

Separation of Ascorbic Acid and 2-Keto-L-gulonic Acid

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Abstract □ The separation of ascorbic acid and 2-keto-L-gulonic acid by molecular sorption on a column of styrene-divinylbenzene copolymer-based sulfonic acid cation-exchange resin, with the relative degree of crosslinking of four, is described.

Keyphrases □ Ascorbic acid—separation from 2-keto-L-gulonic acid, cation-exchange chromatography □ 2-Keto-L-gulonic acid—separation from ascorbic acid, cation-exchange chromatography □ Chromatography with cation-exchange resins—separation of ascorbic acid and 2-keto-L-gulonic acid

The separation and recovery of ascorbic acid by exchange with anion-exchange resins (1–6) and the removal of ionic impurities from solutions of ascorbic acid by ion-exchange resins (7–10) were reported by some workers. However, there seems to be no available study on the separation of ascorbic acid and 2-keto-L-gulonic acid by molecular sorption on cation-exchange resins. The ion-exchange process involves exchange of anions with anion-exchange resin and exchange of cations with cation-exchange resin in equivalent amounts and requires chemical regeneration. On the other hand, molecular sorption on ion-exchange resin involves the sorption of solute on resin and does not involve the exchange process. Therefore, no chemical regeneration is required, and the elution of the sorbed solute can be achieved by solvent. This may provide a useful and economically attractive process for separation problems (11–21).

In this study the separation of ascorbic acid and 2-keto-L-gulonic acid by molecular sorption on cation-exchange resins is described. This is of interest because in the production of ascorbic acid, the conversion of 2-keto-L-gulonic acid to ascorbic acid is not complete. Table I gives representative data for the separation of ascorbic acid and 2-keto-L-gulonic acid.

EXPERIMENTAL

The chemicals were chemically pure, and freshly prepared aqueous solutions of organic acids were used. The resin used was a styrene-divinylbenzene copolymer-based sulfonic acid cation-exchange resin¹, with the relative degree of crosslinking (percentage nominal divinylbenzene content) of four. The resin was conditioned and regenerated into hydrogen form and a column was set up. The column data were: bed volume, 490 ml.; bed length, 210 cm.; and capacity of the resin in the column, 628 meq.

The procedure adopted for a run was as follows. The column was backwashed with distilled water and allowed to settle under gravity. The solution of ascorbic acid of known concentration (~0.05 *N*) was prepared in distilled water. The liquid in the column was brought to the bed level, the organic acid solution (10 ml.) was added, and the column was allowed to flow at 2 ml./min. A sample equal to void volume was first collected. Then samples (10 ml.) were collected and numbered as 1, 2, and so on. When the liquid in the column was again near bed level, distilled water (10 ml.) was added and the

Table I—Separation of 2-Keto-L-gulonic Acid and Ascorbic Acid with Water as Solvent and Eluant

Compound 10 ³ W ^a = Sample Number	2-Keto-L-gulonic Acid + 52.9	Ascorbic Acid 54.1
v.v. ^c	—	—
1–23	—	—
24	0.63	—
25	2.52	—
26	5.04	—
27	9.45	—
28	13.86	—
29	14.49	—
30	6.30	—
31	0.60	—
32	—	0.60
33	—	1.89
34	—	4.41
35	—	7.56
36	—	16.38
37	—	10.71
38	—	7.56
39	—	3.78
40	—	1.26
41	—	—

^a Organic acid content in millimoles in 10 ml. of organic acid solution initially sorbed on resin bed. ^b Organic acid content in millimoles in 10 ml. of effluent sample. ^c Void volume.

column was connected to an overhead reservoir of distilled water. Organic acid was determined in each sample by titration against a standard sodium hydroxide solution. After the run was over, the column was backwashed with distilled water and the liquid level was brought again to the bed level. The run was repeated with 2-keto-L-gulonic acid in distilled water. Such runs indicated that the elution of organic acids was practically complete and the separation of a mixture was feasible. The run was repeated with a mixture of ascorbic acid and 2-keto-L-gulonic acid.

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¹ Dowex 50WX4 (50/100), Dow Chemical Co.

