count for the minimum in the K values at approximately 60% glycol.

This solvent sorting effect may serve to reduce the value of the "microscopic" dielectric constant (in the immediate neighborhood of the ion) below the value of the macroscopic dielectric constant of the mixture so that triple ion formation may occur more readily. It is very probable that absorption spectra studies must be made to give further information on this issue.

It appears that the values of the dissociation constants of thallous chloride in various mixtures of ethylene glycol and water as determined by Black and Garrett[1] are reasonable. This research corroborates their values and suggests possible reasons for the seemingly anomalous behavior which the previous work showed to exist in this thallous chloride–ethylene glycol–water system.

Summary

1. The equivalent conductances of various concentrations of thallous chloride in water, 20, 40, 60 and 80% ethylene glycol in water, and in ethylene glycol were determined.

2. Dissociation constants of the thallous chloride in the various solvents were calculated by various methods.

3. An increase in the thermodynamic dissociation constant with concentration was attributed to association, to triple ion formation, or sorting of solvent molecules.

COLUMBUS, OHIO RECEIVED AUGUST 1, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Molecular Condition of Phenols in Benzene Solution

BY JOHN A. DAVISON[1,2,3]

The early freezing point measurements made by Auwers and Beckmann[4] in aprotic solvents demonstrated that many organic solutes exhibited molecular weights which were much greater than their formula weights. In addition, the molecular weight was observed to vary with the concentration. These investigators divided the compounds that they had studied into three principal classes according to the manner in which the molecular weight varied with concentration.[5]

By far the largest class consisted of polar organic compounds such as ketones, amines, nitro compounds and mercaptans, which gave a small, steady rise in molecular weight as the concentration was increased. Weak hydrogen bonds and dipole–dipole orientation prevail here.

A second distinct group comprised the carboxylic acids. The molecular weight appeared to increase very rapidly at low concentrations, levelling off at approximately double the formula weight. An equilibrium exists between the single and double molecules.[6] The picture of the dimer has been established as an eight-membered ring, in which each acidic hydrogen atom resonates between two oxygen atoms.

The third group included phenols, alcohols, anilides and oximes, whose molecular weights increased almost linearly and apparently without limit as the concentration increased. The infrared absorption spectra of their solutions have shown the existence of hydrogen bonds. Since there is very little possibility of ring formation in these compounds, aggregates of all orders probably are present in equilibrium with one another. Lassettre[7] has shown that once the exact equation connecting the molecular weight with the concentration is known, it is possible to calculate the set of equilibrium constants corresponding to the formation of these aggregates. In using this approach it is assumed that the deviations from the laws of perfect solutions are due to the presence of polymers. It is, therefore, necessary to work in sufficiently dilute solutions so that other deviations from these laws will not interfere. The present work was undertaken in order to cover the range of high dilutions, supplementing the work which has been done over a period of years by users of the Beckmann technique.

Apparatus and Experimental Method

The apparatus used in this work was especially designed to measure freezing points of solutions at 0.002 to 0.10 molal. The freezing point measurement was made with a sensitive thermel and a potentiometer. The principle of the method was to place one arm of the thermel in an equilibrium mixture of pure liquid benzene and solid benzene and the other arm in a mixture of the benzene solution and solid benzene. The apparatus was designed so that both freezing mixtures had the same thermal environment. The twin cell freezing point apparatus was entirely similar to that described by Kraus.[8]

Procedure.—The apparatus was carefully examined while in an unassembled condition and dried in an oven at about 50°. It was then assembled outside the thermo-

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(1) This paper is based on a dissertation presented by John A. Davison to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. June, 1942.

(2) George L. Harrison Fellow in Chemistry, 1939–41; du Pont Fellow in Chemistry, 1941–42. Present address: General Laboratories, United States Rubber Company, Passaic, New Jersey.

(3) The author gratefully acknowledges the assistance and guidance of Professor Martin Kilpatrick throughout this investigation.

