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## SORPTION OF UNSATURATED MONOCARBOXYLIC ACIDS ON ANION-EXCHANGE RESINS AND NON-IONIC RESINS FROM AQUEOUS SOLUTIONS

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### SUMMARY

An increasing number of carbon atoms in unsaturated carboxylic acids gave rise to increased distribution coefficients in sulphate and acetate solutions, both on styrene-divinylbenzene resins and on anion-exchange resins. On the non-ionic resins the double bond led to a large decrease in the retention volume, which was less for 2-alkenoic acids than for isomers with the double bond more distant from the carboxylic acid group. The results indicate that hydrophobic interactions had a larger effect than  $\pi$ -bond interactions with the aromatic resin. For the anion exchangers, hydrogen bonding explains the higher retention of 2-alkenoic than alkenoic acids.

The carboxylate ions derived from 2-alkenoic acids exhibited a higher ion-exchange affinity than those from alkenoic acids. This can be related to the greater acid strength of the parent acid.

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### INTRODUCTION

Only a few comparisons between the sorption of unsaturated and saturated monocarboxylic acids in aqueous solutions onto anion-exchange resins and non-ionic resins have been published<sup>1-4</sup>. In the present paper the behaviour of unsaturated aliphatic acids with three to six carbon atoms is compared with that of the corresponding saturated acids in solutions containing sodium sulphate, sulphuric acid, sodium acetate or acetic acid.

### EXPERIMENTAL

The total retention volumes during the elution of the acids from anion-exchange resins of the quaternary ammonium type and from non-ionic styrene-divinylbenzene resins were determined in jacketed columns. The peak positions were determined with a refractive index detector and UV absorption at 254 nm. The columns were filled by slurry-packing in water and conditioned by pumping the eluent through the column at a high rate (12 cm min<sup>-1</sup>). The bed volume,  $X$ , was determined after the conditioning. No correction was applied for small changes due to compression or

swelling. To suppress the effect of irreversible shrinkage<sup>5</sup> in aqueous media, the non-ionic resins were kept in 0.001 *M* sulphuric acid for at least 20 days before being used for the determination of retention volumes.

The peak elution volume  $\bar{V}$ , determined as the total retention volume minus the dead volumes before and after the resin bed, was calculated in bed volumes,  $\bar{V}/X$ . The interstitial volume is a well-defined quantity for the anion exchangers of the gel type, and the retention is reported as the volume distribution coefficient  $D_v = \bar{V}/X - \epsilon_p$ , where  $\epsilon_p$  is the relative interstitial volume (0.39). For the non-ionic styrene-divinylbenzene resins the interstitial volume depends on test substance<sup>6</sup>. No attempt was made therefore to calculate the distribution coefficients for these resins.

The anion-exchange column packed with Dowex 1-X10 (7–10  $\mu\text{m}$ ) was 200  $\times$  2.5 mm I.D. The column packed with Aminex A-28 (8–12  $\mu\text{m}$ ) was 148  $\times$  2.5 mm I.D. The non-ionic resin Amberlite XAD-2 was crushed and fractionated carefully to obtain a particle size of 0.10–0.12 mm before packing the column (160  $\times$  2.5 mm I.D.). The non-ionic Hitachi gel 3011 was supplied as beads with a particle size of 7–17  $\mu\text{m}$ , and the column dimensions were 337  $\times$  2.55 mm I.D. Propenoic acid was purified by crystallization and distillation under vacuum at 53–56°C. Vacuum distillation was used for 3-butenic acid to remove small amounts of 2-butenic acid. No interfering impurities were found during chromatography of the other acids, which were applied as received from commercial sources. 2-Butenoic, 2-pentenoic and 2-hexenoic acids were in *trans* form.

The carboxylic acids were dissolved in the eluent and introduced through a 100- $\mu\text{l}$  sample loop. In all experiments referred to in the tables, the applied amounts of carboxylic acids were 2.4  $\mu\text{mol}$ . If not otherwise stated, the experiments were performed at 50°C. An increase in the applied amount led to a lower peak elution volume for all systems in which tailing elution peaks were obtained. Hence, the reported retention data are dependent on the concentration of the solute. In experiments on Dowex 1-X10 in 0.01 *M* sodium sulphate, the adjusted retention volume increased by 6% when the loaded amounts of propanoic and butanoic acids were decreased to 0.6  $\mu\text{mol}$ . For pentanoic acid the decrease was 10%. Similar effects were obtained in 0.05 *M* sodium sulphate.

