there was obtained 0.228 g. (47% yield) of pale yellow crystals, m.p. 88–92°. Recrystallization from a small amount of methanol gave small colorless prisms, m.p. 91.5–92.5° (reported[10], 94°), undepressed on admixture with authentic N-acetyl-4-keto-1,2,3,4-tetrahydroquinoline prepared from the free quinolone.[11]

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[10] G. R. Clemo and H. J. Johnson, *J. Chem. Soc.*, 2133 (1930).

[11] W. S. Johnson, E. L. Woroch and B. G. Buell, THIS JOURNAL, **71**, 1901 (1949).

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The Solubility of Lead Chloride in Sodium Chloride, Perchloric Acid and Hydrochloric Acid Solutions[1]

BY S. Z. LEWIN, JOHN E. VANCE AND LAWRENCE B. NELSON

RECEIVED FEBRUARY 13, 1953

In connection with an investigation of the crystal growth of lead chloride, measurements were made of the solubility of that compound at 25° in the media listed in Table I.

TABLE I

SOLUBILITIES OF $PbCl_2$ AT 25°

Medium (conc. in molality)	G. $PbCl_2$ per 1000 g. H_2O	Standard deviation	Lit. values (interpolated)
0.4723 *m* NaCl	1.870	0.008	1.87[a]
1.0125 *m* NaCl	1.784	.008	1.74[a]
2.0265 *m* NaCl	2.743	.010	2.72[a]
4.0216 *m* NaCl	8.367	.014	8.55[a]
0.5375 *m* HCl	1.561	.007	(3.68 g. at 0.50 *m*)[g]
0.5487 *m* $HClO_4$	10.88	.04	
1.0368 *m* $HClO_4$	10.56	.05	
2.3239 *m* $HClO_4$	7.421	.025	
3.4565 *m* $HClO_4$	5.183	.013	
6.4730 *m* $HClO_4$	1.781	.005	
Water	....	...	10.87[a], 10.84[b], 10.86[c], 10.75[d], 10.91[e], 10.76[f], 11.03[g], 10.84[h]

[a] G. E. R. Deacon, *J. Chem. Soc.*, 2063 (1927). [b] L. J. Burrage, *ibid.*, 1703 (1926). [c] W. R. Carmody, THIS JOURNAL, **51**, 2909 (1929). [d] T. P. Goulden and L. M. Hill, *J. Chem. Soc.*, 447 (1945). [e] L. Wilkinson, N. O. Bathhurst and H. N. Parton, *Trans. Faraday Soc.*, **33**, 623 (1937). [f] F. Flöttman, *Z. anal. Chem.*, **73**, 1 (1938). [g] H. E. Armstrong and J. V. Eyre, *Proc. Roy. Soc.* (*London*), **A88**, 238 (1913). [h] P. M. Lichty, THIS JOURNAL, **25**, 469 (1903).

Sealed glass tubes containing solution and excess solid $PbCl_2$ were heated to about 100° for several hours, then placed into a thermostat and rotated at 25.00 ± 0.05° for at least 24 hours, after which samples were removed for analysis by suction through a plug of glass wool.

The concentration of acid was determined in each case by titration with standard NaOH to the brom cresol green end-point. Two procedures were used for the determination of lead chloride; (1) triple evaporation with sulfuric acid, followed by dilution with water and the usual gravimetric procedure with filtration on Selas crucibles, and (2) neutralization to the methyl orange end-point with ammonia, precipitation in hot solution with hydrogen sulfide, followed by solution of the precipitate in nitric acid and conversion to lead sulfate as before. Both procedures were followed in the case of the sodium chloride and hydrochloric acid solutions, and gave concordant results; only procedure (2) was used for the solutions containing perchloric acid. The concentration of sodium chloride was found as the difference between total chloride as obtained by the Volhard titration[2] and the amount of chloride as lead chloride calculated from the gravimetric determination of lead.

Demassieux[3] and Deacon[4] have reported that no double salts are formed between NaCl and $PbCl_2$, whereas Kendall and Sloan[5] offered analytical evidence that the solid phase in equilibrium with NaCl solutions of $PbCl_2$ is $NaCl{\cdot}2PbCl_2$ for all concentrations in excess of 0.5 *N* NaCl. The solid phases in equilibrium with the 1, 2 and 4 *m* NaCl solutions of Table I were analyzed for lead according to procedure (1) above. The solid was removed from the liquid phase by filtration, and dried by pressing between filter papers without washing. The analytical results are given in Table II.

