

resistance was noted. There have been reports of hypovolemia (7) and of redistribution of blood (*e.g.*, cutaneous vasoconstriction) although these latter effects appear to be due to the vasoconstrictor action of ST-155 (16).

It cannot be stated at present if or how the supersensitization to the pressor actions of epinephrine and tyramine are related to the reflex hypotension or bradycardia. Moreover, that central inhibition of cardiac sympathetic nerve fibers by ST-155 does indeed occur must also remain an unresolved postulate until direct studies are made to test this hypothesis and to correlate this with the hypotensive action of ST-155. However, the authors of a related study which appeared shortly after the present investigation was completed, concluded that ST-155 owed its hypotensive action to a central inhibition of "medullary vasomotor and accelerator centers" (19).

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Keyphrases

Hypotensive activity—tolazoline analog
2-(2,6-Dichlorophenylamino)-2-imidazoline
HCl (ST-155)—hypotensive activity
Pressor, depressor activity—ST-155
Cardiovascular activity—ST-155
Central mediation—ST-155 activity

Molecular Sorption on Ion-Exchange Resins: Studies with Coumarin

By R. S. HEGDE, M. J. MEHTA, R. A. BHATT, D. J. PATEL, and S. L. BAFNA

The sorption equilibrium of coumarin on ion-exchange resins of different degree of cross-linking, ionogenic groups, and counter ions in water and aqueous methanols has been studied and the results are discussed.

EARLIER, (1-3) the sorption and separation of coumarins on ion-exchange resins has been reported. This paper covers the study of the sorption equilibrium of coumarin on ion-exchange resins of different degrees of cross-linking, ionogenic groups, and counter ions in water and aqueous methanols at room temperature ($\sim 30^\circ$).

EXPERIMENTAL

Resins—(a) Styrene divinylbenzene copolymer-based sulfonic acid cation-exchange resins¹ of relative degree of cross-linking (% nominal divinylbenzene content) as 4, 8, and 12 (further referred to as X4, X8, and X12) of -100, +200 mesh; the resins were

conditioned, regenerated, and moisture content and capacity were estimated (4, 5).

The different ionic forms of the resins were obtained by passing an excess of the salt or hydroxide solution through the resin bed. The resin was then washed, filtered, air dried, moisture content determined, and the capacity of the air-dried form of the resin calculated from the capacity of the oven-dried resin in the hydrogen form.

(b) Carboxylic acid cation-exchange resins² of relative degree of cross-linking (% nominal divinylbenzene content) $X = 2.5, 5, 10$, and 15 (further referred to as resin CX 2.5, CX 5, CX 10, and CX 15) of -40, +60 mesh; these are presumably based on acrylic acid divinylbenzene copolymers. The resins were conditioned, regenerated, and the moisture content and capacity were estimated as given before (5). The ionic forms of the resins were obtained by passing an excess of the corresponding hydroxide solution through the resin bed. The resins were then washed free of alkali, filtered, air dried, and the moisture content was determined. The capacity of the resins in different forms was calculated from the capacity of the oven-dried resin in the hydrogen form.

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¹ Dowex 50W, Dow Chemical Co., Midland, Mich.

² Zeo-karb 226, Permutit Co., London, England.

(c) IR-200³ of -20, +60 mesh; this is presumably styrene divinylbenzene copolymer-based sulfonic acid cation-exchange resin of relative degree of cross-linking about 20 but has an expanded structure. The resin was conditioned, regenerated, and moisture content and capacity were determined.

(d) IRC-50⁴ of -40, +60 mesh; this is presumably methacrylic acid divinylbenzene copolymer-based carboxylic acid cation-exchange resin of relative degree of cross-linking about 8. The resin was conditioned, regenerated, and the moisture content and capacity were determined and the ionic forms prepared as given in (b).

