saponified and fractionally crystallized to give 3-hydroxy-4-isopropylbenzoic acid.

There also was obtained 6 g. of a compound insoluble in potassium hydroxide which on distillation was found to be 3,4-diisopropylphenyl isopropyl ether (b. p. 248–251°).

**Rearrangement of Isopropyl *m*-Hydroxybenzoate.**—One hundred and thirty grams of ester of b. p. 143–144° (5 mm.) m. p. 59–60°, 190 g. of carbon tetrachloride and 14 g. of boron fluoride were refluxed for one hour. Three grams of 3-isopropoxyisopropylbenzoate (b. p. 138–140°) (12 mm.) and 5 g. of isopropyl 3-isopropoxy-4-isopropylbenzoate b. p. 155–157° (10 mm.) were obtained from the potassium hydroxide insoluble portion. Ninety-one grams of acid was obtained which on heating practically all went into solution, leaving an oil. The oil recrystallized from methyl alcohol and was shown to be 3-isopropoxybenzoic acid (m. p. 88–89°). These acids soluble in water (m. p. 170–180°) were shown to be a mixture of *m*-hydroxybenzoic acid and 3-hydroxy-4-isopropylbenzoic acid by decomposing into phenol and *o*-isopropylphenol.

**Rearrangement of Isopropyl *p*-Hydroxybenzoate.**—Fifty-six grams of ester, b. p. 158–160° (5 mm.), 108 g. of carbon tetrachloride and 9 g. of boron fluoride were refluxed for one hour. From 23 g. of an acid (m. p. 155–160°) obtained from above, 4 g. of methyl-4-isopropoxybenzoate[4] (from acid and methyl alcohol using sulfuric acid) were obtained.

ANALYSIS OF COMPOUNDS

| Name | Calcd., % | | Found, % | |
|---|---|---|---|---|
| | C | H | C | H |
| 4-Isopropoxybenzoic acid[a] | 66.68 | | 65.98 | |
| 3-Isopropoxybenzoic acid[a] | 66.68 | | 66.01 | |
| 3-Isopropyl-4-isopropoxybenzoic acid[a] | 70.23 | | 71.06 | |
| Isopropyl 3-isopropoxybenzoate | 70.23 | 8.14 | 70.19 | 8.10 |
| Isopropyl 4-isopropoxybenzoate | 70.23 | 8.14 | 70.00 | 8.00 |
| Isopropyl 3-isopropoxy-4-isopropyl benzoate | 72.90 | 9.35 | 72.46 | 9.18 |
| Isopropyl 4-isopropoxy-3-isopropyl benzoate | 72.90 | 9.35 | 72.38 | 7.13 |

[a] Rowan, "Wet Combustion," Thesis, University of Notre Dame, 1935.

## Summary

Propylene has been condensed with *m*- and *p*-hydroxybenzoic acids in the presence of boron fluoride.

The course of the condensation and rearrangement has been determined.

Six new compounds have been reported.

NOTRE DAME, INDIANA RECEIVED APRIL 17, 1935

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON]

# The Compressions and Specific Volumes of Aqueous Solutions of Resorcinol and Methanol at 25° and the Behavior of Water in these Solutions

BY R. E. GIBSON

The results obtained in a systematic study of the compressions and volumes of aqueous salt solutions show regularities which we have already discussed.[1] In particular they give experimental confirmation of the generalization that the apparent volumes and the apparent specific compressions of salts in aqueous solutions are linear functions of the square root of the volume concentration[2] or in many cases of the square root of the weight or mole ratio.[3] We have also found that from pure water to 40% acid the apparent specific compression of acetic acid in aqueous solutions varies linearly with the square root of the volume concentration. There are, however, notable exceptions to these rules. Examination of the data available has shown,[4] moreover, that it is probable that such relations also hold in solutions of non-electrolytes such as urea and sucrose. The case of sucrose is doubtful, however, as the deviations from the linear relation are outside the estimated experimental error. The data of Perman and Urry[5] at pressures up to 100 atm. for glucose and raffinose show that except in the highest concentrations the apparent compression of the solute is zero. Evidently solutions of weak or non-electrolytes require further investigation.

With the object of looking into these regularities we have examined solutions of methanol and resorcinol in water. Methanol is a highly compressible liquid infinitely miscible with water, while resorcinol is a solid melting at 110° and very soluble in water. Both solutes are non-electrolytes. The results will be discussed in this paper.

