

the nitrile (XI) was added in 50 cc. of benzene and the mixture was refluxed overnight. The reaction mixture was decomposed by dilute hydrochloric acid, whereupon the imine hydrochloride precipitated and was collected; yield 3.5 g. (83.5%). A sample was purified for analysis by repeated conversion to the free base and reprecipitation from organic solvents by hydrochloric acid.

Anal. Calcd. for $C_{27}H_{24}NCl$: N, 3.52. Found: N, 3.41.

9,10-Diphenyl-9-methyl-10-ethoxy-9,10-dihydroanthracene (XIII, R = C_2H_5).—A mixture of 0.5 g. of the imine hydrochloride (XII) and 15 cc. of 48% hydrobromic acid was refluxed for seven days. At the end of this period, the suspended solid (probably impure bromide) was collected and added to 50 cc. of absolute alcohol. The solution was refluxed for one hour during which the ethyl ether crystallized from the boiling solution. Once recrystallized from alcohol, it gave 0.28 g. (57%) of white plates, m. p. 203–204°.

Anal. Calcd. for $C_{25}H_{26}O$: C, 89.21; H, 6.70. Found: C, 88.93; H, 6.87.

9,10-Diphenyl-9-methyl-10-methoxy-9,10-dihydroanthracene (XIII, R = CH_3) was prepared as described above, but using methyl instead of ethyl alcohol. The product crystallized from methanol as irregular white prisms, m. p. 284–286°.

Anal. Calcd. for $C_{23}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.08, 88.90; H, 6.65, 6.40.

Summary

By cyclization of ketones of such a nature that elimination of water cannot take place, we have been able to offer very strong support to the theory that the cyclization of *o*-benzylphenones does *not* involve enolization.

The function of the acid in this cyclization has been discussed and an effort has been made to show that this reaction is not a modification of the Elbs synthesis, but could most aptly be described as a reaction of the Friedel and Crafts type.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

Molar Polarizations in Extremely Dilute Solutions. II^{1,2}

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The abnormal behavior sometimes observed in the polarization curves at high dilution on plotting polarization values against mole fractions has been supported by some investigators and denied by others.³ The purpose of this investigation was to study the very dilute solution ranges more thoroughly than before^{3a} in an attempt to decide whether an anomalous behavior did exist for certain compounds or whether experimental error was responsible. The molar polarizations and dipole moments of chlorobenzene, nitrobenzene, ethyl benzoate, benzamide, *m*-nitroaniline, *d,l*-pinene, 3,6-dichloro-2,5-dimethoxybenzoquinone, and 2,3-dichloro-5,6-dimethoxybenzoquinone were determined in benzene or in dioxane as the non-polar solvents.

Materials

Benzene.—Thiophene was removed from General Chemical Company technical benzene by either refluxing

over aqueous mercuric acetate or by shaking with concentrated sulfuric acid. After either of these treatments, the benzene was washed with water and dried over calcium chloride. The benzene was distilled over sodium through 3 feet of a 1.5-inch column packed with glass rod, discarding the first 10% and also the residue amounting to 10–20% of the initial volume. After use the benzene was recovered by distilling through the same column discarding the first 10%. The benzene was stored in a glass bottle over sodium wire and used as required.

Dioxane.—Union Carbon and Carbide Co. dioxane was refluxed over sodium for six hours and distilled over sodium through the above column. The first 10–15% and a residue of 20% were discarded. The dioxane after use was recovered by distilling over sodium.

Nitrobenzene.—Eastman Kodak Co. nitrobenzene was distilled through a 10-inch Vigreux column and the middle 50% was collected; b. p. 210–210.5°.

Chlorobenzene.—Coleman and Bell chlorobenzene was distilled as above; b. p. 132°.

Ethyl Benzoate.—Eastman pure ethyl benzoate was distilled as above; b. p. 212.0–212.5°.

Pinene.—Eastman technical *d,l*-pinene was distilled as above; b. p. 162–162.3°.

***m*-Nitroaniline.**—Eastman pure *m*-nitroaniline was recrystallized from water and dried in a desiccator for three days; m. p. 114° (cor.).