In the experiments reported in the tables and figures, the nominal linear (empty tube) flow-rate was 5  $\text{cm min}^{-1}$ . A change by a factor of two had no significant effect on the experiments with the anion exchangers and with the non-ionic resins in acid media.

#### *Non-ionic styrene-divinylbenzene resins*

Most experiments with the non-ionic resins were performed in 0.01 *M* sulphuric acid, which means that the carboxylic acids were virtually non-dissociated. Table I shows that on both non-ionic styrene-divinylbenzene resins the sorption of the saturated as well as of the unsaturated acids increased within each homologous series. For all compounds studied the retention volume on the Hitachi gel was much higher than that recorded on Amberlite XAD-2. The difference between  $\ln \bar{V}/X$  for one acid and that of its next lower homologue, denoted  $\Delta$ , exhibited systematic variations. The values were much larger for the Hitachi gel than for XAD-2. An increase in  $\Delta$  with an increasing number of carbon atoms in the acids was obtained on both resins. The  $\Delta$  values were higher for saturated than for unsaturated acids.

TABLE I

RETENTION DATA IN 0.01 M SULPHURIC ACID ON NON-IONIC STYRENE-DIVINYLBENZENE RESINS

Acids	Amberlite XAD-2			Hitachi gel, 3011		
	$\bar{V}/X$	$\Delta$	$\pi$	$\bar{V}/X$	$\Delta$	$\pi$
Propanoic	1.77			3.29		
Propenoic	1.58		-0.11	2.78		-0.17
Butanoic	5.14	1.07		11.8	1.28	
2-Butenoic	4.02	0.93	-0.25	8.83	1.16	-0.29
3-Butenoic	2.85		-0.59	6.22		-0.64
Pentanoic	20	1.35		52	1.48	
2-Pentenoic	15.0	1.31	-0.29	35	1.37	-0.40
4-Pentenoic	8.98		-0.81	21		-0.91
Hexanoic	91	1.52				
2-Hexenoic	62	1.43	-0.38			

On both resins the unsaturated acids were held less strongly than the corresponding saturated acid. The difference in  $\ln \bar{V}/X$  denoted  $\pi$  was less negative for the 2-alkenoic acids than for those with the double bond more distant from the carboxylic acid group. It has previously been shown that cyclohexylacetic acid is held much more strongly on the Hitachi gel than phenylacetic acid, which is less hydrophobic, and that the same is true for 3-cyclohexylpropanoic acid compared with the corresponding aromatic acid<sup>4</sup>. These and other results led to the conclusion that, in aqueous solution, hydrophobic interactions have a greater influence on the sorption than  $\pi$ -bond interactions between the aromatic compounds and the resins. The results presented in Table I are consistent with these observations. Evidently, the interactions between the double bonds in the solutes and water suppress the hydrophobic contributions to the sorption so effectively that the net result is a significantly decreased retention volume. For molecules with the same number of carbon atoms containing two hydrophilic groups, one of which is terminal (at C-1), the largest hydrophobic interactions will be obtained if the second hydrophilic group is linked to C-2<sup>7</sup>. This explains the larger retention volume of 2-butenic acid compared with 3-butenic acid, and the elution order 4-pentenoic < 2-pentenoic acid.

A slight tailing was observed for the acids with low distribution coefficients, whereas acids which appeared late on the chromatograms exhibited a severe tailing. Mixtures of an organic solvent, e.g. methanol or ethanol, in water can be used as eluents to suppress the tailing. As a complement, chromatograms were recorded in acetic acid. The example presented in Fig. 1A shows that the elution order in 0.5 M acetic acid was the same as that observed in 0.01 M sulphuric acid. Although the retention volumes were lower than in the sulphuric acid, the more hydrophobic acids exhibited a severe tailing.