TABLE II

ANALYSES OF SOLID SAMPLES

Source of sample	$PbCl_2$, %
Mallinckrodt A.R. $PbCl_2$	100.16, 99.84, 99.96
1 *m* NaCl	98.36, 99.17
2 *m* NaCl	99.16, 98.05
4 *m* NaCl	98.13, 99.21

The analyses of the samples from the NaCl solutions are low as a result of contamination by NaCl, but the data clearly support the conclusion that no double salts form between NaCl and $PbCl_2$ for solutions up to 4 *m* in NaCl under the conditions of our experiments.

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[1] This work was supported in part under Contract No. AT (30-1)-1256 between the Atomic Energy Commission and New York University.

[2] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 546, procedure 2.

[3] N. Demassieux, *Ann. chim.*, **20**, 267 (1923).

[4] G. E. R. Deacon, footnote *a* of Table I.

[5] J. Kendall and C. H. Sloan, THIS JOURNAL, **47**, 2306 (1925).

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Anion-exchange Studies. VII.[1,2] Separation of Sulfuric Acid from Metal Sulfates by Anion Exchange

BY KURT A. KRAUS, FREDERICK NELSON AND JOHN F. BAXTER[3]

RECEIVED JANUARY 2, 1953

A strong base anion-exchange resin in the sulfate form (or in combination with other polyvalent anions) might be considered a base which can react with (adsorb) acids according to reactions of the type

$$(SO_4^{=})_r + HX \rightleftharpoons (HSO_4^{-})_r + (X^{-})_r \qquad (1)$$

where subscript r stands for resin. In the case of the adsorption of sulfuric acid by a sulfate resin equation (1) becomes

$$(SO_4^{=})_r + H_3O^+ + HSO_4^- \rightleftharpoons 2(HSO_4^-)_r + H_2O \qquad (2a)$$

and

$$(SO_4^{=})_r + 2H_3O^+ + SO_4^{=} \rightleftharpoons 2(HSO_4^-)_r + 2H_2O \qquad (2b)$$

The fact that such acid adsorption, possibly according to equations (1) and (2), actually takes place can readily be demonstrated by passing sulfuric acid solutions through sulfate columns, and noting that a considerable volume of effluent is free of acid.

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper, K. A. Kraus and G. E. Moore, THIS JOURNAL, **75**, 1460 (1953).

[3] Summer Participant (1951) at Oak Ridge National Laboratory.

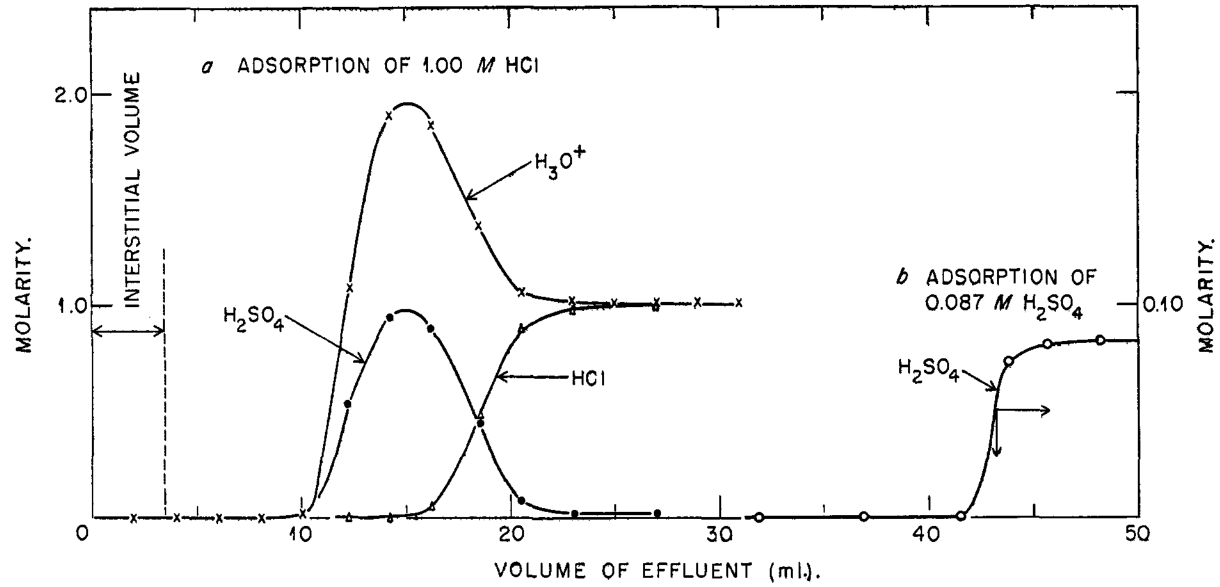

Fig. 1.—Adsorption of HCl and H_2SO_4 by Dowex-1-sulfate (0.488 cm.² × 16.9 cm. column).

