[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES

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RECEIVED APRIL 20, 1926 PUBLISHED JULY 6, 1926

The introduction of the "vacuum" or "three-electrode" tube has made possible several accurate methods for the measurement of the dielectric constant. These measurements serve to test the newer theories of atomic structure[1] in the case of the pure non-conducting liquids, and the later theories of electrolytic solutions[2] in the case of conducting systems.

The determination of the dielectric constants of several binary mixtures was undertaken, and in this paper are presented the results on mixtures of benzene and toluene, chlorobenzene and bromobenzene, and carbon tetrachloride and benzene. The dielectric constants of the components of these solutions were also determined and are included in the tables. It has been shown[3] that few solutions, if any, are strictly ideal. The results here presented are in agreement with that conclusion.

Method

The method used for the determination of the dielectric constant of the liquids was one of the so-called "electrical resonance methods."[4] It does, however, contain several novel features.

A diagram of the apparatus used is shown in Fig. 1. In the first circuit oscillations are generated by an electron tube in a so-called Hartley circuit. The grid and filament of the tube in this particular circuit are connected to the branched circuit containing inductance, L_1, and capacitance, C, which constitute the oscillatory circuit. The fundamental constituent of the waves generated in this circuit may be changed at will to any desired frequency by adjustment of the capacity in the circuit, and made to equal that of the second circuit.

Circuit No. 2 may be described as a regenerative receiving circuit. It consists of a simple wave-meter circuit containing inductance and capacitance, with a two-stage amplifier, inductively coupled, connected in series. The circuit is caused to oscillate by means of the "Feed Back Regeneration" principle. This oscillation is maintained constant, great care being taken to prevent variations in batteries, inductance and capacitance in the circuit. The telephone receivers are connected in series in the plate cir-

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[1] Lewis, "Valence and the Structure of the Atom," Chemical Catalog Company, New York, **1924**.

[2] Debye-Hückel, *Physik. Z.*, **24**, 185 (1923); **25**, 145 (1924).

[3] Williams and Daniels, THIS JOURNAL, **47**, 1490 (1925).

[4] Hyslop and Carman, *Phys. Rev.*, **15**, 243 (1920). Waibel, *Ann. Physik*, **72**, 161 (1923). Fritts, *Phys. Rev.*, **23**, 345 (1924), and others.

cuit of the second vacuum tube. This circuit then acts as both an oscillatory circuit and receiving circuit, thereby eliminating a third circuit which is generally employed for the reception of the beats in the usual heterodyne method for the measurements of capacities.

The dielectric container, C_x, which is used for the determination of the dielectric constant of the liquid is connected in parallel with condenser, C_1, of Circuit 1. C_1 consists of two standard variable air condensers connected in parallel. One was manufactured by the Leeds and Northrup Company of Philadelphia and the other is a Standard Precision Condenser (Type 222) made by the General Radio Company of Cambridge, Massachusetts. The dielectric cell was especially designed for the purpose in hand and constructed in the University of Wisconsin Shops. It is contained in a Pyrex glass vessel and is fitted with a hard rubber cover. External to the dielectric cell is a perforated copper container which is bolted to a thermostat, thus allowing the water of the thermostat to circulate about the cell. This copper container serves as a shield to protect the condenser from stray capacity effects. The depth of the cell is such that the plates of the condenser are remote from any ungrounded metallic portions of the cell cover. The variable condensers are carefully grounded and shielded to prevent external capacity effects.

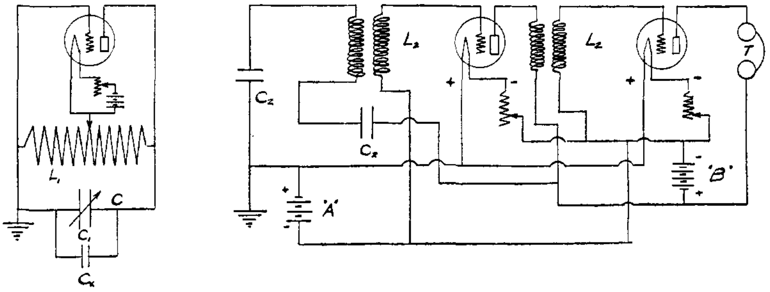

Fig. 1.