Benzamide.—Eastman pure benzamide was recrystallized from water and dried as above; m. p. 130° (cor.).

2,3-Dichloro-5,6-dimethoxybenzoquinone was furnished through the courtesy of the Dow Chemical Company and was used without further purification.

(1) Presented in part at the Detroit meeting of the American Chemical Society, September, 1940.

(2) Abstracted from the Master's Thesis of Raymond Davis, University of Maryland, June, 1940.

(3) (a) Svirbely, Ablard and Warner, *THIS JOURNAL*, **57**, 652 (1935); (b) Maryott, *ibid.*, **63**, 3079 (1941); (c) Halverstadt and Kumler, *ibid.*, **64**, 2988 (1942); (d) Hoecker, *J. Chem. Phys.*, **4**, 431 (1936); (e) Pohl, Hobbs and Gross, *Annals of the New York Academy of Sciences*, **40**, 389 (1940). These are but a few papers referring to the subject.

3,6-Dichloro-2,5-dimethoxybenzoquinone was also furnished by the Dow Chemical Company. It was recrystallized from methyl alcohol, washed with water and dried for one week in a desiccator; m. p. 146–146.5° (cor.).

Experimental Method

The dielectric constants were measured at a frequency of 1000 kilocycles with a crystal controlled heterodyne beat apparatus, designed and built in this Laboratory. The outfit is exceptionally stable even under the most adverse humidity conditions. The details of design and calibration will appear in a later publication.

TABLE I

SUMMARY OF DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS IN SOLUTIONS BEHAVING NORMALLY

N_2	ϵ	d	P_2
Nitrobenzene in Benzene at 30° (2 runs)			
0.0000	2.2574	0.86672	
.003785	2.3397	.86814	348.3
.004421	2.3534	.86844	346.4
.004731	2.3609	.86850	348.7
.006202	2.3921	.86905	344.3
.008478	2.4430	.87017	342.2
.01098	2.4958	.87095	336.9
.01179	2.5156	.87125	338.3
.01228	2.5254	.87142	336.6
.01259	2.5315	.87160	335.2
.01496	2.5828	.87250	331.7
.02006	2.6957	.87450	325.9
.02674	2.8440	.87710	317.8
Nitrobenzene in Dioxane at 30.1°			
0.0000	2.1965	1.02205	
.006070	2.3346	1.02332	353.2
.01002	2.4246	1.02416	346.9
.0206	2.6669	1.02637	331.6
.02494	2.7687	1.02735	327.2
.03176	2.9233	1.02865	317.6
.03552	3.0129	1.02955	313.7
.03882	3.0895	1.03009	310.0
Chlorobenzene in Benzene at 30°			
0.0000	2.2567	0.86655	
.001147	2.2604	.86681	79.6
.001767	2.2623	.86705	76.8
.002450	2.2648	.86717	79.8
.003245	2.2672	.86739	78.5
.004009	2.2704	.86759	81.2
.004696	2.2722	.86775	79.6
.005110	2.2735	.86785	79.4
.006917	2.2799	.86836	80.1
.01047	2.2926	.86926	81.1
.01456	2.3064	.87034	80.7
.02218	2.3327	.87232	80.7
.03181	2.3650	.87479	80.1
.04273	2.4032	.87761	80.3
<i>m</i> -Nitroaniline in Benzene at 30°			
0.0000	2.2596	0.86653	
.005331	2.4438	.86938	524.6
.007454	2.5145	.87052	512.0
.01022	2.6087	.87203	501.7
.01289	2.7019	.87347	494.6

<i>m</i> -Nitroaniline in Dioxane at 30.1°			
0.0000	2.1935	1.02219	
.006224	2.4323	1.02448	564.0
.008221	2.5099	1.02532	556.3
.01064	2.6025	1.02615	545.6
.01493	2.7716	1.02768	531.5
.01927	2.9379	1.02922	513.9

Benzamide in Dioxane at 30.1°			
0.0000	2.1988	1.02212	
.004083	2.2821	1.02295	322.4
.01064	2.4169	1.02431	315.2
.01680	2.5443	1.02558	308.3
.02682	2.7543	1.02765	298.4
.03445	2.9209	1.02917	292.8
.04340	3.1062	1.03084	283.1

