# Chloride–Sulfate Equilibria and Transport Processes in Benzidine–Formaldehyde and Other Anion-Permeable Membranes

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## Synopsis

Exchange equilibria, ohmic resistances, concentration and bi-ionic potentials, diffusion coefficients, and transport numbers were measured for the chloride–sulfate–oxalate system in anion-permeable membranes with quaternary ammonium and benzidine exchange sites. The benzidine membranes showed a greater selectivity for sulfate than chloride as compared with the quaternary ammonium membranes, but a lower transport number. These phenomena were interpreted in terms of an ion-binding mechanism. Fair agreement was observed between measured transport numbers and those calculated from selectivity coefficients, diffusion coefficients, and equivalent conductances.

This contribution describes the preparation and electrochemical properties of a heterogeneous anion-permeable membrane containing a benzidine-formaldehyde condensate. This membrane and others available commercially were characterized by their anion-exchange equilibria, ohmic resistances, concentration and bi-ionic potentials, exchange-diffusion coefficients, and transport numbers, all measured by using the chloride-oxalate–sulfate system. Benzidine was selected as the active anion-exchange group because it forms a rather insoluble precipitate with sulfate.[1,2] Its specificity to sulfate could be the result of a sandwichlike structure with two benzidine molecules arranged atop one another, with the adjacent terminal aminogroups forming diaminosulfate complexes. Ion-pairing probably can also occur between o-phenylenediamine and the sulfate anion, but the resulting reduction in polarity is presumably insufficient to lead to precipitation. Membranes containing an exchange group which forms complexes with counterions have been described by Woermann et al.[3] and by Gregor and Wetstone.[4] A study of chloride-sulfate transport across a pyridinium-type anion-permeable membrane was reported by Kosaka and Emura.[5]

## Experimental

A condensate was prepared by adding 10 g. of benzidine to a mixture of 500 ml. of water and 250 ml. of a 36% (by weight) solution of sulfuric

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acid. At room temperature only about 20% of the benzidine dissolved. Then, 250 ml. of a 37% (by weight) formaldehyde solution was added, the system heated to 100°C. and then allowed to cool to 40°C., the latter temperature being maintained for 20 hr. with constant stirring. No visible changes were observed, but the particles of solid benzidine were replaced by ones which were insoluble in a number of solvents. This resin slurry was cooled, filtered and washed with water, then dried for 12 hr. *in vacuo* at 60°C. The resin was ground, washed repeatedly in acetone until the washings were clear, and redried as before; the material passing a 100-mesh screen was used to make membranes (designated B). A similar resin was prepared by the same procedure but by employing 36% hydrochloric acid instead of sulfuric acid. Its properties were quite similar (within 20%), so it was assumed that no specific properties were imparted to the resin by being formed in the sulfate state.

Heterogeneous membranes were cast as described by Bieber et al.[6] with the acrylonitrile–vinyl chloride copolymer NYGL (Union Carbide Company) as a 15% solution in dimethylformamide as matrix. One part of dry resin dispersed in 3.3 parts (by weight) of polymer solution was cast onto a glass plate, dried at 70°C. in air for 12 hr. and then used. The commercially available anion-permeable membrane also studied was Nalfilm 2 (Nalco Chemical Co.). This has quaternary ammonium exchange groups, and is designated N. Chloride was determined according to Mohr[1] and was accurate to ±0.2%. The Blacher titration for sulfate[7] is reported to be accurate to ±1%, but in solutions containing only chloride and sulfate with a total normality of 0.05 and with the sulfate normality ranging from 0.005 to 0.05, it gave results accurate to ±0.3%. Oxalate determined by titration with standard permanganate[1] was accurate to ±0.2%.

Exchange equilibria were determined with 100 cm.[2] samples brought to equilibrium with a solution 0.025$N$ in sodium chloride and 0.025$N$ in sodium oxalate. The membranes were blotted quickly to remove surface solution and their ionic content eluted with 1$M$ sodium nitrate. Chloride-oxalate equilibria were examined here because the titration for sulfate was not sufficiently accurate. The pertinent physical properties of oxalate and sulfate were assumed to be quite similar, a point which will be discussed later. All experiments reported herein were performed at 25 ± 1°C. For details of the experimental procedures and computations, the thesis[8] should be consulted.

