as the size of the electrodes increases, the range and possible accuracy within the range increase. So choosing the cells that the resistance in them is large is not equivalent experimentally to increasing the size of the electrodes.

3. Cells have been designed, with the aid of Washburn's equations, which do not change in resistance with a change in frequency and which with the Washburn Type A Cell cover the range from 2×10^{-3} to 2×10^{-7} reciprocal ohms.

4. The method of cleansing and drying the electrodes has been found to be of far greater importance than any of the other factors involved, the errors from this source alone often being as high as 2 to 3%. The usual method of cleansing and drying seemed to make the cell, filled with its solution, not a resistance and a capacity but a voltaic cell, which gives the effect of an abnormally high resistance. A method is given for cleansing the cells which has for its underlying principle the production of 2 electrodes having as nearly as possible the same contact potential when immersed in the same solution; it involves thoroughly "scrubbing" the electrodes after any treatment with an acid cleaning mixture and keeping the electrodes short-circuited during all the processes of cleaning, drying and the bringing of the cell to temperature equilibrium.

5. It is believed that the difference in the potential developed by different electrodes when subjected to the same treatment accounts for the change in resistance with a change in the impressed voltage, and for the fact that some observers have not been able to eliminate the change by thorough cleansing while others have. The term "clean" applied to conductance cells should be more rigidly defined, if comparable values are to be obtained by different workers.

New York, N. Y.

[Contribution from the Chemical Laboratory of Johns Hopkins University]

THE OSMOTIC PRESSURES OF AQUEOUS SOLUTIONS OF PHENOL AT 30°

By Arthur Grollman and J. C. W. Frazer

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Introductory

The only reference to be found in the literature of an attempt to determine experimentally the osmotic pressure of phenol solutions is that of Naccari,[1] whose results, being much lower than those theoretically expected and incapable of either duplication or accurate determination, were rejected by Naccari as unsatisfactory. Owing to the crudity of the method employed, which at its best could give but qualitative results, his data are of interest only from an historical standpoint.

[1] Naccari, *Atti. accad. Lincei,* **6,** 32 (1897).

Indeed, even with the experimental refinements of the later methods as developed by Morse and Frazer, and their co-workers, only such compounds as the sugars were capable of accurate measurement. Failure to obtain results with substances of a low molecular weight were attributed to permeability of the cupric ferrocyanide membrane, or to the disintegration of the latter in the presence of such substances. Recent improvements in cell structure, which have been made in this Laboratory, have enabled the methods of direct osmotic-pressure measurements to be applied to a variety of substances hitherto considered beyond experimental determination, with an accuracy comparable to that of the best results obtained with cane sugar.

Phenol, presenting as it does rather anomalous behaviors in aqueous solution, was chosen for measurement, to determine whether the results so obtained could be correlated with its other properties. The great uncertainty existing regarding certain of its actions, such as cryoscopic behavior, hydration, etc., demanded an attack from another point of view in order to throw light on these subjects. The fact that it forms solutions with two coexisting phases was also suggestive. Moreover, all substances hitherto measured have approximated ideal solutions and obey the van't Hoff osmotic-pressure formula more or less closely. Phenol was, therefore, chosen, as it diverges widely from such behavior.

Experimental Part

The measurements were carried out throughout the solubility range at 30°, with nitrogen-filled manometers in a bath constant to 0.05°. The method was essentially that described and used by Frazer and Myrick[2] for sugar solutions, manometers being used, however, instead of the resistance gage there described. For low pressures, the manometric method is the most accurate though not the most convenient mode of measurement.

The solutions were analyzed with a Zeiss water-interferometer which permitted an accuracy exceeding that required by the manometric readings with a cathetometer.

The cells were perfected in a manner to be described in a later article;

TABLE I

RESULTS

Concn. of phenol per 1000 g. of H_2O Moles	O. p. obs. Atm.	Ratio: o. p. to concn.	Concn. of phenol per 1000 g. of H_2O Moles	O. p. obs. Atm.	Ratio: o. p. to concn.
0.0986	1.42	1.45	0.2965	3.89	1.31
.1006	1.47	1.46	.3831	4.90	1.28
.1992	2.73	1.42	.5214	6.67	1.28
.1999	2.83	1.42	.6672	8.42	1.26
.2716	3.73	1.37	.8936	11.20	1.25

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[2] Frazer and Myrick, THIS JOURNAL, **38**, 1907 (1916).

upon them were deposited the usual membrane of cupric ferrocyanide. These allowed but a slight permeability of the phenol, which was finally corrected for by analysis of the solutions. Equilibrium was obtained in less than 6 hours, even with the most concentrated solutions.

Table I and Fig. 1 give the results obtained. The curve is practically linear, tending to slope slightly towards the X axis with increasing concentration. The third and sixth columns show this tendency.