(e) Styrene divinylbenzene copolymer-based strongly basic anion-exchange resins⁵ of relative degrees of cross-linking: 2, 4, and 8 (further referred to as 1X2, 1X4, and 1X8), of -20, +50 mesh; these have presumably trimethyl ammonium groups as ionogenic groups. The resins were conditioned, regenerated, and moisture content was determined. For the estimation of capacity weighed samples (\sim 0.5 Gm.) of air-dried resin were mixed with 100 ml. of 0.05 *N* hydrochloric acid in well-stoppered flasks with frequent shaking. The next day, the remaining hydrochloric acid was estimated by titrating the aliquots with standard sodium hydroxide solution and the capacity was then calculated. Chloride form of these resins was obtained by passing sodium chloride solution through the resin bed in an excess of, the resin was then washed, filtered, air dried, and the moisture content was determined. The capacity was calculated from an oven-dried capacity of the hydroxyl form of the resins.

(f) Styrene divinylbenzene copolymer-based strongly basic anion-exchange resins⁵ of relative degrees of cross-linking as 4 and 8 (further referred to as 2X4 and 2X8) of -20, +50 mesh; these presumably have dimethyl methylol ammonium groups as ionogenic groups. The resins were conditioned, regenerated, the moisture content and capacity of the resins were determined, and the chloride forms prepared.

(g) Styrene divinylbenzene copolymer-based weakly basic anion-exchange resin G⁷ of relative degree of cross-linking about 8 and -14, +52 mesh; the ionogenic groups are presumably diethylamino groups. The resin was conditioned, regenerated, and the moisture content was determined. For the estimation of capacity, a weighed sample (\sim 1 Gm.) of air-dried resin was mixed with 50 ml., 1 *N* in NaCl and 0.1 *N* in HCl of solution with frequent shaking. The next day, the remaining hydrochloric acid was estimated by titrating the aliquots with standard sodium hydroxide solution and the capacity was then calculated.

Chemicals and Solvents—Chemicals were of A.R. or C.P. grade. Aqueous methanols were prepared by volume; for example, 10% methanol was prepared by making 100 ml. of methanol to 1 L. with distilled water. The dielectric constant of each solvent was measured on Multi-Dekameter-type DK 06 (WTW) using 1.8 m./cs. frequency at room temperature (\sim 30°).

Procedure—Coumarin solutions of different con-

centration and of known volume were mixed with weighed amounts of air-dried resins in well-stoppered flasks, with frequent shaking at room temperature (\sim 30°). After sufficient time, after the equilibrium was reached, the initial and the equilibrium concentrations were determined by ultraviolet absorption (6) with a Beckman model DU spectrophotometer using 10-mm. quartz cells.

RESULTS AND DISCUSSION

The synthetic organic ion-exchange resins (7, 8) consist of an irregular, three-dimensional network of hydrocarbon chains, to which ionogenic groups are attached and the surplus electric charge is balanced by mobile counter ions. The hydrocarbon network is hydrophobic but the ionogenic groups are hydrophilic. Hence, when the resin particle is placed in water, it sorbs water and swells to a limited extent. The amount of water sorbed and the extent of swelling depend on the degree of cross-linking and the counter ions. If the external solvent contains a nonelectrolyte, it is also sorbed to a certain extent and after some time a state of equilibrium is reached. The amount sorbed will depend on several factors (7), which include the London (dispersion) interactions, the dipole-dipole interactions, the relative solubility of the solute in the medium inside and outside the resin particle, the solvent uptake and the volume of the swollen resin particle, the equilibrium concentration of the solute in the external solution, and the temperature. Besides these, there may also be specific interactions in a particular system.

A sorption equilibrium study involves three substances: the resin, the solvent, and the solute. For the resin, the variables may include the matrix structure, the relative degree of cross-linking, the type and the acid or base strength of the ionogenic group, and the charge, shape, size, and hydration of the counter ions. The solvent may be aqueous, mixed, or organic, it may be polar or nonpolar, and have different dielectric constants and solvation of the ionogenic groups and the solute molecules. For the solute, the variables may include the shape, size, polarity, and the relative solubility in the medium inside and outside the resin particle.

The amount of the solute sorbed per unit capacity of the resin at a given temperature will hence be determined by the overall effect and a complex behavior is to be expected; the systematic study of the variables may help toward better understanding of the phenomenon and with this object this study was undertaken.

