**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Reverse Osmosis Separation of Some Organic Acids from Their Aqueous Solutions

M. Malaiyandi[a]; S. M. Shah[a]; V. S. Sastri[b]
[a] ENVIRONMENTAL HEALTH CENTRE HEALTH PROTECTION BRANCH HEALTH AND WELFARE CANADA TUNNEY'S PASTURE, OTTAWA, CANADA [b] MINERAL SCIENCES LABORATORIES CANMET DEPARTMENT OF ENERGY, MINES AND RESOURCES, OTTAWA, CANADA

**To cite this Article** Malaiyandi, M. , Shah, S. M. and Sastri, V. S.(1982) 'Reverse Osmosis Separation of Some Organic Acids from Their Aqueous Solutions', Separation Science and Technology, 17: 8, 1065 — 1074
**To link to this Article: DOI:** 10.1080/01496398208060270
**URL:** http://dx.doi.org/10.1080/01496398208060270

SEPARATION SCIENCE AND TECHNOLOGY, 17(8), pp. 1065–1074, 1982

# Reverse Osmosis Separation of Some Organic Acids from Their Aqueous Solutions

---

M. MALAIYANDI* and S. M. SHAH

ENVIRONMENTAL HEALTH CENTRE
HEALTH PROTECTION BRANCH
HEALTH AND WELFARE CANADA
TUNNEY'S PASTURE, OTTAWA, CANADA K1A 0L2

V. S. SASTRI

MINERAL SCIENCES LABORATORIES
CANMET
DEPARTMENT OF ENERGY, MINES AND RESOURCES
OTTAWA, CANADA

## Abstract

Cellulose acetate membranes were characterized as previously described and were found to reject 91.7% of sodium chloride. The reverse osmosis separation behavior of benzoic, 2-chlorobenzoic, 2-nitrobenzoic, 2-hydroxybenzoic, and 2-aminobenzoic acids as a function of pH was studied. Experimentally obtained $pK_a$ values are compared with literature values. The calculated polar substituent constant $\sigma^*$ values for the *o*-substituents were also found to agree with literature values.

## INTRODUCTION

Reverse osmosis (RO) is a promising separation technique for the concentration and separation of both inorganic and organic solutes from aqueous solutions, and the process does not involve phase transformation of the liquid (*1*). Some of the attractive features of RO are low expenditure requirements, simplicity of processing technology, and operation at ambient temperature. However, high-pressure RO suffers from disadvantages such as high capital investment, fouling, and severe membrane compaction problems.

---

*To whom correspondence should be addressed.

On the other hand, low-pressure RO systems involve comparatively low capital investment and an insignificant amount of membrane compaction.

RO separation of organic compounds using asymmetric cellulose acetate membranes is often practical and of great interest from the mechanistic, wastewater treatment, and water pollution abatement points of view (*1–4*). Kesting et al. (*2*) studied the separation of some alcohols and organic acids using 1% by weight of the organic compound in water at a pressure of 102 atm and correlated the experimental results with the hydrogen bonding ability of the solute. RO separation of alcohols and acids was studied by Duvel and co-workers (*4*) using a feed concentration in the range of $10^{-2}$ to $10^{-3}$ $M$ at a pressure of 600 psig and a temperature of 40°C. From RO studies of several alcohols and monocarboxylic acids, Matsuura et al. (*5*) concluded that preferential sorption of water on the membrane accounted for solute separation, and this was governed by the hydrogen bonding ability of the organic compound in the undissociated form and by electrostatic repulsion of ions when the molecule is in the dissociated form.

Studies on the behavior of cellulose acetate membranes for the separation and concentration of organic solutes have been initiated in our laboratories since knowledge of separation characteristics of RO membranes is extremely important in the production of high quality water for laboratory, potable, food processing, and clinical purposes. Moreover, it is highly desirable to develop specific technology for concentrating ultratrace amounts of polar and nonpolar organics in water from the analytical and toxicological points of view, since these aspects have relevance in establishing water quality standards. The total organic carbon content of tap water is on an average about 3600 ppb (*6*) of which only about 2% is extractable using XAD-2 macroreticular resin columns (*7*), and thus facilitating only the analysis of nonpolar organics. The remaining dissolved organic carbon is often in the form of semipolar and polar organics with some significance in routine water quality assessment. Hence a study of the separation of selected model polar compounds, such as organic acids, was undertaken using asymmetric cellulose acetate membranes. The results are reported in this paper.