(4) See Lassettre, *Chem. Rev.*, **20**, 259 (1937).

(5) Beckmann, *Z. physik. Chem.*, **2**, 715 (1888).

(6) MacDougall, THIS JOURNAL, **58**, 2585 (1936).

(7) Lassettre, *ibid.*, **59**, 1383 (1937).

(8) (a) Kraus and Vingee, *ibid.*, **56**, 511 (1934); (b) Batson and Kraus, *ibid.*, **56**, 2017 (1934).

stat. A stream of dry air was introduced. About 350 ml. of benzene was distilled into each cell directly. Shaved ice was packed around each of the cells and the stirrers were started. About one-quarter of the benzene froze out, forming a cylinder of solid benzene on the walls of the cell. The cells were then inserted into Dewar flasks and the entire apparatus was immersed in a low temperature bath. The apparatus was left submerged in the bath for not less than twelve hours, usually until the following day. This time was required for all parts of the system to come to an equilibrium temperature. When the difference in temperature between the two cells was less than 0.006°, and steady to 0.00006° over a period of at least two hours, a solute was added with a spatula or pipet to one of the cells. After stirring intermittently for an hour, the temperature was measured with the thermel and a 10-ml. sample was siphoned out of the cell. By means of a density determination on the sample and a previous determination of the relation between density and concentration for that particular solute, the concentration of the solute could be calculated. From the value of the observed depression of the freezing point and the concentration of the solution, the molecular weight was calculated.

Temperature Measurement.—The temperature standard was a platinum resistance thermometer used in connection with a Mueller bridge. The thermel was calibrated against the resistance thermometer at various temperatures and gave a reading of 6.5746×10^{-4} deg./microvolt at 5.5°. The resistance thermometer was used also to determine the temperature in the reference cell during a run.

The thermel was constructed of forty junctions of copper and constantan wire in the manner described by Kraus.[8] Twenty junctions could be measured separately from the others. In this manner half of the thermel could be opposed to the other half, providing a test for complete attainment of equilibrium of the thermel with its surroundings. The e. m. f. of the thermel was measured with a potentiometer designed by W. P. White and manufactured by the Leeds and Northrup Company. The galvanometer used had a sensitivity of 24.0 mm./microvolt, critical damping resistance of 440 ohms and a period of 10.5 sec. Parasitic e. m. f.'s in the leads to the galvanometer and thermel together with leakage currents were the largest sources of error in the measurements. The leads were shielded and completely enclosed with magnesia pipe-covering. The batteries, the potentiometer, and the galvanometer also were shielded. These precautions greatly improved the precision of the measurements.

Measurement of Concentration.—Samples were removed from the cryoscopic apparatus when a freezing point was determined. The concentration was determined by measurement of the density of the solution by a flotation method. The apparatus used was similar to that of Hall[9] in that a magnetically controlled float was used. The float was made from a soft glass ampule in which was inserted a soft iron core centered with paraffin. The containing vessel for the liquid and float was made of Pyrex and fitted into a holder so as to center the float reproducibly in the field of a magnet. The magnet was taken from a telegraph fixture.

Samples were siphoned into the density cell directly from the freezing point apparatus. The float and the liquid were kept at constant temperature. The weight of the float was approximated by adding or removing small platinum weights until the float was a trifle too light. Then the float was pulled down to the bottom of the vessel by passing a current through the magnet. By reducing the current slowly, a value of the current was obtained which just prevented the float from rising. Since the value of the current in milliamperes which was equivalent to one mg. weight could be determined by changing weights on the float, the total weight of the float at equilibrium could be calculated.

It is not necessary to compute actual densities for the solvent or any of the solutions, although this can be done. Over a small range the change in density of a solution may be taken as proportional to the change in the weight of the float. Flotation measurements were made on several solutions of low concentration for every solute. These determinations were used in calculating the concentrations of unknown solutions drawn from the freezing point apparatus.