The sorption equilibrium studies were carried out at room temperature, since the small variation in temperature did not make substantial change. The values of *S* were calculated from $S = (C_0 - C_e)/C_r$, where *C*₀ and *C*_e are the initial and equilibrium concentration of solute, gram moles per liter, and *C*_r is the capacity of air-dried resin (Table I) in equivalents added per liter of solution, and then *S* was plotted against *C*_e. The plots were linear. Figure 1 gives a typical example to illustrate this. The slope of such plots is termed as *B* (4).

Table II gives the values of *B* for the sorption of coumarin on sulfonic acid cation-exchange resins in hydrogen form in water and aqueous methanols. It is observed that with increase in the % methanol

³ Amberlite IR-200, Rohm & Haas Co., Philadelphia, Pa.

⁴ Amberlite IRC-50, Rohm & Haas Co., Philadelphia, Pa.

⁵ Dowex 1, Dow Chemical Co., Midland, Mich.

⁶ Dowex 2, Dow Chemical Co., Midland, Mich.

⁷ Deacidite G, Permutit Co., London, England.

TABLE I—CAPACITY OF ION-EXCHANGE RESINS

Cation-Exchange Resins		Anion-Exchange Resins	
Resin	Oven-dried Capacity, meq./Gm.	Resin	Oven-dried Capacity, meq./Gm.
X4	5.06	1X2	3.9
X8	4.89	1X4	3.5
X12	4.85	1X8	3.6
IR-200	4.78
CX 2.5	10.6	2X4	3.5
CX 5	9.77	2X8	2.67
CX 10	8.70
CX 15	6.84	G	4.0
IRC-50	10.4

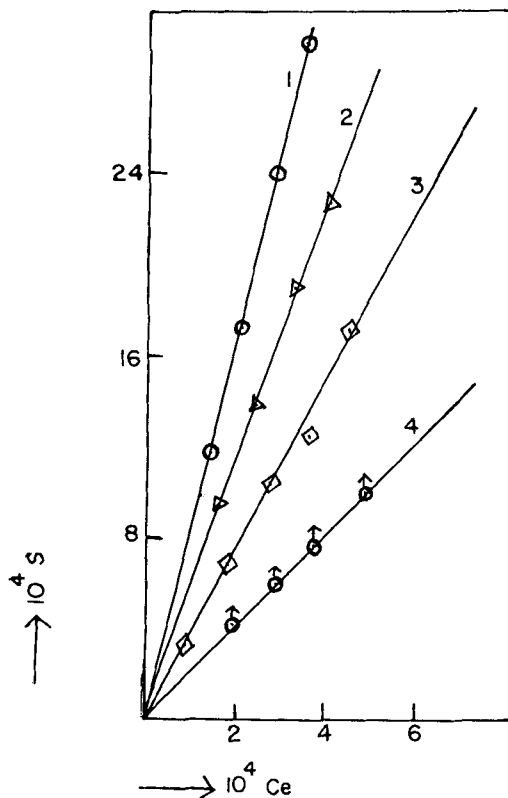


Fig. 1—Plots of S against Ce for the resin X4 in hydrogen form in water (1), 10% methanol (2), 19% methanol (3), and 30% methanol (4).

in the external solvent, B decreases. Figure 2 gives the plot of $\log B$ against $\log D$ (D is the dielectric constant of the external solvent) and the plots are linear; the values of slopes m , and the intercepts i are given in Table II. With the increase in the degree of cross-linking, X and m increase but i and B decrease.

For resin IR-200 (Table II) also, B decreases as the methanol content of the solvent increases, but the values of B are lower than what may be expected for 50W-type resin of $X = 20$. This implies that for sulfonic acid cation-exchange resins, the sorption is relatively less on a resin of expanded structure than that on a gel-type resin.