Ethyl Benzoate in Benzene at 30°			
0.0000	2.2587	0.86658	
.0008321	2.2625	.86683	117.8
.001642	2.2670	.86704	120.4
.003249	2.2755	.86757	118.1
.004274	2.2806	.86780	118.3
.005360	2.2861	.86807	118.4
.007353	2.2965	.86859	118.9
.01004	2.3123	.86943	118.7
.01622	2.3421	.87103	118.5
.02603	2.3920	.87368	117.8
.03611	2.4427	.87638	117.1
.05258	2.5253	.88069	116.1

3,6-Dichloro-2,5-dimethoxybenzoquinone in Benzene at 30°			
0.0000	2.2563	0.86666	
.003980	2.2792	.87121	140.5
.006832	2.2945	.87445	140.1

2,3-Dichloro-5,6-dimethoxybenzoquinone in Benzene at 30°			
0.0000	2.2568	0.86644	
.002631	2.2901	.86949	232.8
.004108	2.3084	.87115	231.0
.005091	2.3206	.87229	230.2
.008562	2.3632	.87622	227.5
.01192	2.4057	.88002	227.0
.01867	2.4867	.88749	222.3

<i>d,l</i> -Pinene in Benzene at 30.1°			
0.0000	2.2588	0.86646	
.001077	2.2588	.86640	48.4
.002194	2.2589	.86638	49.1
.003538	2.2588	.86634	47.7
.004496	2.2588	.86626	48.0
.007517	2.2596	.86614	49.5
.01051	2.2596	.86599	49.1
.01595	2.2596	.86572	48.7
.02352	2.2602	.86544	48.8
.03179	2.2619	.86506	49.4
.04142	2.2630	.86466	49.4

The measuring condenser was a modification of one first described by Sayce and Briscoe⁴ and later used by Ball⁵

(4) Sayce and Briscoe, *J. Chem. Soc.*, 315 (1925).

(5) Ball, *ibid.*, 570 (1930).

TABLE II

Compound	MR_D	Solvent	Method	P_∞	$\mu \times 10^{18}$ obs.	$\mu \times 10^{18}$ literature values
Nitrobenzene	32.7	Benzene	Linear	353	3.96	3.95 ^a
			Hoecker	352	3.95	
Nitrobenzene	32.7	Dioxane	Linear	361	3.99	4.72 ^b , 4.94 ^c
			Hoecker	539	5.00	
<i>m</i> -Nitroaniline	29.4	Benzene	Linear	539	5.00	4.72 ^b , 4.94 ^c
			Hoecker	544	5.02	
<i>m</i> -Nitroaniline	29.4	Dioxane	Linear	586	5.22	3.6 ^d
			Hoecker	580	5.19	
Benzamide	33.05	Dioxane	Linear	325	3.77	3.6 ^d
			Hoecker	315	3.71	
Ethyl benzoate	45.54	Benzene	Linear	120	1.88	1.8 ^e , 1.91 ^f , 2.14 ^g
			Hoecker	121	1.89	
Chlorobenzene	31.20	Benzene	Linear	80.4	1.53	1.54 ^h , 1.56 ⁱ
			Hoecker	80.9	1.54	
<i>dl</i> -Pinene	43.95	Benzene	Linear	49.0	0.36	
			Hoecker	49.0	0.36	
3,6-Dichloro-2,5-dimethoxy- benzoquinone	49.05	Benzene	Linear	141	2.09	
			Hoecker	140	2.08	
2,3-Dichloro-5,6-dimethoxy- benzoquinone.	49.05	Benzene	Linear	234	2.99	

^a Muller, *Physik. Z.*, **34**, 689 (1933). ^b Hojendahl, *ibid.*, **30**, 391 (1929). ^c Taganik, *Z. physik. Chem.*, **B14**, 135 (1931). ^d Devoto, *Gazz. chim. ital.*, **63**, 495 (1933). ^e Estermann, *Z. physik. Chem.*, **B1**, 422 (1928). ^f Bergmann and Weizmann, *THIS JOURNAL*, **57**, 1755 (1935). ^g Svirbely, Ablard and Warner, *ibid.*, **57**, 652 (1935). ^h Müller, *Physik. Z.*, **38**, 283 (1937). ⁱ Smyth, Morgan and Boyce, *THIS JOURNAL*, **50**, 1536 (1928).

