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A. F. Findeis^a & J. A. Lubkowitz^a

^a University of Alabama, University Alabama

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A Study of the Quenching Properties of Alcohols in Liquid Scintillator Solutions

A. F. FINDEIS and J. A. LUBKOWITZ

University of Alabama, University, Alabama

Abstract—A study has been made of the quenching properties of alcohols in liquid scintillator solutions. Sixteen alcohols, *n*-C-1—*n*-C-10, and branched chain alcohols up to C-5 were studied in two of the more common scintillator solutions (toluene and dioxane base), using carbon-14 and tritium. Irrespective of the composition of the scintillator and independent of the activity, the quenching decreased with increasing molecular weight of the quenching agent when expressed on a volume basis. The converse is true when the composition is expressed on a molar basis. Branched chain alcohols show a decreasing quenching ability with increasing substitution on the alpha-carbon. Quenching properties of binary mixtures of alcohols are intermediate between the quenching curves of the pure alcohols. The quenching behavior of the alcohols was compared with that of compounds containing the same number of carbons but different functional groups. Quenching is dependent not only upon the number of molecules but also on the steric factors affecting the functional group primarily responsible for the quenching.

1. Introduction

One of the severe limitations of liquid scintillation counting is the property of the majority of organic compounds to quench due to color, which absorbs the radiation emitted by the phosphor, or because of inhibition of energy transfer from solvent to solute. The quenching condition has given rise to numerous papers⁸ for the correction and determination of the internal efficiency of the sample being counted.

The sample is usually accompanied by an organic solvent foreign to the scintillator solution in order to satisfy its solubility requirements. The resulting counting efficiency is lowered. Unfortunately, due to sophisticated methods of standardization present in modern instruments, there has been a considerable gap in the study of the quenching effects of organic compounds. Consequently it is not possible to predict *a priori* the quenching effect of two suitable choices of closely related solvents for the sample being counted.

This study was started in order to obtain a correlation between the quenching effect of alcohols and their structure in different scintillator solutions and in the presence of carbon-14 and tritium activities. The availability and extensive use of alcohols makes an investigation of their quenching properties desirable. The quenching of mixtures of alcohols has been studied in order to obtain a knowledge of the resulting quenching effect.

Kerr, Hayes and Ott⁴ studied the quenching properties of a number of organic compounds with the purpose of establishing a guide to quenching parameters of such compounds in liquid scintillator solutions. Guinn² has given a quenching order for a few organic compounds. Lerch and Cosandey have reported the quenching effects of the normal alcohols through *n*-pentanol by measurement of the mean pulse height and the square of the resolution power using Sn¹¹³ activity.⁵

The Stern-Volmer equation which applies to the solute quenching in photofluorescence is not applicable to the quenching of liquid scintillator solutions.⁸ Since previous quenching studies have shown that the counting efficiency decreases as an exponential function of the concentration of the quencher, it has been the choice in this work to present the data in an exponential form.

2. Experimental

Apparatus

The liquid scintillation spectrometer used was a Tri-Carb Model 314 F, manufactured by Packard Instrument Co. All samples were counted in 20-ml. glass vials which were obtained from Packard Instrument Co. The photomultiplier tubes were located in a freezer maintained at 1°C.

Scintillator Solutions

In this work two types of scintillator solutions were used. The first solution contained 5 grams of 2,5-diphenyloxazole (PPO), and 0.3 gram of 1,4-bis-2-(4-methyl-phenyloxazolyl)-benzene (dimethyl POPOP) per liter of solution. Toluene, reagent grade (J. T. Baker Chemical Company) was used as solvent. This solution will be referred to as the toluene base scintillator solution (hereafter called TBS solution). The second solution used in this work was reported by Davidson and Feigelson¹ and also

used by Horrocks and Studier.³ A modification was made in which the secondary solute was dimethyl POPOP instead of POPOP. This solution is a mixture in volume ratios of 75% *p*-dioxane, 12.5% 1,2-dimethoxyethane and 12.5% anisole with the scintillators in concentrations of 7 grams of PPO and 50 mg of dimethyl POPOP per liter. This solution will be referred to as the dioxane base scintillator solution (hereafter called DBS solution). The scintillator solutes were of scintillation grade and were obtained from Packard Instrument Company. The 1,2-dimethoxyethane and the *p*-dioxane were Eastman Organic Chemicals White Label grade. The anisole was reagent grade (Matheson Coleman and Bell).