## Experimental

The densities and the compressions of the solutions under an increase of pressure from 1 to 1000

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[1] Gibson, (a) THIS JOURNAL, **56**, 4 (1934); (b) **56**, 865 (1934); (c) **57**, 284 (1935). These papers may be consulted for explicit definitions of the terms used here.

[2] See Gucker, *ibid.*, **55**, 2709 (1933). In this article reference to the earlier work will be found.

[3] Adams, *ibid.*, **54**, 2229 (1932).

[4] Gucker, *Chem. Reviews*, **13**, 128 (1933). See, however, Redlich and Klinger, *Monatsh.*, **65**, 137 (1934).

[5] See Thomas and Perman, *Proc. Roy. Soc.* (London), **A146**, 640 (1934).

bars were measured with apparatus which has already been described.[1] *Resorcinol* from the Eastman Kodak Co. was recrystallized twice from water and thoroughly dried. The sample froze between 108.5 and 108.9°. Andrews, Lynn, and Johnston[6] give 109.6–109.7° for the freezing point of a very pure sample of resorcinol. A second sample was also recrystallized twice from ether and dried. From these two portions aqueous solutions of approximately 40% resorcinol were made and their densities at 25° were compared. They agreed to within 1 part in 10,000, indicating that the material was of adequate purity for the purposes of this work.

Reagent absolute *methanol* (free from acetone) from Merck was fractionated, the middle fraction coming over within 0.05° being collected. This sample was dehydrated by the method of Lund and Bjerrum,[7] the process being carried out twice. The alcohol was stored in Jena glass bottles kept in a desiccator. The density in grams per milliliter at 25° of the sample so obtained was 0.78655. Lund and Bjerrum give 0.78651; Vosburgh, Connell and Butler[8] used for accurate work methyl alcohol with densities ranging between 0.78651 and 0.78653. The value calculated from the equation in the "International Critical Tables"[9] is 0.78660.

**The Compression of Methanol.**—In Table I the values for the compressions of methanol for various pressure increases as determined in this work are compared with the work of previous investigators. A relatively large number of experiments were made because of the large discrepancy between our results and those of Bridgman and of Amagat. The values of *k* at 500 and 1000 bars are means of six independent results.

TABLE I

COMPRESSIONS OF METHANOL AT 25°

| Pressure range, bars | *k*, Gibson | *k*, Bridgman | *k*, Amagat | *k*, Richards |
|---|---|---|---|---|
| 1–1000 | 0.08007 | 0.0723 | 0.0747 | ... |
| 1– 800 | .06817 | .... | .0638 | ... |
| 1– 500 | .04785 | .0429 | .0442 | 0.0474 |
| 1– 300 | .0316 | .... | .0288 | .0313 |

In both cases the maximum deviations from the mean were 0.00005. As a check on the purity of the alcohol, experiments were made with a sample of methanol obtained in sealed tubes from the Bureau International des Étalons Physico-chimiques in Brussels through the National Bureau of Standards. This sample gave results at 500 and 1000 bars which were indistinguishable from those obtained with our own preparation. The values of *k* (Bridgman) were interpolated from his final table of volumes,[10] the pressure unit being converted from kg./sq. cm. to bars. In constructing this table Bridgman appears to have leaned heavily on Amagat's[11] results, his own high-pressure apparatus being ill adapted to accuracy at low pressures. On page 39 of the paper quoted, Bridgman gives "experimental values of the changes of volume" at 20° for low pressures. While the 500 atm. result does not agree with ours, the value of the volume change from 1 to 1000 atm. gives a value of *k* for 1000 bars of 0.0797 at 20° which corresponds to 0.0817 for *k* at 25°. It is probable that this figure is closer to the correct one than the figures at low pressures given in his table. It appears likely that Amagat's sample of methanol was not very pure, as his volumes at atmospheric pressure differ widely from those now accepted. If his sample contained much water his results would undoubtedly be too low, as water has a large effect on the compression of methanol.

Richards and his students[12] measured compressions of methanol at 20° up to 500 bars. From this they obtained so-called mean compressibilities. Unfortunately, their results only begin at 100 bars and it is the very large compressibility of methanol at low pressures that renders extrapolation so difficult. We plotted Richards' average compressibilities against the pressure together with the compressibility at 1 bar determined by sound velocity measurements.[13] From this curve values of *k* at 20° for the pressure intervals 1–300 and 1–500 bars were computed and converted to *k* at 25° by the temperature coefficient from Amagat's data. The final values are tabulated under *k* (Richards) and are in good agreement with our results. The compressibility of methanol changes very rapidly with pressure, a circumstance which seems to have vitiated the extrapolation of earlier workers.

