The Solubility of Water in Normal Perfluoroheptane

By G. J. Rotariu, D. W. Fraga and J. H. Hildebrand

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Following our recent determination of the solubility of water in phosphorus,[1] a non-polar liquid with a very high solubility parameter, it appeared desirable to determine its solubility in one having an extremely low parameter, such as *n*-perfluoroheptane. The Fisher reagent could again be used without the procedural complications necessary with phosphorus.

The fluorocarbon was purified by passing very slowly through a 1 meter long column of silica gel, then distilled, taking a middle portion boiling at 81.8° at 747.5 mm. It showed no ultraviolet absorption down to 2400 Å. Its density was 1.7192. For the measurements at 50°, the material had to be repurified. This was done by repeated washings with (1) concd. H_2SO_4, (2) 10% NaOH, (3) water and (4) mercury, drying over Drierite, filtering, passing through silica gel, and finally distilling, giving a density of 1.7186 and a boiling point of 82.0° at 755.7 mm. These figures agree satisfactorily, taking account of the uncertain amount of air dissolved, with the density 1.7180 and the boiling point, 82.5° at 760 mm. reported by Oliver, Blumkin and Cunningham.[2] Our material gave an infrared spectrum identical with the one reported by these investigators. We determined that as little as 0.1% of hydrocarbon could be detected by its C–H band at 2930 cm.$^{-1}$.

The solubility of water was determined by rocking for 24 hours about 80 cc. of the fluorocarbon with 10 cc. of water and removing much of it for analysis through a special pipet, with a turned-up tip, from which could be removed by blowing any water caught as the tip was thrust through the water into the interior of the perfluoroheptane. During the removal and the analysis with the Fisher reagent the liquid was exposed only to dry nitrogen. The analysis was carried out in a flask equipped with a magnetic stirrer. The following results were obtained, expressed as mg. H_2O/100 g. of *n*-C_7F_{16}.

25.06°:	2.0	1.5	2.4	2.5	2.4	mean 2.2
50.00°:	5.6	4.4	5.5	6.0	5.3	mean 5.4

Upon introducing the mean value for 25° into the general solubility equation applicable to solutions from which hydrogen bonds are absent, as was done for other liquids in the paper on the solubility of water in phosphorus,[1] we calculate an empirical solubility parameter for water, δ_2, and extend the table previously given to include perfluoroheptane, with the results given in Table I. It is remarkable that the values for δ_2 show no more variation than they do in view of the 200-fold range in solubility and the strong dipole of water. The interaction of water with these solvents involves unusually large induced dipole effects superimposed upon the London dispersion effect. The drift in the calculated δ_2 values with changing δ_1 is therefore not surprising. By allowing for this, it seems evident that considerable confidence could be placed in a calculated value for the solubility of water in another non-polar liquid.

TABLE I

THE SOLUBILITY PARAMETER OF WATER δ_2 CALCULATED FROM ITS SOLUBILITY IN VARIOUS LIQUIDS AT 25°

Solvent	Wt., %	Vol., %	δ_1 (solvent)	δ_2 (water)
P_4	0.38	0.67	14.4	26.2
CS_2	.014	.020	10.0	26.1
CCl_4	.010	.016	8.6	24.7
n-C_7H_{16}	.013	.009	8.1	24.7
n-C_7H_{16}	.0022	.0037	5.9	23.8

The increase in solubility from 25 to 50° may be attributed to the increase in the vapor pressure of water, 23.76 to 92.51 mm. If the water were applied as vapor at 50° at the same pressure as at 25°, its solubility, applying Henry's law, would be only 1.4 weight per cent. less than at 25°, in accord with the smaller δ_1 of perfluoroheptane at the higher temperature.

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[1] G. Rotariu, E. A. Haycock and J. H. Hildebrand, THIS JOURNAL, **74**, 3165 (1952).

[2] G. D. Oliver, S. Blumkin and G. W. Cunningham, *ibid.*, **73**, **5722** (1951).