Chemicals

The following chemicals used, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, *t*-butyl alcohol, isobutyl alcohol (spectrophotometric grade), isopentyl alcohol, *t*-pentyl alcohol, were Baker Analyzed Reagents (J. T. Baker Chemical Company); the *sec*-butyl alcohol, *n*-pentyl alcohol, *n*-hexyl alcohol, *n*-heptyl alcohol, *n*-octyl alcohol, *n*-decyl alcohol, and cyclopentanone, were Eastman Organic Chemicals Yellow Label grade; the *n*-valeric acid, was of technical grade (Brothers Chemical Company); the *n*-pentane used was pure grade (Phillips Petroleum Company); the methyl alcohol used was acetone free and anhydrous (Merck & Co., Inc.); the absolute ethyl alcohol was obtained from U.S. Industrial Chemical Company; the *n*-nonyl alcohol was of practical grade (Matheson Coleman and Bell).

Radioactive Isotopes

Two radioactive sources were used: carbon-14 toluene and tritiated toluene (Packard Instrument Company). The carbon-14 toluene had a specific activity of 4×10^5 dpm/ml. The tritiated toluene had a specific activity of 2.09×10^6 dpm/ml.

Procedures

Those alcohols which contained moisture were dried with calcium hydride and distilled. The remaining alcohols were distilled and a fractions collected which had boiling points and refractive indexes corresponding to literature values. In the case of methyl, ethyl, and *n*-propyl alcohols, the moisture was removed by distillation after formation of the Grignard adduct.

Studies of the Quenching of Alcohols in the Different Solvent Systems.

A 200 μ l aliquot of carbon-14 toluene was added with a calibrated syringe to 10 ml of each of the scintillator solutions which were contained in a 20 ml sample vial. In the study using tritiated toluene, 200 μ l of the activity was introduced to 10 ml of the TBS solution. The alcohols were added in increments of 1 ml with a calibrated buret having a teflon and glass needle valve. The sample was introduced into the freezer where it was counted to approximately 0.2% standard deviation.

Studies of the Quenching Properties of Mixtures of Alcohols. For the calibration curves, the mixtures were prepared by addition of known volumes of the two alcohols to pre-weighed volumetric flasks. For each mixture, five standards were prepared containing approximately 100, 75, 50, 25, and 0 mole per cent of the more volatile component. Throughout a mixture study the same batch of scintillator solution was used. The test mixtures were prepared in identical fashion as the standards. Ten aliquots of 4 ml were introduced in pre-weighed glass vials and the weight of the 4 ml test mixture was recorded. This was followed by the addition of 10 ml of the TBS solution and 100 μ l of carbon-14 toluene.

Quenching Standards for the Studies of Alcohols. A series of standards was prepared containing 4 ml of each of the sixteen alcohols studied. Each standard contained 10 ml of the TBS solution and 100 μ l of carbon-14 toluene. A standard containing no alcohol was also prepared. A similar series of standards were also prepared, each sample containing the same number of moles of alcohol.

Selection of the Operative Conditions for the Liquid Scintillation Spectrometer

For determining the balance point operation of the instrument a carbon-14 toluene and a tritiated toluene standard were prepared. The lower discriminator (Gate), and upper discriminator were chosen as previously described^{1,10}. The following settings were used during these studies: carbon-14 toluene was counted in a 100-900 division window, tap 5, 65% efficiency, with a background counting rate of 23 cpm; tritiated toluene was counted in a 100-900 division window, tap 7, 34% efficiency with a background counting rate of 31 cpm. In this study no effort was made to remove dissolved oxygen from the samples, although the effects of it have been studied elsewhere.¹¹

3. Results and Discussion

Each alcohol added to the scintillator solutions showed unique quenching properties. The volume quenching curves in TBS solution are shown in Fig. 1 for the straight-chain alcohols. This shows that the decrease in cpm, as a function of the volume of the alcohol added, follows an exponential-like function, but does not show the linearity which has been previously reported for very dilute concentrations of quenching material.⁴ As the volume of the alcohol was increased the counting efficiency decreased as expected. As the molecular weight of the straight-chain alcohol increased, for a constant volume added, the cpm increased. The same quenching order for the straight-chain alcohols was observed in the DBS solution using carbon-14 toluene activity and in TBS solution using tritiated toluene as the radioactive source.

