

An Olfactory Indicator for Acid Base Titrations

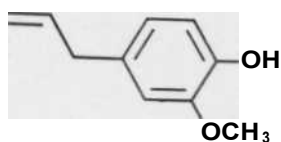
A Laboratory Technique for the Visually Impaired

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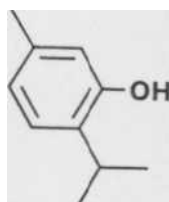
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While it is impossible for the blind student to be completely self-sufficient in the chemical laboratory, experimental modifications leading to greater autonomy for these individuals should be pursued. It is desirable to develop techniques that can serve to help integrate handicapped students into chemistry and provide a more meaningful laboratory experience. A good olfactory acid-base indicator would be of great utility in increasing the participation of the visually impaired in the chemistry laboratory. Although assistance will still be required in most phases of experimental work, the ability to perform titrations would clearly enhance the value of the laboratory for the student.³

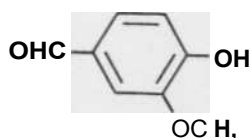
The use of olfactory indicators has been described.⁴ For our specific purpose we have examined four compounds as potential olfactory indicators: eugenol, thymol, vanillin, and thiophenol.



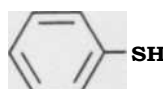
Eugenol



Thymol



Vanillin



Thiophenol

In each of the experiments, a small amount of the potential indicator was dissolved in 25 mL of 2 M NaOH. The basic solution was then titrated with 2 M HCl. The equivalence point (endpoint) in these titrations was determined based upon the smell of the titrated mixture. Equivalence points were later verified using phenolphthalein indicator.

As olfactory indicators, thymol and vanillin do not provide clear endpoints in acid-base titrations. Thymol has a pungent phenolic odor that, in our hands, seems to linger, masking the titration endpoint. It may also be that endpoint detection is inhibited by numbing of the sense of smell in the case of thymol. Vanillin, on the other hand, is unsuitable due to its relative lack of odor at the equivalence point, owing perhaps to its relatively high solubility in water (vanillin, 1 g/100 mL; thymol, 1 g/1000 mL).⁵

Thiophenol, even in minute quantities, possesses a strongly disagreeable odor, but it did behave as expected. Although there is always the lingering smell even in basic solutions, at the equivalence point the repulsive, penetrating stench becomes overpowering. While this is chemically noteworthy, it

Table 1. Titration of 25.00-mL Portions of 2 M NaOH Solutions with 2 M HCl Solutions (Reproducibility Study)

Run	Eugenol	Vol. HCl (mL) Phenolphthalein	Difference
1	27.57	27.57	0.00
2	27.38	27.50	0.12
3	27.50	27.70	0.20
4	27.41	27.65	0.24

Table 2. Titration of 2 M NaOH Solution with 2 M HCl Solution (Reversibility Study)

Vol. NaOH (mL)	Vol. HCl (mL)	Additional base/acid
25.00	27.54	
30.00	33.35	5.00/5.81
35.00	38.58	5.00/5.23
40.00	44.10	5.00/5.52
50.00	55.13	10.00/11.03

cannot be seen as an alternative indicator; thiophenol is both toxic and obnoxious.

Eugenol proved to be completely successful as an olfactory indicator for acid-base titrations both in terms of the obvious endpoint of the titration (the pungent fragrance of cloves bursts out of the titration mixture at the equivalence point) and the consistency of the results. The results of our titrations using both eugenol and phenolphthalein are summarized in Tables 1 and 2. The data in Table 1 show that titrations using a eugenol indicator are as reproducible as those using phenolphthalein. Note, however, that the eugenol endpoints require about two drops less acid than the phenolphthalein endpoints. That is, after the endpoint of the titration was determined by the strong smell of cloves, phenolphthalein indicator was added giving a pink solution and titration continued until the visual endpoint (colorless) was obtained. The difference in endpoints is perhaps due to the difference in pK_a values for the indicators (pK_a of eugenol = 10.0, pK_a of phenolphthalein = 9.7, and pK_a of thiophenol = 6.5⁶).

The reversibility of this titration technique is illustrated by the data in Table 2. Adding additional base in 5-mL portions, and continuing the titrations still gives sharp, detectable endpoints. Two drops of eugenol are distinctly pun-

¹ U. A. H. undergraduate, 1988-1990.

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³ For articles on teaching and laboratory aids for the visually impaired, see: (a) Crosby, G. A. J. *Chem. Educ.* 1981, 58, 206-208; (b) Tombaugh, D. J. *Chem. Educ.* 1981, 58, 222-226; (c) Smith, D. J. *Chem. Educ.* 1981, 58, 226-227; (d) Lunney, D.; Morrison, R. C. J. *Chem. Educ.* 1981, 58, 228-231.

Abe, S.; Kon, S.; Matsuo, T. *Anal. Chim. Acta* 1978, 96, 429-434.

⁵ *The Merck Index*, 9th ed.; Merck: Rahway, NJ, 1976.

⁶ Dean, J. A. *Handbook of Organic Chemistry*; McGraw-Hill: New York, 1987.

gent in 55+ mL of liquid. Because the fragrance disappears when the eugenol solution is re-basified, back-titrations are feasible. It is suspected that a small amount of eugenol (about 2 drops) would suffice for titrations of even large volumes of solution. A blank for comparison is easily prepared using the desired volume of water and two drops of eugenol. It should be observed that the pungent clove odor is uniformly strong even in large quantities of water.