The dielectric constant of a liquid is determined as follows. The filaments of the vacuum tubes in both circuits are lighted from isolated sets of storage batteries, the current being carefully maintained constant by means of suitable rheostats. Circuit 2 is caused to oscillate by increasing the plate current in the tubes until regeneration begins. The circuit is now maintained perfectly constant so that the waves generated have a constant frequency. Circuit 1 is now adjusted to this frequency by means of condensers, C_1. The dielectric cell, C_x, is connected in the circuit at all times. The position of resonance just mentioned is determined with the plates in air and set at a definite and perfectly reproducible position, which may be called "A." The plates are now adjusted to a position "B" and the circuit is again brought to resonance with the constant Circuit 2. The difference in capacity of the dielectric cell in air with the plates in these two positions is determined by means of the calibrations of the standard condensers in C_1. The difference in capacity between these positions, A and B, of the dielectric cell with the plates immersed in the liquid whose dielectric constant is to be measured is now determined. The dielectric constant of the liquid is then calculated by dividing the difference in capacity between positions A and B when the plates are immersed in the liquid by the difference in capacity in air between these positions. The dielectric cell is so constructed that a number of settings may be used for each liquid, making check determinations easy to obtain. These measurements may be made easily and very rapidly. This method entirely eliminates any correction for the capacity of the leads, etc., a distinct advantage since these capacities, though small, are uncertain, and should be avoided for accurate determinations.

The accuracy and consistency of the measurements are illustrated by fifteen consecutive observations made on benzene at 25° which gave a mean value of 2.282, with an average deviation from the mean of ± 0.0025, and a maximum deviation from the mean of 0.004.

Purification of Materials

Benzene.—The benzene, obtained from the Eastman Kodak Company, was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide solution and with distilled water. It was frozen out twice and fractionated, and showed no blackening with mercury. The drying agent used was phosphorus pentoxide. The liquid gave practically the same physical constants that are given by Richards and Shipley.[5]

Toluene.—This material was obtained from the Mallinckrodt Chemical Works. It was shaken with concd. sulfuric acid, washed with dil. sodium hydroxide and distilled water. After standing over mercury for a week it was dried with phosphorus pentoxide and fractionated.

Carbon Tetrachloride.—The preparation (obtained from Merck and Company) was refluxed over mercury and washed with concd. sulfuric acid to remove sulfides. It was then washed with dil. sodium hydroxide solution and water, dried over fused calcium chloride and fractionated.

Chlorobenzene.—This material was obtained from the Eastman Kodak Company. It was carefully dried and fractionated.

Bromobenzene.—The liquid was also obtained from the Eastman Kodak Company. It was treated as was the chlorobenzene.

Experimental Results

The dielectric constants of benzene, toluene, carbon tetrachloride, bromobenzene and chlorobenzene at 25° were obtained. In all cases the frequency was of the order 10^6 cycles per second. The dielectric constant of air was taken as unity.

The results on systems of benzene-toluene, benzene-carbon tetrachloride and bromobenzene-chlorobenzene are summarized in Table II and in Figs.

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[5] Richards and Shipley, This Journal, **41**, 2022 (1919).

TABLE I

DIELECTRIC CONSTANTS AT 25°

Liquid	Dielectric constant	B. p., °C.
Benzene	2.282 ± 0.0020	80.10- 80.15
Toluene	2.378 ± .0030	110.60-110.80
Carbon tetrachloride	2.230 ± .0030	76.45- 76.52
Bromobenzene	5.397 ± .0050	156.20-156.30
Chlorobenzene	5.610 ± .0050	131.85-132.15

2, 4 and 5, where percentage composition is plotted against dielectric constant.

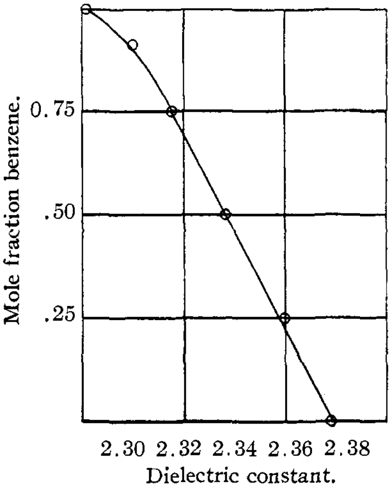

Fig. 2.—C_6H_6—C_7H_8.

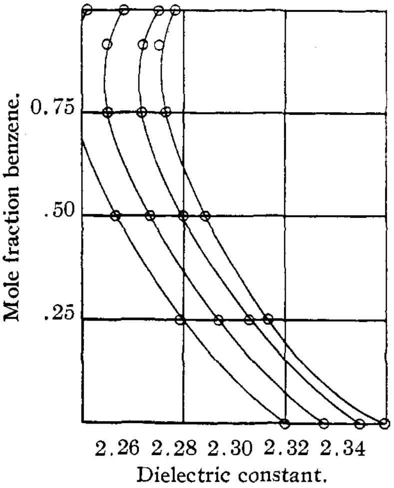

Fig. 3.—C_6H_6—C_7H_8. Grützmacher.