Experiments with butanoic, 3-butenic and 2-butenic acids on the Hitachi gel in 0.5 M acetic acid showed that the retention volume decreased with increasing temperature. The change in enthalpy was estimated from plots of  $\ln \bar{V}/X$  versus  $1/T$  ( $T$  = thermodynamic temperature). The most negative value was obtained for butanoic

TABLE II  
RETENTION DATA IN SULPHURIC ACID AND SODIUM SULPHATE ON DOWEX 1-X10

Acids	pK	0.01 M Sulphuric acid			0.01 M Sodium sulphate			0.05 M Sodium sulphate			0.25 M Sodium sulphate		
		$D_v$	$A$	$\pi$	$D_v$	$A$	$\pi$	$D_v$	$A$	$\pi$	$D_v$	$A$	$\pi$
Propanoic	4.87	1.32			2.16			2.06			1.94		
Propenoic	4.25	1.98		0.40	4.0		0.62	3.22		0.45	2.70		0.33
Butanoic	4.80	2.42	0.60		3.50	0.48		3.13	0.42		2.80	0.37	
2-Butenoic	4.70	2.89	0.38	0.18	4.9	0.20	0.34	4.2	0.25	0.28	3.80	0.35	0.31
3-Butenoic	4.35	2.33		-0.03	4.6		0.27	3.7		0.16	3.12		0.11
Pentanoic	4.80	5.3	0.79		7.5	0.76		6.9	0.78		5.4	0.66	
2-Pentenoic	4.74	5.9	0.71	0.10	9.6	0.67	0.25	8.5	0.72	0.22	7.3	0.65	0.29
4-Pentenoic	4.67	3.9		-0.31	6.3		-0.17	5.4		-0.24	4.9		-0.10
Hexanoic	4.80	12	0.82		18	0.90		16	0.86		17	1.15	
2-Hexenoic	4.75	12	0.71	0.0	18	0.66	0.0	18	0.74	0.12	17	0.85	0

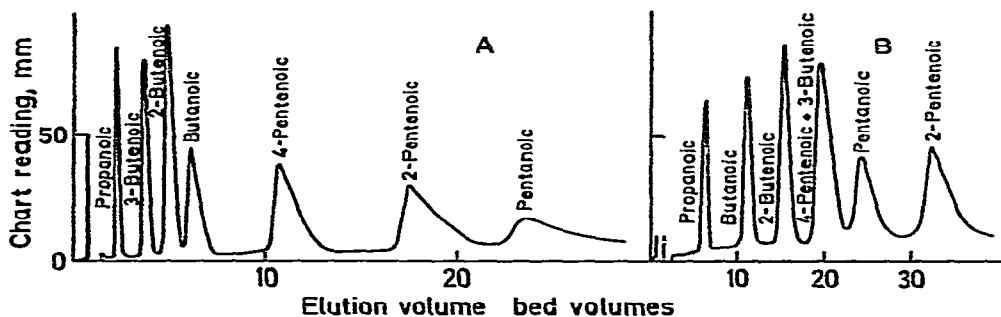


Fig. 1. Chromatography of aliphatic carboxylic acids in 0.5 *M* acetic acid. A, Non-ionic resin (Hitachi gel). B, Anion-exchange resin (Aminex A-28).

acid ( $\Delta H = -9.5$ ), while the values obtained for 2-butenoic and 3-butenoic acids were  $-8.9$  and  $-6.7$   $\text{kJ mole}^{-1}$ , respectively.

As expected, much lower retention volumes were observed when the acids were chromatographed as carboxylate ions. Hence, the peak elution volume of propanoate on XAD-2 in 0.05 *M* sodium acetate correspond to *ca.* one bed volume, whereas pentanoate and hexanoate appeared after three and six bed volumes, respectively, of the eluent had passed through the column. The elution curves exhibited a severe fronting, and the peak positions depended on the amount of solute applied to the column. From a practical point of view, it is important that the adsorption of long-chain fatty acids is suppressed when the acids are converted into anions, but it should be noted that they are still held so strongly that large amounts of aqueous eluents are required to displace higher homologues from the resin. For this reason, organic solvents containing a neutralizing agent such as sodium hydroxide or ammonia are applied when strongly hydrophobic acids are to be displaced from non-ionic styrene-divinylbenzene resins.