## EXPERIMENTAL

### Reverse Osmosis Cell and Apparatus

The low volume, fast flow, stainless steel (s.s.) RO cell consists of detachable upper and lower parts (Fig. 1). The membrane is supported on an s.s. porous plate embedded in the lower part of the cell. The lower part is also provided with an outlet for the product water which is received in a collection

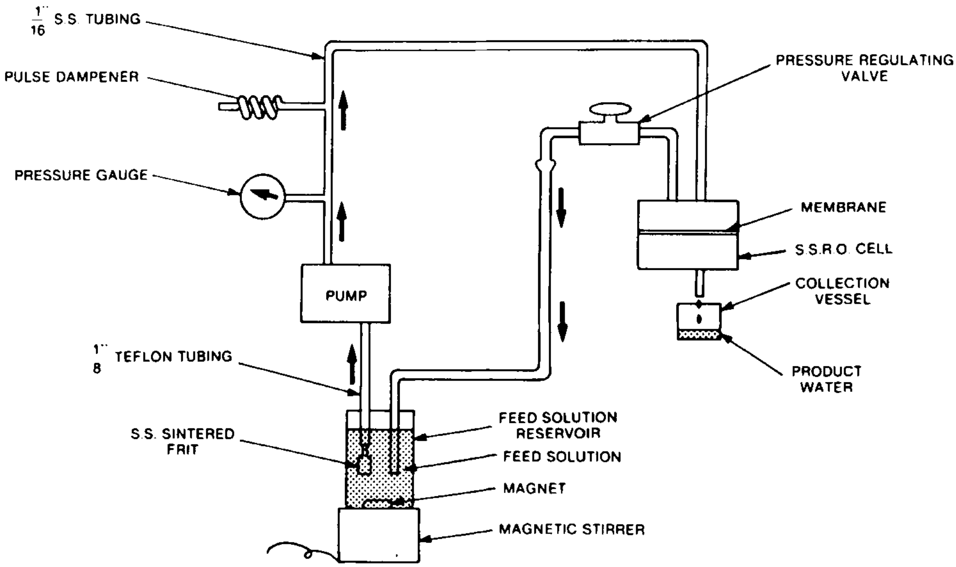

FIG. 1. Reverse osmosis apparatus.

tube at atmospheric pressure. The upper part of the cell has an inlet and an outlet through which the feed solution enters and exits at high pressures. The exit end is attached to a pressure regulating valve so as to maintain the desired pressure. The free end of the regulating valve is connected to 1/8 in. polytetrafluoroethylene (PTFE) tubing, the other end of which is returned to the feed solution reservoir.

The two parts of the RO cell are fitted with prewashed neoprene O-rings and tightly sealed together by means of s.s. cap screws. The effective area of the asymmetric cellulose acetate membrane is 13.4 $cm^2$. Feed solutions of suitable pressures are achieved by using an Altex high pressure pump Model 110 A in conjunction with an integrated pulse dampener and pressure gauge. The inlet of the pump is connected to an s.s. fritted filter (25 $\mu$m) by means of 1/8 in. PTFE tubing. The fritted filter is submerged in the feed solution which is vigorously stirred by means of a magnetic stirrer.

## Reverse Osmosis Procedure

The acid solution is made by suspending 500 mg of purified acid (98–99%) in 4 L of specially purified water (*6*) in a 5-L volumetric flask. The solution is heated with stirring to 50–60°C until all the solute is dissolved, then cooled to room temperature and made to volume with purified water. After filtering the solution using a 0.45 μm membrane filter, the solution is stored in darkness or shielded from light by wrapping the container with aluminum foil. An aliquot (200 mL) is used for each RO experiment. The pH of the solution is adjusted to the second decimal place using dilute solutions of hydrochloric acid or sodium hydroxide.

## Analysis

Sodium chloride solutions were analyzed by conductance measurements. The concentration of benzoic and *o*-substituted benzoic acids were determined by UV spectrometry and by high pressure liquid chromatography. The liquid chromatographic conditions chosen were: Instrument: Waters Scientific High Pressure Liquid Chromatograph Model A 202 with Model M 6000 pump; Column: ODS reverse phase 5 μm packing in 25 cm × 0.4 cm i.d.; Eluent: *n*-BuOH:HOAC:MeOH:$H_2O$ (5:2:25:68); Mobile phase flow: 0.7 to 1.2 mL/min depending on the acid used; Sample size: 20 μL; Detector: UV-VIS Spectrometer Model SP 8400 at 242 nm; Recorder: 10 mV Varian Model A 25 and SP 4000 Printer/Plotter.