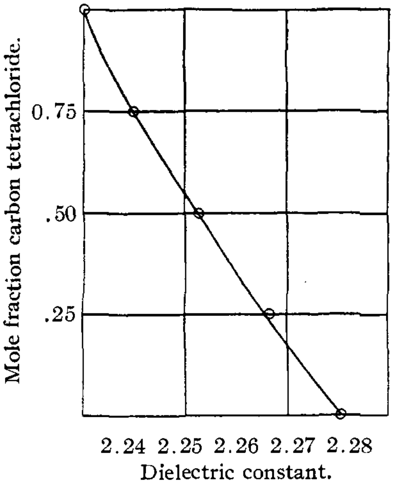

Fig. 4.—C_6H_6—CCl_4.

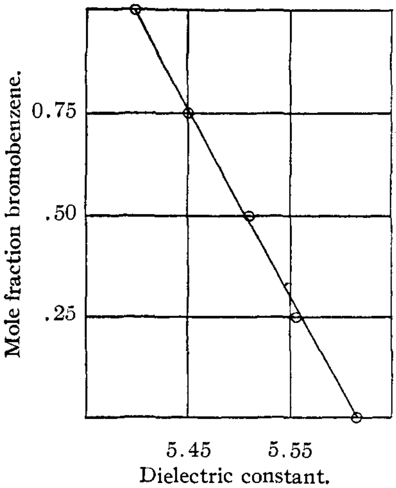

Fig. 5.—C_6H_5Cl—C_6H_5Br.

Discussion of Results

A. Pure Liquids

Concerning the dielectric constants of the pure liquids, it may be stated that with the exception of chlorobenzene the values obtained are in good agreement with the commonly accepted values. For example, in the case of benzene Turner[6] obtained 2.289 ± 0.003 at 18°. Since $\frac{d\ (\text{D.C.})}{dt} = -0.001$ (approximately), his value at 25° would be 2.282.

The dielectric constant of chlorobenzene is decidedly different from that reported by Veley.[7] This author reports a value of 10.95 at 10.8°, which has been accepted by the Landolt-Börnstein "Tabellen" and has been used in many theoretical discussions, for example, by Hildebrand.[8] It is hard to understand why chlorobenzene should have such a radically different dielectric constant from bromobenzene (5.397) and iodobenzene[8] (4.6), especially since other physical properties such as specific heat, molecular refraction, molecular volume, etc., show periodic changes as bromine and iodine are substituted in place of chlorine.

TABLE II

DIELECTRIC CONSTANT—COMPOSITION DATA FOR MIXTURES AT 25°

	Benzene-toluene					Benzene-carbon Tetrachloride			Bromobenzene-Chlorobenzene		
		Dielectric constant					Dielectric Constant			Dielectric Constant	
Mole fraction A[a], %	n_D^{25}	Obs.	Dev.	Grütz-macher	Dev.	n_D^{25}	Obs.	Dev.	n_D^{25}	Obs.	Dev.
100	1.— 49780	2.282	.....	2.277	.....	1.— 49780	2.282	.....	1.— 55711	5.397	.....
91.5	49724	2.304	+0.014	2.271	−0.013	...	...	.....	...	...	.....
75	49649	2.315	+ .008	2.273	− .026	48770	2.267	−0.002	54874	5.448	.....
50	49653	2.337	+ .007	2.289	− .031	47766	2.253	− .003	54059	5.510	+0.006
25	49460	2.362	+ .006	2.314	− .027	46747	2.240	− .003	53179	5.557	− .002
0	49392	2.378	.....	2.360	.....	45724	2.230	.....	52343	5.610	.....

[a] In each case the first named component is designated by A.

Again, data on chlorobenzene-bromobenzene mixtures (vapor-pressure relations, heats of mixing and volume changes) by Young[9] and specific heat relations[3] lead to the conclusion that this system is at least approximately ideal, but if the dielectric constant of chlorobenzene were over twice that of bromobenzene (as previously given) it would have been expected that the various physical constants for these solutions would show greater deviations from those calculable on the basis of Raoult's law, since it has been suggested by Kendall,[10] and by Hildebrand[8] that the dielectric constant may be considered as being the most direct evidence of polarity

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[6] Turner, *Z. physik. Chem.*, **35**, 385 (1900).

[7] Veley, *Phil. Mag.*, [6] **11**, 73 (1906).