Experimental Errors.—The precision measure of a single flotation measurement was 5×10^{-6} g./ml., resulting in a probable error of ±0.5% in estimating the concentration of the solutes.

The probable error of the temperature measurement varied from ±0.6% at a concentration of 0.005 molal to ±0.4% at 0.05 molal.

The corresponding probable error of $n = M/M_0$ was calculated to be ±1.1% at 0.05 molal and ±0.8% at 0.05 molal.

In addition to the errors which have been estimated above, there was an unknown and variable error produced by small quantities of moisture. In addition to their contribution to the freezing point depression, the water molecules formed hydrogen bonds with the solute, thus altering the equilibria between the polymers. This error was larger than that due to any other cause.

Purification of Materials.—Benzene (Baker, C. P., thiophene-free) was treated successively with sulfuric acid, water, concentrated sodium hydroxide solution and water. It was then purified by fractional crystallization and distilled. The benzene was distilled from over metallic potassium just prior to making measurements. The freezing point was 5.496°, as determined with a thermohm.

Phenol, *o*-cresol, *p*-cresol and nitrobenzene were given the following treatment. The compound was distilled through a small column, then fractionally frozen until it gave a constant melting point with a 0.1° thermometer (±0.2°). The material was then stored in a desiccator. Just before the material was to be used, it was distilled to remove water and any oxidation products that might have accumulated.

Triphenylmethane, *m*-nitrophenol, *p*-nitrophenol and 2,4-dinitrophenol were sublimed once and then were ready to use.

Results

Determination of the Cryoscopic Constant for Benzene.—The freezing points of a series of solutions of triphenylmethane in benzene were determined, using the apparatus and technique described in the previous section. Assuming that this solute did not associate, the results were used to calculate the constant, K_f, of the equation

$$\frac{M}{M_0} = \frac{RT_0M_{\text{solvent}}}{L_f\,\Delta T \times 10^3} = \frac{K_fm}{\Delta T}$$

where M is the observed mol. wt. of the solute, M_0 is the formula wt. of the solute, M_{solvent} is the mol. wt. of the solvent, T_0 is the f. p. of the pure solvent, ΔT is the observed f. p. depression, and m is the formula wt. of solute/1000 g. solvent.

It was shown earlier that K_f is a function of both temperature and concentration. Therefore the data were fitted to an empirical equation, $K_f = K_f^0 - b\Delta T$. The value of b was computed from the data of Bury and Jenkins[10] on the freezing points of solutions of carbon tetrachloride in benzene. These data extend over a temperature range of 5°; consequently the value of b obtained is fairly accurate. It was found that $b = 0.0548$. Using this value of b, the value of K_f^0 was computed by the method of least squares from the

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[9] Hall and Jones, THIS JOURNAL, **58**, 1915 (1936).

[10] Bury and Jenkins, *J. Chem. Soc.*, 668 (1934).

author's data on triphenylmethane solutions in benzene. It was found that K_f^0 = 5.088 deg./mole. The average deviation of the author's results from the equation

$$K_f = 5.088 - 0.0548\Delta T$$

was ±0.5% (see Table I). Figure 1 shows the plot of the combined results of this investigation

TABLE I

CRYOSCOPIC DATA FOR SOLUTIONS OF TRIPHENYLMETHANE IN BENZENE

Formula weight = M_0 = 244.32.

Molality × 10^3	ΔT °K. × 10^3	$\Delta T/m$	M
4.17	21.10	5.06	245.5
9.65	48.88	5.065	245.3
11.50	58.46	5.083	244.3
19.85	101.2	5.097	243.6
28.68	146.2	5.097	243.6
33.87	172.6	5.095	243.6
42.20	215.1	5.096	243.3
56.79	287.6	5.063	244.8
60.78	307.5	5.060	244.8

together with those of Bury and Jenkins; the line shown represents the empirical equation just mentioned.