Feed solution, product water, and reject solution were diluted if necessary and analyzed in duplicate and interspersed with standard solutions of nearly equal absorbance and quantitated by peak height measurements. The same samples were also analyzed by directly measuring straight UV absorbance at 242 nm using a UV-visible spectrometer. Replicate experiments were carried out. The accuracy of analysis was within ±5%. All the experiments were carried out at laboratory temperature (22–23°C).

The membranes obtained from Osmonics Inc. were preconditioned at 85°C for 1/2 h and cooled at 10°C for a 2-h period and characterized as before (*8*). After installing the membranes in the RO cell, the membranes were pressurized with purified water at 2750 kPa for 2 h before use. Subsequent experiments were carried out at 1030 kPa and at a constant flow-rate of 4 mL/min of feed solution pumped to the RO cell. The reject water was returned to the feed reservoir and thoroughly mixed by magnetic stirring. The pressure was maintained by adjusting the regulating valve to obtain a ratio of 1:27 (v/v) of product water to the reject solution so as to minimize concentration polarization (vide infra, ≈90% rejection of acids). After thorough mixing, the aliquot of feed solution was sampled at the outset of the experiment and after collecting 20 mL of product water.

By this procedure the rate of production of permeate water was 8 mL/h. When a volume of 20 mL of product water was collected, the reservoir containing the feed solution was replaced by another containing distilled water. After each experiment the RO system was thoroughly washed to remove any sorbed solutes by increasing flow rates to 7 mL/min for a period of at least 2 h. This wash solution was discarded.

The pure water permeation rate, permeation rate of test solutions through the membrane of a given area, and the solute separation factor (*f*) were determined at preset conditions (*8*). A feed solution containing 3500 and 100 mg/L of sodium chloride were used to characterize the membranes. Since low concentrations of the acids were used in this experiment (≈100 mg/L), the solute separation factor (*f*) data were calculated using the relation

$$f = \frac{\text{amount of solute/mL in original feed} - \text{amount of solute/mL in product}}{\text{amount of solute/mL in orginal feed}}$$

## RESULTS AND DISCUSSION

To enable comparison of the relative performance of the asymmetric cellulose acetate membranes for feed solutions containing solutes for which physicochemical data such as osmotic pressure and other pertinent data are not available, it is necessary to provide specifications for the membranes in terms of experimentally obtainable parameters for well-studied reference system such as sodium chloride (*8*). Using the well-characterized membranes, the separation factors for 3500 and 100 mg/L sodium chloride solutions were 0.917 and 0.862, respectively.

On the basis of the solution–diffusion mechanism (*9–11*), the relative permeabilities of solute and solvent through a medium determine the rejection characteristics of the medium. Further, it is also known that solute permeability is the product of distribution coefficient and diffusion coefficient. In general, it is expected that highly ionized solutes are effectively rejected by the membrane whereas weakly ionized solutes and nonelectrolytes would be poorly rejected by this process. Moreover, compounds which are strongly adsorbed on the membrane would also be poorly rejected (*8, 12*). These observations point out the intrinsic relationship between solute rejection and distribution coefficient and suggest that rejection parameters for the benzoic acid–benzoate ion–membrane system depend more specifically on solute distribution coefficient than the solute diffusion coefficient.

The available separation data relating to solute molecules using cellulose acetate membranes indicate that the degree of rejection of solutes by RO is dependent on the applied pressure. However, in this investigation, constant low pressure was applied to study the effects of pH on separation properties of cellulose acetate membranes. Further, in the case of dilute aromatic acid solutions where the solutes are dissociated to varying degrees, the separation of these solutes depends on their dissociation constants, since dissociated species are rejected while undissociated species with aromatic rings are fairly sorbed to the membrane. Alteration of pH of the solution would therefore play a significant role in the rejection factor of the solutes. A highly ionized acid is generally more soluble in the aqueous phase but less soluble in the membrane phase, and therefore more effectively rejected by the cellulose acetate membrane. In such situations, the dissociation constant $K_a$ has to be incorporated in the treatment of the distribution coefficient similar to the solvent extraction theory (*13*).