[8] Hildebrand, "Solubility," Chemical Catalog Company, New York, **1924**, pp. 89–90.

[9] Young, *J. Chem. Soc.*, **81**, 768 (1902).

[10] Kendall, THIS JOURNAL, **39**, 2323 (1917).

or association in a liquid, and since association in a liquid is usually (though not always[3]) a cause for the formation of a non-ideal solution.

The value obtained, 5.610 at 25°, for chlorobenzene was carefully checked and samples of the material from several different sources were used, giving the same results within the limits of experimental error. The final samples used had considerably better physical constants than those of the chlorobenzene described under purification of materials and used for the binary mixtures. It was necessary to use larger quantities for them, and it was not practicable to confine the distillate to very narrow ranges.

B. Binary Mixtures

The binary mixtures were studied with the purpose of continuing the study of the thermodynamics and the mechanism of solutions.[3] An attempt has been made to account for the deviations from the ideal solution by a study of the dielectric constants of certain mixtures, since that property has been considered to be the most direct evidence of association or polarity. In general, a polymerized molecule has a greater electrostatic moment than the simple molecule.[11] This means that the dielectric constant of the solvent will be greater in its associated state, and if a de-association takes place on solution, the dielectric constant of that component in solution will be less than that of the pure liquid. And, conversely, if two liquids unite chemically the electrostatic moment of the molecules will very probably be increased and the forces holding the electric charge will be weakened, causing the dielectric constant of a component to be greater in solution than in its pure state.

On this basis it should be possible to predict whether the dielectric constant of a solvent in solution will be greater or less than that of the pure solvent. However, the problem is not simple, and it has already been shown[3] that in some cases there are at least two simultaneous reactions taking place when liquids are mixed—a de-association of the liquids and a combination between the two liquids. These factors lead to opposing tendencies in any physical property. It is not possible with the data here presented to do more than point out in a qualitative way the factors which are operating for the binary mixtures studied.

With these general considerations in view, a brief discussion of each of the three systems studied will be given.

Benzene-Toluene.—The dielectric constants for solutions of benzene and toluene over a considerable range of temperature have recently been determined by Grützmacher.[12] If we determine (by graphic interpolation of his data) the values of the dielectric constants at 25°, 30°, 40° and 50°, of the various solutions examined by this investigator and plot dielectric

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[11] Creighton and Fink, "Electrochemistry," Wiley and Sons, Inc., New York, **1924**, Vol. I, pp. 58–59.

[12] Grützmacher, *Z. Physik*, **28**, 342 (1924).

constant-composition curves for these values, curves shown in Fig. 3 are obtained. It will be noted from these curves that there is a distinct minimum in the dielectric constant at 85 mole fractions benzene, 15 mole fractions toluene, and that over the whole range of composition the dielectric constants as determined are considerably less than those which would be calculated, assuming an ideal solution.

The results obtained in this investigation have already been presented. It will be noted (Fig. 2) that the dielectric constants of all mixtures lie between those of the two components, and that in solutions in which the benzene content is less than 0.75 mole fraction the points lie practically on a straight line. It was evident from the slope of this line, however, that the extrapolation to 1.00 mole fraction benzene would not give the previously determined value for pure benzene. Therefore it was necessary to determine the dielectric constant of a 0.915 mole fraction benzene-0.085 mole fraction toluene solution to complete the curve. Since all points on the curve were determined with a mean possible error of not greater than ± 0.0025 it is believed that the deviations of the observed results from those calculated using Raoult's law and presented in Table IV are significant. It will be evident from the curves and the table that these values are hard to reconcile with those of Grützmacher. After the first curve had been constructed the values of Table II for the solutions were redetermined. Very pure benzene and toluene were finally and thoroughly dried over metallic sodium, and the dielectric constants of the mixtures determined immediately. In all cases the previous values were verified within the limits of experimental error. The value of the 0.915 mole fraction benzene-0.085 mole fraction toluene solution was repeatedly checked to ± 0.002.

From previous measurements of the physical properties of benzene-toluene solutions large deviations from the law of ideal solutions are not to be expected. Fig. 2 and Table II show this to be true in the case of their dielectric constants. The deviations are significant, however, especially in the case of the 0.915 mole fraction benzene-0.085 mole fraction toluene solution. In the previous paper of this series,[3] it was shown that in the higher concentrations of benzene, the partial molal heat capacity of the benzene in solution was less than the molal heat capacity of the pure benzene, and that the partial molal heat capacity of the benzene increased as its mole fraction decreased. The results on the dielectric constants of the mixtures constitute an excellent check on these results, for the deviations from the ideal solution exactly parallel to those of the heat capacity relations. In the more concentrated benzene solutions the dielectric constant of the benzene in solution is greater than that of the pure liquid and this quantity becomes less as the concentration of the benzene is decreased.