The System Sodium Metaphosphate–Calcium Metaphosphate

By George W. Morey

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The ability to "sequester" calcium ions, preventing their precipitation as calcium soaps and thus effectively softening water, is an outstanding property of glassy sodium metaphosphate. The mechanism of this sequestering action is not known, but it has been suggested that a slightly dissociating complex anion which contains the calcium is formed. In connection with such speculations, it is of interest to see what compounds, if any, exist in the binary system $NaPO_3$–$Ca(PO_3)_2$ or $Na_2O{\cdot}P_2O_5$–$CaO{\cdot}P_2O_5$.

The method used was to make known mixtures of the two end members by fusion and to determine the melting point by the quenching method used in this Laboratory, details of which, including calibration of the thermocouples, have been described by Morey and Ingerson.[1] No difficulties were encountered, and the phase equilibrium diagram is a simple one. Details are given in Table I and in the diagram in Fig. 1. The melting point of $NaPO_3$ is 627.6°[1]; of $Ca(PO_3)_2$, 977°.[2] A binary compound is formed, $4NaPO_3{\cdot}CaP_2O_6$ or $2Na_2O{\cdot}CaO{\cdot}3P_2O_5$, which melts congruently at 738°. Its optical properties[3] are: biaxial, negative, $2V = 80°$; $\alpha = 1.518$, $\beta = 1.564$, $\gamma = 1.581$. The eutectic between $NaPO_3$ and $2Na_2O{\cdot}CaO{\cdot}3P_2O_5$

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[1] George W. Morey and Earl Ingerson, *Am. J. Sci.*, **242**, 1 (1944).

[2] W. L. Hall, G. T. Faust and D. S. Reynolds, *ibid.*, **242**, 457 (1944).

[3] The measurements of the optical properties were made by Miss Jewell Glass, of the U. S. Geological Survey, to whom I am glad to express my obligation.

TABLE I

THE SYSTEM $Na_2O \cdot P_2O_5$–$CaO \cdot P_2O_5$

No.	Weight fraction $CaO \cdot P_2O_5$	Liquidus, °C.	Crystalline
1	0	627.6	$Na_2O \cdot P_2O_5$
	0.046	625	Eutectic
		661	$2Na_2O \cdot CaO \cdot 3P_2O_5$
2	.094	696	$2Na_2O \cdot CaO \cdot 3P_2O_5$
3	.258	734[a]	$2Na_2O \cdot CaO \cdot 3P_2O_5$
4	.328 (2:1)	738[a]	$2Na_2O \cdot CaO \cdot 3P_2O_5$
5	.404	734[b]	$2Na_2O \cdot CaO \cdot 3P_2O_5$
6	.448	728[c]	$2Na_2O \cdot CaO \cdot 3P_2O_5$
7	.492	739	$CaO \cdot P_2O_5$
8	.700	834	$CaO \cdot P_2O_5$
9	.898	927	$CaO \cdot P_2O_6$
10	1.0	977	$CaO \cdot P_2O_5$

[a] No. 3 and 4 together at 733°; 3, very few crystals; 4, hardly sintered. [b] No. 3 and 5 together at 734°; 3, hardly sintered; 5, very few crystals. [c] The eutectic is near; 4° below liquidus both kinds of crystals were present.

is at 625°. The composition was not determined exactly, but it is assumed to be about 0.01 weight fraction CaP_2O_6. The eutectic between $2Na_2O \cdot CaO \cdot 3P_2O_5$ is at 725°, 0.46 weight fraction CaP_2O_6. The eutectic composition was obtained by extrapolating the two liquidus curves to their intersection.

