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William Rieman Iii[ab]; Nancy Luque[ab]; Juan Jiménez[ab]
[a] WRIGHT LABORATORY RUTGERS UNIVERSITY, NEW BRUNSWICK, NEW JERSEY [b] UNIVERSIDAD PERUANA CAYETANO HEREDIA, LIMA, PERU

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The Equilibria between Solutions of (−)-*N*-(1-Naphthyl)methyl-α-methylbenzylammonium Benzenesulfonate in Nitrobenzene and Aqueous Solutions of Sodium (±)-Mandelate

WILLIAM RIEMAN III,* NANCY LUQUE, and JUAN JIMÉNEZ

WRIGHT LABORATORY
RUTGERS UNIVERSITY, NEW BRUNSWICK, NEW JERSEY 08903
AND
UNIVERSIDAD PERUANA CAYETANO HEREDIA
LIMA, PERU

Abstract

Solutions of the optically active liquid anion exchanger named in the title were equilibrated with aqueous solutions of sodium mandelate. Racemic mandelate was used in some experiments, active mandelate in others. Some of the aqueous solutions also contained sodium benzenesulfonate. The analysis of the equilibrated phases yielded data from which the several anion-exchange selectivity coefficients were calculated, most importantly (+)-mandelate vs benzenesulfonate and (+)-mandelate vs (−)-mandelate. The results indicate that this liquid anion exchanger has important advantages over the analogous chloride in chloroform for the resolution of mandelate and other racemic anions. Some properties of *S*-amine and *S*-ammonium benzenesulfonate are reported.

INTRODUCTION

A previous paper (*1*) described the study of (−)-*N*-(1-naphthyl) methyl-α-methylbenzylammonium chloride in chloroform as an agent for the resolution of mandelate ion and two other racemic anions. Although

* Deceased, October 29, 1972.

36 mmole of each enantiomer of sodium mandelate was obtained at an optical purity of 99% or better in one separation by Craig countercurrent extraction, this liquid anion exchanger has two disadvantages. In the first place, the solubility in water, or more importantly the ratio of this solubility to the solubility in chloroform, is too large. This results in the extraction of an appreciable quantity of the anion exchanger from the organic phase into the aqueous phase. This loss of exchanger from the organic phase is probably the major cause of the rather large discrepancies between the observed and theoretical graphs when the Craig countercurrent apparatus was applied in a method analogous to elution chromatography, Fig. 1 of Ref. 1. In the second place, when aqueous sodium hydroxide is employed as a displacing agent in the Craig procedure analogous to displacement chromatography, the hydroxide ion not only displaces the (+)-mandelate ion from the organic phase, but also attacks the solvent:

$$CHCl_3 + 4OH^- \longrightarrow HCOO^- + 3Cl^- + 2H_2O \quad (1)$$

Therefore a better optically liquid anion exchanger was sought. The cation, (−)-$C_{10}H_7$–CH_2–$\overset{+}{N}H_2$–$CH(C_6H_5)CH_3$ (hereinafter denoted S-ammonium or SaH^+), was considered to be satisfactory; but a search was made for an anion better than chloride and a solvent better than chloroform. The system selected was *S*-ammonium benzenesulfonate in nitrobenzene.

Appreciable hydrolysis of the mandelate ion occurs in the aqueous solution with subsequent anion exchange of the resultant hydroxide ion

$$Ma^- + H_2O \rightleftharpoons HMa + OH^- \quad (2)$$

$$OH^- + \overline{SaHSu} \rightleftharpoons \overline{Sa} + Su^- + H_2O \quad (3)$$

The overall reaction is

$$Ma^- + H_2O + \overline{SaHSu} \rightleftharpoons HMa + \overline{Sa} + Su^- + H_2O \quad (4)$$

Ma^- and Su^- denote mandelate and benzenesulfonate ion, respectively. Solutes in the organic phase are denoted by the overline. This hydrolysis was unfortunately neglected in the previous paper (*1*).

EXPERIMENTAL

Reagents

To prepare *S*-ammonium benzenesulfonate, 0.713 mole of *S*-amine (*1*), 2 liters of water, and 0.720 mole of benzenesulfonic acid were mixed and

stirred several days until the oily phase disappeared and copious colorless crystals were formed. The crystals were filtered on sintered glass, washed with 1 liter of water, and dried to constant weight. The yield was 0.653 mole or 91.6%. The concentration of saturated solutions of this compound at 25° in some solvents were 0.01198 M (σ = 0.00008 M) in water saturated with nitrobenzene, 0.0123 M (σ = 0.0003 M) in pure water, 0.507 M in nitrobenzene saturated with water and 0.128 M (σ = 0.004 M) in pure nitrobenzene. The molar rotation in water at 365 nm was 56° (σ = 4).