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Determination of CMC of Polysorbate 20 in Aqueous Solution by Surface Tension Method

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Abstract □ The CMC of polysorbate 20 was determined using a surface tension method; the concentration (C) of polysorbate 20 studied varied from 0.001 to 10.000 mg./ml. The results show clearly that the surface tension (γ) decreases linearly with $\log C$ up to a concentration of 0.06 mg./ml. and is practically constant for more concentrated solutions. This suggests that the CMC of polysorbate 20 is in the vicinity of 0.06 mg./ml., which is in excellent agreement with the values obtained by other methods.

Keyphrases □ CMC—polysorbate 20, surface tension method □ Polysorbate 20—determination of CMC by surface tension method □ Surface tension method—determination of CMC for polysorbate 20

Among other methods, the surface tension method has been widely used to determine the CMC of a variety of nonionic surfactants (1), and the validity of this technique has been well established (2). However, the surface tension method has not been used to determine the CMC of the polysorbate family of surfactants, probably because of their alleged heterodisperse nature. Becher (1) cataloged the CMC values of polysorbate surfactants as determined by light-scattering and iodine solubilization methods, but no application of the surface tension method was mentioned. The surface tension method for the determination of CMC is more accurate than the light-scattering technique; with solubilization methods, one is always doubtful whether or not the solubilized material lowered the actual CMC.

Phares (3) studied the surface and interfacial behavior of polysorbate 20 and tabulated the values of surface tension (γ) as a function of concentration (C), but he did not discuss the CMC. His data did not yield a definite value of the CMC because of the difficulties outlined later. In the present article, results are reported on the surface tension behavior of polysorbate 20 and the value of the CMC derived from the plot γ versus $\log C$.

EXPERIMENTAL

The label of the polysorbate 20¹ sample used read polyoxyethylene (20) sorbitan monolaurate, HLB, 16.7. A stock solution containing 10.0 mg./ml. of polysorbate 20 was prepared using distilled water; from this stock solution, solutions of varying concentrations in the range 10.0–0.001 mg./ml. were prepared by dilution. As the molecular weights of such nonionics is not known with certitude, the concentrations are expressed in milligrams per milliliter. Surface tension (γ) values were obtained using an interfacial tensiometer²; the correction factor was calculated as suggested by Harkins and Jordan (4). The measured values of γ for toluene and water were in good agreement with literature values. The following important points concerning the actual experimental conditions and the mode of measuring γ for polysorbate 20 solutions should be mentioned.

1. All measurements were made at 28°.
2. The solutions used were 9–10 hr. old, *i.e.*, 9–10 hr. elapsed after the dilution and before the measurement of γ .
3. The fresh solution–air interface was left undisturbed for 3–5 min. before measurement of γ ; this procedure was necessary to obtain reliable and constant values of γ . During this interval (3–5 min.), γ decreased quite appreciably (in some cases by 5–6 dynes/cm.); after that time, γ values were quite concordant. The change of γ during this initial period could be attributed to the diffusion of surfactant molecules from the bulk to the interface.

RESULTS AND DISCUSSION

The plot of γ versus $\log C$ is shown in Fig. 1. It is clear that initially γ varies linearly with $\log C$ up to a concentration of 0.06 mg./ml. and then stays practically constant for more concentrated solutions, *i.e.*, up to 10.0 mg./ml. (which is 160 times 0.06 mg./ml.). To be precise, γ decreases slightly (1.0 dyne/cm.) in the concentration range from 0.06 to 1.00 mg./ml. and is essentially constant for higher concentrations. Furthermore, the break in the plot of γ versus $\log C$ is quite sharp considering the broad molecular distribution of the nonionic, which suggests that the CMC value for polysorbate 20 is in the vicinity of 0.06 mg./ml. If the two straight-line portions in Fig. 1 are extended, they cross at a concentration of 0.05 mg./ml.; this indicates that the CMC of polysorbate 20 determined by the extrapolation procedure is 0.05 mg./ml. In any case, the present results suggest clearly that the CMC of polysorbate 20 lies

¹ Tween 20, Atlas Chemical Industries, Wilmington, Del.

² Cenco Du Nouy.