Transport experiments were performed in a four-compartment cell, with the anode and cathode compartments containing silver–silver chloride electrodes in 0.05$M$ sodium chloride, separated from the two middle compartments by a cation-permeable membrane (Nalfilm 1). The membrane (exposed area of 11.4 cm.[2]) separated two middle solutions of 170 ml. each, 0.025$N$ in sodium chloride and in sodium sulfate. This arrangement was necessary because silver–silver chloride electrodes did not function properly in these chloride–sulfate mixtures. The current density

was 2 ma./cm.$^2$, and about 25% of the anions originally present were transported.

Diffusion-exchange experiments were carried out in a simple two-compartment cell, with adequate agitation such that at the relatively high concentration used (0.1$N$), the rate of the diffusive process was controlled by that in the membrane phase.[9]   Here 0.1$N$ sodium oxalate was allowed to diffuse against 0.1$N$ sodium sulfate, and 0.1$N$ sodium chloride against 0.1$N$ sodium nitrate.   At intervals aliquots were analyzed; a plot of equivalents exchanged against time was linear for the first 5 or 6 hr., intersecting the abscissa at a point corresponding to about 10 min., the time required to establish the steady state.

Diffusion-exchange coefficients in the membrane phase were calculated by using Fick's law.   The diffusion path length was the membrane thickness as measured in each solution (100 $\mu$ for N and 175 $\mu$ for B).   The molar exchange anion concentration for each membrane was determined.   In the univalent anionic state, it was 0.79 $\times$ 10$^{-3}$ mole/cm.$^3$ for N and 0.55 $\times$ 10$^{-3}$ mole/cm.$^3$ for B; with divalent anions, the molar capacity was half these values, within experimental error.   The concentration gradients in the membrane phases were then computed from these values.   Concentration potentials were measured across 0.2/0.1$M$ potassium chloride with the use of saturated calomel reference electrodes.   Each measured potential was corrected for differences in the potentials of the two calomel electrodes,

TABLE I
Membrane Properties

|  | Membrane N | Membrane B |
|---|---|---|
| Specific conductance, ohm$^{-1}$-cm.$^{-1}$ |  |  |
|    0.1$M$ KCl | 1.8 $\times$ 10$^{-4}$ | 11.7 $\times$ 10$^{-4}$ |
|    0.05$M$ K$_2$SO$_4$ | 1.3 $\times$ 10$^{-4}$ | 5.3 $\times$ 10$^{-4}$ |
| Concentration potential, mv.[a] | −15.87 | −16.03 |
| Bi-ionic potential, mv. |  |  |
|    0.01$N$ Cl$^-$/0.01$N$ SO$_4^=$ | 22.1 | −2.6 |
|    0.025$N$ Cl$^-$/0.025$N$ SO$_4^=$ | 10.3 | −10.7 |
|    0.025$N$ Cl$^-$/0.025$N$ Ox$^=$ | 13.1 | −9.2 |
|    0.1$N$ Cl$^-$/0.1$N$ SO$_4^=$ | −7.4 | −15.1 |
| Exchange-diffusion coefficient, cm.$^2$/sec. |  |  |
|    $\bar{D}$ for oxalate vs. sulfate | 0.81 $\times$ 10$^{-8}$ | 6.8 $\times$ 10$^{-8}$ |
|    $\bar{D}$ for chloride vs. nitrate | 2.6 $\times$ 10$^{-8}$ | 30 $\times$ 10$^{-8}$ |
| Selectivity (molar ratio of sorbed Ox$^=$Cl$^-$)[b] | 0.92 | 1.16 |
| Transport number |  |  |
|    $t_{Na}$ (meas.) | 0.039 | 0.084 |
|    $t_{Cl}$ (meas.) | 0.434 | 0.450 |
|    $t_{Cl}/t_{SO_4}$ (meas.) | 0.821 | 0.964 |
|    $t_{Cl}/t_{SO_4}$ (calc. from resist.) | 0.746 | 0.961 |
|    $t_{Cl}/t_{SO_4}$ (calc. from diffusion) | 0.860 | 0.990 |

  [a] Maximum potential ($t_-$ = 1) is −16.11 mv.
  [b] From solution 0.025$N$ each in chloride and oxalate.

for the potential at the salt bridge–liquid junction,[10] and to 25.0°C. Bi-ionic potentials were measured in the same manner. Ohmic resistances were measured in the usual manner.

Table I summarizes the results obtained.

## Discussion

The benzidine–formaldehyde resin B showed a significant but not marked preference for oxalate over chloride when compared with the quaternary ammonium resin N (1.26:1) by selectivity coefficient measurements. The conductance ratio of chloride over sulfate was greater in resin N (1.4) than in resin B (2.2), but here we employed sulfate and not oxalate; the degree of specific binding is expected to be greater for sulfate than for other divalent anions. The relationship between the specific conductivity, diffusion coefficient, valence, and molar concentration as predicted by the Nernst-Einstein equation is satisfied to within ±15% for both resin types with chloride and oxalate ions.