Both enantiomers of mandelic acid were purchased and found to be 99% optically pure. Other reagents were of analytical grade or the best available.

Equilibrations

In all the equilibrations, each solvent was previously saturated with the other. Equal volumes, usually 10.00 ml, of the original solutions in water and nitrobenzene were stirred magnetically in a closed weighing bottle for 20 min. The concentration of the original solutions are given in Table 1.

Titrations

After the equilibration and separation of the phases, a carefully measured volume, usually 1.000 ml, of the aqueous solution was transferred to a 50-ml beaker and evaporated to dryness. The residue was dissolved in 10 ml of a mixture of equal volumes of ethylene glycol and propanol-2, usually called G-H solvent (*2*). The mandelate ion was then determined by titration with standard 0.1 M perchloric acid, also dissolved in G-H solvent. To prevent excessive absorption of moisture from the air, the beaker was loosely closed by a rubber stopper through which passed glass and calomel electrodes and a Guilmont buret.

Another carefully measured portion of the equilibrated aqueous phase, usually 5.00 ml, was transferred to a 20-ml beaker and titrated with standard, aqueous, carbonate-free 0.1 M sodium hydroxide. Glass and calomel electrodes were used, and an atmosphere free of carbon dioxide was provided. There are two jumps in this titration graph. The first one marks the neutralization of the mandelic acid produced by Reaction (4). The second jump marks the complete conversion to *S*-amine of the *S*-ammonium ion extracted from the organic phase as either sulfonate or mandelate by the aqueous phase. Somewhere between the two jumps in the titration, the solution becomes turbid because of the limited solubility of *S*-amine in water. The solubility of the *S*-amine can be calculated from

TABLE 1

Concentrations (molarity $\times 1000$) of the Solutions before Equilibration

No.	In water			In nitrobenzene
	(+)-Ma$^-$	(−)-Ma$^-$	Su$^-$	SaH Su
A1	25.4	25.4	0.0	91.5
A2	49.7	49.7	0.0	91.5
A3	75.0	75.0	0.0	91.5
A4	99.8	99.8	0.0	91.5
B1	26.3	26.3	188	91.5
B2	49.6	49.6	203	95.5
B3	75.0	75.0	200	91.5
B4	99.6	99.6	200	91.5
C1	26.6	26.6	400	91.5
C2	48.7	48.7	403	91.5
C3	75.0	75.0	400	91.5
C4	100.0	100.0	400	91.5
D1	25.2	25.2	799	91.5
D2	45.8	45.8	800	91.5
D3	75.0	75.0	799	90.2
D4	100.0	100.0	800	91.5
E1	25.0	25.0	0.0	46.4
E2	25.0	25.0	154.3	46.4
E3	50.0	50.0	103.0	46.4
E4	75.0	75.0	51.5	46.4
E5	100.0	100.0	0.0	46.4
F1	100.0	100.0	0.0	202
G1	10.30	41.1	0.0	92.8
G2	14.8	32.8	0.0	92.8
G3	20.0	29.8	0.0	92.8
G4	34.9	14.5	0.0	92.8
G5	39.2	10.0	0.0	92.8

the amount of sodium hydroxide used between the first jump and the appearance of incipient turbidity. Because of the gradual development of the turbidity, however, the determination is not accurate.

A carefully measured volume of the equilibrated organic phase, usually 2.00 ml, was transferred to a 50-ml beaker, mixed with 10 ml of G-H solvent and titrated with the standard perchloric acid. Although two reactions occur during this titration,

$$SaHMa + HClO_4 \longrightarrow SaHClO_4 + HMa \quad (5)$$

$$Sa + HClO_4 \longrightarrow SaHClO_4 \quad (6)$$

there is only one jump, which occurs at the completion of both reactions. Thus this titration serves to determine the sum of the concentrations of *S*-ammonium mandelate and free *S*-amine in the organic phase. Since the latter concentration is equal to the concentration of mandelic acid in the aqueous phase by Reaction (4), the concentration of *S*-ammonium mandelate is readily computed.