A classification of the quenching properties of the alcohols is meaningless unless accompanied by a statement as to whether the comparison

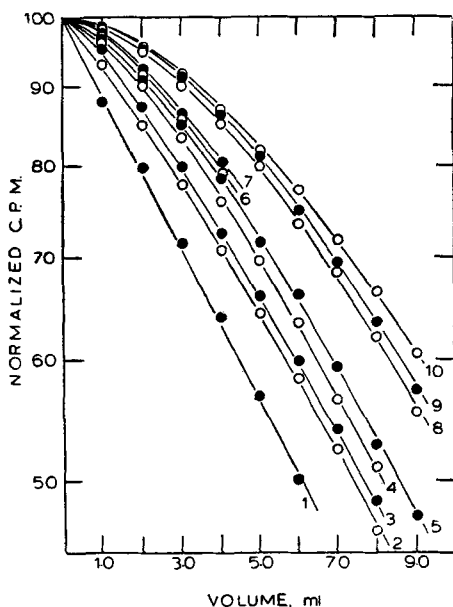


Figure 1. Volume quenching curves for the straight-chain alcohols in the TBS solution using Carbon-14 as the activity.

Alcohols

1. C_1 ; 2. C_2 ; 3. $n-C_3$; 4. $n-C_4$; 5. $n-C_5$; 6. $n-C_6$; 7. $n-C_7$; 8. $n-C_8$; 9. $n-C_9$; 10. $n-C_{10}$

is made on a mole, mole fraction, volume, or weight basis. The particular range of these quantities must also be specified. In Fig. 2 the quenching curves for the alcohols in TBS solution are plotted in terms of the moles added. A reversal of the quenching order is observed. Similar type curves were obtained in the other scintillator solutions previously mentioned.

A separate study was made in which a series of standards were prepared containing 4 ml of each of the alcohols and 10 ml of the TBS solution with carbon-14 toluene activity. These standards were counted and normalized to 100 per cent with respect to the counts obtained for a sample of 10 ml of the same scintillator solution with an identical amount of radioactivity, but no quenching material. This procedure was followed in order to compensate for any drift in the instrument which may have taken place during prior experiments, and to minimize any other variables which may have contributed to prior data. No difference was noted in the order of quenching obtained from these data and that obtained from the quenching curves shown in Fig. 1. Data for the DBS solution containing carbon-14 activity and TBS solution containing tritium activity were obtained from curves similar to those shown in Fig. 1. These data are shown in Table 1. Figure 3 shows a plot of the normalized

TABLE 1 Normalized Counting Rates as a Function of Volume and Moles Added

Alcohol	TBS solution C ¹⁴ Toluene		DBS solution C ¹⁴ Toluene		TBS solution H ³ Toluene	
	4 ml	5.00 × 10 ⁻² mole	4 ml	6.00 × 10 ⁻² mole	4 ml	5.00 × 10 ⁻² mole
Methyl	68.4	79.5	31.6	42.6	29.7	44.7
Ethyl	72.9	78.6	37.1	41.4	34.6	42.7
<i>n</i> -Propyl	75.4	75.0	43.8	39.7	39.0	40.3
<i>n</i> -Butyl	77.7	71.2	50.7	38.1	40.6	36.4
<i>n</i> -Pentyl	81.3	71.0	54.0	35.5	44.7	34.8
<i>n</i> -Hexyl	80.0	61.9	54.8	26.4	44.0	28.5
<i>n</i> -Hyptyl	82.6	59.8	60.3	28.0	46.7	26.3
<i>n</i> -Octyl	87.1	66.0	65.8	28.7	51.8	29.8
<i>n</i> -Nonyl	88.6	62.3	68.0	23.6	54.8	28.7
<i>n</i> -Decyl	89.6	60.8	69.1	21.5	56.8	27.6
Isopropyl	78.9	78.5	52.8	46.5	42.0	43.5
Isobutyl	77.5	71.7	48.0	35.6	40.0	35.4
<i>sec</i> -Butyl	80.4	74.7	60.3	46.4	43.7	39.0
<i>t</i> -Butyl	87.2	83.7	67.8	54.7	53.8	48.2
Isopentyl	81.8	70.7	53.9	34.4	44.0	34.4
<i>t</i> -Pentyl	85.8	72.7	65.0	42.5	50.0	37.3

cpm versus the number of carbon atoms in the straight-chain n-alcohols. This plot shows that, at constant volume, as the molecular weight increases the increment of quenching per unit of chain-length decreases. The data in Table 1 shows that a similar trend is observed in all of the scintillator solutions studied. It is clear that the nature of the radioactive source and the nature of the scintillator solvent affect the magnitude of quenching although the same order of quenching is observed.