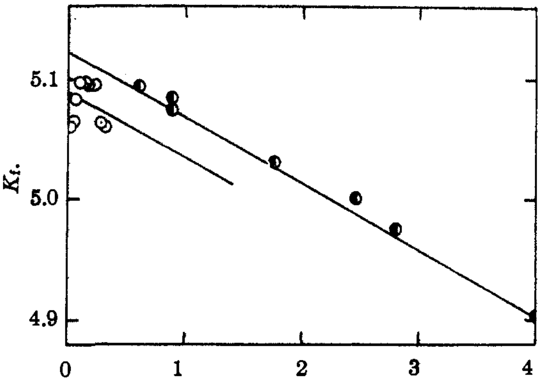

Fig. 1.—Variation of the cryoscopic constant with temperature: O, triphenylmethane, this investigation; ◐, carbon tetrachloride, Bury and Jenkins.

It will be noticed from Fig. 2 that the values of K_f determined in the present investigation fall in about the center of those reported in the literature which have been determined in dilute solutions.[11] The earliest values reported by Beckmann[5] and Auwers[12] were about 5.3 deg. per mole. Bury and Jenkins[10] found 5.122, while Kraus[8b] reported 5.070. It is also probably true that each design of apparatus may give a slightly different value for the constant. These systematic differences are probably due to the balance achieved between the heat output to the surroundings and the heat input from formation of solid benzene in the apparatus. The difference between the freezing point recorded on the thermometer, T_t, and the true value, T, is given by[13]

$$T_t - T = \kappa(T_c - T_t)/s$$

where T_c is the temperature of the cooling bath, s is the number of degrees of supercooling, and κ is a constant for a given design of apparatus. For apparatus with good insulation, κ is small. Since users of the Beckmann technique invariably employed a bath of ice and water surrounding the measuring cell and little insulation, the freezing points of the solution recorded were always too low. The higher the concentration of the solution being measured, the smaller this error became, so that in extrapolating the results to infinite dilution, the limiting value obtained was always too high. Now, when a differential type of apparatus is employed, the effects of heat transfer should be minimized. This is shown by the fact that several workers have obtained results agreeing to within 1% or less. However, within this limit, there are still systematic differences which are probably due to the degree of balance achieved between the various heat quantities in the apparatus. The value 5.072 deg./mole reported by Kraus[8b] is probably very close to the correct value, but because the result is a function of the apparatus, the author's own value was used in this work.

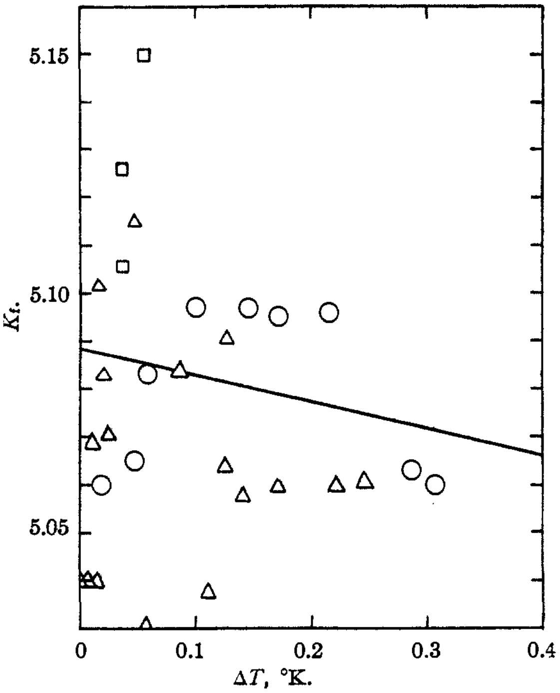

Fig. 2.—Determinations of the cryoscopic constant in dilute solutions: ○, this investigation; △, Kraus; □, Peterson and Rodebush.

Results on Phenol.—Cryoscopic measurements on phenol solutions are shown in Table II and in Fig. 3. It can be seen that the molecu-

(11) Peterson and Rodebush, *J. Phys. Chem.*, **32**, 709 (1928).