For example, 13 cc. of a 0.496 *M* and 42 cc. of a 0.082 *M* H_2SO_4 solution could be passed through 0.488 cm.² × 14.5 and 17.0 cm. columns of the quaternary amine polystyrene–divinyl benzene resin Dowex-1 in the sulfate form, before the *p*H of the effluent dropped below 4 (see also Fig. 1).

Other acids (*e.g.*, HCl, $HClO_4$) have been similarly adsorbed by the sulfate form of the resin. The adsorption of HCl is typical of the behavior of strong acids and the results are shown in Fig. 1. A 1 *M* HCl solution was passed into a column of Dowex-1 in the sulfate form. The effluent initially had a $pH > 4$. Its acidity reached a maximum of *ca.* 2 *M* H_3O^+ and then decreased to 1 *M* H_3O^+. The increase in the acidity of the effluent over that of the eluent apparently is due to the fact that sulfuric acid is first eluted and that chloride ions substitute for acid sulfate (HSO_4) ions. The bulk of the sulfuric acid portion of the effluent was relatively free of chloride ions as also shown in Fig. 1.

This adsorption of sulfuric acid by a strong base exchanger implies that these resins can be used to separate sulfuric acid from non-adsorbable or weakly adsorbable metal sulfates. This separation is demonstrated below using a mixture of copper sulfate and sulfuric acid.

One-ml. portions of copper sulfate in sulfuric acid were placed on a 0.187 cm.² × 9.3 cm. column (bed volume 1.74 cc.) filled with (well-washed) Dowex-1 in the sulfate form. The column was then eluted with distilled water. Approximately 1-ml. fractions of the effluent were collected and tested for copper and sulfuric acid. The copper concentration was determined spectrophotometrically after making aliquots 0.5 *M* in NH_3. The sulfuric acid concentration was determined either by *p*H measurements combined with a calibration curve or by titrations. The results of two experiments using 0.1 *M* $CuSO_4$–0.1 *M* H_2SO_4 and 0.1 *M* $CuSO_4$–0.5 *M* H_2SO_4 are shown in Fig. 2. Good separation of copper sulfate from the acid was obtained in both experiments with the copper containing effluent having a $pH > 4.5$.

The volume at which acid appears in the effluent depends on the amount of acid initially passed into the column (loading with respect to sulfuric acid) since in the water "elution" the acid will have to be moved through the remaining part of the sulfate column. In the experiment with 0.1 *M* H_2SO_4 acid appeared after *ca.* 8 column volumes of water while in the experiment with 0.5 *M* H_2SO_4 acid appeared after *ca.* 2 column volumes. In these experiments *ca.* 7.2 and 36%, respectively, of the adsorptive capacity of the column for H_2SO_4 were utilized (capacity 1.62 equivalents/1 bed).

Although the removal of sulfuric acid from the $CuSO_4$ solution was quite satisfactory the regeneration of the resin (removal of H_2SO_4 from the resin) using water only, rather than a stronger base, takes place slowly as also shown in Fig. 2. *Circa* 22 column volumes were necessary before the *p*H of the effluent rose to *ca.* 4.5.

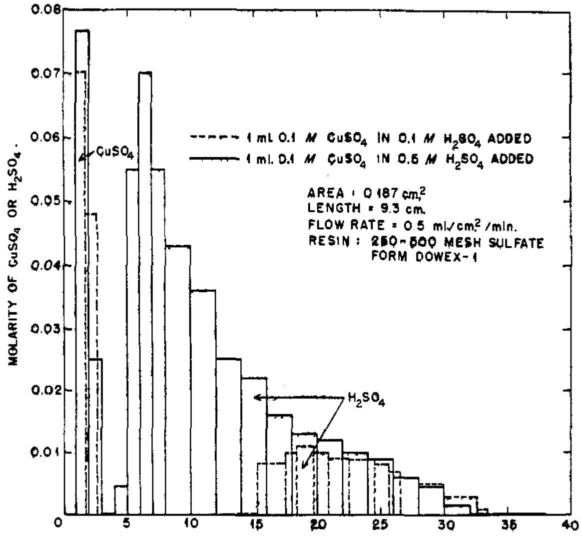

Fig. 2.—Anion exchange separation of $CuSO_4$ and H_2SO_4 by elution with water (25°).