**Specific Volumes and Compressions of the Solutions.**—All the solutions were made up

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(6) Andrews, Lynn and Johnston, THIS JOURNAL, **48**, 1281 (1926).

(7) Lund and Bjerrum, *Ber.*, **64**, 210–213 (1931).

(8) Vosburgh, Connell and Butler, *J. Chem. Soc.*, 936 (1933).

(9) "International Critical Tables," Vol. III, p. 27.

(10) Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 40 (1913).

(11) Amagat, *Ann. chim. phys.*, **29**, 508 (1893).

(12) Richards, Stull, Mathews and Speyers, THIS JOURNAL, **34**, 988 (1912).

(13) Freyer, Hubbard and Andrews, *ibid.*, **51**, 759 (1929).

independently from known masses of the components. The specific volumes and compressions were determined immediately and the results are recorded in Tables II and III.[14] For solutions of resorcinol $k$ and $-\Delta_P v$ decrease with concentration over the entire range considered, but for the methanol solutions the curve of bulk compression *vs.* concentration passes through a minimum, while all solutions from pure water to 15% methanol appear to have exactly the same specific compressions $(-\Delta_P v)$.

TABLE II

COMPRESSIONS AND SPECIFIC VOLUMES OF AQUEOUS SOLUTIONS OF RESORCINOL. EXPERIMENTAL RESULTS AT 25°

| $100\ x_2$ | $10^4 k$ | $v$ | $10^4\ A$ | $10^4(k_{\text{obs.}} - k_{\text{calcd.}})^a$ |
|---|---|---|---|---|
| 0.00 | 393.5 | 1.00293 | 0.0 | ... |
| 5.18 | 386.3 | 0.99274 | − 9.9 | 1.1 |
| 10.92 | 377.3<br>376.6 | .98134 | − 20.6 | 0.0 |
| 20.00 | 364.9 | .96318 | − 44.8 | .4 |
| 29.97 | 350.9<br>351.9 | .94320 | − 78.6 | − .3 |
| 40.00 | 339.5 | .92303<br>.92311 | −127.7 | .3 |
| 50.34 | 327.1<br>326.8 | .90224 | −199.4 | .2 |

[a] $k$ (calcd.) computed by Eqn. 1.

**Changes in Apparent Volume with Pressure.** **(a) Resorcinol.**—The apparent compression of resorcinol in aqueous solutions $(-\Delta_P\phi_2)$ is a linear function of $c_2^{1/2}$, the relation being

$$10^4 \times \Delta_P\phi_2 = -146.7 - 67.0\ c_2^{1/2} \qquad (1)$$

which fits the data well within the experimental error. This equation differs from those for the apparent compressions of salts in aqueous solutions in that $\Delta_P\phi_2$ is negative in infinite dilution and that it decreases much less rapidly with concentration—all indicating a closer approach to ideal behavior in resorcinol solutions as contrasted with salt solutions.

**(b) Methanol.**—The apparent compression of methanol in aqueous solutions is distinctly not a linear function of the square root of the concentration, as an inspection of Fig. 1 will reveal, the curve of $\Delta_P\phi_2$ *vs.* $c_2^{1/2}$ passing through a minimum.

TABLE III

COMPRESSIONS AND SPECIFIC VOLUMES OF AQUEOUS SOLUTIONS OF METHANOL. EXPERIMENTAL RESULTS AT 25°

| $100\ x_2$ | $10^4\ k$ | $v$ | $-\Delta_P v \times 10^4$ (average) | $(k_{\text{obs.}} - k_{\text{calcd.}})^b \times 10^4$ |
|---|---|---|---|---|
| 100.000 | 800.7 | 1.27136 | 1018.0 | |
| 95.335 | 749.3<br>748.9 | 1.24985 | 936.3 | 0.3 |
| 91.400 | 710.0 | 1.23262 | 875.2 | − .1 |
| 83.952 | 642.6<br>641.9 | 1.20232 | 772.1 | −2.3 |
| 75.137 | 576.5 | 1.17032 | 674.7 | −0.6 |
| 69.995 | 542.2 | 1.15325 | 625.3 | − .4 |
| 59.769 | 486.3<br>486.8 | 1.12255 | 546.1 | 2.9 |
| 50.310 | 444.4 | 1.09760 | 487.8 | 3.8 |
| 40.342 | 412.3 | 1.07464 | 443.1 | 4.8 |
| 20.290 | 382.4 | 1.03733 | 396.7 | 3.8 |
| 19.994 | | 1.03684[a] | | |
| 12.169 | 383.7 | 1.02413 | 393.0 | 2.5 |
| 8.232 | 387.2 | 1.01759 | 394.0 | 0.7 |
| 5.451 | 390.1<br>389.0 | 1.01283 | 394.5 | −2.6 |
| 4.019 | 390.1<br>390.0 | 1.01034 | 394.0 | −6.6 |
| 2.314 | 392.4<br>391.2<br>391.2<br>391.5 | 1.00728 | 394.5 | −7.4 |
| 0.000 | 393.5 | 1.00293 | 394.6 | |