and Sugden.⁶ The cell consisted of two concentric glass tubes having outside diameters of approximately 32 and 35 mm., respectively. The tubes were sealed together at one end and rounded off at the other. The outer tube was silvered on the inside and the inner tube silvered on the outside having a gap of 1 mm. between the plates. The inner silvered surface served as the high potential plate and the outer silvered surface was grounded. The leads to the plates were made through platinum wires sealed through glass tubes and making contact with the silvered surfaces. Filling and emptying tubes were sealed to the cell, which was rigidly supported in an oil thermostat.

The cell was always rinsed out with the solution to be used before final introduction of the solution. The dielectric constant and the density of the non-polar solvent used in preparing the solutions were measured every time a new run was made. Care was exercised to keep water from being picked up during a run by closing the inlet and outlet tubes with corks while the cell with its contents was reaching temperature equilibrium.

Densities were measured by the bobbin method.

Experimental Results

All our experimental results are summarized in Tables I and III.

Table I gives the experimental values of the dielectric constants, ϵ , the densities, d , the mole fractions of the solute, N_2 , and the molar polarizations, P_2 , obtained in solutions where the usual linear plot of P_2 versus N_2 was obtained. Table III lists mole fractions, N_2 , and the molar polarizations, P_2 , obtained in the more dilute solution ranges for the compounds listed.

(6) Sugden, *J. Chem. Soc.*, 768 (1933).

TABLE III

SUMMARY OF DATA OBTAINED IN SOLUTIONS BEHAVING ABNORMALLY

N_2	P_2	N_2	P_2
Nitrobenzene in Benzene at 30°		<i>m</i> -Nitroaniline in Benzene at 30°	
0.0002332	432	0.001532	579
.0003746	381	.002576	555
.0004402	386	.003307	541
.0007377	369	.004129	539
.001303	362	<i>m</i> -Nitroaniline in Dioxane at 30.1°	
.001445	364		
.001516	362	0.0008960	599
.002557	355	.002005	588
.003002	351	.002920	580
		.003914	586
		.005180	560

Table II lists in the second column the values of MR_D , the molar refraction for the sodium D line. These values were either taken directly from Landolt-Börnstein or were calculated from the atomic or molecular refractions given there. In the fifth column are listed not only the values of molar polarizations, P_∞ , obtained by extrapolation to $N_2 = 0$ of the values of P_2 given in Table I, but also the values of the molar polarizations, P_∞ , obtained by Hoecker's method^{8d} using some of the combined data of Tables I and III. In column six are given the dipole moments calculated in the usual manner using the P_∞ values of column 5. $P_E + P_A$ was taken equal to $1.05 P_E$.

The dielectric constants of the different samples of pure benzene given in Table I varied at the most ± 0.0018 from the average value of 2.2578 at 30°. Plots of dielectric constant against N_2 for a series of solutions made from any particular sample of benzene indicated that the data were consistent to better than 0.1%. The densities of the different samples of pure benzene were consistent to 0.03%. Actually the densities of any particular set of solutions made from a particular sample of benzene were consistent to 0.01%.

The dielectric constants of the different samples of pure dioxane varied at the most ± 0.003 from the average value of 2.1966 at 30°. Consistency between the dielectric constants for a series of solutions was better than 0.1%. The densities of the different samples of pure dioxane as well as those of a set of solutions made from any particular sample were consistent to better than 0.01%.

The estimated error in mole fraction was of an order less than 0.1%.

Discussion of Results

On plotting values of P_2 against N_2 given in Tables I and III, the usual linear relationship was observed for all cases in the more concentrated range, that is above a mole fraction of 0.005. In the more dilute concentration range, the polarization curves for nitrobenzene and *m*-nitroaniline rose sharply while the curves for ethyl benzoate and chlorobenzene had a slight tendency to dip down. Examination of the data in Tables I and III will show these trends. To account for such trends one would have to assume in these cases either abnormal behavior in dilute solutions or some systematic experimental error which becomes quite important in the dilute solution range. That non-systematic errors in the experimentally determined values of dielectric constant, density and mole fraction which actually result in quite large errors in P_2 at low concentration cannot be the answer for the abnormalities can be shown as follows.