The possibility of a volume change resulting in a change in counting efficiency of these scintillator solutions was checked by measuring the effect of dilution on adding solvent to the scintillator solution. The addition of up to 10 ml of toluene to the TBS solution resulted in a decrease in counting efficiency of carbon-14 of less than five per cent. The addition of dioxane base solvent to the DBS solution yielded similar results. The values reported in this work are uncorrected for the quenching effect on dilution which is of much less magnitude than the quenching effect of the compounds investigated. Such a correction could be only estimated from dilution on adding pure solvent. It is not a simple matter to evaluate all factors contributing to the quenching curves such as increased photon transmission as a result of volume increase and decrease of photon emission due to diminished scintillator concentration.

Alcohols have a lower ultraviolet transmission limit than toluene as is evidenced by their use as solvents in the region 215–285 $m\mu$, in which toluene absorbs strongly. Alcohols should therefore enhance energy transfer if transparency of the solvent was the only criterion. The fact that the photon yield is decreased shows that the quenching effect is the predominant factor in the overall process. The addition of alcohols to the DBS solution does not greatly affect the ultraviolet transmission since that scintillator solvent is much more transparent in the ultraviolet region of the spectrum. The cut-off point for dioxane is at 220 $m\mu$ as compared with the cut-off point for toluene of 285 $m\mu$. The quenching effect is primarily the result of the functional group consideration in the quenching molecule which in this case is not compensated by any significant increase in transmission of the solvent.

From Table 1 the following quenching order for the alcohols is observed in TBS solution using carbon-14 activity: *n* propyl > isopropyl; *n* butyl = isobutyl > *sec*-butyl > *t*-butyl; *n* pentyl = isopentyl > *t*-pentyl. In the case of the DBS solution and the TBS solution using

tritiated toluene the primary branched-chain alcohols are greater quenchers than the secondary alcohols which are in turn greater quenchers than the tertiary alcohols. The experiments on the linear alcohols in these solvents were conducted on different days and thus are not included for comparison. It is possible to generalize, however, that the counting rate increases with increasing substitution on the alpha carbon. The significance of these observations is that steric effects on the alpha-carbon play an important role in the shielding of the functional group responsible for the quenching which in this case is the OH group. This principle may also be applied to the quenching behavior of the normal alcohols. As can be seen from Fig. 2, the quenching curves, when represented on a moles added basis, become closer together as the chain length of the alcohol increases. When a smooth curve is drawn through the experimental data, obvious deviations are noted for *n*-hexanol and *n*-heptanol. It was first thought that these deviations resulted from impurities in these alcohols and they were fractionally distilled several times prior to use. The deviations persisted after each fractionation

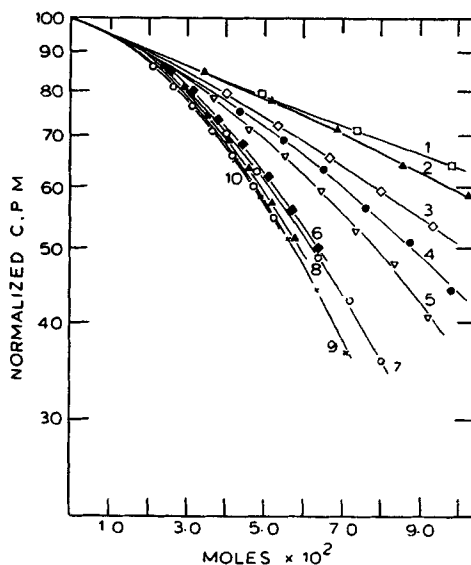


Figure 2. Mole quenching curves for the straight-chain alcohols in the TBS solution using Carbon-14 as the activity.