Obviously the sum of the concentrations of mandelate found as Ma^-, HMa, and $\overline{SaHMa}$ should equal the concentration (both enantiomers) of sodium mandelate originally in the aqueous solution. Because of experimental errors, the ratio of mandelate taken to mandelate found was seldom exactly 1.000, but the mean of all the experiments except Series G was 0.999 ($\sigma = 0.017$).

Measurement of Rotation

In most cases, 1.548 ml of the aqueous phase was mixed with a few drops of 12 *M* perchloric acid to convert the mandelate ion to mandelic acid. The solution was then diluted to 2.01 ml, and the rotation was measured with a Perkin-Elmer Polarimeter, #141, at 436 nm. The error of the instrument is stated to be 0.002° or less.

Four of the experiments were done at Universidad Peruana Cayetano Heredia where the best polarimeter available was a visual instrument with a sodium lamp. To compensate partly for the lesser sensitivity of this instrument, larger volumes of the two phases were equilibrated, and a portion of the aqueous phase was concentrated by evaporation to a known volume before the measurement of rotation.

The rotations of the acidified aqueous phases were due largely to the mandelic acid. Nevertheless, in each case there was sufficient of the negatively rotating *S*-ammonium ion present to exert a small effect on the rotation. Therefore a correction was applied for the rotation due to this cation as calculated from its concentration and molar rotation, 56. This correction never exceeded −0.004°.

To calculate the excess of either enantiomer of mandelic acid in the acidified aqueous solution, it was necessary to know the molar rotation of mandelic acid. Since this changes appreciably with the composition of the solution, a known solution was prepared for each experiment identical in composition to the acidified and diluted aqueous phase except that it

contained (−)-mandelic acid at a concentration equal to the sum of the two enantiomers of mandelic acid in the other solution.

In the early part of the work, an attempt was made to confirm the enantiomeric composition of the mandelic acid in the aqueous phase by measuring the rotation of the mandelic acid isolated from the *S*-ammonium mandelate in the organic phase. Obviously, except in Series G, the excess of (−)-mandelic acid in the acidified aqueous phase should equal the excess of (+)-mandelic acid obtained from the organic phase. The organic phase was treated with an excess of aqueous sodium hydroxide to convert the *S*-ammonium mandelate to sodium mandelate and to extract the latter. The extraction was completed by three treatments with water. The aqueous extracts were combined, acidified with perchloric acid, diluted to a definite volume, and subjected to a measurement of rotation. In 14 such experiments the ratio of the excess of (+)-mandelic acid from the organic phase to the excess of (−)-mandelic acid from the aqueous phase was 0.94 with a standard deviation of 0.11. The agreement is not good. Since the measurement of the aqueous phase is simpler, presenting less opportunity for error, and since the results from the aqueous phase gave more concordant results for the selectivity coefficient of (+)-mandelate relative to (−)-mandelate, the results from the organic phase were discarded.

CALCULATIONS

The titrations furnish the data for the calculation of the concentrations of each species in the equilibrated phases except that they give no information regarding the enantiomeric composition of the species Ma^-, HMa, or $\overline{SaHMa}$. The concentration of sulfonate transferred from the organic to the aqueous phase is

$$\Delta[Su^-] = [\overline{SaHMa}] + [HMa] + [SaH^+] \tag{7}$$

Then

$$[Su^-] = [Su^-]_i + \Delta[Su^-] \tag{8}$$

and

$$[\overline{SaHSu}] = [\overline{SaHSu}]_i - \Delta[Su^-] \tag{9}$$

The subscript i denotes the concentrations before equilibration.

The measurements of the rotation of the acidified aqueous phase furnish the data for the calculation of the enantiomeric compositions.

