dithizone in one-liter portions and the procedure followed as indicated above from this point.

Summary

The apparent lead content of normal urine as indicated by dithizone measurements is greater than the true lead content as measured by chemical separation of the total lead from large volumes of such urine. A rapid micromethod for the determination of lead is described which permits the objective separation and precise evaluation of minute amounts in drinking water and in urine without the necessity of ashing.

WASHINGTON, D. C. RECEIVED JUNE 16, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Electric Polarization and Association in Solution. III. The Dipole Moments of Some Alcohols in Very Dilute Benzene Solutions

BY ARTHUR A. MARYOTT[1]

Numerous determinations of the electric polarization of alcohols in non-polar solvents have been made previously. Hennings,[1a] and more recently Hückel,[2] have made rather complete studies of the polarization of various alcohols over a wide concentration range. They used benzene, hexane, and several other non-polar solvents. The polarization as a function of concentration exhibited quite complex behavior, showing maxima and minima which were interpreted by assuming the existence of a number of associated alcohol complexes. Goss[3] has made use of the partial molar polarizations to interpret the behavior of alcohols in solution and Rodebush[4] has examined several alcohols in carbon tetrachloride and interpreted the data on the basis of the Onsager theory.[5]

In none of the above-mentioned work, however, did the concentration range studied extend sufficiently low to eliminate entirely any association effects; consequently, any calculation of the dipole moment of the unassociated alcohol would necessarily involve some uncertainty. In cases where dilution sufficient to eliminate association was obtained,[6] the polarization values appeared to be quite anomalous. Apparently, there exist no data in the literature at either low enough concentration or of sufficient reliability to furnish very dependable dipole moments for the alcohols from solution measurements.

In the present work the polarizations and dipole moments of methyl, ethyl, isopropyl, and *t*-butyl alcohols have been determined in benzene at concentrations ranging from approximately 10^{-4} to 10^{-2} mole fraction with the object of obtaining accurate solution values for the moments of these alcohols and to study association effects if they existed at these low concentrations.

Materials

Methyl Alcohol.—Merck absolute methanol was dried over magnesium ribbon and distilled in a 180-cm. Dufton column. The boiling point of the middle fraction was 64.51° (cor.). The critical solution temperature in carbon disulfide was found to be 35.2°. This value is slightly lower than that found for anhydrous methyl alcohol by McKelvy and Simpson.[7] Since drying with magnesium is superior to the method used by the latter workers, it is quite probable that our alcohol is more nearly anhydrous than that used by these authors.

Ethyl Alcohol.—A best grade absolute ethanol was purified in the same manner as methanol, b. p. 78.34° (cor.). The critical solution temperature in carbon disulfide was −23.5°, indicating less than 0.1% moisture.[8]

Isopropyl Alcohol.—Eastman Kodak Company best grade alcohol was purified in the same manner as methyl and ethyl alcohol. As a check on the purity, a part of the best fraction was again refluxed over magnesium ribbon and distilled. Polarization measurements on this repurified sample agreed with those of the other fraction. The b. p. was 82.33–82.39° (cor.).

***t*-Butyl Alcohol.**—Eastman best grade *t*-butanol was first distilled over sodium. The best fraction was then fractionally recrystallized from its own melt until no change in melting point occurred upon further recrystallization; m. p. 24.85–25.0°.

Experimental

The experimental procedure and most of the apparatus have been described previously.[9] An entirely new hetero-

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[1] The author is indebted to the Ethyl-Dow Chemical Company for the grant of a Post-Doctorate fellowship which enabled this problem to be undertaken.

[1a] Hennings, *Z. physik. Chem.*, **B28**, 267 (1935).

[2] Hückel and Schneider, *ibid.*, **B47**, 227 (1940).

[3] Goss, *J. Chem. Soc.*, 888 (1940).

[4] Rodebush, Eddy and Eubank, *J. Chem. Phys.*, **8**, 889 (1940).

[5] Onsager, THIS JOURNAL, **58**, 1486 (1936).

[6] Hoecker, *J. Chem. Phys.*, **4**, 431 (1936).

[7] McKelvy and Simpson, THIS JOURNAL, **44**, 105 (1922).

[8] Schoorl and Regenbogen, *Rec. trav. chim.*, **41**, 125 (1922).

[9] Pohl, Hobbs and Gross, *J. Chem. Phys.*, **9**, 408 (1941).

dyne-beat oscillator circuit which operated on 110 volt a. c. current was used. A detailed report of this circuit will appear in a later publication.