[a] Gives 1.03733 for $v$ at $x_2 = 0.20290$ by interpolation.
[b] $k$ (calcd.) computed from Eqn. 2.

On the other hand, the *apparent compression of water in methanol solutions* may be well represented as a linear function of the square root of the concentration of water over a wide range of concentration, for although the complete curve is undoubtedly S-shaped,[15] the region of inflection is so drawn out that equation (2) expresses the experimental data with fair approximation:

$$10^4\ \Delta_P\phi_1 = 1017.9 - 1427.6\ c_1^{1/2} \qquad (2)$$

The deviations between the observed values of $k$ and those computed by equation (2) are given in the last column of Table III. The curve of $\Delta_P\phi_1$ *vs.* $c_1^{1/2}$ is shown in Fig. 1. The differences between the characteristics of the two $\Delta_P\phi - c^{1/2}$ curves in Fig. 1 are noteworthy and suggest the possibility of drawing a distinction between the solvent and the solute even in a binary mixture of two completely miscible substances on the basis of their relative compressibilities or their cohesive energy densities.

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(14) The symbols used in this paper are as follows. The subscripts 1 and 2 refer to water and the other component, respectively. $x$ is the weight fraction, $c$ the concentration in grams per cc., $X$ the mole fraction, $M$ the molecular weight; $v$ is the specific volume of a solution, $v_w$ and $v_s$ are specific volumes of the water and other component, $\bar{v}_1$ and $\bar{v}_2$ are partial volumes, $\phi$ is the apparent volume, $P$ is the pressure and $k$ the bulk compression for a given rise in pressure usually from 1 to 1000 bars. The operator $\Delta_P$ indicates the increase with pressure in the particular quantity to which it is prefixed. $A$ denotes $(\Delta_P v/x_1 - \Delta_P v_w)$.

(15) It should be remarked that a curve with a point of inflection may be taken as or mistaken for a straight line if the region considered is small enough. The curve for the partial molal volumes *vs.* square root of the concentration for cobalt sulfate in aqueous solutions is distinctly S-shaped. See Cantelo and Phifer, THIS JOURNAL, **55**, 1336 (1933).

**The Apparent and Partial Volumes of the Components at 1 and 1000 Bars. (a) Resorcinol.**—The apparent and partial volumes of resorcinol in aqueous solutions at 25° are given in Table IV. It should be observed that $\phi_2$ is not a linear function of $c_2^{1/2}$. The partial volumes were computed from the apparent volumes by the relation

TABLE IV

APPARENT AND PARTIAL VOLUMES IN AQUEOUS SOLUTIONS OF RESORCINOL AT 25°

| $x_2$ | $\phi_2$ | $v_2$(1 bar) | $v_1$(1 bar) | $-\Delta_P v_1$ | $v_1$(1000 bars) |
|---|---|---|---|---|---|
| 0.0518 | 0.8061 | 0.8050 | 1.0030 | 0.0395 | 0.9635 |
| .1092 | .80515 | .8038 | 1.0031 | .0393 | .9638 |
| .2000 | .80420 | .8029 | 1.0033 | .0392 | .9640 |
| .2997 | .80361 | .8027 | 1.0033 | .0389 | .9644 |
| .4000 | .80327 | .8025 | 1.0035 | .0386 | .9649 |
| .5034 | .80294 | .8021 | 1.0038 | .0379 | .9658 |

