

$BaSO_4$, g.	10	10	10	2
Ba salt adsorbed	Bromide	Iodide	Thiocyanate	Formate
Init. concn., molar $\times 10^3$	1	1	1	1
Final concn., molar $\times 10^3$	0.52	0.54	0.63	0.73
Adsorbed in %	48.0	45.9	36.8	27.0
$x/m \times 10^5$	0.24	0.23	0.18	0.67

Discussion

1. One of the most interesting results of this study is that the Freundlich adsorption isotherm, was found to hold for the adsorption of barium salts on barium sulfate from a medium of 50% ethanol. One certainly would expect to be dealing here with the adsorption of a "potential determining ion,"[6] in which case it is claimed[7] that the relation between the amount adsorbed x and the concentration c is given by an expression

$$\Delta x = k \Delta \log c \qquad (2)$$

and not by the expression

$$\log x = k \Delta \log c \qquad (3)$$

The only experimental proof of the validity of expression (2) has been found in the case of silver iodide[8] where the adsorption of silver and of iodide apparently occurs on the active surface. In our study we worked with well-aged barium sulfate. Although in none of the cases investigated (Tables II–VI) a saturated surface corresponding to a monomolecular layer of adsorbed barium salt was obtained, it is quite evident that in the present study we are mainly dealing with an adsorption on the normal surface and not on active surface. In the derivation of expression (2) assumptions have been made which, theoretically, are not entirely justified. On the basis of the present study it becomes doubtful whether equation (2) holds generally for the adsorption of potential determining ions. That the barium ions actually behave as potential determining ions is evidenced by their peptizing effect upon the barium sulfate. When the solid (average diameter about 0.14 micron) is shaken with aqueous solutions of barium nitrate or other barium salts a clear centrifugate is obtained readily. In 50% ethanol solutions of barium salts, it is difficult to obtain a clear centrifugate after shaking with barium sulfate. As much as two hours of centrifuging at 3000 r. p. m. was required to obtain a clear supernatant liquid. A maximum peptizing effect was found at a certain concentration of the barium salt, in the case of barium bromate in 0.002 molar solutions.

There is a possibility that only a small fraction of the adsorbed barium acts as potential determining ion and that we are dealing mainly with a "true adsorption" on the entire surface comparable to the adsorption of salts having no ion in common with the lattice, for which expression (3) holds within wide limits of concentration.[7b] Actually it was found that salts such as potassium bromate and calcium bromate from solutions in 50% ethanol gave a pronounced adsorption on barium sulfate. Upon shaking 10 g. of barium sulfate with 50 ml. of 0.002 molar potassium bromate, 15.7% of the salt was found to be adsorbed, corresponding to 1.6×10^{-6} mol per g. of barium sulfate. Equivalent amounts of cation and anion were adsorbed. The adsorption of calcium bromate was measured at different concentrations by determining the bromate content before and after adsorption. The results are given in Table VII; it is seen that the percentage of bromate adsorbed changes in an irregular way with the concentration. In order to decide whether an equivalent adsorption of calcium and bromate occurred, it was decided to determine the amount of calcium adsorbed from the 0.001 molar solution (first solution in Table VII). It was found that 45.7% of the calcium was adsorbed, which is just double the amount of bromate adsorbed (23.6%). This result indicates that a hydrolytic adsorption has taken place and that the salt is adsorbed in the form of $Ca(OH)(BrO_3)$. In agreement with this conclusion it was found that the supernatant liquid after the adsorption

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(6) E. Lange and R. Berger, *Z. Elektrochem.*, **36**, 171 (1930).

(7) (a) M. Andauer and E. Lange, *Z. physik. Chem.*, **A156**, 241 (1931); (b) E. J. W. Verwey, *Chem. Rev.*, **16**, 363 (1935).

(8) E. Lange and R. Berger, *Z. Elektrochem.*, **36**, 171, 980 (1930); E. J. W. Verwey and H. R. Kruyt, *Z. physik. Chem.*, **A167**, 149 (1933); I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **58**, 1528 (1936).

showed a strongly acid reaction. The hydrolytic adsorption accounts for the irregular change of the bromate adsorption at different salt concentrations as it will be a function of the *p*H of the solution in equilibrium with the solid.