RO rejection of benzoic acid and its *o*-substituted, namely 2-chloro (2-Cl—), 2-nitro ($2\text{-}NO_2$—), 2-hydroxy (2-OH—) and 2-amino ($2\text{-}NH_2$—), derivatives was investigated at different pHs ranging from 2.0 to 6.5. (Note: The cellulose acetate membrane is suspectible to hydrolysis beyond these pH ranges.) The resulting data were analyzed and the rejection factor ($f$) of the acids was plotted as a function of pH and is shown in Fig. 2 and Figs. 3a to 3d.

The behavior of benzoic acid is depicted in Fig. 2. The percent rejection of benzoic acid shows a sharp increase between pH 4 and 5 and also between pH 5 and 6. This rejection profile clearly resembles that of an acid–base titration curve of a weak acid. Further, at higher pHs beyond the p$K_a$ of benzoic acid, i.e., 4.2 (*14*), rejection of benzoic acid by the cellulose acetate membrane is very good and reaches a maximum of nearly 90% at pH 6.5. This high rejection is expected since, at these higher pHs, the acid is in the form of its benzoate ion and hence it is highly ionized.

Similarly, the 2-Cl, $2\text{-}NO_2$, 2-OH, and $2\text{-}NH_2$ substituted benzoic acids show high rejection (96% at pH 6.5, 95% at pH 6.0, 85% at pH 6.5, and 85% at pH 6.5, respectively, Figs. 3a to 3d) at higher pHs irrespective of their p$K_a$s.

It is further observed that, at low pHs, the rejection of benzoic acid is lower and the curve goes through a minimum near pH 3.0, its lowest rejection, and is followed by an increase in rejection with further lowering of pH. Since lowering of pH is attained in these dilute solutions by the addition of strong acid, namely hydrochloric acid, benzoic acid is apparently protonated to give $\phi\text{-}COOH_2^+ + Cl^-$, resulting in discrete ionic species. Therefore, rejection of benzoic acid is enhanced at a pH lower than 3.0.

Similar observations are also made with the *o*-substituted benzoic acids. In the case of 2-nitrobenzoic acid with a p$K_a$ of 2.17 (*15*), the inflection is very sharp in the low pH region and minimum rejection (6%) was observed at pH 2.5 (Fig. 3b). The 2-chlorobenzoic acid [p$K_a$ = 3.01 (*17*)] (Fig. 3a) and 2-hydroxybenzoic acid (Fig. 3c) [p$K_a$ = 3.07 (*16*)] have also sharp but slightly broader transition zones than 2-nitrobenzoic acid. The 2-aminobenzoic acid with a p$K_a$ of 4.98 (18) shows a very broad inflection (Fig. 3d) and the rejection is about 42 to 43% at pH 2.0. This enhanced rejection may be due

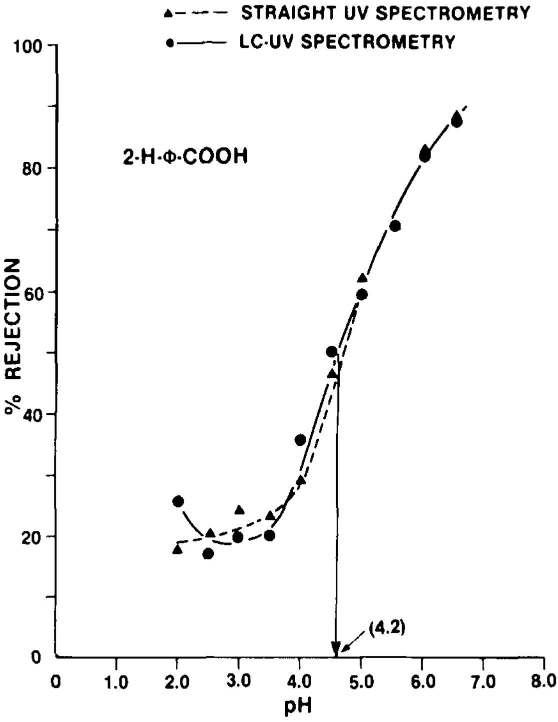

FIG. 2. Curve showing rejection of benzoic acid versus pH.

to formation of the substituted ammonium chloride which dissociates to give the substituted ammonium and chloride ions.