From the equation for ideal solutions,

$$P = \frac{RT}{V_0}\left(x + \frac{1}{2}x^2 + \frac{1}{3}x^3 + \;\ldots\ldots\right) \qquad (1)$$

where P is the osmotic pressure, V_0, the molecular volume of solvent and x, the molar fraction of solute, we can, neglecting the association of water,[3] calculate the theoretical osmotic pressures of phenol solutions. This has been done in Cols. 2 and 6 of Table II. By interpolation of the observed values in Table I, the values for exact concentrations are obtained in Cols. 3 and 7.

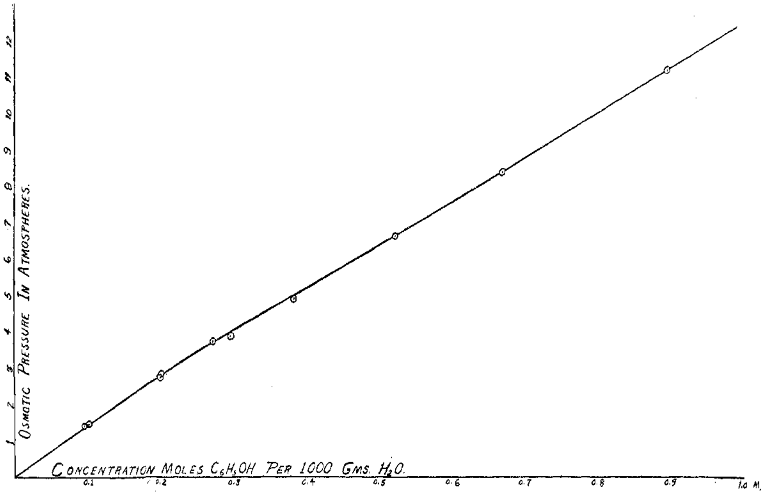

Fig. 1

TABLE II

COMPARISON OF THEORETICAL WITH EXPERIMENTAL RESULTS

Concn.	O. p. calc. from Formula I	O. p. obs.	Calc. o. p. / Obs. o. p. = degree of assoc.	Concn.	O. p. calc. from Formula I	O. p. obs.	Calc. o. p. / Obs. o. p. = degree of assoc.
0.1	2.46	1.46	1.68	0.6	14.73	7.62	1.93
.2	4.92	2.84	1.73	.7	17.16	8.82	1.95
.3	7.38	3.93	1.88	.8	19.59	10.05	1.95
.4	9.83	5.12	1.92	.9	22.02	11.28	1.95
.5	12.28	6.40	1.92	...	..	...	..

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[3] Kendall, THIS JOURNAL, **36**, 1222, 1722 (1914); **37**, 149 (1915); **38**, 1309, 1712 (1916); **42**, 2131 (1920).

A comparison of the observed values in Cols. 3 and 7 and the theoretical values calculated in Cols. 2 and 6 shows, as Cols. 4 and 8 indicate, that the former are approximately $^1/_2$ the latter, thus showing the probability of association of 2 molecules of phenol in aqueous solution to form a diphenolic complex.

If α is the degree of association of phenol, we must introduce this factor in Equation 1. Assuming the association to take place exclusively according to the equation, $2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$, instead of C, the molar concentration, we must use $\frac{\alpha c}{2} + (1-\alpha)c$ or $c\left(1-\frac{\alpha}{2}\right)$ and x, the molar fraction, becomes

$$\frac{c\left(1-\frac{\alpha}{2}\right)}{55.5 + c\left(1-\frac{\alpha}{2}\right)}$$

Making these substitutions in Equation 1 and substituting for the osmotic pressure, P, the observed values, we are able to calculate, α, the degree of association at the various concentrations. The decrease in the relative osmotic pressures with increasing concentrations is due to an increase in the degree of association of phenol with higher concentrations. The value of α increases from 86% for 0.1 M to 99% for 0.9 M solutions.

Beckmann and Maxim[4] have derived values for the association of phenol in carbon tetrachloride and bromoform in various concentrations and at temperatures varying from the freezing points of the above-mentioned solvents to their boiling points under normal pressure. The degree of association is found to be most sensitive to dilution, rising for example from the value 1.21 for a solution of 0.599 g. of phenol in 100 g. of carbon tetrachloride at 54.1° to the value 1.58 when the same amount of solvent contains 2.738 g. The results in Table II, Cols. 4 and 8, derived from the osmotic pressure studies, lead us to the same conclusion, namely, that dilution is a potent factor in decreasing the association of phenol. This decrease of association with dilution may explain the great variance in the behavior of phenol in aqueous solutions on bromination. The formation of tribromophenol and tribromophenol bromide (tetrabromocyclohexadienone) may be due to the presence of both the simple molecule and the associated form in solution. Attention may be called to alternative explanations of the above phenomena, as due to the presence of a quinoid form,[5] or as due to the presence of hydrobromic acid.[6]

The Association of Phenol

The above conclusion that phenol exists in solution in an associated form is supported by its behavior in other respects, both physical and

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[4] Beckmann and Maxim, *Z. physik. Chem.*, **89**, 411 (1915).

[5] Dinwiddie and Kastle, *Am. Chem. J.*, **46**, 502 (1911).