Using the definitions

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{M_2 N_2 + M_1 N_1}{d} \quad (1)$$

and

$$P_2 = \frac{P_{12} - P_1(1 - N_2)}{N_2} \quad (2)$$

one can obtain by the usual method the error equation

$$\Delta P_2 = \left[\frac{(M_2 - M_1)(\epsilon - 1)}{N_2 d (\epsilon + 2)} + \frac{(P_1 - P_{12})}{N_2^2} \right] \Delta N_2 +$$

$$\left[\frac{M_1(1 - N_2) + M_2 N_2}{N_2 d (\epsilon + 2)^2} \right] \Delta \epsilon - \left[\frac{M_1(1 - N_2) + M_2 N_2 (\epsilon - 1)}{N_2 d^2 (\epsilon + 2)} \right] \Delta d - \left[\frac{N_1}{N_2} \right] \Delta P_1 \quad (3)$$

In order to show the relative magnitude of the errors, part of the data on nitrobenzene have been substituted in equation 3. An arbitrary error of 0.1% was assumed for ΔN_2 , $\Delta \epsilon$, Δd , and ΔP_1 , and the values for each separate term of equation 3 are given in Table IV. It is obvious that when one uses the linear extrapolation method (*i. e.*, P_2 vs. N_2 plot), the error in P_2 due to experimental errors in N_2 , ϵ , d and P_1 is quite large especially at low concentrations. The actual error in P_2 is impossible to evaluate since the errors due to N_2 , ϵ and d might be either positive or negative for any particular solution. The error due to P_1 would, however, have the same sign, that is, be either positive or negative for every solution in the series since it is usually based on the measurement of the pure solvent from which all the solutions were made. The second column in Table IV gives the differences between the experimental values of P_2 and those picked off the line which runs through the more concentrated points. It is apparent on

TABLE IV

N_2 Nitrobenzene	P_2 calcd. - P_2 linear	Linear extrapolation method Error in P_2 due to experimental errors of			
		$\Delta N_2 =$ 0.1%	$\Delta \epsilon =$ 0.1%	$\Delta d =$ 0.1%	$\Delta P_1 =$ 0.1%
0.0002332	79.3	0.36	144.4	114.5	114
.0004402	33.5	.37	76.4	60.3	60.4
.001303	10.3	.35	25.8	20.8	20.4
.002557	5.3	.33	13.1	10.7	10.4
.004421	- 0.8	.33	7.59	6.33	6.0
.008478	0.8	.33	3.95	3.45	3.1
.01179	1.2	.33	2.83	2.57	2.2
.01496	- 1.0	.32	2.23	2.08	1.8

comparing this column with the others that there occurred a certain amount of cancellation of errors in each solution as should have been the case. However, since the error due to P_1 is always in the same direction, the resultant error in any P_2 value will usually be in the same direction and the polarization curve will go either up or down although the points due to a series of solutions might be spotty depending entirely on the magnitude of the other errors. Using a method developed in this

TABLE V

Solvent	Extrap. ⁶⁰	Exp.	Variation, %	Polarization curve behavior with dec. concn.
Nitrobenzene	2.2582	2.2574	+0.04	Upswing
<i>m</i> -Nitroaniline	2.2645	2.2596	+ .2	Upswing
Ethyl benzoate	2.2583	2.2587	- .02	Downswing (slight)
Chlorobenzene	2.2562	2.2567	- .02	Downswing (slight)
Pinene	2.2588	2.2588	00	Scattering

Laboratory,⁷ we have plotted the dielectric constants against mole fractions for some of the solutions and from the extrapolation of the straight lines obtained the values of ϵ_0 listed in the second column of Table V. In the fourth column of Table V are listed the percentage variations between the extrapolated and experimental ϵ_0 's and it is observed that when the extrapolated values were higher, then the polarization curves went up, when the extrapolated values were lower, then the curves went down. From the equation

$$P_1 = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} \quad (4)$$

one obtains the following error equation for P_1 due to ϵ alone

$$\Delta P_1 = \frac{M}{d} \frac{3}{(\epsilon + 2)^2} \Delta \epsilon \quad (5)$$

Substituting in equation (5) the proper values of M , d , and ϵ for benzene, one observes that an arbitrary 0.1% error in ϵ will make an error of 0.1% in P_1 . This will create extremely large errors in P_2 in the dilute solution range as reference to Table IV will show.