$$v_2 = x_1x_2\frac{d\phi_2}{dx_2} + \phi_2 \qquad (3)$$

the slope, $d\phi_2/dx_2$, being obtained by graphical interpolation of tabular differences. Both $\phi_2$ and $v_2$ *decrease* as the concentration of solute increases—a phenomenon never encountered in salt solutions. As a consequence, the partial volumes of water in resorcinol solutions *increase* with the concentration and they are always greater than the specific volume of pure water.[16] At 1000 bars the partial volumes change in the same direction but more rapidly as the concentration increases. This means that a gram (or mole) of water appears to expand when added to a very large amount of a resorcinol solution—the greater the concentration of the solute or the pressure the greater the expansion. Such an effect is quite unusual even for non-electrolytes. For example, the partial volumes of urethan in water increase with concentration according to calculations from density data.[17] At 30° the partial volumes of resorcinol in ethyl acetate solutions, as computed from the density data of Cohen, de Meester and Moesveld,[18] increase from 0.738 to 0.802 over a concentration range from 13.8 to 68.5%. By extrapolation these authors obtain the value 0.809 cc. for the specific volume of liquid resorcinol at 30°, a value which is probably slightly high.

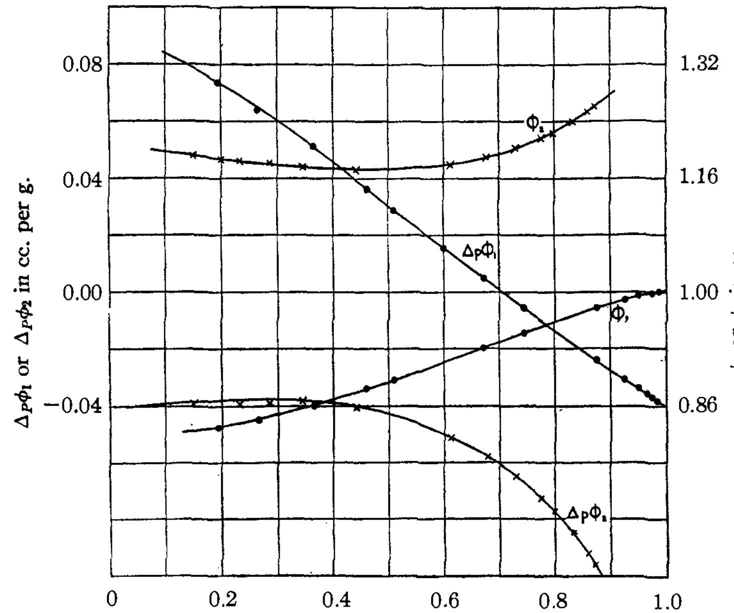

Fig. 1.—Curves of the apparent volume $\phi_1$ and the apparent compression $\Delta_P\phi_1$ of water in methanol solutions *vs.* the square root of mass of water per cc. $c_1^{1/2}$; and curves of the corresponding quantities for methanol $\phi_2$ and $\Delta_P\phi_2$ *vs.* the square root of the mass of methanol per cc.

According to vapor-pressure measurements[19] the activity coefficient of water in resorcinol solutions, $p/p_0X_1$ ($p$ and $p_0$ being the vapor pressures of solution and water, respectively) is always greater than unity, indicating positive deviations from Raoult's law. On the other hand, the solubility of resorcinol in water[20] is slightly greater than the ideal solubility calculated from the thermodynamic properties of resorcinol, showing slight negative deviations from Raoult's law. Extrapolation of the heat of melting to lower temperatures and the change in phase[21] of solid resorcinol around 70° make the calculation of the ideal solubility somewhat uncertain. At 30° the ideal solubility of resorcinol as computed by Walker, Collett and Lazzell is $X_2$ = 0.2216. In water the observed solubility at this

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[16] It should be noted, however, that the partial volumes differ absolutely very little from the specific volumes in the pure state and vary only slightly with concentration, thereby approximating to one of the necessary conditions for an ideal solution.

[17] Richards and Palitzsch, THIS JOURNAL, **41**, 59 (1919).

[18] Cohen, de Meester and Moesveld, *Z. physik. Chem.*, **108**, 103 (1924).

[19] Boswell and Cantelo, *Canadian Chemistry and Metallurgy*, **6**, 109 (1922).

[20] Walker, Collett and Lazzell, *J. Phys. Chem.*, **35**, 3264 (1931).

[21] Lautz, *Z. physik. Chem.*, **84**, 611 (1913); Denecke, *Z. anorg. Chem.*, **108**, 1 (1919).

temperature is 0.2425 and in ethyl acetate it is $X_2 = 0.4619$ according to Cohen, de Meester and Moesveld. Undoubtedly the ethyl acetate solutions of resorcinol deviate more from ideal behavior than do the aqueous solutions according to this criterion, and this is in accord with the observed volume changes.