The transport number ratios $t_{Cl^-}/t_{SO_4^-}$ given in Table I show that chloride transport is favored when a sulfate-binding group is present in the membrane. The relative transport ratios are equal to the corresponding ratios of the products of the concentration, valence, and equivalent conductances or the concentration, diffusion coefficient, and square of valence, all in the membrane phase. Accordingly, one can calculate the transport number ratio from the membrane composition and its ohmic resistance or its diffusion-exchange coefficients. This assumes that the membrane composition during the transport experiments was nearly the same as at zero current; at the low current densities employed, this assumption is reasonable. Further, it is assumed that diffusion coefficients or equivalent conductances measured with but a single anionic species present are unchanged in mixtures of ions. The measured transport ratios $t_{Cl^-}/t_{SO_4^-}$ given in Table I are compared with the ratios calculated from conductance and diffusion-exchange data. In most cases, agreement is reasonable, particularly since the diffusion measurements were made with oxalate rather than sulfate.

The bi-ionic potential data shows that chloride against sulfate and chloride against oxalate give approximately the same potentials, and that the transport of sulfate over chloride is favored as the total concentration is decreased. Bi-ionic potential values calculated by using the theoretical treatment of Helfferich and Ocker[11] show only qualitative agreement, doubtless due to errors in estimating the parameters needed in this treatment.

## References

1. I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, MacMillan, New York, 1947.
2. J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*, Wiley, New York, 1941.
3. D. Woermann, K. F. Bonhoeffer, and F. Helfferich, *Z. Physik. Chem. (Frankfurt)*, **8**, 265 (1956).
4. H. P. Gregor and D. M. Wetstone, *Discussions Faraday Soc.*, **21**, 162 (1956).
5. Y. Kosaka and N. Emura, *Sci. Rept. Toyo Soda Mfg. Co.*, **6**, No. 2, 44 (1962).
6. H. H. Bieber, P. F. Bruins, and H. P. Gregor, *Ind. Eng. Chem.*, **50**, 1273 (1958).
7. F. J. Welcher, *Organic Analytical Reagents*, Vol. 2, Van Nostrand, New York, 1947.
8. R. M. Kramer, thesis, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., June 1959.
9. M. A. Peterson and H. P. Gregor, *J. Electrochem. Soc.*, **106**, 1051 (1959).
10. K. Sollner and H. P. Gregor, *J. Phys. Chem.*, **51**, 299 (1947).
11. F. Helfferich and H. D. Ocker, *Z. Physik Chem. (Frankfurt)*, **10**, 213 (1957).

## Résumé

On a mesuré des équilibres d'échange, les résistances ohmiques, les potentiels de concentration et bi-ionique, les coefficients de diffusion et les nombres de transport pour des systèmes chlorure–sulfate–oxalate dans des membranes anioniques perméables contenant des sites d'échange ammonique et benzidinique quaternaires. Les membranes benzidiniques montraient une plus grande sélectivité pour le sulfate que le chlorure comparés aux membranes à base d'ammonium quaternaire; par contre elle présentaient un nombre de transport plus faible. Ces phénomènes ont été interprêtés sur la base d'un mécanisme de liaisons d'ion. Un accord satisfaisant a été observé entre les nombres de transport mesurés et ceux calculés au départ des coefficients de sélectivité, des coefficients de diffusion et des conductances équivalentes.

## Zusammenfassung

Austauschgleichgewicht, ohmscher Widerstand, Konzentrations- und biionisches Potential, Diffusionskoeffizient sowie Überführungszahlen wurden am Chlorid–Sulfat–Oxalatsystem in anionendurchlässigen Membranen mit quaternärem Ammonium und Benzidin als Austauschergruppen gemessen. Die Benzidinmembranen zeigten im Vergleich zu den quaternären Ammoniummembranen eine grössere Selektivität für Sulfat als für Chlorid, jedoch eine niedrigere Überführungszahl. Diese Erscheinungen wurden auf der Grundlage eines Ionenbindungsmechanismus interpretiert. Gute Übereinstimmung wurde zwischen den gemessenen Überführungszahlen und den aus Selektivitätskoeffizienten, Diffusionskoeffizienten und der Äquivalentleitfähigkeit berechneten beobachtet.