It does not seem probable that the dielectric constants of benzene-toluene solutions should deviate so much from those calculated on the basis of Raoult's law as is required by the data given by Grützmacher.[12] Neither does it seem probable that this deviation should be greatest in the region of equal molal fractions of the components, since measurements of other physical properties show that solutions, with the exception of those in which the mole fraction of benzene is high, behave in a manner which approaches that of the ideal solution.

Benzene-Carbon Tetrachloride.—Systems of these components have been subjected to many physicochemical studies. They show for the most part deviations from "ideality" corresponding to a slight de-association of complex molecules, although the data are somewhat conflicting. From the measurements of vapor pressure,[13,14] heats of mixing[15] and specific heats[3] it has been suggested that association has been diminished on solution.

It is evident from Table II that the solutions show a slight deviation from the ideal condition as regards their dielectric constants. The fact that these observed dielectric constants are slightly less than those calculated on the basis of Raoult's law tends to indicate that association has been diminished and the number of molecules increased since the observed values are consistently less than the calculated ones. However, the magnitude of the deviations is so small that it is hardly possible to draw any definite conclusions as to what happens on solution.

Chlorobenzene-Bromobenzene.—The results of the measurements on this system, as summarized in Table II, indicate that chlorobenzene and bromobenzene form solutions which are ideal within the limits of experimental error, a conclusion which Young[9] arrived at from measurements of vapor pressure, heats of mixing and volume changes.

The value obtained for the dielectric constant of chlorobenzene has been discussed. This new value makes it probable that only slight deviations from the ideal solution for any physical property of these solutions may be expected. The dielectric constants of the components are comparatively high, which is considered to be evidence of polarity or association, but it has been pointed out[3] that the mere existence of association in a pure liquid is not a sufficient cause for the formation of a non-ideal solution.

Conclusions

The study of the causes of deviations of physical properties of solutions from Raoult's law has been discussed by Hildebrand.[16] The results here presented confirm the impression given that the changes taking place on solution are intricate indeed. The study is being extended to other solutions which it is hoped will give more definite evidence for either one or

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[13] Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).

[14] Dolezalek, *ibid.*, **64**, 727 (1908).

[15] Young and Fortey, *J. Chem. Soc.*, **83**, 45, 68 (1903).

[16] Ref. 8, Chap. 7.

the other of the two fundamental factors which are being recognized in explaining the properties of solutions, namely, the formation of compounds, and the breaking down of complex molecules present in the liquids.

Summary

1. An electrical resonance method, making use of several novel features, for the determination of the dielectric constants of liquids has been presented.

2. The dielectric constants at 25° of pure benzene, toluene, carbon tetrachloride, bromobenzene and chlorobenzene have been redetermined. A new value, and it is believed a more exact one, has been found for chlorobenzene.

3. The dielectric constants of three binary mixtures at 25° have been determined at various concentrations. The systems studied are benzene-toluene, benzene-carbon tetrachloride and chlorobenzene-bromobenzene, all of which may be considered as being nearly ideal solutions.

4. Each of the systems studied has been critically discussed, and an attempt made to explain the nature of the changes taking place on solution, from a consideration of values of the dielectric constants of the solutions.

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[Contribution from the National Bureau of Standards, United States Department of Commerce]

THE RATE OF FLAME PROPAGATION IN GASEOUS EXPLOSIVE REACTIONS[1]

By F. W. Stevens

Received April 30, 1926 Published July 6, 1926

In the case of gaseous explosive reactions the energy transformation of the chemical system is brought about by the spatial propagation within the explosive gases of a thin, sharply defined area of reaction marked by flame.[2] The expression, then, rate of flame propagation, should refer to the linear rate of displacement of this area relative to the active gaseous components in which it propagates itself. This rate may be expressed by

$$s = v_p/ta \quad (1)$$

where v_p is the volume at constant pressure of the active components passing an element of the flame front in time t; a is the area of this element.[3,4,5,6]

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] Luther, *Z. Elektrochem.*. **12**, 597 (1906).

[3] Bunsen, *Phil. Mag.*, **34**, 1 (1867).

[4] Gouy, *Ann. chim. phys.*, [5] **18**, 18 (1879).

[5] Michelson, *Ann. Phys. Chem.*, **37**, 1 (1887).

[6] Mache, "Die Physik der Verbrennungserscheinungen," Viet and Co., Leipzig, **1918**.