In an attempt to increase the efficiency of the regeneration process an experiment was carried out at 60° since it was believed that slow rates of equilibration might be in part responsible for the trailing edge in the sulfuric acid elution. Operation at higher temperature not only does not improve the regeneration but actually the removal of H_2SO_4 takes more water (*ca.* 32 column volumes) than at lower temperature indicating that the tailing in the elution band is not due to slow rates of equilibration. It probably arises from a pronounced non-linearity of the adsorption isotherm. It is interesting to note that the copper band at 60° definitely showed some adsorption, the apparent elution constant E[4] being *ca.* 1 instead of the theoretical maximum *ca.* 2.5 when no adsorption takes place. At the lower temperature the copper band was less strongly adsorbed, but did not travel with elution constant as large as 2.5.

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[4] E has been defined (K. A. Kraus and G. E. Moore, THIS JOURNAL, **73**, 9 (1951), as the distance (cm.) a band moves under equilibrium conditions, per cc. of eluent in a 1-cm.^{2} column.

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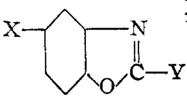
Preparation of Certain Derivatives of Benzoxazole

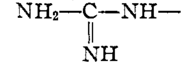
BY TOYOYUKI NAGANO, MOTOKO ITOH AND KONOMU MATSUMURA

RECEIVED DECEMBER 22, 1952

This note describes the preparation of several 2,5-disubstituted benzoxazoles, in the hope that they may be of therapeutic value.



X (5 position): Cl, HO_2C—, or BuO_2C—
Y (2 position): SH, OH, NH_2, or



$NH_2\text{—}C(\text{=}NH)\text{—}NH\text{—}$

Experimental

2-Benzeneazo-4-chlorophenol.—A modification of the method of Krause[1] was found to prevent the formation of tar. A solution of benzenediazonium chloride made from 0.1 mole (9.3 g.) of aniline was added at −3 to 0° with stirring over a period of two hours to a cold solution of 0.1 mole (12.9 g.) of *p*-chlorophenol, 4.0 g. of sodium hydroxide and 2.9 g. of sodium carbonate crystals in 100 ml. of 90% ethanol and 200 ml. of water. The stirring was maintained until there was no color reaction with alkaline β-naphthol, the solution then acidified with acetic acid, filtered, and the solid product (23 g. of orange yellow needles melting at 105–107°) washed with water. Recrystallization from 60% acetic acid gave orange prismatic needles melting at 110–111°.

2-Amino-4-chlorophenol.—To a stirred mixture of 4.64 g. of 2-benzeneazo-4-chlorophenol in 10 ml. of ethanol and 20 ml. of water was added 12.6 g. of sodium hydrosulfite during 15 minutes. Stirring was maintained until the mixture became colorless, and the ethanol was then removed on a water-bath. After standing overnight, the solution deposited 2.4 g. (83%) of colorless plates, melting at 138–140° with preliminary softening. Recrystallization from 50 ml. of hot water gave colorless rhombic plates melting at 140–141°. Popov[2] reported a melting point of 137–138°, and Korczynski and Obarski[3] a melting point of 185° for this product.

Anal. Calcd. for C_6H_6ClNO: N, 9.76. Found: N, 9.78.

The diacetyl derivative of 2-amino-4-chlorophenol gave colorless plates from benzene, melting at 173–175°. Korczynski and Obarski[3] reported a melting point of 201° for this derivative.

Anal. Calcd. for $C_{10}H_{10}ClNO_3$: N, 6.15. Found: N, 6.13.

The hydrochloride of 2-amino-4-chlorophenol gave colorless prisms from ethanol, melting at 258° with decomposition.