Alcohols

1. C_1 ; 2. C_2 ; 3. *n*- C_3 ; 4. *n*- C_4 ; 5. *n*- C_5 ; 6. *n*- C_6 ; 7. *n*- C_6 ; 8. *n*- C_9 ; 9. *n*- C_7 ; 10. *n*- C_{10}

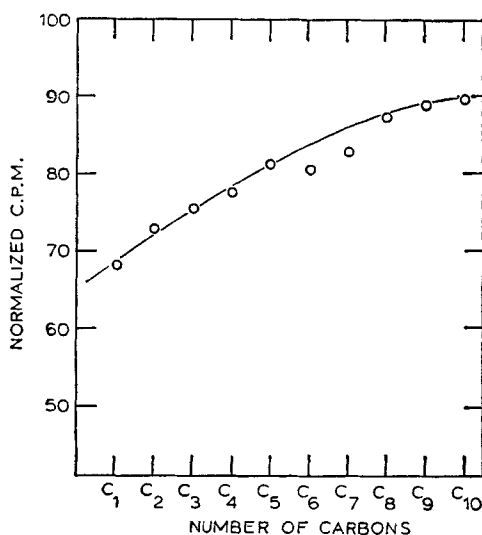


Figure 3. Quenching of the straight-chain alcohol standards at 4 ml in the TBS solution using Carbon-14 as the activity.

procedure. This suggests that the anomalous quenching behavior results from a property of the molecules rather than from a non-alcoholic impurity which we were unable to discern from gas chromatographic data. Alcohols in solution may exist in coiled or extended configurations. Those up to *n*-pentanol cannot assume a configuration in which the carbon chain can interfere with the hydroxyl group. At a carbon chain length of six the terminal methyl group can interfere with the OH group. This also is true for the higher alcohols. However, if one considers the possibility of interaction only between a terminal methyl group and the hydroxyl group to form a hydrogen bonded species, the most favorable conformation for linear hydrogen bonding occurs for *n*-hexanol and *n*-heptanol. The existence of steric factors such as these have been noted many times previously. For example, a coiled configuration in solution has been postulated for the relative constant rate of esterification for the carboxylic acids above *n*-butyric acid. This has been referred to as the rule of six.⁶

For very small amounts of alcohols present in the scintillator solutions the difference in quenching is not significant. This is illustrated by the data shown in Fig. 4 and 5 in which differences in per cent quenching are not appreciable. On the other hand, Fig. 6 clearly reveals the

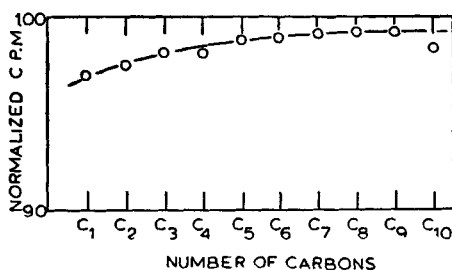


Figure 4. Quenching of the straight-chain alcohols after addition of 0.5×10^{-2} mole to the TBS solution using carbon-14 as the activity.

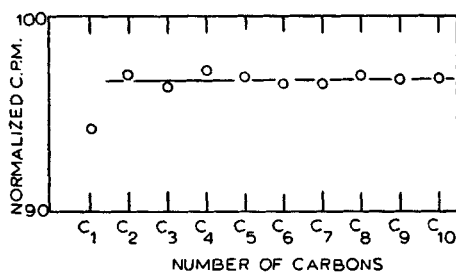


Figure 5. Quenching of the straight-chain alcohols after addition of 1.0×10^{-2} mole to the TBS solution using carbon-14 as the activity.

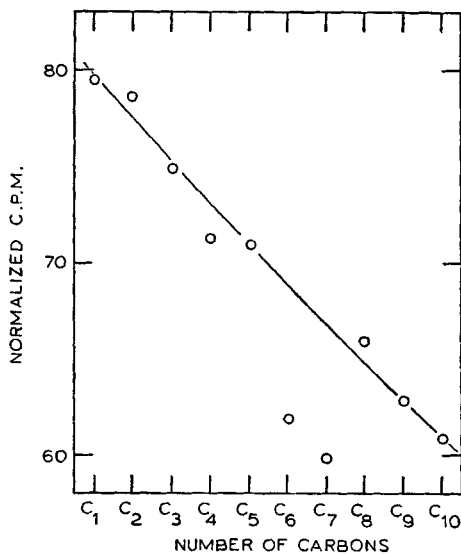


Figure 6. Quenching of the straight-chain alcohol standards containing 5×10^{-2} mole in the TBS solution using carbon-14 as the activity.

marked differences in quenching which are measured at an amount added which is five times greater than that in Fig. 5. These data contradict the statement made in a prior work² that all alcohols at the same mole fraction would be expected to quench to the same degree.