(12) Auwers, *Z. physik. Chem.*, **12**, 689 (1893).

(13) Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 637.

TABLE II

CRYOSCOPIC DATA FOR SOLUTIONS OF PHENOL IN BENZENE

Formula weight = M_0 = 94.11.

Molality $\times 10^3$	ΔT °K. $\times 10^3$	M	M/M_0
10.56	31.99	157.5	1.674
26.44	76.47	165.0	1.753
30.03	87.55	163.7	1.739
31.96	97.60	156.2	1.660
44.26	133.7	157.8	1.677
54.00	159.2	161.7	1.718
61.02	182.6	159.2	1.692
74.82	222.3	160.3	1.704
91.44	270.6	160.8	1.709
109.8	322.9	161.8	1.719

lar weight of phenol appears to be nearly twice the formula weight at 0.004 molal and shows no tendency to approach a lower value. Since this result is completely at variance with those obtained by the isopiestic method at 25 and 50°, and is not duplicated by any other phenol, it is quite probable that a solid solution is formed.[14] Using the equation[15]

$$T = K_f \cdot m(1 - K')$$

the partition coefficient, K', of phenol between the solid and liquid phases was calculated to be 0.41. This is in fair agreement with the value 0.47 found by Bury and Jenkins.[10]

Results on Nitrobenzene.—This solute was selected as being a typical member of Auwers' third class. The deviations from ideality are far smaller than in the case of the cresols, for example; however, they show that dipole–dipole interactions may contribute appreciably to the association of highly polar phenols. Work at high concentrations led Bury and Jenkins[10] to believe that solid solutions were formed as in the case of phenol, and a partition coefficient of 0.05 was calculated. The results in Table III and in Fig. 3 now prove this to be erroneous.

TABLE III

CRYOSCOPIC DATA FOR SOLUTIONS OF NITROBENZENE IN BENZENE

Formula weight = M_0 = 123.11.

Molality $\times 10^3$	ΔT °K. $\times 10^3$	M	M/M_0
5.50	27.63	124.3	1.010
13.71	71.26	120.1	0.976
19.08	98.59	120.7	0.981
26.18	131.2	124.4	1.011
29.50	150.8	122.0	0.991
36.08	187.4	120.0	0.975
43.55	215.8	125.8	1.022
48.88	244.6	124.6	1.012
51.11	257.2	123.8	1.005
70.63	351.1	125.2	1.017

Results on *o*-Cresol and *p*-Cresol.—The data for these solutes are gathered in Tables IV and V

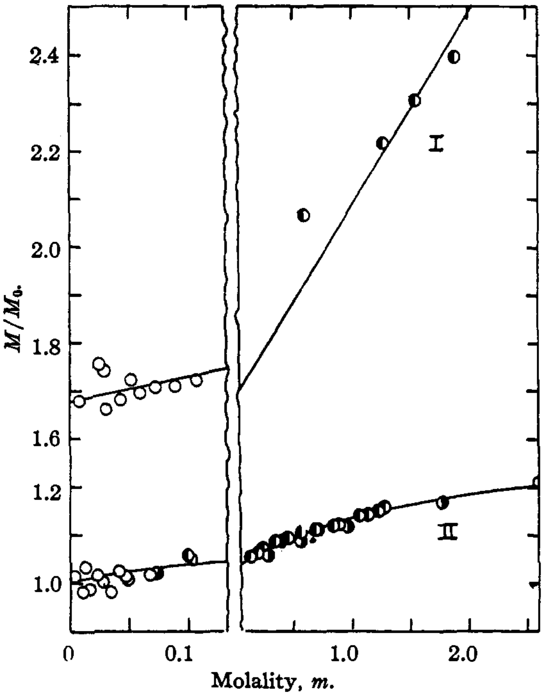

Fig. 3.—Molecular weights of phenol (I) and nitrobenzene (II) in benzene: ○, this investigation; ◐, Bury and Jenkins; ◑, Beckmann.