The liquid measuring condenser had been dismantled and reassembled since the last work was reported. A recalibration of the air capacity gave 932.5 $\Delta\ C$ units (a ΔC unit being the arbitrary calibrating unit equal about 0.4 mmf.) instead of the value 912.5 previously reported. The sensitivity of the apparatus was such that a capacity change of 0.0004 mmf. could be detected.

The polarizations were calculated from the experimental data using a simplified, expanded form of the Debye equation.[10]

$$P_2 = \frac{M_2 \dfrac{W_1}{W_2}\left[\dfrac{\Delta\epsilon}{\epsilon + 2} - \dfrac{(\epsilon - 1)\ \Delta d}{d} - \dfrac{\epsilon - 1}{\epsilon + 2}\,\dfrac{\Delta d\ \Delta\epsilon}{d}\right] + M_2(\epsilon + \Delta\epsilon - 1)}{(\epsilon + \Delta\epsilon + 2)(d + \Delta d)}$$

where M_2 = molecular weight of solute
W_1 = weight of solvent
W_2 = weight of solute
ϵ = dielectric constant of solvent
$\Delta\epsilon$ = dielectric constant increment
d = density of solvent
Δd = change in density upon addition of solute

Table I lists the essential experimental data for the alcohols and chlorobenzene. The first column contains, f_2, the mole fraction of solute; the second, the capacity change, ΔC expressed in terms of the arbitrary calibrating unit; and the last column, P_2, the polarization of the solute. At the bottom of each set of data is given $\Delta d/f_2$, the ratio of the change in density to mole fraction. Chlorobenzene has been included in the measurements to show the reliability of the polarization values at low concentrations and also to serve as a check on the apparatus.

Discussion

In Table II are given some of the data on the alcohols together with a comparison of the dipole moments obtained by other workers. P_∞ is the polarization extrapolated to infinite dilution; P_E, the electronic polarization calculated from the atomic refractivities; $\mu_{\text{obs.}}$, the experimentally obtained moment, μ_{benzene}, the corresponding moment found by other workers in benzene; and μ_{gas}, the gas value of the moment. The moments have been calculated in the usual manner using the equation, $\mu = 0.221\ (P - P_E)^{1/2}$ since the temperature was 30°. Atomic polarization has been neglected in our calculations.

In general, the values reported in the present communication are slightly lower than those obtained in the same solvent by other investigators. This might be expected if association effects were not entirely eliminated in the previous work. In addition, water as an impurity in the alcohol would give values for the moments[10a] that were too high, and apparently in some of the previous work no special precautions were taken to eliminate water. In methyl and ethyl alcohols the vapor value of the moment is definitely slightly higher than the solution value, indicating a negative solvent effect. If atomic polarization had been taken into account in our calculations, this difference would be further increased by approximately 0.02 *D*. It had been previously concluded by Higasi[11] that the alcohols exhibited a positive solvent effect. The more recent measurement of Hoecker,[12] however, on the moment of ethyl alcohol in carbon disul-

TABLE I

CHLOROBENZENE IN BENZENE AT 30°

$f_2 \times 10^3$	ΔC	P_2
0.1355	0.447	83.0
.1535	.499	82.2
.2360	.770	82.6
.4798	1.577	82.8
.5292	1.725	82.3
1.362	4.506	83.1
1.439	4.697	82.3

$\Delta d/f_2 = 0.264$

$P = 82.6$ $P_E = 31.4$ $\mu = 1.58\ D$

METHYL ALCOHOL IN BENZENE AT 30°

$f_2 \times 10^3$	ΔC	P_2
0.2078	0.655	62.2
.3199	1.008	62.2
.5867	1.827	61.6
1.439	4.497	61.8
1.687	5.298	61.9
3.693	11.59	61.7
3.838	12.14	62.1

$\Delta d/f_2 = -0.035$

ETHYL ALCOHOL IN BENZENE AT 30°

$f_2 \times 10^3$	ΔC	P_2
0.1325	0.432	69.9
.2750	0.899	69.9
.7110	2.284	69.0
1.801	5.847	69.5
2.110	6.849	69.5
3.370	10.97	69.5
4.603	15.01	69.6
8.500	28.57	70.8

$\Delta d/f_2 = -0.067$

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[10] Pohl, Hobbs and Gross, "Dielectrics," *Ann. New York Acad. Sci.*, **40**, 389 (1940).

[10a] A preliminary measurement was made on a sample of ethyl alcohol which was later shown to have approximately 1% water according to the critical solution temperature in carbon disulfide. The moment obtained from this measurement was 1.70 *D*.

[11] Higasi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **28**, 284 (1936).

[12] Hoecker, *J. Chem. Phys.*, **5**, 372 (1937).