In the case of an acid, the dissociation constant $K_a$ is represented by

$$K_a = \frac{[\phi\text{-COO}^-][\text{H}^+]}{[\phi\text{-COOH}]} \tag{1}$$

from which the relationship between dissociation constant and hydrogen ion concentration can be derived to give

$$\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]} \tag{2}$$

At the point of 50% neutralization, the ratio of salt to acid is unity and hence Eq. (2) reduces to $\text{pH}_{50\%} = \text{p}K_a$. Applying this concept to the curve shown in

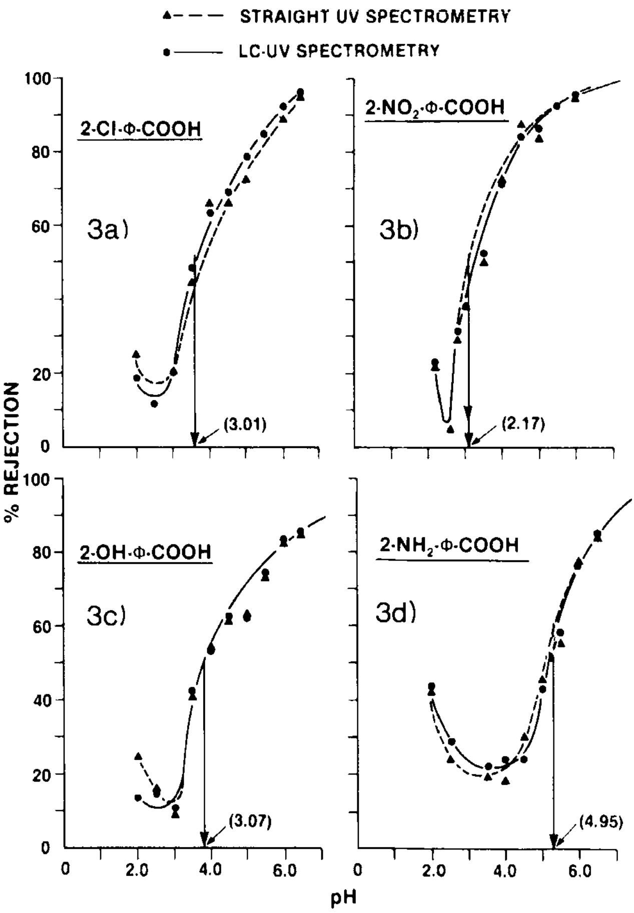

FIG. 3. Curves showing rejection of *o*-substituted benzoic acids versus pH.

Fig. 2, the 50% rejection of benzoic acid was obtained at a pH value of 4.6 which is close to the p$K_a$ of benzoic acid (4.2) obtained from other methods. Similar analyses were performed and the p$K_a$s are shown in Fig. 3a to 3d.

It can be seen that the p$K_a$s of 2-$NO_2$—, 2-Cl—, 2-OH—, and 2-$NH_2$—benzoic acids were observed to be 3.1, 3.6, 3.8, and 5.3, respectively, as compared to the literature values of 2.19, 3.01, 3.07, and 4.98 (*15–18*). Except for 2-nitrobenzoic acid, most of the observed p$K_a$ values are in fair agreement with the literature values. From these data it is apparent that, as far as the present work is concerned, RO rejection characteristics of aromatic organic acids as a function of pH allow the evaluation of p$K_a$ values of these acids.

## Evaluation of Taft $\sigma^*$ Parameter for *o*-Substituents

The effects of structure on rates of reactions or ionic equilibria are determined in part by the polar effects of substituents in the molecule. For *o*-substituted aromatic acids, the Taft equation (*19*) is

$$\log(k/k_0) = \rho^*\sigma^* \qquad (3)$$

and can be applied to determine $\sigma^*$. Here $k$ and $k_0$ are the rates of reactions (in this case, dissociation constant $K_a$-substituted and $K_a$-benzoic acids) respectively of $\rho^*$, the proportionality or susceptibility constant. Using the observed p$K_a$ values derived from RO data, $\sigma^*$ values have been calculated and are compared with the literature values. From this study, the p$K_a$s of the *o*-substituted benzoic acids with respect to the parent acid are derived from the RO separation, and $\rho^*$ for the substituted benzoic acids is taken to be 1.787 (*19*). Therefore, from these data it is possible to calculate $\sigma^*$ values and to compare with the values of $\sigma^*$ reported in the literature.