#### *Anion-exchange resins in sulphuric acid*

Table II shows that the retention volumes on Dowex 1-X10 in 0.01 *M* sulphuric acid increased with an increasing number of carbon atoms, both for the saturated and for the unsaturated acids. Again, the  $\Delta$ -values, here calculated from the  $D_v$  values, increased within each homologous series and were lower for the unsaturated than for the saturated species. The  $\Delta$ -values were much lower than those observed for the non-ionic resins in the same medium. A comparison with the retention volumes given in Table I shows that propanoic acid, which is less hydrophobic and has a much higher dissociation constant than any of the other acids, was retained more strongly by Dowex 1-X10 than by Amberlite XAD-2. All other acids were held much more strongly by the non-ionic resin. The largest differences between  $\ln D_v$  found on the two resins were observed for the most hydrophobic acids.

These results support the conclusions that hydrophobic interactions, although less important than for the non-ionic resin, contribute markedly to the sorption of the carboxylic acids onto the sulphate form of the anion-exchange resin and that this contribution is most important for the higher homologues. The high swelling pressure in the resin phase of the anion exchanger will suppress the sorption of molecules

with large partial molar volumes more effectively than that of smaller molecules<sup>8</sup>. Evidently, this factor has a comparatively small influence on the net adsorption.

Since the acids were virtually non-dissociated, ion exchange cannot be of great importance. On the other hand, the opposite effect of the double bond in the  $\alpha$ -position (positive  $\pi$ -values) compared with the non-ionic resins, indicates that interactions between the carboxylic acid group in the acids and the sulphate form of the anion exchanger contribute to the sorption of the carboxylic acids. One known mechanism for the sorption of free carboxylic acids onto anion-exchange resins is hydrogen bonding<sup>9</sup>. Sulphate ions are known to enter into hydrogen bonding, serving as proton acceptors<sup>10</sup>. Hence, the results suggest that besides non-polar interactions, including hydrophobic interactions, hydrogen bonding with the resin contributes to the sorption of carboxylic acids on the sulphate form of anion exchangers. The effect of the hydrogen bonding with the resin increases with an increasing strength of the acid<sup>11</sup>.

The acids with the double bond in the  $\alpha$ -position are stronger than the corresponding saturated acids. The largest difference between the  $pK$  values is that between propanoic and propenoic acids. As shown in the table, the  $\pi$ -value was larger for propenoic acid than for the other 2-alkenoic acids. A negative  $\pi$ -value was observed for 3-butenic acid, although this acid has a higher acid strength than butanoic acid. Lowered hydrophobic interactions explain this result. As expected, the most negative  $\pi$ -value was observed for 4-pentenoic acid. These results support the conclusion that hydrogen bonding between the carboxylic proton and the resin contributes markedly to the sorption of the carboxylic acids onto the sulphate form of the anion exchanger in acid solution.

#### *Anion-exchange resins in sodium sulphate solution*

The experiments in sodium sulphate solutions were made without any addition of sulphuric acid or alkali. The pH of the solutions was *ca.* 6.5. Some tailing was obtained with the lower homologues, and the tailing increased with an increasing number of carbon atoms. As shown in Table II, the distribution coefficients of the carboxylic acids (carboxylate anions) decreased with an increasing concentration of sodium sulphate. In the idealized case, where the dissociation is complete and the activity coefficients and invasion of cations into the resin phase can be disregarded, an increase in the concentration of sodium sulphate by a factor of 5 should, according to mass-action law, lead to a  $D_v$  equal to that at the lower concentration multiplied by  $5^{-0.5}$ . The results given in the table show that the observed decrease was much smaller. The decrease in the activity coefficients of sodium sulphate with an increasing concentration contributes markedly to the observed effect. The very small influence of the sulphate concentration and the difference in concentration dependency observed for different carboxylate anions show that the deviations from the idealized conditions are very large. It is noteworthy that for hexanoic acid a slight effect on  $D_v$  in the opposite direction (salting out) was observed when the eluent concentration was changed from 0.05 to 0.25 *M*. Similar salting-out effects have been observed for aromatic carboxylate anions, in sodium salt solutions<sup>12</sup>.

As previously shown<sup>13</sup>, the distribution coefficients for hydrophilic carboxylate anions decrease with an increasing partial molar volume. This is in agreement with the Gibbs-Donnan theory. For the ions studied in the present work, this effect

was offset by the non-polar interactions. Accordingly, positive  $\Delta$ -values were obtained, both for the saturated and unsaturated carboxylate anions on the anion exchanger in the sulphate form.