It appears therefore both from the data presented here and from unpublished data⁷ that the abnormal trend in the polarization curves observed in very dilute solutions is without significance and is really due to experimental error in obtaining the dielectric constant of the pure solvent. This error even if quite small becomes important in very dilute solutions.

To avoid introducing experimental and calculation errors at low concentrations, Hoecker suggested plotting the product of $P_2 N_2$ against N_2 and using the slope of the resulting line as P_∞ . It is evident from the expression

$$\frac{d(P_2 N_2)}{dN_2} = \frac{P_2 dN_2 + N_2 dP_2}{dN_2} \quad (6)$$

that the slope is equal to P_∞ only if P_2 is constant. Careful inspection of large-scale $P_2 N_2$ vs. N_2 plots of our data shows that the experimental

(7) J. J. Lander, Thesis, University of Maryland, 1942 (unpublished as yet). Lander has shown that if the value of ϵ_0 obtained for a pure solvent by extrapolation of an ϵ vs. N_2 plot to $N_2 = 0$ is higher than the experimental value of ϵ_0 , then an upswing in the corresponding polarization curve will result if the experimental ϵ_0 is used in the calculations. If the extrapolated ϵ_0 is lower than the experimental ϵ_0 , then a downswing occurs in the polarization curve if one uses the experimental ϵ_0 in all calculations. If the extrapolated and the experimental are the same, then a scattering of points results. As little a variation as 0.03% in the extrapolated and experimental values of ϵ_0 caused deviations from linearity in the polarization curves. Obviously the method corresponds to obtaining the true dielectric constant of a pure solvent by graphical methods. In all cases considered, a linear relationship was observed and consequently extrapolation was quite simple.

points fall on a straight line at concentrations up to approximately a mole fraction of 0.005 for *m*-nitroaniline, nitrobenzene and benzamide while above a mole fraction of 0.005 the plots tend to curve toward decreasing P_2 values. The compounds with smaller moments, ethyl benzoate, chlorobenzene and pinene were linear throughout the entire concentration range studied. The slopes of the linear portions of all plots were determined by the method of least squares and are listed in Table II. It is apparent that Hoecker's method when applied over the concentration range where P_2 is constant gives results of P_∞ almost identical with those obtained by extrapolating P_2 to $N_2 = 0$ in a linear P_2 vs. N_2 plot, *i. e.*, in the range where the P_2 curve behaves rationally.

The experimental agreement between the values of P_∞ obtained by the two methods should be examined more closely, however, since Hoecker's method in some cases utilized data obtained only in the extremely dilute solution range where the polarization curves changed slope markedly. The empirical equation for such a curve can be expressed by the equation

$$P_2 = P_\infty - AN_2 + B(1/N_2) \quad (7)$$

At high concentrations the first two terms are important, approximating a straight line and at low concentrations the third term on the right becomes important, yielding a curve approximating a hyperbola. The fact this hyperbolic trend has no physical significance and is due to a systematic experimental error is of no consequence. If the experimental data can be expressed by an equation of the above form, then it becomes apparent that the Hoecker method of calculating P_∞ should yield the same or very nearly the same value of P_∞ as obtained by the usual linear extrapolation method. Multiplying equation (7) by N_2 and differentiating one obtains

$$d(P_2 N_2)/dN_2 = P_\infty - 2AN_2 \quad (8)$$

The limitations of Hoecker's method are easily obtained from equation (8) and are as follows. First, the Hoecker slope is equal to P_∞ only if A is equal to zero. This is true only if the polarization curve is parallel to the concentration axis in the usual method of plot. Second, the Hoecker slope is very nearly equal to P_∞ only if A and N_2 are quite small. This is in agreement with our experience with nitroaniline, nitrobenzene and benzamide where constancy of slope only occurred up to a mole fraction of 0.005. Third, the

Hoecker method of plot should in principle never lead to a constant slope except when A is zero. Within experimental error, however, in case A is not equal to zero, the plot can be considered constant in extremely dilute solutions.