If a denotes the rotation of this solution, corrected for the small concentration of S-ammonium ion, and if F represents the dilution factor, usually 1.158/2.01,

$$[(-)\text{-Ma}^-] + [(-)\text{-HMa}] - [(+)\text{-Ma}^-] - [(+)\text{-HMa}] = \frac{-10a}{\phi F} = y \tag{10}$$

In this paper, the enantiomeric compositions are expressed in terms of the two active isomers rather than in terms of the racemic mixture and the excess of one active enantiomer:

$$[(-)\text{-Ma}] + [(-)\text{-HMa}] = \frac{[\text{Ma}^-] + [\text{HMa}] + y}{2} \tag{11}$$

Since both enantiomers of mandelic acid have the same ionization constant:

$$\frac{[(-)\text{-Ma}^-]}{[(-)\text{-HMa}]} = \frac{[(+)\text{-Ma}^-]}{[(+)\text{-HMa}]} = \frac{[\text{Ma}^-]}{[\text{HMa}]} \tag{12}$$

From Eq. (11) and (12), the concentrations of each enantiomer in the equilibrated aqueous phase can be readily calculated. Then

$$[\overline{\text{SaH}(-)\text{-Ma}}] = [(-)\text{-Ma}^-]_t - [(-)\text{-Ma}^-] - [(-)\text{-HMa}] \tag{13}$$

and an analogous equation can be used to calculate $[\overline{\text{SaH}(+)\text{-Ma}}]$.

RESULTS AND DISCUSSION

The composition and pH values of the equilibrated aqueous phases are given in Table 2. To save space, the concentrations in the organic phase are not given; they can be calculated from the data of Tables 1 and 2. Nevertheless the values of R_1 are included to facilitate the discussion.

Since four anions (benzenesulfonate, hydroxide, and two enantiomeric mandelate ions) participate in the exchange reactions, six selectivity coefficients can be calculated from the data of each of the 27 experiments. However, only three of these selectivity coefficients are independent. It is most advantageous to consider as the three independent coefficients those between (a) (+)-mandelate and benzenesulfonate, (b) (+)- and (−)-mandelate, and (c) hydroxide and benzenesulfonate, denoted respectively E_{Su}^{+}, E_{-}^{+}, and $E_{\text{Su}}^{\text{OH}}$.

The Selectivity Coefficient of (+)-Mandelate vs Benzenesulfonate

Table 2 reveals that this coefficient varies from 1.03 to 2.39, far too much to be explained as experimental errors. Since a selectivity coefficient

TABLE 2

$$R_1 = \frac{[\overline{SaH(+)\text{-}Ma}]}{[\overline{SaH(+)\text{-}Ma}] + [\overline{SaHSu}]}$$

No.	[(+)-Ma^-] ×1000	[(−)-Ma^-] ×1000	[HMa] ×1000	[SaH^+] ×1000	[Su^-] ×1000	R_1	$E_{Su}{}^+$	R_2	$E_-{}^+$
A1	6.94	8.01	4.59	1.47	37.4	0.232	1.63	0.522	1.26
A2	21.73	24.47	6.00	1.04	54.1	0.402	1.67	0.534	1.28
A3	42.44	45.26	7.10	0.58	62.9	0.505	1.51	0.527	1.19
A4	63.81	66.89	7.59	0.40	69.3	0.592	1.58	0.527	1.17
B1	15.54	16.67	3.72	0.67	209	0.113	1.71	0.537	1.25
B2	32.37	34.73	3.99	0.60	236	0.196	1.78	0.544	1.28
B3	53.55	55.95	5.68	0.42	241	0.269	1.66	0.536	1.21
B4	74.23	77.27	6.37	0.43	248	0.339	1.71	0.538	1.21
C1	18.43	19.37	3.10	0.50	416	0.081	1.99	0.540	1.24
C2	35.45	37.75	3.43	0.55	428	0.141	1.98	0.560	1.34
C3	57.90	60.16	5.20	0.39	432	0.197	1.83	0.543	1.24
C4	79.62	82.48	5.66	0.40	438	0.248	1.82	0.546	1.25
D1	19.34	20.15	2.48	0.57	810	0.054	2.39	0.552	1.28
D2	36.93	38.07	3.06	0.48	817	0.090	2.18	0.541	1.23
D3	62.38	64.52	3.62	0.49	823	0.140	2.15	0.555	1.30
D4	84.38	86.61	5.12	0.49	830	0.174	2.08	0.548	1.24
E1	10.79	11.61	5.50	0.81	28.3	0.389	1.67	0.525	1.18
E2	17.14	17.77	4.21	0.44	169.8	0.158	1.86	0.535	1.18
E3	36.98	38.02	5.57	0.34	128.3	0.327	1.83	0.529	1.15
E4	58.01	59.28	6.61	0.19	84.4	0.504	1.48	0.526	1.13
E5	80.02	81.48	7.26	0.26	38.7	0.680	1.03	0.524	1.12
F1	43.20	47.91	6.82	0.80	109.8	0.368	1.48	0.524	1.21
G1	2.67	12.9	5.67	1.41	37.3	0.108	1.69	0.222	1.38
G2	3.70	9.7	5.49	1.44	35.6	0.153	1.61	0.334	1.32
G3	5.30	9.33	5.42	1.41	36.5	0.184	1.55	0.428	1.31
G4	9.5	4.39	5.47	1.62	37.1	0.279	1.52	0.720	1.19
G5	10.88	3.03	5.38	1.42	36.8	0.301	1.46	0.803	1.16