It is interesting to point out that the per cent quenching difference between *n*-propyl alcohol and isopropyl alcohol is the same, within experimental error, as that obtained between *n*-butyl and *sec*-butyl alcohol in the TBS scintillator solution using carbon-14 activity. This would suggest the per cent change in quenching due to the introduction of a methyl group on the alpha carbon is constant. The data for the DBS solution and the TBS solution using tritium activity, although not subject to the precise control of the TBS solution using carbon-14 activity, shows a similar per cent difference for these alcohol pairs.

Figures 7 and 8 show the moles required to decrease the normalized counting rate to 50% versus the molecular weight and versus the per cent OH group for the straight chain alcohols. The latter is a straight line except for *n*-hexyl, *n*-heptyl and methyl alcohols. It is apparent from these observations that the quenching behavior is not only dependent on the functional group in the molecule, but also on the steric factors which may affect the functional group primarily responsible for the quenching.

Volume quenching curves for the carboxylic acids are shown in Fig. 9. The acids, in terms of volume added, become lesser quenchers

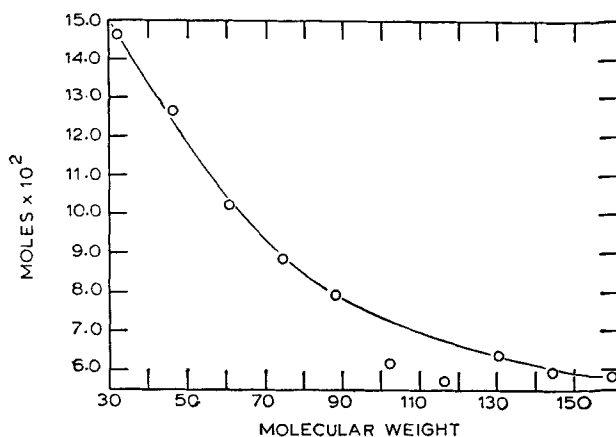


Figure 7. Moles required to reduce the counting to 50% versus the molecular weight of the straight-chain alcohol in the TBS solution using Carbon-14 as the activity.

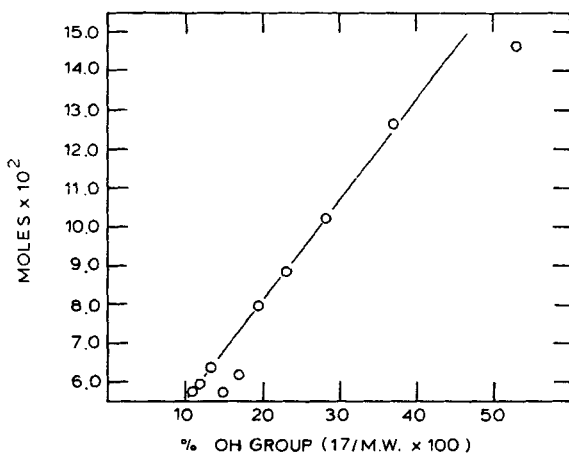


Figure 8. Moles required to reduce the counting to 50% versus the % OH group in the TBS solution using Carbon-14 as the activity.

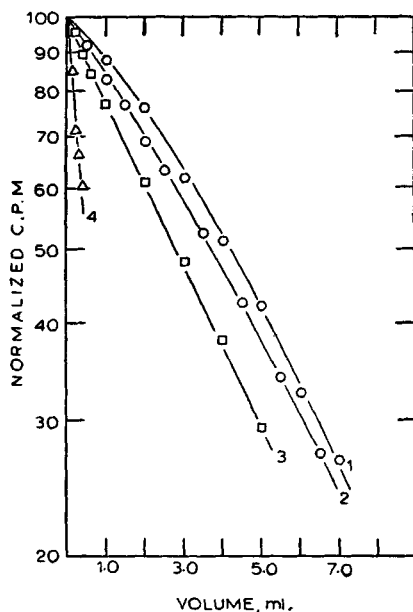


Figure 9. Volume quenching curves for the straight-chain carboxylic acids in the TBS solution using Carbon-14 as the activity.