Table III gives the values of B for sorption of coumarin on the sulfonic acid cation-exchange resins of degree of cross-linking 4, 8, and 12 in H^+ , Li^+ , Na^+ , K^+ , and NH_4^+ forms. With the increase

TABLE II—SORPTION OF COUMARIN ON SULFONIC ACID CATION-EXCHANGE RESINS IN WATER AND AQUEOUS METHANOLS

Resin	B in Solvent with Methanol % =				m	i
	0	10	19	30		
X4	8.5	5.8	3.8	2.1	7.6	-13.53
X8	7.3	4.3	2.6	1.2	9.6	-17.42
X12	6.3	3.5	2.0	0.9	10.6	-19.38
IR-200	1.8	0.8	0.41

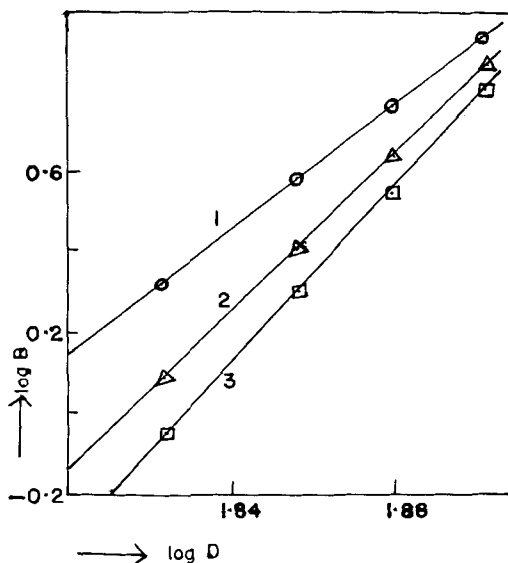


Fig. 2—Plots of $\log B$ against $\log D$ for the resins X4 (1), X8 (2), and X12 (3) in hydrogen form.

TABLE III—SORPTION OF COUMARIN ON SULFONIC ACID CATION-EXCHANGE RESINS WITH DIFFERENT COUNTER IONS

Resin	B When Counter Ion is				
	H^+	Li^+	Na^+	K^+	NH_4^+
X4	8.5	6.4	6.2	5.8	5.3
X8	7.3	6.8	7.9	7.9	6.8
X12	6.3	7.6	8.6	8.6	7.8

in X , for the hydrogen form of the resin, B decreases, but for Li^+ , Na^+ , K^+ , and NH_4^+ forms, B increases. For resin X4, B is in the order $H^+ > Li^+ > Na^+ > K^+ > NH_4^+$, for resin X8 in the order $K^+ \sim Na^+ > H^+ > Li^+ > NH_4^+$, and for resin X12 in the order $K^+ \sim Na^+ > Li^+ > H^+ > NH_4^+$. Thus the order for H^+ , Li^+ , and Na^+ forms for resin X4 is reversed for resin X12. B for NH_4^+ form is always less than that for K^+ and Na^+ forms.

The sorption of coumarin was studied in water on resin X4 in different ionic forms. The values of B (Table IV) may be arranged in the order $H^+ > Fe^{+3} \sim Al^{+3} > Ca^{+2} > Ni^{+2} \sim Co^{+2} \sim Li^+ > Na^+ > Fe^{+2} > Cu^{+2} > K^+ \sim Sr^{+2} > Ba^{+2} > NH_4^+ > C_5H_5NH^+ > Ce^{+4}$.

Table V gives the values of B for sorption of coumarin on carboxylic acid cation-exchange resins of different X and ionic form. With increase in X , B first increases and then decreases for H^+ , Li^+ , Na^+ , and K^+ forms, but for NH_4^+ form B increases with increase in X ; for the ionic forms, B decreases in the order $H^+ > Li^+ > Na^+ > K^+ > NH_4^+$.

TABLE IV—SORPTION OF COUMARIN ON SULFONIC ACID CATION-EXCHANGE RESIN X4 WITH DIFFERENT COUNTER IONS (C.I.)