It might thus be concluded that the Hoecker method is less sensitive to a systematic error in P_1 when measurements are made in very dilute solutions. In more concentrated solutions, however, it is applicable only to those solutions where little or no slope in the usual polarization curves is obtained.

The calculated moments using the P_∞ values obtained by both methods are in excellent agreement as reference to Table II will show. It suggests that the Hoecker method could be used to evaluate the moments of substances of limited solubility.

In the last column of Table II are given for comparison some of the dipole moments obtained by other workers. The agreement between our results and those of Mueller for nitrobenzene and chlorobenzene is excellent. Upon considering the measuring technique, reproducibility of

results and agreement with previous workers, it might be concluded that the dipole moments reported here are within 1 per cent. of their actual value in the non-polar solvents used.

Summary

1. The dipole moments of nitrobenzene, *m*-nitroaniline, benzamide, ethyl benzoate, chlorobenzene, *d,l*-pinene, 3,6-dichloro-2,5-dimethoxybenzoquinone and 2,3-dichloro-5,6-dimethoxybenzoquinone were measured in either benzene or dioxane as the non-polar solvent.

2. The method of computing molecular polarizations suggested by Hoecker has been considered and found quite satisfactory under the proper conditions. It is suggested that this method be applied to measurements made on relatively insoluble compounds.

3. The abnormal behavior in polarization curves frequently obtained in very dilute solutions appears to be due to experimental error in measuring P_1 and thus has no physical significance.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Activity Coefficients of Thallous Chloride in Ethylene Glycol-Water Solutions Determined by E. m. f. and Solubility Data at 25°

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Electromotive force and solubility data on thallous chloride in ethylene glycol-water solutions serve to supplement the data on a thermodynamic study of thallous chloride in alcohol-water solutions.¹

Ethylene glycol lends itself well to the study of the relative solvation-dielectric constant effects because of its dihydric character. The cell data are used to determine (a) the value of $(1/m_\pm)_{\mu=0}$ and (b) the values of γ to saturation; the solubility data are used to determine the value of γ above saturation and also to give a qualitative idea of the degree of dissociation of thallous chloride.²

Experimental

The temperature was 25.00 \pm 0.01°. The solubility data were obtained in the manner previously described.¹ The samples were analyzed by potentiometric titration

(1) Hogge and Garrett, *THIS JOURNAL*, **63**, 1089 (1941).

(2) The symbols used throughout this paper are consistent with those used by Lewis and Randall "Thermodynamics," The McGraw-Hill Book Co., New York, N. Y., 1923.

with a silver electrode, using an excess of standard potassium iodide as the precipitant and back titrating with standard silver nitrate. A few drops of nitrobenzene were used in each sample to reduce the solubility of the thallous iodide (reduce the reverse reaction) as was recommended for silver chloride by Caldwell and Moyer.³

The Cell.—The Ag/AgCl/TlCl/Tl-Hg cell was used.⁴ The silver chloride electrodes were prepared by chloridizing 999 fine silver in 0.05 *m* hydrochloric acid at 5 volts with an initial amperage of 150 ma. This procedure gave a firm white coating of silver chloride. The electrodes reached equilibrium rapidly and gave a potential difference of less than 0.1 mv. among themselves. New electrodes were prepared for each cell. Cell data were first obtained for thallous chloride in pure water and compared with similar data obtained by Cowperthwaite, LaMer and Barksdale.⁵ Agreement was obtained in the activity coefficients to within 0.2 of 1%.

The e. m. f. of the cells was measured with a Leeds and Northrup type K-2 potentiometer. The standard cell was calibrated by a cell certified by the National Bureau of Standards.

(3) Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

(4) Carmody, *THIS JOURNAL*, **51**, 2005 (1929).

(5) Cowperthwaite, LaMer and Barksdale, *ibid.*, **56**, 544 (1934).