TABLE I (*Concluded*)

ISOPROPYL ALCOHOL IN BENZENE AT 30°

$f_2 \times 10^3$	ΔC	P_2
0.1609	0.510	74.4
.2434	.779	75.0
.5054	1.585	73.9
.6016	1.899	74.2
1.354	4.284	74.3
1.808	5.722	74.4
3.385	10.80	74.6
5.333	17.24	75.2

$\Delta d/f_2 = -0.111$

t-BUTYL ALCOHOL[a] IN BENZENE AT 30°

$f_2 \times 10^3$	ΔC	P_2
0.1908	0.575	77.4
.2500	.779	79.1
.3418	1.066	79.1
.3642	1.099	77.4
.6535	2.020	78.6
.7928	2.422	78.2
1.708	5.226	78.2
3.212	9.898	78.5
5.108	15.68	78.1
9.295	28.77	78.3
13.33	41.34	78.2

$\Delta d/f_2 = -0.132$

[a] These values are representative of a total of twenty-three points with an average P_2 of 78.3 cc. and a mean deviation slightly less than 0.4 cc.

TABLE II

Substance	P_∞	P_E	$\mu_{obs.}$	$\mu_{benzene}$	μ_{gas}
Methyl alcohol	61.9	8.3	1.62	1.64[a] 1.68[c]	1.68[b] 1.69[i] 1.70[h]
Ethyl alcohol	69.7	12.9	1.66	1.74[a] 1.74[c] 1.70[f]	1.70[b] 1.67[i] 1.69[e]
Isopropyl alcohol	74.3	17.6	1.66	1.74[a] 1.78[k] 1.72[d] 1.70[j] 1.63[m]	1.58[i] 1.68[g]
t-Butyl alcohol	78.3	22.1	1.66	1.65[l] 1.71[d] 1.55[m]	

[a] Stranathan, *Phys. Rev.*, **31**, 653 (1928). [b] Miles, *ibid.*, **34**, 964 (1929). [c] Wolf and Gross, *Z. physik. Chem.*, **B14**, 305 (1931). [d] Donle, *ibid.*, **B14**, 326 (1931). [e] Knowles, *J. Phys. Chem.*, **36**, 2554 (1932). [f] Hoecker, *J. Chem. Phys.*, **4**, 431 (1936). [g] Stranathan, *ibid.*, **5**, 828 (1937). [h] Stranathan, *ibid.*, **6**, 395 (1938). [i] Kubo, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **26**, 242 (1935). [j] Higasi, *ibid.*, **28**, 284 (1936). [k] Mahanti, *J. Ind. Chem. Soc.*, **6**, 743 (1929). [l] Smyth and Dornte, THIS JOURNAL, **53**, 545 (1931). [m] Hennings, *Z. physik. Chem.*, **B28**, 267 (1935).

fide is in accord with the present measurements in that it indicates a negative solvent effect. According to solvent theories based on the sign of the Kerr constant, both methanol and ethanol should exhibit no very appreciable solvent effect since the Kerr constants are indistinguishable from zero. In the last two alcohols listed there is not a sufficient number of gas measurements to draw conclusions concerning the solvent effect.

Examination of Table II shows that the moments of all the alcohols studied are practically constant. The moment of methanol is slightly lower than the others; but the moments of the primary alcohol, ethanol; the secondary alcohol, isopropanol; and the *t*-alcohol, *t*-butanol, are the same.

The present data are not in agreement with the other very dilute solution measurements which showed a rather marked rise in polarization of the alcohols beginning around 5×10^{-3} mole fraction and increasing rapidly as the concentration was decreased. It has been suggested that such behavior is perhaps inherent in polarization measurements at low concentrations, possibly because of some solute influence affecting the polarization of the solvent. Hoecker[6] measured the polarization of ethyl alcohol in benzene at concentrations as low as 7×10^{-5} mole fraction and found a gradual rise for the polarization as the concentration decreased so that an extrapolation to zero concentration was impossible. He resorted to an unusual method of analyzing the data which, in effect, practically neglected the points in the more dilute region. Consequently, his measurements had no particular advantage over other measurements which did not extend to such low concentrations. The moment of 1.70 *D* found by Hoecker is somewhat higher than the value reported here. Apparently the only other alcohol measurements which have approached a dilution as great as 10^{-3} mole fraction are those of Müller.[13] The lower limit of Müller's work on methyl alcohol in benzene was about 2×10^{-3} mole fraction. As in the work of Hoecker, the polarization began to rise rather rapidly in the most dilute region. Figure 1 gives a comparison of our data with those of Müller and of Hoecker. The temperature at which these latter measurements were made was not the same as in the case of our measurements, and consequently the polarization at a given concentration should not have the same value. However, in Fig. 1 the polarizations reported by these latter authors have been corrected on the as-

(13) Müller and Mortier, *Physik. Z.*, **36**, 371 (1935).

sumption that no association existed at such low concentrations to 30° to make them strictly comparable with our results. The graph clearly shows the deviation from linearity of the polarizations in the case of the previous workers and also indicates, according to the present work, that the polarization of the alcohols is independent of concentration in the region from 10^{-4} to 10^{-3} mole fraction.