TABLE IV

CRYOSCOPIC DATA FOR SOLUTIONS OF *o*-CRESOL IN BENZENE

Formula weight = M_0 = 108.13.

Molality $\times 10^3$	ΔT °K. $\times 10^3$	M	M/M_0
16.28	81.19	110.0	1.017
18.60	91.93	110.9	1.026
23.11	112.9	112.2	1.038
25.88	125.7	112.8	1.043
31.06	149.6	113.7	1.052
36.29	177.4	111.9	1.036
38.55	191.1	110.5	1.022
45.03	220.8	111.7	1.033
50.96	245.7	113.5	1.050
62.98	304.4	113.2	1.047

TABLE V

CRYOSCOPIC DATA FOR SOLUTIONS OF *p*-CRESOL IN BENZENE

Formula weight = M_0 = 108.13.

Molality $\times 10^3$	ΔT °K. $\times 10^3$	M	M/M_0
11.01	54.36	111.0	1.027
11.42	57.99	108.0	0.999
14.92	73.67	111.0	1.027
17.42	90.11	105.9	0.980
24.78	119.7	113.4	1.049
27.86	134.2	113.7	1.052
29.74	149.3	109.2	1.010
35.89	178.8	109.9	1.017
46.12	229.7	109.9	1.016
70.95	342.8	113.2	1.047

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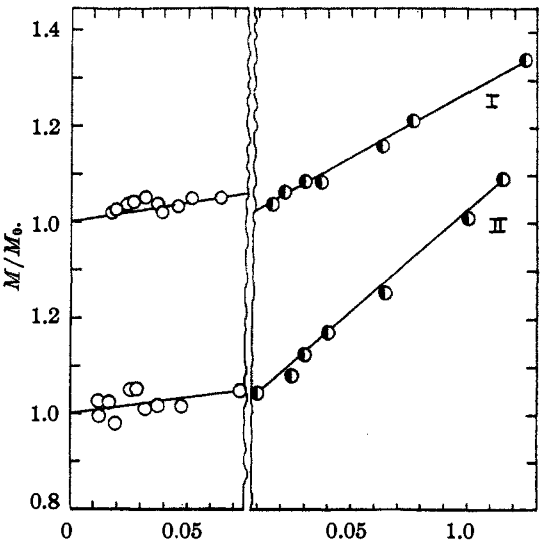
(14) Lassettre and Dickinson, THIS JOURNAL, **61**, 54 (1939).

(15) Reference (13) above, p. 641.

and in Fig. 4. Previous measurements of Bury and Jenkins[10] at higher concentrations are also shown in the graph. Unfortunately, the deviations from ideality in dilute solutions are so small as to be just outside the experimental error.



Molality, *m*.

Fig. 4.—Molecular weights of *o*-cresol (I) and *p*-cresol (II) in benzene: ○, this investigation; ◐, Bury and Jenkins.

Results on *m*-Nitrophenol, *p*-Nitrophenol and 2,4-Dinitrophenol.—(See Tables VI, VII and VIII and also Fig. 5.) Because of the large density differences between these solutes and benzene, it was possible to study these compounds at much lower concentrations than the others. This was especially fortunate, inasmuch as *p*-nitrophenol forms a eutectic mixture with benzene at 0.055 molal. The deviations from the expected formula weight are large, considering the low concentrations involved. *m*-Nitrophenol is considerably less associated, resembling the cresols in this respect. The experimental points

TABLE VI

CRYOSCOPIC DATA FOR SOLUTIONS OF *m*-NITROPHENOL IN BENZENE

Formula weight = M_0 = 139.11.