- | | |
|---------------------------|---------------------------|
| 1. <i>n</i> -valeric acid | 2. <i>n</i> -butyric acid |
| 3. acetic acid | 4. formic acid |

as the molecular weight increases. This is a similar result to that obtained for the alcohols. The quenching order of four membered straight chain carbon molecules is *n*-butyraldehyde > *n*-butyl bromide > *n*-butyric acid > *n*-butyl alcohol. Figure 10 shows the volume quenching curves

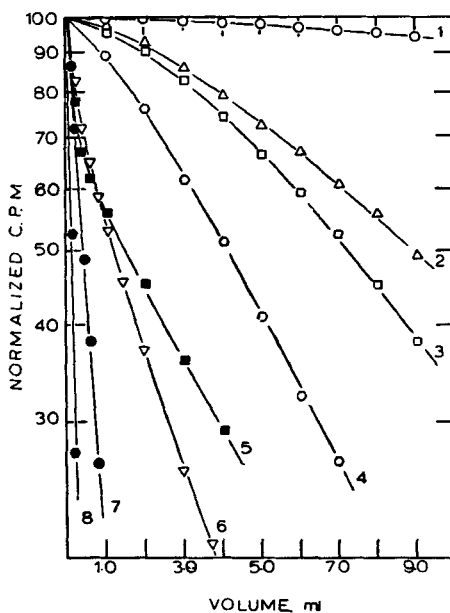
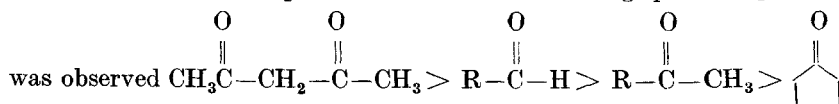


Figure 10. Volume quenching curves for the five-carbon compounds possessing different functional groups in the TBS solution using carbon-14 as the activity 1. *n*-pentane 2. *n*-pentyl alcohol 3. cyclopentyl alcohol 4. *n*-valeric acid 5. cyclopentanone 6. methylpropylketone 7. *n*-valeraldehyde 8. 2,4-pentanedione

for the five carbon compounds studied. The following quenching order



$> \text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{OH} > \text{cyclopentanol} > \text{ROH} > \text{RH}$. These orders were observed at all concentrations with the exception of cyclopentanone. This order does not agree with the order given by Guinn.⁴

The orders observed are the same as reported by Hayes *et al.*⁴ However, that work showed that the quenching order was dependent upon the nature of the solvent although no uniform measure of comparison

was used. Half quenching values are purposely not tabulated since a simple exponential relation is not observed. Furthermore, the values reported in this paper do not have the character of universal reproducibility and depend on the amplification of the instrument⁷ and on the nature of the scintillator solution.

The quenching curves obtained for mixtures of methyl and *t*-butyl alcohols are plotted in Fig. 11. The curves are similar to those obtained for the pure compounds. Figure 12 shows the relation between the per cent quenching and the mole per cent of the methyl alcohol in this mixture for 4-ml samples. It is noted that the quenching is very nearly additive. Similar data was obtained for many binary mixtures. For all binary mixtures of alcohols the quenching for a precise amount of mixture may be used for analyses if a calibration curve is constructed. Table 2 shows the results of a study of the deviations in the analysis of a selected mixture of methyl alcohol and *t*-butyl alcohol. It should be pointed out that the empirical equation of Peng⁷, $S_a = S_o e^{-(q_1 c_1 + q_2 c_2)}$ is not applicable here. That equation is valid only for very low concentrations of quenchers. If quenching differences are not appreciable the analyses of mixtures is not possible. Calibration curves for mixtures

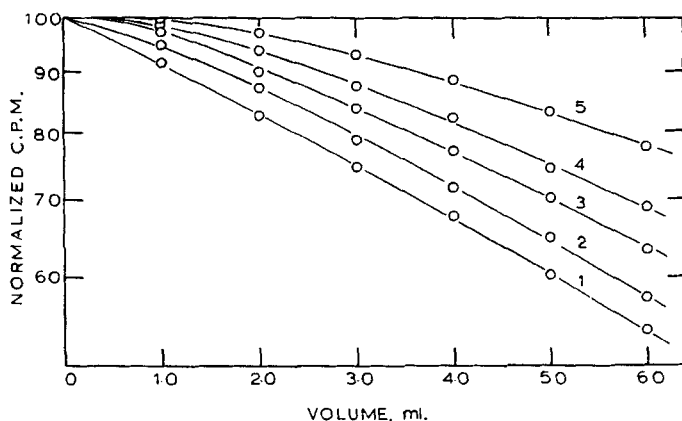


Figure 11. Volume quenching curves for the methyl and *t*-butyl alcohol mixtures.