Table 1 gives the calculated values of $\sigma^*$ from known p$K_a$s of these acids and from p$K_a$s derived from the RO data, and these values are compared with the ones reported (*1*).

The calculated $\sigma^*$ values based on p$K_a$ values obtained from RO rejection data from 2-Cl, 2-OH and 2-$NH_2$ benzoic acids agree fairly well with the values reported in the literature except for the slightly lower $\sigma^*$ value calculated for 2-nitrobenzoic acid from the literature p$K_a$ value. Most of the reported $\sigma^*$ values are derived from rate constants of acid and base hydrolysis of esters of the substituted benzoic acids. In this study the $\sigma^*$ are calculated from RO data obtained from simple separation techniques involving less vigorous chemical conditions.

Since the p$K_a$ values obtained from RO rejection data compare well with

TABLE 1

$\sigma^*$ Values of *o*-Substituted Benzoic Acid[a]

| Substituent | $\sigma^*$ calculated from p$K_a$ | | $\sigma^*$ reported |
|---|---|---|---|
| | p$K_a$ (Literature) | p$K_a$ (RO) | |
| $-NO_2$ | 1.14 | 0.84 | 0.80 |
| —Cl | 0.67 | 0.56 | 0.20 |
| —OH | 0.63 | 0.45 | — |
| $-NH_2$ | −0.43 | −0.39 | — |

[a] Ref. *1*, p. 13.

the values reported in the literature, it is concluded that the RO separation method can be used for the evaluation of $pK_a$ and $\sigma^*$ values for some organic acids.

## Acknowledgments

The authors wish to thank T. Matsuura and P. Blais for helpful discussions and reviewing the manuscript, and P. Toft for his continued interest in our work.

## REFERENCES

1. S. Sourirajan, "Physico-Chemical Criteria for Reverse Osmosis Separations," in *Reverse Osmosis and Synthetic Membranes* (S. Sourirajan, ed.), National Research Council Canada, Publication No. 15627 (1977).
2. R. E. Kesting and J. Eberlin, *J. Appl. Polym. Sci.*, *10*, 961 (1966).
3. E. Hindin, P. J. Bennett, and S. S. Narayanan, *Water Sew. Works*, *116*, 466 (1969).
4. W. A. Duvel, T. Helfgott, and E. J. Genetelli, Paper Presented at the American Chemical Society Meeting, Chicago, Sept. 1970.
5. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, *15*, 2905 (1971).
6. M. Malaiyandi, M. H. Sadar, P. Lee, and R. O'Grady, *Water Res.*, *14*, 1131 (1980).
7. G. LeBel, Private Communication.
8. M. Malaiyandi, P. Blais, and V. S. Sastri, *Sep. Sci. Technol.*, *15*, 1483 (1980).
9. H. K. Lonsdale, U. R. Merten, and R. L. Riley, *J. Appl. Polym. Sci.*, *9*, 1341 (1965).
10. R. L. Riley, H. K. Lonsdale, C. R. Lyons, and U. R. Merten, *Ibid.*, *11*, 2143 (1967).
11. H. K. Lonsdale, B. P. Cross, F. M. Graber, and C. E. Milstead, *J. Macromol. Sci.—Phys.*, *5B*, 167 (1971).
12. M. E. Heyde, C. R. Peters, and J. E. Anderson, *J. Colloid Interface Sci.*, *50*, 476 (1975).
13. D. Dyrssen. J. O. Lilijenzin, and J. Rydberg. *Solvent Extraction Chemistry*, North Holland, Amsterdam, 1976, p. 517.
14. R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, *75*, 2421 (1953).
15. J. F. J. Dippy, *Chem. Rev.*, *25*, 151 (1939).
16. B. Jones and J. C. Speakman, *J. Chem. Soc.*, p. 19 (1944).
17. S. G. Vandenberg, G. Hewrich, and J. M. Vandenbelt, *Anal. Chem.*, *25*, 726 (1954).
18. D. Peltier and A. Pichevin, *C. R. Hebd. Seances Acad. Sci., Ser. C*, *245*, 436 (1957).
19. R. W. Taft, Jr., "Separation of Polar Steric and Resonance Effects in Reactivity," in *Steric Effects in Organic Chemistry* (M. S. Newman, ed.), Wiley, New York, 1956, pp. 556–675.

*Received by editor December 28, 1981*