Molality $\times 10^3$	ΔT °K. $\times 10^3$	M	M/M_0
5.00	23.27	151.5	1.089
7.11	34.21	146.6	1.054
8.97	43.64	145.1	1.043
12.92	59.34	153.5	1.104
14.25	67.57	148.7	1.069
17.74	82.86	151.0	1.086
21.86	106.8	144.4	1.038
24.28	116.4	147.1	1.058
30.52	149.0	144.4	1.038
30.75	147.6	146.9	1.056
39.93	190.4	147.7	1.062
46.75	223.8	147.1	1.057

TABLE VII

CRYOSCOPIC DATA FOR SOLUTIONS OF *p*-NITROPHENOL IN BENZENE

Formula weight = M_0 = 139.11.

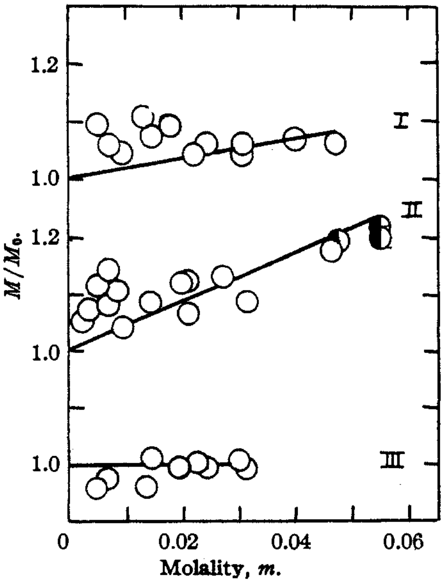
Molality $\times 10^3$	ΔT °K. $\times 10^3$	M	M/M_0
1.86	9.03	145	1.04
3.16	14.97	149	1.07
4.50	20.49	155.0	1.114
6.52	29.03	158.5	1.139
6.56	30.93	149.6	1.076
8.25	37.85	153.8	1.106
9.34	45.67	144.2	1.037
13.99	65.09	150.6	1.082
19.35	88.03	155.0	1.114
20.46	92.64	155.8	1.120
20.95	100.1	147.6	1.061
26.63	119.6	157.0	1.128
31.16	146.7	149.7	1.076
45.80	198.0	163.0	1.172

TABLE VIII

CRYOSCOPIC DATA FOR SOLUTIONS OF 2,4-DINITROPHENOL IN BENZENE

Formula weight = M_0 = 184.11.

Molality $\times 10^3$	ΔT °K. $\times 10^3$	M	M/M_0
4.42	23.58	175.1	0.951
6.08	31.82	178.4	0.969
13.09	69.36	176.2	0.957
13.91	70.15	185.1	1.005
18.71	95.68	182.5	0.991
21.97	111.4	183.9	0.999
23.69	121.5	182.0	0.989
29.39	148.5	184.6	1.003
30.32	155.9	181.5	0.986



Molality, *m*.

Fig. 5.—Molecular weights of *m*-nitrophenol (I); *p*-nitrophenol (II), and 2,4-dinitrophenol (III) in benzene: ○, this investigation; ◐, Bury and Jenkins.

do not fall very well along the expected line; adsorption of the *m*-nitrophenol may occur, causing the intercept, M/M_0, to be greater than unity. 2,4-Dinitrophenol was found to be essentially an ideal solute over the small range studied. The chelation in this compound undoubtedly accounts for its difference in behavior compared to *p*-nitrophenol.

Calculation of Equilibrium Constants.—The mean polymerization number, n, was found to be a linear function of the concentration, m, for all of the solutes examined. Thus, $n = M_0/M = 1 + \alpha m$, where α is a constant. Now Lassettre[7] found that a unique set of equilibrium constants K_L for the formation of polymers would account for this behavior, where L was the order of the individual polymer.

$$K_L = \frac{(\alpha \cdot L)^{L-1}}{L!}$$

The equilibrium constant for the dimer ($L = 2$) turns out to be $K_2 = \alpha$. This quantity has been calculated from the author's own data and also from that of earlier workers, using the method of least squares. The values for the cresols are in poor agreement, due to the small deviations that must be measured in dilute solutions. The equilibrium constants for the nitrophenols are found to be high, especially for the para compound.