Mole % methyl alcohol	
1. 100.0	3. 50.32
2. 77.83	4. 20.79
5. 0.000	

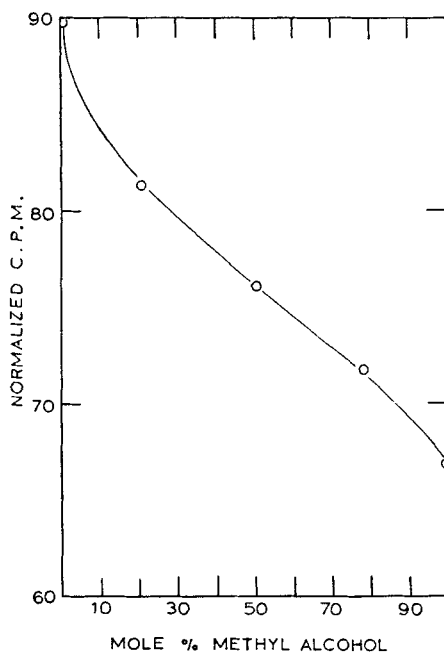


Figure 12. Standard calibration curve for the methyl and *t*-butyl alcohol mixtures obtained from the third count of the 4 ml standards.

TABLE 2 Composition and C.P.M. of the Methyl and *t*; Butyl Alcohol Test Mixtures

Volume added, ml.	Weight added, grams	Mole % methyl alcohol prepared	3rd count, ^a c.p.m.	Mole % methyl alcohol read
4.00	3.1036	61.09	74.4	60.4
4.00	3.1476	61.09	74.1	62.0
4.00	3.0988	61.09	75.0	56.3
4.00	3.1328	61.09	74.5	59.6
4.00	3.2305	61.09	74.9	56.9
4.00	3.0715	61.09	73.6	65.3
4.00	3.1358	61.09	75.0	56.3
4.00	3.1151	61.09	74.6	59.0
4.00	3.1238	61.09	74.3	60.5
4.00	3.1303	61.09	74.3	60.5
Average, %				59.7
Standard deviation, %				2.7
Relative error of the mean, %				2.2

^aThe counts are normalized to 100.00 c.p.m.

were not linear therefore the deviation in the evaluation of composition depends on the composition of the mixture.

The data obtained for the TBS system were repeated several times. It was evident that the order of the quenching curves never changed regardless of the manner of addition to the scintillator solution. The efficiency obtained after addition of a certain volume of alcohol can be reproduced, within experimental error, if the same scintillator solution is used and if not too great a period of time is allowed between duplicate runs (3-4 days). This is due to instrument drift or to changes in the scintillator solution which can occur since oxygen was not removed from the scintillator solutions. All samples were counted to a per cent standard deviation of $\pm 0.2\%$ or better.

Acknowledgements

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Discussion

King: Are these aerated samples or are these degassed or de-oxygenated?

Findeis: These are aerated samples and they had to be for the simple reason that when you make up a precise mixture for calibration purposes and you bubble nitrogen through it, you change the composition not only of the solvent, but also of any solute. We felt it was best to stick with aerated samples which were defined by the partial pressure of oxygen, rather than trying to degas the samples or to handle them in an inert atmosphere.

King: Well, then, have you looked at the fluorescence of these by u. v. excitation, because sometimes alcohols result in considerable enhancement of fluorescence and if you haven't sorted this out from your other effects, it may be a little difficult to...

Findeis: No we have not; we did not have a fluorescence apparatus available.

King: Well, I've seen some effects as large as 20% enhancement.

Findeis: We have seen similar effects in the solvent extraction of 2,2'-bi-pyrimidine complexes of iron in which there was almost a 200% increase in the efficiency of counting of Fe^{59} . This is a case where an organic complex can act as an aid to energy transfer.

King: Would it be possible that the change in efficiency was the result of charge donation by the alkyl groups.

Findeis: You mean an inductive effect? Well, I would prefer to think of this in terms of the actual entropy of the system before and after the introduction of the functional group. It's a thermodynamic property of the solution.