is in reality the equilibrium constant of an ion-exchange reaction expressed without regard for the activity coefficients in either phase, this variation is not surprising. A completely satisfactory explanation of the variation of $E_{Su}{}^+$ as a function of the composition of both phases can not be given. However, it follows moderately well the empirical equation

$$E_{Su}{}^+ = 0.60\mu + f(R_1) \tag{14}$$

where μ is the ionic strength of the aqueous phase and $f(R_1)$ is an empirical

function of R_1, presented graphically in Fig. 1:

$$R_1 = \frac{\overline{[SaH(+)\text{-}Ma]}}{\overline{[SaH(+)\text{-}Ma]} + \overline{[SaHSu]}} \tag{15}$$

In this figure, the continuous line pertains to the experiments of Series A, B, C, D, and G, where the concentration of the exchanger in the organic phase is between 0.091 and 0.095; the discontinuous line pertains to the experiments of Series E where this concentration is 0.046; and the circle pertains to Experiment F1 where the concentration is 0.202. For Series A, B, C, D, and G, the experimentally determined values of E_{Su}^{+} agree with those calculated by Eq. (14) with a maximum deviation of ± 0.14 and an average deviation of 0.05 (signs disregarded).

The major cause of these discrepancies is probably the inadequacy of Eq. (14). At the high ionic strengths of the aqueous solutions, the activity

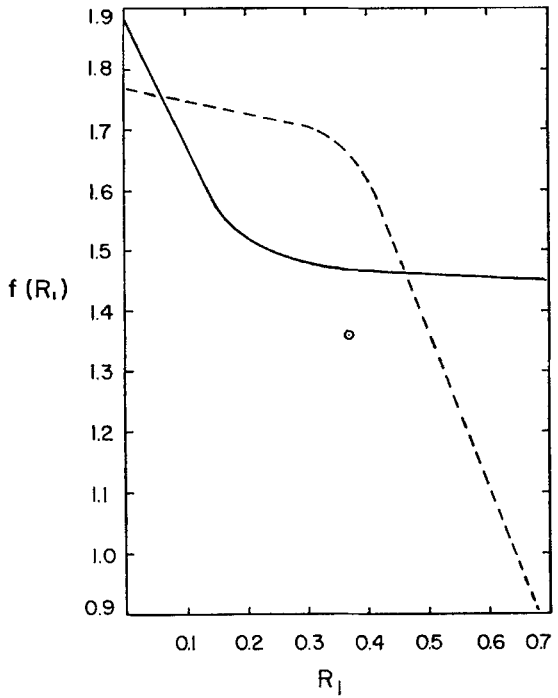

FIG. 1. Plot of $f(R_1)$ vs R_1. (——) Series A, B, C, D, and G. (- -) Series E. (◉) Experiment F1.

coefficients of the mandelate and sulfonate ions depend not only on the total ionic strength but also on the ratio of mandelate to sulfonate concentration. Likewise, in the organic phase, the activity coefficients depend not only on R_1 and the total concentration of exchanger, but also on the concentrations of *S*-amine and *S*-ammonium (−)-mandelate. An equation taking all these variables into account would be too cumbersome for convenient use. Furthermore Eq. (14) is sufficiently accurate to enable the investigators to select rationally the best conditions for the countercurrent resolution of racemic mandelate by either liquid–liquid chromatography or the Craig apparatus.

The Selectivity Coefficients of (+)-Mandelate vs (−)-Mandelate

This is, of course, the most important coefficient for the resolution of mandelate.

Table 2 reveals that the mean value of E_-^+ for Series A, B, C, and D is 1.25 ($\sigma = 0.04$). Since this variation is within the experimental error, the selectivity coefficient can be considered constant under the conditions of these experiments, i.e., racemic mandelate in the unequilibrated aqueous phase and 0.0902 to 0.0915 *M* exchanger in the organic phase.