TABLE IX

EQUILIBRIUM CONSTANTS FOR FORMATION OF DIMERS FOR VARIOUS PHENOLS

Solute	$K_2 = \alpha$	Workers
o-Cresol	1.1	This investigation
	0.28	Bury and Jenkins[10]
p-Cresol	1.1	This investigation
	0.42	Bury and Jenkins[10]
m-Nitrophenol	2.3	This investigation
p-Nitrophenol	5.2	This investigation

Summary

An apparatus for measuring the freezing points of dilute solutions (0.002 to 0.1 molal) has been described. The freezing points of solutions of triphenylmethane in benzene have been determined, and the cryoscopic constant of benzene was found to be 5.088 − 0.0548 ΔT.

The freezing points of solutions of phenol in benzene have been determined. The results were interpreted as due to the formation of solid solutions of phenol in benzene. The partition coefficient of the solute between solid and liquid benzene was calculated to be 0.41.

Cryoscopic data were obtained for solutions of nitrobenzene in benzene. The ideal law was obeyed to ±2% below 0.1 molal. There was no evidence that nitrobenzene formed solid solutions with benzene.

The freezing points of solutions of *o*-cresol, *p*-cresol, *m*-nitrophenol, *p*-nitrophenol and 2,4-dinitrophenol in benzene have been measured. Equilibrium constants for the formation of dimers have been calculated. Except for 2,4-dinitrophenol, which is chelated, the deviations from ideality increase in the order mentioned.

PASSAIC, N. J. RECEIVED AUGUST 7, 1944

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

Isomeric Lactone Pairs Related to Cyclohexanone-2-acetic Acid[1]

BY MELVIN S. NEWMAN AND CALVIN A. VANDERWERF[2]

Because of their relation to the aglucones of the important cardiac glycosides, unusual interest has attended a study of $\Delta^{\alpha,\beta}$- and $\Delta^{\beta,\gamma}$-unsaturated γ-lactones, particularly from the standpoint of a comparison of their properties and reactions.[3]

Most of the early knowledge concerning the chemistry of isomeric unsaturated lactones was due to the classical work of Thiele,[4] who reported an extensive series of investigations involving a number of unsaturated lactone pairs prepared by the removal of water from γ-ketonic acids.

To our knowledge, however, no isomeric pair of unsaturated lactones of the $\Delta^{\alpha,\beta}$- and $\Delta^{\beta,\gamma}$-type in which the lactone ring is fused to a second ring has heretofore been reported. The present paper describes such a pair, namely, the unsaturated lactones, IV and V, related to cyclohexanone-2-acetic acid, III, as well as the corresponding pair of stereoisomeric saturated lactones, I and VII. The method used for the synthesis of the lactones is illustrated by the chart.

The lactone, I, prepared according to Coffey[5] possessed physical constants in agreement with those reported.[5] Our lactone, however, in direct contrast to that of Coffey, was hydrolyzed to give a quantitative yield of an unusually stable hydroxy-acid, cyclohexanol-2-acetic acid, II. Upon direct oxidation of II with chromic anhydride in acetic acid, cyclohexanone-2-acetic acid, III, was obtained in good yield.

Treatment of III with boiling acetic anhydride

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[1] The material in this paper is largely contained in the Ph.D. thesis of C. A. V. W., The Ohio State University, August, 1941.

[2] Now Assistant Professor of Chemistry at the University of Kansas, where several additional experiments were performed.

[3] See for example: (a) Jacobs and Collins, *J. Biol. Chem.*, **61**, 387 (1924); (b) Jacobs, Hoffmann and Gustus, *ibid.*, **70**, 1 (1926); (c) Jacobs and Scott, *ibid.*, **87**, 601 (1930); (d) **93**, 139 (1931); (e) Paist, Blout, Uhle and Elderfield, *J. Org. Chem.*, **6**, 273 (1941).

[4] Thiele. *Ann.*, **319**, 144 (1901), and subsequent articles.

[5] Coffey, *Rec. trav. chim.*, **42**, 387 (1923).