(b) **Methanol.**—The curves of $\phi_2$ *vs.* $c_2^{1/2}$ and $\phi_1$ *vs.* $c_1^{1/2}$ for methanol solutions at 1 bar show the same characteristics as do the corresponding curves for the apparent compressions, except that the linear region on the $\phi_1$ *vs.* $c_1^{1/2}$ curve is less than on the curve of $\Delta_P\phi_1$ *vs.* $c_1^{1/2}$ (see Fig. 1). From $x_1 = 0.16$ to $x_1 = 0.87$ the line

$$\phi_1 = 0.74167 + 0.26821\, c_1^{1/2} \qquad (4)$$

fits the data with an average deviation without regard to sign of 0.0006—not a very good fit. The partial volumes of water and methanol in the solutions, $v_1$ and $v_2$, were computed by equation (3), $d\phi_1/dx_1$ being estimated by graphical interpolation of the tabular divided differences of $\phi_1$ as a function of $x_1$. In Fig. 2 values of $(v_1 - v_w)$ and $(v_2 - v_s)$ are plotted against the weight percentage of methanol. Striking features of this diagram are (a) the minima on the curves of $(v_2 - v_s)$ (or the maxima on the curves of $(v_1 - v_w)$) and (b) the displacement of these extremals to a higher concentration of methanol at the higher pressure. In dilute solutions the partial volume of water is greater than the specific volume of pure water.

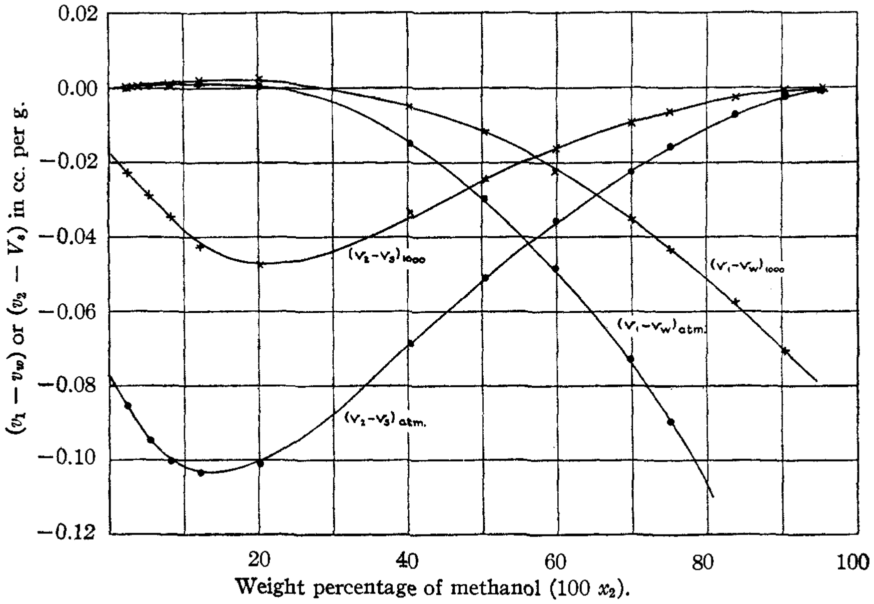

Fig. 2.—Curves showing the specific expansions of water and methanol when these compounds are introduced into mixtures of various concentrations at atmospheric pressure and at 1000 bars at 25°.

**The Behavior of Water in Solution with Methanol and Resorcinol.**—These experimental facts concerning volume relations in aqueous solutions of resorcinol and methanol at the water end may be satisfactorily correlated with other properties of these solutions on the assumption that these *solutes increase the association of the water.* From many points of view it is immaterial whether one elaborates the picture of association in water in terms of polymerized molecules, mono-, di-, or trihydrol, etc.,[22] or in terms of a fourfold coördination of water molecules with a fairly definite orientation,[23] the important thing is that, if molecular association in water is to explain the observed physical properties of water at all, the groups of associated molecules must be formed from the simple molecules with increase in volume and evolution of heat. Hence both increase of pressure and of temperature should decrease the fraction of associated molecules present in the liquid, if the principles of thermodynamics may be applied to such a homogeneous system. In most cases the observed facts lead to the conclusion that addition of solute also decreases the fraction of associated molecules present. On the other hand, the volume relations in the solutions discussed here may be explained if we assume that the predominating effect at the water end is the expansion in volume of the water when its degree of association is increased by the presence of resorcinol or methanol. Furthermore, the effect of a given amount of solute in increasing the fraction of associated water molecules should be proportional to the percentage of non-associated molecules initially present and inversely proportional to the percentage of associated

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[22] The literature is extensive. See Chadwell, *Chem. Reviews,* **4,** 375 (1927); Bancroft and Gould, *J. Phys. Chem.,* **38,** 197 (1934).