[6] *J. Chem. Soc.*, **121**, 2810 (1922).

chemical. Essex[7], from a study of the compressibility of phenol, applied the principle of Tammann[8] whereby molecular magnitudes of anisotropic phases are determined, and finds that phenol exists as two forms of $(C_6H_5OH)_2$, a third species —C_6H_5OH— being enriched at higher temperatures. Turner and English[9] found, by a study of the freezing points in benzene, that the molecular weight of phenol varies from 149.6 to 194.5; these results are in the same order of magnitude as those derived from the osmotic-pressure measurements. Walden,[10] by a study of the specific cohesion, reaches the same conclusion. The surface-tension measurements of phenol solutions,[11] cryoscopic measurements, etc., all point to association of phenol.

In its chemical reactions, also, phenol shows a tendency towards reacting not as a simple molecule but rather in an associated form. Thus the following compounds have been isolated: $2C_6H_5OH.H_2O$;[12] $2C_6H_5OH.TeCl_4$;[13] a series of compounds having the structure $2C_6H_5OH.Ca(OH)_2\ x\ H_2O$;[14] $(C_6H_5OH)_2H_2SO_4$;[15] as well as numerous other addition products. In all of these compounds 2 molecules of phenol react, which points to the probability that phenol reacts as the dimolecular compound —$(C_6H_5OH)_2$, as indicated by the values of the osmotic pressures.

Effect of Temperature on the Degree of Association

Solution of phenol is accompanied by a large absorption of heat. The measurements of various properties, such as ebullioscopic, etc., all give results indicating a decrease in the degree of association with increasing temperature. Applying the Le Chatelier principle, it is obvious that the compound formation must be exothermic and, *vice versa*, the dissociation of the double molecule takes place with an absorption of heat. We must, therefore, attribute the negative heat effect resulting on dissolving phenol as due to the breaking down of the more complicated structure with the formation of a certain percentage of simple molecules. The pure substance, therefore, exists practically entirely in an associated form; experimental studies of the molten material corroborate this (as, for example, Essex's work quoted above).

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[7] Essex, *Z. anorg. Chem.*, **88**, 189 (1914).

[8] Tammann, *Z. physik. Chem.*, **84**, 293 (1913).

[9] Turner and English, *Proc. Roy. Soc.*, **105**, 1786 (1914).

[10] Walden, *Z. physik. Chem.*, **65**, 189, 266 (1908).

[11] Morgan and Egloff, THIS JOURNAL, **38**, 844 (1916). Feustel, *Ann. Physik*, [4] **16**, 61 (1905).

[12] Smits and Maarse, *Proc. acad. Sci. Amsterdam*, **14**, 192 (1911). Rhodes and Markley, *J. Phys. Chem.*, **25**, 527 (1921).

[13] *Ber.*, **30**, 2832 (1898).

[14] *J. Russ. Phys. Chem. Soc.*, **45**, 1535 (1914); *Chem. Centr.*, **1914**, I, 110.

[15] THIS JOURNAL, **36**, 2507; *ibid.*, 1222 (1914).

Summary

1. The osmotic pressures of phenol solutions have been determined throughout the solubility range at 30.0°.

2. From the results so obtained the degree of association of phenol in aqueous solution has been calculated, and it is found that the percentage of simple molecules existing in the dimolecular form varies from 86% for 0.1 *M* solution to 99% for 0.9 *M* solution. The pure material is entirely associated.

3. It is suggested that the variance in the chemical compounds formed on direct bromination of aqueous phenol solutions of varying concentration is attributable to the different molecular combinations present.

4. The great absorption of heat attending the solution of phenol is due to the partial decomposition of higher molecular forms, the reaction $(C_6H_5OH)_2 \longrightarrow 2C_6H_5OH$, being endothermic.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

IMPROVEMENTS IN THE MODE OF MEASUREMENT OF OSMOTIC PRESSURE

BY ARTHUR GROLLMAN AND J. C. W. FRAZER

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Introduction

Of the various experimental physicochemical methods, none is of greater importance than the measurement of osmotic pressure. The thermodynamic considerations of solutions are based on the concept of an osmotic pressure and all other properties of solutions are derivable from osmotic-pressure data. Of paramount importance is the fact that osmotic-pressure measurements are capable of the greatest refinement, being measurable with an extreme accuracy. Though we possess other accurate means of measurement such as of the freezing point and the vapor pressure, these are very limited, the former being confined to one temperature, the latter applicable over only a limited range of temperature. Osmotic-pressure measurements, on the other hand, can be carried out with equal precision over the range of temperature in which the solvent in question exists in the liquid form and throughout all possible concentration limits.

Despite these desirable conditions and advantages, measurements of osmotic pressures have been limited to a few substances, such as sugar and glucose. Substances of lower atomic weight, and especially electrolytes, have defied measurement and it has usually been assumed in the case of electrolytes that measurement is impossible because of the destructive effect on the semipermeable membrane and the permeability of the latter to such substances. The object of this investigation was so