C.I.	B	C.I.	B	C.I.	B	C.I.	B	C.I.	B
H ⁺	8.5	Li ⁺	6.4	Ca ⁺²	6.6	Fe ⁺²	6.0	Fe ⁺³	7.4
NH ₄ ⁺	5.3	Na ⁺	6.2	Sr ⁺²	5.8	Cu ⁺²	5.9	Al ⁺³	7.4
C ₆ H ₅ NH ⁺	4.8	K ⁺	5.8	Ba ⁺²	5.1	Co ⁺²	6.4	Ce ⁺⁴	2.6
						Ni ⁺²	6.4		

TABLE V—SORPTION OF COUMARIN ON CARBOXYLIC ACID CATION-EXCHANGE RESINS WITH DIFFERENT COUNTER IONS

Resin	B when the Counter Ion is				
	H ⁺	Li ⁺	Na ⁺	K ⁺	NH ₄ ⁺
CX 2.5	4.1	2.8	2.5	1.9	0.24
CX 5	9.0	5.9	4.2	3.7	0.71
CX 10	19.5	10.3	8.9	5.4	2.8
CX 15	9.1	9.0	6.9	6.4	5.8
IRC-50	6.7	2.9	1.7	1.3	0.74

TABLE VI—SORPTION OF COUMARIN ON ANION-EXCHANGE RESINS IN CHLORIDE FORM IN WATER AND AQUEOUS METHANOLS

Resin	B in Solvent with % Methanol =			
	0	10	20	30
1X2	9.0	6.1	5.0	2.9
1X4	21.0	12.5	9.2	6.2
1X8	21.0	12.5	9.2	6.2
2X4	13.9	8.7	6.9	4.3
2X8	38.0	21.0	16.7	9.0
G	23

For IRC-50, the same order is valid, but the values of *B* are relatively lower than those expected for carboxylic acid cation-exchange resin type resin of *X* ~ 8. This implies that the sorption for acrylic and methacrylic acid-based resins is significantly different.

Table VI gives the values of *B* for the sorption of coumarin on anion-exchange resins in chloride form, with different *X* and type of ionogenic groups, in water and aqueous methanols. With increase in the methanol content and hence decrease in the dielectric constant of the solvent, *B* decreases. For 1X2, 1X4, and 1X8 resins, *B* increases with increase in the degree of cross-linking from 2 to 4 and is practically constant for increase in *X* for 4 to 8. For 2X4 and 2X8 resins, *B* increases when *X* increases from 4 to 8. *B* for 1X4 is greater than that for 2X4, but for 1X8 is lower than those for 2X8. *B* for the weak base anion-exchange resin G is greater than that for resin 1X8 but less than that for resin 2X8.

Table VII gives the values of *B* for sorption of coumarin on strong base anion-exchange resins in the hydroxyl form of different *X* in water and aqueous methanols. For 1X2, 1X4, and 1X8 resin, *B* increases with increase in *X* from 2 to 8 in water and 10% aqueous methanol; for 40% and 70% aqueous methanols, *B* first increases for increase in *X* from 2 to 4 and then decreases for increase in *X* from 4 to 8. For 2X4 and 2X8 resins, *B* varies in a similar manner for increase in *X* from 4 to 8. The values of *B* for 1X2, 1X4, and 1X8 resins are greater than those for the corresponding 2X4 and 2X8 resins of same *X*.

With increase in % methanol of the solvent and hence decrease in the dielectric constant of the solvent, *B* for resin 1X2 increases, for resin 1X4 decreases and then increases, and for resin 1X8 decreases. For resins 2X4 and 2X8, *B* decreases with increase in % methanol of the solvent. For the strong base anion-exchange resins, *B* for hydroxyl form is considerably greater than that for chloride form. This may be attributed to the strongly alka-

TABLE VII—SORPTION OF COUMARIN ON STRONGLY BASIC ANION-EXCHANGE RESINS IN HYDROXYL FORM IN WATER AND AQUEOUS METHANOLS

Resin	B in Solvent with % Methanol =			
	0	10	40	70
1X2	24	26	31	75
1X4	97	82	79	117
1X8	121	117	75	69
2X4	68	40	30	23
2X8	106	52	15	9

line nature of the resins in the hydroxyl form and the relatively greater solubility of coumarin in alkaline medium; this comparison also suggests that in water 1X2, 1X4, and 1X8 resins should be more basic than the corresponding 2X4 and 2X8 resins of the same *X*.

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Keyphrases

Ion-exchange resins
 Coumarin adsorption equilibrium—ion-exchange resins
 Ionic resin forms—prepared
 Solvent effect adsorption equilibrium
 UV spectrophotometry—analysis