Several authors have observed that for ions of similar size and structure, those corresponding to a parent acid of high acid strength are held more strongly than those derived from weaker parent acids<sup>7,14</sup>. In agreement with this rule, propenoic acid exhibited the largest  $\pi$ -values. Again 4-pentenoic acid gave negative values. The small difference in  $pK_a$  for hexanoic and 2-hexenoic acids, together with lower hydrophobic interactions for unsaturated species, explains the observation that these acids exhibited very similar distribution coefficients.

#### *Anion-exchange resins in sodium acetate*

The acids can in rough calculations be considered as completely ionized in the sodium acetate solution. The results given in Table III show that the  $D_v$  of propanoic acid in 1 M sodium acetate was in agreement with that calculated by dividing the  $D_v$  in 0.25 M solution by 4. For propenoic acid the calculated  $D_v$  in 1 M sodium acetate was lower than that calculated by this method, whereas for the anions with more than three carbon atoms the opposite was found. Salting-out effects on ion-exchange equilibria in sodium acetate have been observed for other hydrophobic anions<sup>12</sup>.

Both for the alkanate and the alkenate ions the distribution coefficients increased with an increasing number of carbon atoms. Evidently, non-polar interactions have a decisive influence. The  $\Delta$  values increased within each homologous series.

Despite the lower hydrophobic interactions, the 2-alkenate ions exhibited higher distribution coefficients than the corresponding alkanate ions. This observation, and the fact that only 4-pentenoic acid exhibited negative  $\pi$ -values, strongly support the theory that when other factors are virtually constant, the anion exchange affinities increase with an increasing strength of the parent acid.

Some other anions held very strongly at a low acetate concentration were studied in 1 M sodium acetate. As could be predicted with regard to the increased hydrophobic interactions, heptanate ions ( $D_v = 62$ ) exhibited a higher  $\Delta$ -value than

TABLE III  
RETENTION DATA IN SODIUM ACETATE AND ACETIC ACID ON AMINEX A-28

Acids	0.25 M Sodium acetate			1 M Sodium acetate			0.20 M Acetic acid		
	$D_v$	$\Delta$	$\pi$	$D_v$	$\Delta$	$\pi$	$D_v$	$\Delta$	$\pi$
Propanoic	6.3			1.6			9.2		
Propenoic	10.4		0.50	2.3		0.35	39		1.44
Butanoic	10.8	0.54		3.4	0.75		17.4	0.66	
2-Butenoic	16.2	0.44	0.40	4.3	0.63	0.23	30	-0.26	0.54
3-Butenoic	13.2		0.20	3.7		0.08	40		0.83
Pentanoic	25	0.84		8.1	0.87		41	0.85	
2-Pentenoic	35	0.77	0.33	10	0.85		62	0.73	0.42
4-Pentenoic	19.3		-0.27	5.8		-0.34	37		-0.10
Hexanoic	66	0.97		19.9	0.90		106	0.95	
2-Hexenoic				26	0.95	0.26	141	0.82	0.29

the carboxylate ions listed in Table III. A larger decrease in  $D_v$  resulting from a double bond than for the other unsaturated ions could be predicted for 6-heptanate ions ( $D_v = 30$ ). Accordingly, the  $\pi$ -value was much more negative than that observed for 4-pentenate ions.

A comparison between phenylacetate and cyclohexylacetate ions was also made in this medium. Phenylacetate ions exhibited a  $D_v$  of 44, whereas cyclohexylacetate had a  $D_v$  of 47, *i.e.* a slightly higher value. The hydrophobic interactions are much larger for cyclohexane derivatives of this type than for the corresponding aromatic compounds<sup>4</sup>. The small difference in  $D_v$  is ascribed to the fact that the parent acid is much stronger in the case of phenylacetate.

The effect of a double bond in a cyclohexane ring was also studied. The  $D_v$  of cyclohexanecarboxylate was 21, and a lower value ( $D_v = 17$ ) was obtained for 3-cyclohexenate anions. Decreased hydrophobic interactions as a result of  $\pi$ -bond interactions with the water seem to have a greater influence than other factors.