The experiments of Series E were performed with a lower but constant concentration of exchanger. As is to be expected, these values of E_-^+ are lower than those of Series A, B, C, and D but constant among themselves (mean = 1.15, $\sigma = 0.03$).

The one experiment of Series F, done at a greater concentration of exchanger, was expected to yield a greater value of E_-^+ than that of Series A, B, C, and D. However, the value 1.21 is equal to mean of these four series within the experimental error. It appears that the value of 1.25 can not be exceeded by the use of greater concentrations.

The experiments of Series A, B, C, and D were done with racemic mandelate in the unequilibrated aqueous phase. Then after equilibration, the organic phase contained slightly more (+)-mandelate than (−)-mandelate. If R_2 is defined as

$$R_2 = \frac{\overline{[\text{SaH(+)-Ma}]}}{\overline{[\text{SaHMa}]}} \tag{16}$$

the mean value of R_2 for these series is 0.541, $\sigma = 0.010$. This variation of R_2 is not great enough to reveal a dependence of E_-^+ on R_2. Therefore, Series G was performed with wide variation in the enantiomeric composition of the mandelate in the initial aqueous phase and hence in the value of R_2.

As is to be expected, E_{-}^{+} decreased with increasing values of R_2. A plot of E_{-}^{+} vs R_2 is a straight line following the equation

$$E_{-}^{+} = 1.46 - 0.37R_2 \tag{17}$$

The maximum deviation of an experimental point from this line is only 0.02. However, this excellent agreement is fortuitous because experimental errors have increasing effects on E_{-}^{+} as R_2 approaches either zero or unity.

Selectivity Coefficient of Hydroxide vs Benzenesulfonate

The equation for this exchange is

$$E_{\mathrm{Su}}^{\mathrm{OH}} = \frac{[\overline{\mathrm{Sa}}][\mathrm{Su}^-]}{[\overline{\mathrm{SaHSu}}][\mathrm{OH}^-]}$$

According to Reaction (4)

$$[\overline{\mathrm{Sa}}] = [\mathrm{HMa}] \tag{18}$$

The concentration of hydroxide ion can be calculated from the pH of the aqueous phase provided that the ionic strength is small enough to permit the calculation of ionic activity coefficients from Kielland's (*3*) atomic radii. Actually these calculations were done for Experiment B1 and all experiments of Series A and G. The average value of $E_{\mathrm{Su}}^{\mathrm{OH}}$ is 3.9×10^7, $\sigma = 0.8 \times 10^7$. This large value is not surprising because the exchanger has acidic properties by virtue of its secondary nitrogen atom.

Solubility of *S*-Amine in Aqueous Salt Solutions

In the potentiometric titration of the equilibrated aqueous phase, if the observer notes the buret reading when the solution first becomes turbid because of the precipitation of *S*-amine, as well as the buret reading of the jump marking the complete neutralization of mandelic acid, these data enable him to calculate the solubility of *S*-amine. This was done for 14 of the first 16 experiments. The solubility in moles per liter follows the salting-out Eq. (*4*) is

$$\log S = -4.20 - 0.30\mu \tag{19}$$

where μ denotes the ionic strength of the solution at incipient turbidity, not that of the equilibrated aqueous phase. Because of the difficulty in detecting the first trace of turbidity, the relative error in the determination of S is about 10%.

Protolysis Constant of *S*-Ammonium Ion

In the titration of the equilibrated aqueous phases with sodium hydroxide, the buret readings between the first equivalence point and the appearance of the turbidity furnish the data needed for the calculation of the concentrations of *S*-ammonium ion and of *S*-amine. The concentration of hydrogen ion can be calculated from the pH readings provided that the ionic strength is small enough to permit the use of Kielland's ionic radii in the evaluation of the activity coefficient of hydrogen ion. Thus the protolysis constant of *S*-ammonium ion can be calculated. These computations were done for four of these titrations. The mean value of the constant is 1.0×10^{-8}, $\sigma = 0.3 \times 10^{-8}$.

CONCLUSIONS

The liquid anion-exchange system (−)-*N*-(1-naphthyl)methyl-α-methylbenzylammonium benzenesulfonate in nitrobenzene offers two important advantages over the solution of the chloride of the same cation in chloroform for the resolution of mandelate and other racemic anions: (a) Solubilities are more favorable, and (b) aqueous sodium hydroxide does not attack the solvent.

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