TABLE VII

ADSORPTION OF BROMATE FROM CALCIUM BROMATE

10 g. of $BaSO_4$; 50 ml. of solution

Init. concn., molar × 10^3	1	0.5	0.4	0.2
Final concn., molar × 10^3	0.764	0.358	0.303	0.169
Adsorbed BrO_3^- in %	23.6	28.4	24.3	15.5
$x/m \times 10^5$	0.12	0.071	0.049	0.015

2. In Table VIII the relation is given between adsorbability from and solubility of the barium salts in 50% ethanol. The value of the constant *a* in the expression for the adsorption isotherm (equation 1) is taken as a measure of the adsorbability. From the experimental data, *a* and $1/n$ were calculated for four barium salts, an average value of 0.38 for $1/n$ being found. For the other barium salts, the adsorption of which was determined at one concentration only, the value of $1/n$ equal to 0.38 was used in the calculation of the "*a*" values.

TABLE VIII

SOLUBILITY AND ADSORBABILITY

	Barium salt	Order of absorbability expressed in $a \times 10^4$	Relative solubility in 50% ethanol	Order of increasing solubility
1	Bromate	1.80	1	1
2	Formate	0.91	81	3
3	Nitrate	.69	33	2
4	Perchlorate	.59	1610	7
5	Chloride	.54	223	4
6	Bromide	.37	848	5
7	Iodide	.35	1477	6
8	Thiocyanate	.26	1663	8

It is seen that there is no close parallelism between adsorbability and solubility.[9] Barium formate is adsorbed more strongly than the nitrate, although the latter is much less soluble. Particularly the perchlorate is out of place. Its adsorbability is of the same order as that of the chloride and much greater than that of the bromide or iodide, although its solubility in 50% ethanol is greater than that of the halides.

Summary

1. The adsorption of barium salts on barium sulfate and of salts not having an ion in common with the lattice is much greater from 50% ethanol than from water.

2. Contrary to the expectation, the adsorption of barium salts from 50% ethanol on barium sulfate follows the Freundlich adsorption isotherm.

3. No close parallelism has been found between adsorbability and solubility.

4. Potassium bromate gives an equivalent adsorption of cations and anions. Calcium bromate yields a hydrolytic adsorption and was found to be adsorbed in the form of $Ca(OH)(BrO_3)$.

[9] For a similar conclusion on the adsorption of silver salts on silver iodide compare the study of J. S. Beekley and H. S. Taylor, *J. Phys. Chem.*, **29**, 942 (1925).

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The Primary and Secondary Dissociation Constants of Malonic, Succinic and Glutaric Acids by Potentiometric Titration

BY WILLIAM L. GERMAN AND ARTHUR I. VOGEL

The primary thermodynamic dissociation constants at 25° of malonic, succinic and glutaric acids have been determined by conductivity methods by Jeffery and one of us[1] but it has not yet been found possible to calculate the true secondary dissociation constants satisfactorily from conductivity data alone. Attention was therefore directed to the potentiometric method for the simultaneous evaluation of both constants. Previous electrometric titrations for these three acids have been carried out by Britton[2] at 18°, Gane and Ingold[3] at 25° for malonic acid; by Bjerrum[4] at 18°, Auerbach and Smolczyk[5] at 20°, Britton[2] at 18°, Kolthoff and Bosch[6] at 18°, Gane and Ingold[3] at 25°, Ashton and Partington[7] at 25° for succinic acid; and by Gane and Ingold[3] at 25°

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[1] Jeffery and Vogel, *J. Chem. Soc.*, **21** (1935).

[2] Britton, *ibid.*, **127**, 1906 (1925).

[3] Gane and Ingold, (a) *ibid.*, 1594 (1928); (b) 2158 (1931).

[4] Bjerrum, *Z. physik. Chem.*, **106**, 227 (1923); *cf.* Larsson, *Z. anorg. allgem. Chem.*, **125**, 291 (1925).

[5] Auerbach and Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924).

[6] Kolthoff and Bosch, *Rec. trav. chim.*, **47**, 861 (1928).

[7] Ashton and Partington, *Trans. Faraday Soc.*, **30**, 598 (1934).