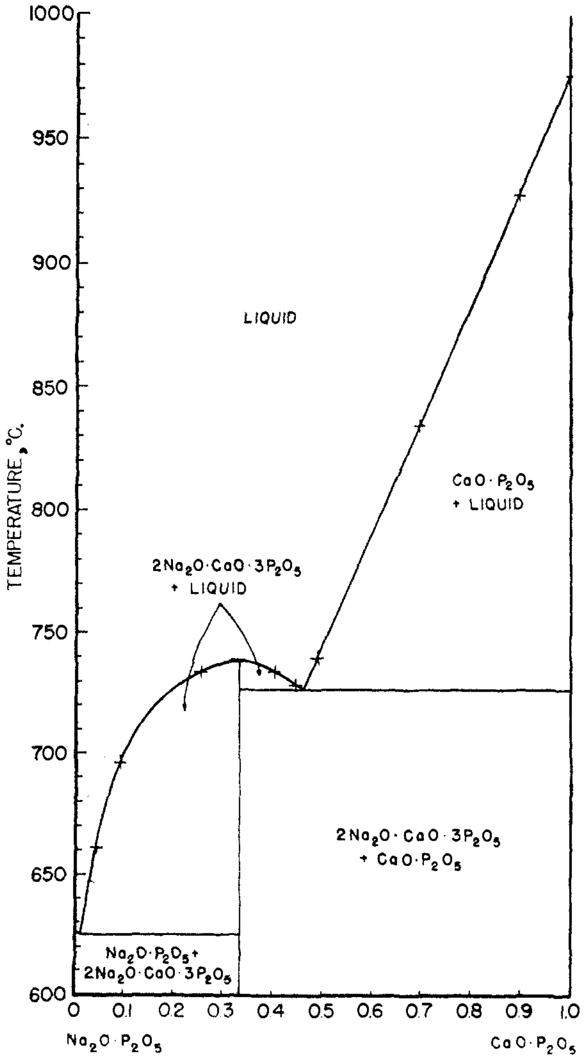

Fig. 1.—The binary system $Na_2O \cdot P_2O_5$–$CaO \cdot P_2O_5$.

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Color Reactions of Lignin in Solution Compared to Similar Reactions in the Solid State

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In previous work, the color reactions of lignin with phenols[1] and with strong acids[2] were found to be caused by the presence of a substituted coniferylaldehyde group in the lignin. The colors developed with Brauns' spruce "native lignin" in solution had absorption maxima at the same wave length as those produced with coniferylaldehyde and the respective reagent. With spruce wood sections, the maxima occurred at higher wave lengths, comparable to those resulting with the reagent and solutions of coniferylaldehyde substituted in the 5-position with a propenyl group. This was believed to indicate the presence of a side chain in the 5-position in the color-reacting group of the lignin in spruce wood. Adler,[3] however, found absorption at a higher wave length when certain dyestuffs were measured in the solid or adsorbed state than in solution and a similar effect when wood, in which the color reacting group had been destroyed, was impregnated with the colored solution produced by the reaction of coniferylaldehyde with phloroglucinol and then dried. Similar results were obtained with impregnated filter paper. In view of these observations, it seemed desirable to re-examine the color reactions described in the above papers.

The maximum absorption of the colored solution formed by the condensation of coniferylaldehyde with resorcinol was found at a higher wave length (from 579 to 590 mμ) when measured on filter paper that had been impregnated with the solution and dried. The situation with wood sections, however, may not be comparable, since in this case the chromophoric groups developed are probably more or less dispersed throughout the wood substance.

In order to avoid any effects of the solid state on the measurement of the resorcinol color with spruce wood, an attempt was made to put the chromophoric groups into solution. By using spruce wood ground in a vibratory ball mill[4] and a suitable mixture of concd. hydrochloric acid and ethanolic hydrogen chloride for the reaction vehicle, it was possible to develop and extract concurrently a portion of the colored substance. This extract had a maximum absorption at 586 mμ as compared to 579 mμ for spruce "native lignin" or coniferylaldehyde when reacting with resorcinol. Wood sections under the same conditions had a maximum at 593 mμ.

The proportion of the coloring matter from the

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(1) J. C. Pew, THIS JOURNAL, **73**, 1678 (1951).

(2) J. C. Pew, Abstract of Papers, XIIth International Congress of Pure and Applied Chemistry, 616 (1951).

(3) E. Adler, private communication.

(4) F. H. Forziati, W. K. Stone, J. W. Rowen and W. D. Appel, *J. Research Natl. Bur. Standards*, **45**, 109 (1950).