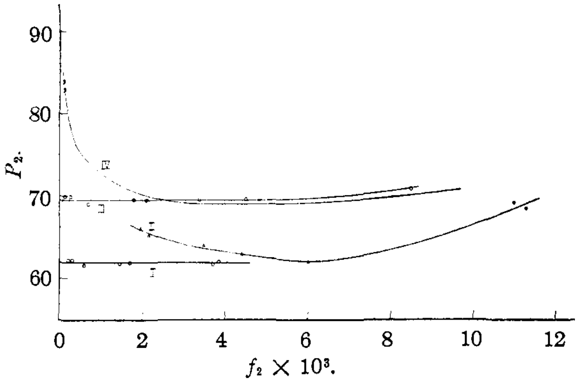

Fig. 1.—Comparison of present polarization data on methyl and ethyl alcohol in benzene at low concentrations with Müller's and Hoecker's data. I, present data [MeOH in C_6H_6]; II, Müller's data [MeOH in C_6H_6]; III, present data [EtOH in C_6H_6]; IV, Hoecker's data [EtOH in C_6H_6].

It has been well established that the polarizations of the alcohols exhibit a marked rise in benzene beginning at a few hundredths mole fraction at room temperature. In the present work the upper limit of concentration was not above 10^{-2} mole fraction. In order to show this dependence of polarization on concentration throughout a wide range of concentration our data on ethyl alcohol in benzene together with those of Mortier[14] which extended to much higher concentrations have been represented in Fig. 2. For purposes of comparison, our data have been recalculated for 20°, which was the temperature of Mortier's work. Because of the wide concentration range, the graph has been divided into two sections so that the scale divisions on the right-hand side are an order of magnitude greater than those on the left. As is evident from the graph, our data in the more concentrated region overlap and are in fair agreement with those of the most dilute region measured by Mortier.

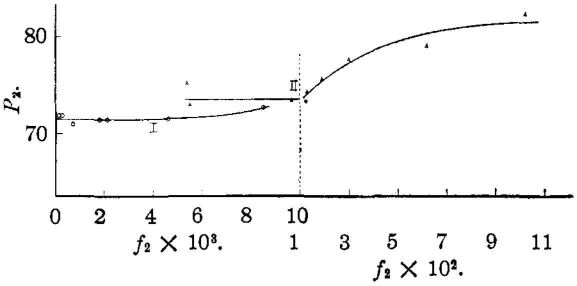

Fig. 2.—Comparison of present polarization data on ethyl alcohol in benzene with those of Mortier. I, present data; II, Mortier's data.

Our polarization measurements on the alcohols agree with other independent methods in indicating a lack of association in very dilute benzene solutions. Ethyl and isopropyl alcohols exhibit no rise in polarization with increasing concentration until approximately 5×10^{-3} mole fraction and probably no appreciable association exists below this concentration. Methyl and *t*-butyl alcohols show no indication of association up to the most concentrated solutions studied. While the alcohols are strongly associated in benzene at moderate concentrations as evidenced by cryoscopic, ebullioscopic, infra-red, and polarization measurements, they are far less associated than the carboxylic acids[9] in very dilute solutions. For example, polarization measurements on acetic acid in benzene at 30° and at a concentration of approximately 10^{-3} mole fraction indicate 70% association but under corresponding conditions and at the same concentration there is no detectable association of the alcohols. Peterson and Rodebush[15] from cryoscopic measurements on methyl and ethyl alcohol in benzene concluded that there was little or no association in the concentration range 5×10^{-4} to 5×10^{-3} mole fraction. Errera[16] found little or no indication of association from infrared studies on ethyl alcohol in carbon tetrachloride below a concentration of 0.02 mole fraction.

Summary

The electric polarizations of MeOH, EtOH, *i*-PrOH, and *t*-BuOH have been determined in benzene at concentrations in the range 10^{-4} to 10^{-2} mole fraction. Using the polarizations extrapolated to infinite dilution, values for the dipole moments have been calculated. The moments for MeOH, EtOH, *i*-PrOH, and *t*-BuOH are 1.62, 1.66, 1.66, and 1.66 *D*, respectively. These values are in general somewhat lower than the corresponding moments obtained by other

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[14] Mortier, *Bull. de l'Acad. de Belgique*, **21**, 594 (1935).