The temperature dependency of the ion-exchange behaviour in sodium acetate solution was very small (Fig. 2). In contrast to results obtained with strongly hydrophilic carboxylate ions<sup>15</sup>, straight-line relationships were obtained between  $\ln D_v$  and  $1/T$ . No influence of the temperature on  $D_v$  was traced for propanate ions. For the other ions the change in enthalpy was negative. It is noteworthy that for the saturated acids the enthalpy change was more negative for higher than for lower homologues. This suggests that hydrophobic interactions (dependent on the water structure) cannot be solely responsible for the increase in  $D_v$  with an increasing number of carbon atoms. As expected, the change in enthalpy was more negative for the alkenate ions than for the alkanate ions. Among the studied ions, 2-pentenate exhibited the most negative value ( $-5.5 \text{ kJ mol}^{-1}$ ).

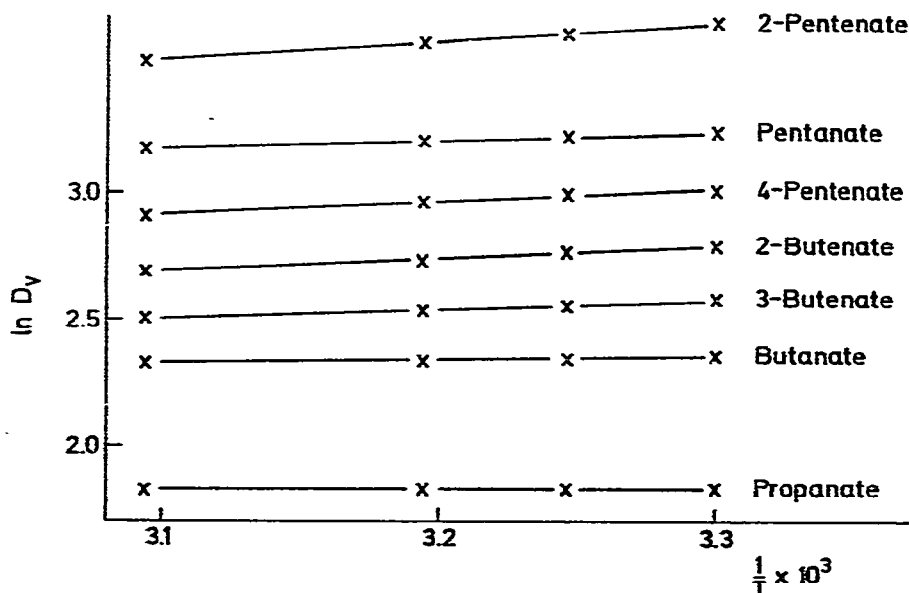


Fig. 2. Influence of the thermodynamic temperature ( $T$ ) on the distribution coefficients of aliphatic carboxylic acids in 0.25  $M$  sodium acetate on Aminex A-28.



*Anion-exchange resins in acetic acid*

In agreement with previous<sup>2</sup> determinations of the  $D_v$  values on an anion exchange resin in 3 *M* acetic acid, propenoic acid exhibited a much higher  $D_v$  in 0.2 *M* acetic acid than propanoic acid (Table III). Similarly, 2-butenic acid was in both media held more strongly than butanoic acid. The results are mainly explained by a strengthened hydrogen bonding for the stronger acids. Accordingly, 3-butenic acid, which is stronger than 2-butenic acid, exhibited the highest  $D_v$  among the acids with four carbon atoms. Again, all other unsaturated acids, except 4-pentenoic acid, were held more strongly than the alkanic acids with the same number of carbon atoms. The same elution order was found in 0.5 *M* acetic acid. Some results are shown in Fig. 1B. A complete separation was obtained of most species. 4-Pentenoic and 3-butenic acids appeared, however, in the same elution band as shown in Table III, the separation factor for these acids was unfavourable also in 0.2 *M* solution. In this medium pentanoic was also eluted very close to these acids, whereas in 0.5 *M* acetic acid pentanoic appeared later.

A change in the acetic acid concentration affects both the proportion of carboxylate anions and free acids and the formation of associated species by hydrogen bonding, both in the resin and in the eluent. At a high concentration the hydrophobic interactions and the dielectric constant are altered to an appreciable extent. The net result is a decrease in the distribution coefficients with increasing acetic acid concentration.

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