More than 10 titrations were performed over the two studies with eugenol, and yet there appeared to be little "numbing" of the sense of smell. It might be supposed that there is a saturation point of some sort where the nose would become numb and thus temporarily "deadened" to the fragrance of eugenol; this was not, however, observed.

Experimental

Eugenol and thiophenol were obtained from Aldrich Chemical Company and were used without further purification. Thymol was

obtained from Fisher Scientific Company and vanillin from Eastman Chemical Company. Titrations were performed using approximately 2 M NaOH and 2 M HCl.

Reproducibility Study. In each titration, two drops of eugenol were dissolved in 25.00 mL of NaOH solution. The mixture was titrated with HCl solution, using magnetic stirring. Endpoints were determined by olfaction, then confirmed with phenolphthalein. The results are compiled in Table 1.

Reversibility Study. Two drops of eugenol were dissolved in 25.00 mL 2 M NaOH and titrated to the olfactory endpoint. An additional 5.00 mL base was added to the mixture, erasing the eugenol fragrance, and the mixture was again titrated to the olfactory endpoint. This process was repeated several times, for a total of five blind trials, which are summarized in Table 2.

Thymol. Ten drops of 50% (w/v) thymol in ethanol were added to 25 mL NaOH solution; then titrated with HCl.

Vanillin. Ten drops of a saturated solution of vanillin in ethanol were added to 25 mL NaOH solution; then titrated with HCl.

Thiophenol. Two drops of thiophenol were added to 25 mL NaOH solution which was then titrated with HCl.

Calculation of Equilibrium Constant in Esterification Reactions

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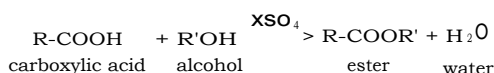
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Various techniques such as spectroscopy, polarimetry, and thermochemistry have been successfully employed to determine the equilibrium constant of a reaction, K_{eq} . Although K_{eq} is seldom calculated directly from the equilibrium concentrations of reactants and products, the following experiment, describing the determination of K_{eq} values for a series of esterifications, is an instance where the equilibrium concentrations are easily measured.

General Education



Experimental

Two-tenths mole each of the carboxylic acid and the alcohol from which the ester is to be prepared are placed in a 100-mL round-bottom flask, and the contents are mixed by swirling the flask. A 1-mL aliquot is withdrawn with a pipet, diluted with 20 mL water, and titrated with a stock solution (approximately 0.5 N) NaOH using phenolphthalein as the indicator (V1). Eight drops of concentrated sulfuric acid are added to the remainder of the alcohol/carboxylic acid solution in the round-bottom flask, and the mixture is refluxed for 1.5 h. While the mixture is refluxing, a solution is prepared by adding 8 drops (same dropper!) of concentrated sulfuric acid to a

volume of water equal to the volume of the alcohol/carboxylic acid mixture. A 1-mL aliquot is withdrawn and titrated against the same stock NaOH solution. The volume of NaOH used (approximately 0.5 mL) will constitute a "correction factor" attributed to the presence of sulfuric acid in the reaction mixture. After refluxing, the reaction mixture is allowed to cool to room temperature and another 1-mL aliquot is removed and titrated as above (V2). The "corrected" volume V_2' ($V_2' = V_2 -$ "correction" factor) will represent the number of moles of carboxylic acid remaining at equilibrium (which is equivalent to the number of moles of alcohol). The difference between the original titration value and the corrected final volume ($V_1 - V_2'$) is proportional to the number of moles of ester formed (which is equivalent to the number of moles of water formed). Thus,

$$K_{eq} = \frac{[\text{ester}][\text{water}]}{[\text{carboxylic acid}][\text{alcohol}]}$$

is determined as

$$K_{eq} = \frac{(V_1 - V_2')^2}{(V_2')^2}$$

To ensure that equilibrium has been attained, the reaction mixture can be refluxed for an additional 30 min and another 1-mL aliquot titrated as above. Titration values should agree to within 0.2 mL.

The table lists a series of alcohols and carboxylic acids with corresponding equilibrium constants at reflux temperatures. No systematic study of these alcohols and acids is reported in the literature, but the value for primary alcohols and straight-chain carboxylic acids is approximately 4.² For steric reasons it is reasonable to expect that larger alcohols and acids require larger activation energies and, therefore, take more time to reach equilibrium. Our results show that, generally, as the size of alcohol and acid increase, the equilibrium constants decrease.

Equilibrium Constants for Esterification Reactions at Reflux Temperature

Alcohol/Acid	Equilibrium Constant		
	Ethanoic	Propanoic	n-Butanoic
Methanol	5.03	4.72	4.08
Ethanol	4.86	2.13	2.28
1-Propanol	4.21	4.10	2.33
1-Butanol	2.85	1.10	1.34
2-Methyl-1-propanol	2.02	1.23	0.92

^a nButanoic acid has an obnoxious odor, and it should be poured in the hood.

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² For instance see: Weininger, S. J.; Stermitz, F. R. *Organic Chemistry*; Academic: Orlando, FL, 1984; p 651. Brewster, R. Q.; Vanderwerf, C. A.; McEwen, W. E. *Unitized Experiments in Organic Chemistry*; Wadsworth: Belmont, 1977; p 227. Euranto, E. K. *The Chemistry of Carboxylic Acids and Esters*; Patai, Ed.; Interscience: New York, 1969; p 522. Nollan, C. R. *Chemistry of Organic Compounds*, 3rd ed; Saunders: Philadelphia, 1965; p 184.