[15] Peterson and Rodebush, *J. Phys. Chem.*, **32**, 709 (1928).

[16] Errera, Gaspart and Sack, *J. Chem. Phys.*, **8**, 63 (1940).

workers and indicate a slight negative solvent effect instead of the generally predicted positive one. Contrary to previous data there appears to be no change of polarization with concentration in the more dilute region.

DURHAM, N. C. RECEIVED AUGUST 1, 1941

[CONTRIBUTION FROM THE GRADUATE SCHOOL OF APPLIED SCIENCE OF THE UNIVERSITY OF CINCINNATI]

Molecular Size Distribution in Three Dimensional Polymers. I. Gelation[1]

BY PAUL J. FLORY[2]

Polymerizations may be divided into two types: those which lead exclusively to soluble products regardless of the extent to which the reaction is carried toward completion, and those which lead to gelled, or insoluble, products provided that the reaction is carried far enough. The former behavior is characteristic of bifunctional systems, *e. g.*, the ethylene glycol–phthalic acid reaction, in which linear polymers are formed; the latter behavior is observed in systems of higher functionality where the reactants are functionally capable of producing indefinitely large three-dimensional molecules, *e. g.*, the glycerol–phthalic acid reaction. Since gelation occurs only when there is the possibility of unlimited growth in three dimensions, the conclusion that it is the result of the formation of infinitely[3] large molecules has been irresistible.[4] Carothers[5] pointed out that when one intermolecular linkage has been formed per initial monomeric molecule, all of the polymerizable material must be bound into one gigantic molecule, and possibilities for further *intermolecular* reaction are exhausted. In the reaction of two moles of glycerol with three of phthalic acid, for example, the extent of intermolecular reaction of the functional groups could not exceed $^5/_6$, or 83.3%, there being six potential linkages per five units. It was recognized by Carothers, however, that indefinitely large molecules might be formed at lower extents of reaction.[6] For example, a small fraction of the units might unite to form "infinite"[3] molecules, while the remaining units yield comparatively small molecules. Gelation, in this case, if due to infinitely large molecules, would occur when fewer than one intermolecular linkage had been formed per unit of the entire polymer mixture. Interspersed with the networks of the infinite molecules there would be many smaller molecules of varying complexity. Common experience shows that gelation occurs in three dimensional polymerizations long before all of the material is bound together in one molecule. Usually it is possible to extract soluble material, the molecular weight of which is not extremely large, from the gelled polymer.

The existence of a sharply defined gel point at a certain critical extent of reaction (independent of temperature, amount of catalyst, etc.) is a significant characteristic of such polymerizing systems. Apparently, gelation occurs when a critical number of intermolecular linkages has been exceeded. Although this implication of numerous experimental results has been recognized for some time, quantitative formulation of the necessary conditions for gelation has not been attempted heretofore.

In the present paper (I) a method will be presented for deducing theoretically the critical conditions for the formation of infinitely large three dimensional molecules. The calculated critical points will be compared with experimental gel points for two types of polyesters. In II and III[7,8] of this series three dimensional polymers will be subjected to statistical treatment in an effort to gain some insight into their composition. It will be shown that the observed characteristics of multifunctional polymerizations are in harmony with the hypothesis that gelation is the result of the formation of infinitely large three dimensional networks.

It should be made clear at the outset that in the papers of this series the term "gel" is meant to include only those polymeric materials portions of which are insoluble in all solvents that do not

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(1) Presented before the Organic Plastics Section of the Paint and Varnish Division at the Detroit Meeting of the American Chemical Society, September 10, 1940.

(2) Present address: Esso Laboratories of the Standard Oil Development Company, Elizabeth, New Jersey.

(3) The term "infinitely large molecule" refers to a molecule having dimensions of an order of magnitude approaching that of the containing vessel. Of course such molecules are finite in size, but by comparison with ordinary molecules they may be considered infinitely large.

(4) W. H. Carothers, *Chem. Rev.*, **8**, 402 (1931).

(5) W. H. Carothers, *Trans. Faraday Soc.*, **32**, 44 (1936). See in particular the Carothers functionality expression equation (2).

(6) See case (b), p. 46, ref. 5.

(7) P. J. Flory, THIS JOURNAL, **63**, 3091 (1941).

(8) P. J. Flory, *ibid.*, **63**, 3096 (1941).