[23] Bernal and Fowler, *J. Chem. Phys.,* **1,** 515 (1933); Katzoff, *ibid.,* **2,** 841 (1934).

molecules initially present. As increase of pressure decreases the degree of association of water, it would be expected that a relatively larger expansion due to increase in degree of association should occur when 1 g. of water at 1000 bars is introduced into a solution at that pressure than when the same process takes place at 1 bar. Figure 2 and Table IV show that this conclusion is in accord with the facts.

This explanation of the partial volume-concentration-pressure relations for solutions of resorcinol and methanol is consistent with the fact that the temperature of maximum density of dilute aqueous solutions of methanol is not lower than that of water,[24] and with the fact that the specific heats of dilute methanol solutions are greater than the specific heat of pure water.[25] Moreover, Rabinovich,[26] after an examination of the effects of salts on the viscosity of water, concluded that the so-called negative viscosity (solutions having a lower viscosity than water) is due to the breaking up by the salt of the more highly associated water complexes with consequent increase in fluidity. Conversely, increase in association of water should be accompanied by increase in viscosity and this is borne out by the data for methyl and ethyl alcohol solutions.[27] The maximum on the viscosity–concentration curve for ethyl alcohol–water mixtures has been explained by the hypothesis of compound formation.[28] The activity coefficients of the components in aqueous solutions of methanol, ethanol, propanol, and butanol which have been recently measured at 25°[29] indicate, however, that compound formation in these systems is extremely unlikely, as the solutions all show pronounced positive deviations from Raoult's law.

Computations made on the existing density data at 15° for methanol solutions[30] and for ethanol solutions at 25° show that the apparent and partial volumes in these solutions also vary with concentration in the way illustrated in Figs. 1 and 2, and the foregoing remarks may all be applied to these solutions.

Although the expansion due to increase in association of the water appears to be the predominating effect when water is added to a dilute solution of methanol, the results show that the chief effect in more concentrated solutions is a large contraction. It is of interest to note that on dissolving at different pressures methanol suffers a contraction per gram which is roughly proportional to its compressibility. Figure 2 shows that $(v_2-v_s)$ is closer to zero at 1000 bars than at 1 bar, in fact, over the range from 40 to 100% of methanol (where the disturbing effects of association of the water are minimized), the ratio $(v_2-v_s)_{1000}/(v_2-v_s)_{atm.}$ lies between 0.35 and 0.48, while the ratio of the compressibility of methanol at 1000 bars to that at 1 bar is approximately 0.46. The diminution of the contraction of methanol on dissolving at the higher pressures furnishes another reason why the expansion due to association of the water is obvious at higher concentrations at 1000 bars than at atmospheric pressure.

We have in these solutions a case of positive deviations from Raoult's law being accompanied by negative departures from the ideal law of mixtures for volumes. As

$$\left(\frac{\partial \ln f_2}{\partial P}\right)_{T,X} = \frac{M_2}{RT}(v_2 - v_s) \qquad (5)$$

where $f_2$ is the activity coefficient of the methanol and is unity in pure methanol, we see from Fig. 2 that $\ln f_2$ decreases with pressure at a rate which diminishes as the pressure is raised. The positive deviations from Raoult's law decrease at the higher pressures, but approximate calculations indicate that it is doubtful that $\ln f_2$ ever becomes zero over the whole concentration range even at high pressures. As a first approximation it will be seen that $d \ln f_2/dP$ is proportional to the compressibility of methanol. Two interesting consequences may be deduced from the diminution of $\ln f_2$ with pressure. First, it is known that high positive deviations from Raoult's law lead to liquid immiscibility. This is well illustrated by the results of Butler, Thomson and Maclennan[31] for the series of aliphatic alcohols, where $\ln f_2$ increases as the carbon chain of the alcohol lengthens. As there is a marked similarity in the thermodynamic properties of these alcohols in aqueous solutions, it may be presumed that $\ln f_2$ decreases with pressure in all cases and hence the tendency to immiscibility in aqueous solutions of the higher alcohols will be diminished by pressure. Second, if the correlation between $\ln f_2$ and the energy of mixing computed from surface

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(24) McHutchinson, *J. Chem. Soc.*, 1898 (1926).