Butyl 4-Hydroxy-3-benzeneazobenzoate.—It has been found that the reaction of benzenediazonium chloride with 4-hydroxybenzoic acid gives only a small yield of 4-hydroxy-3-benzeneazobenzoic acid (the chief product being 2,4-bis-benzeneazophenol), but that substitution of the ethyl ester of the acid gives a good yield of ethyl 4-hydroxy-3-benzeneazobenzoate.[4] For this reason the butyl ester of 4-hydroxybenzoic acid was used in the present investigation.

A solution of benzenediazonium chloride made from 0.2 mole (18.6 g.) of aniline was added with stirring at −5 to −3° to a cold solution of 0.2 mole (38.8 g.) of butyl 4-hydroxybenzoate and 24 g. of sodium hydroxide in 400 ml. of water. After standing in the cold until there was no color reaction with alkaline β-naphthol, the solution was acidified with acetic acid, filtered and washed repeatedly with water. The product, crystallized from 100 ml. of 90% ethanol, weighed 46.0 g. (77%) and separated as orange yellow prisms (m.p. 75°), quite soluble in benzene and petroleum ether, and fairly soluble in warm ethanol and 80% hot acetic acid.

Anal. Calcd. for $C_{17}H_{18}N_2O_3$: N, 9.39. Found: N, 9.30.

The above coupling reaction also proceeds smoothly in sodium carbonate solution, although less rapidly than in sodium hydroxide.

Butyl 4-Hydroxy-3-aminobenzoate.—The reduction of butyl 4-hydroxy-3-benzeneazobenzoate, by the sodium hydrosulfite method outlined above, gave almost the theoretical yield of product melting at 72°. Recrystallization from glacial acetic acid gave colorless plates melting at 113°, but recrystallization from a chloroform–petroleum ether mixture gave colorless needles melting at 72°. Cavill[5] reported a melting point of 64–65° for this product.

Anal. (72°) Calcd. for $C_{11}H_{15}NO_3$: N, 6.70. Found: N, 6.69. *Anal.* (113°) Calcd. for $C_{11}H_{15}NO_3 \cdot C_2H_4O_2$: N, 5.20; $C_2H_4O_2$, 22.3. Found: N, 5.35, 5.10; $C_2H_4O_2$, 20.2 (titration).

Analysis indicated that crystallization from glacial acetic acid gives an acetate. Two recrystallizations of the acetate from chloroform–petroleum ether gave the substance melting at 72°.

The hydrochloride, prepared from the aminobenzoate and 10% hydrochloric acid, crystallized as colorless columns melting at 234° with decomposition.

4-Hydroxy-3-aminobenzoic acid was obtained by refluxing the ester with five times its weight of 20% hydrochloric acid for an hour. The acid separated as colorless rhombic plates melting at 202° with decomposition; the melting point is in agreement with that reported by Cavill,[5] and Auwers and Röhrig.[6] The hydrochloride of the free acid crystallized as colorless rhombic prisms melting at 250° with decomposition.

Hydrolysis of 5,5′-Dicarboxylic-dibenzoxazole-2,2′-disulfide.—A 400-mg. sample of the disulfide was dissolved in the calculated quantity of sodium carbonate solution, and the solution was immediately acidified with hydrochloric acid. Vigorous evolution of sulfur dioxide[7] (identified by odor and by a blue violet color with congo red paper) was followed by the separation of 300 mg. of solid melting at 265–271° with foaming. This material was separated into two fractions by recrystallization from 90% ethanol.

The more insoluble fraction, weighing 170 mg. and melting at 280° with foaming, separated as prismatic needles and was identified as 5-carboxylic-benzoxazole-2-thion by mixed melting point and analysis.

Anal. Calcd. for $C_8H_5NO_3S$: N, 7.18. Found: N, 7.55.

The more soluble fraction, weighing 110 mg. and melting at 248–249° with foaming, separated as prismatic needles

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[1] M. Krause, *Ber.*, **32**, 126 (1899).

[2] Popov, *Anilinokrasochnaya Prom.*, **3**, 391 (1933).

[3] Korczynski and Obarski, *Bull. soc. chim.*, [IV] **33**, 1823 (1923).

[4] Grandmougin and Freimann, *J. prakt. Chem.*, [2] **78**, 385 (1908).

[5] Cavill, *J. Soc. Chem. Ind.*, **64**, 212 (1945).

[6] K. Auwers and H. Röhrig, *Ber.*, **30**, 992 (1897).

[7] To our knowledge, the escape of sulfur dioxide has not heretofore been reported in similar reactions.