(25) "International Critical Tables," Vol. V, p. 116.

(26) Rabinovich, THIS JOURNAL, **44**, 954 (1922).

(27) "International Critical Tables," Vol. V, p. 22.

(28) Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, 1922, p. 177.

(29) Butler, Thomson and Maclennan, *J. Chem. Soc.*, 674 (1933).

(30) "International Critical Tables," Vol. III, p. 115.

(31) *Op. cit.*, p. 677.

forces by Butler, Thomson and Maclennan[32] holds, it would follow that the surface area of the methanol or the surface energy of mixing or both diminish with pressure. In other words, the sum of the cohesive energies of alcohol and of water seems to approximate to the adhesive energy of water and alcohol as the pressure increases.

## Summary

The specific volumes and compressions of six solutions of resorcinol and fifteen solutions of methanol in water have been measured at 25° and the corresponding apparent and partial quantities computed. The apparent compression of resorcinol varies only slightly with concentration and an equation linear in the square root of its concentration expresses this variation within experimental error. The apparent volumes of resorcinol and the apparent volumes and compressions of methanol in aqueous solutions are certainly not linear functions of the square roots of their concentrations. On the other hand, the curves of the apparent compressions and the apparent volumes of water in methanol solutions against the square root of the concentration of water are S-shaped but have the region of inflection so drawn out that a linear function gives a very fair representation of the data even over the whole concentration range.

Analysis of the effect of concentration on the partial volumes of the components indicates that methanol and resorcinol promote the association of water, thereby differing from most other types of solutes. This effect is correlated with the variation with concentration of other significant properties of these solutions. It is noteworthy that the specific compressions (to 1000 bars) of all solutions of methanol from 0 to 15% are the same as the specific compression of pure water.

New values of the compressions of pure methanol at various pressures up to 1000 bars are given and it is pointed out that these do not agree with values already in the literature.

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[32] *Op. cit.*, p. 683.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# Some Reactions of δ-Aminovaleric Acid and its Derivatives

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δ-Aminovaleric acid is closely related to the physiologically important amino acids, arginine, citrulline, ornithine and proline, and seemed to us to be a suitable starting material for the synthesis of these products. However, when an attempt was made to brominate δ-benzoylaminovaleric acid according to the procedure recently described for the corresponding caproic acid derivative,[1] the product obtained was a mixture of the α-bromo-δ-benzoylaminovaleric acid which Fischer and Zemplén have obtained[2] and N-benzoyl-β,β-dibromo-α-piperidone. Likewise, bromination of α-carbomethoxyaminovaleric acid resulted in cyclization to give β,β-dibromo-α-piperidone.[3] It is interesting to note that no such cyclization was observed in the case of ε-benzoylaminocaproic acid, which would have to give a seven-membered ring if this type of reaction were to occur.

Convenient procedures for the production of δ-aminovaleric acid and its benzoyl, carboethoxy and carbomethoxy derivatives have been developed. δ-Ureidovaleric acid has also been prepared and its bromination studied. The product of this bromination has not been identified.

## Experimental Part

**δ-Aminovaleric Acid Hydrochloride.**—Cyclopentanonoxime was converted to α-piperidone by the general procedure of Wallach.[4] The details of the procedure are those which have been described for the rearrangement of cyclohexanonoxime.[1] After neutralization of the acid solution, the α-piperidone was extracted with chloroform and distilled. The yields were about 60% of the theoretical amount. The α-piperidone was hydrolyzed to δ-aminovaleric acid hydrochloride by boiling with concentrated hydrochloric acid, and the amino acid hydrochloride was obtained in pure condition by decolorizing the solution with charcoal and evaporating to dryness under reduced pressure. The yield was about 80% of the theoretical amount of a product which melted at 92–94°. It is unnecessary to put the hydrolysis mixture in a sealed tube as described by Wallach.

**δ-Benzoylaminovaleric Acid.**—This product was obtained in 60% yields by the procedure of Wallach.[4] We

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[1] Eck and Marvel, *J. Biol. Chem.*, **106**, 387 (1934).

[2] Fischer and Zemplén, *Ber.*, **42**, 1022 (1909).

[3] Heymons, *ibid.*, **66**, 847 (1933).

[4] Wallach, *Ann.*, **312**, 171 (1900).