DISCUSSION

To unravel the secrets Nature has locked up in petroleum, to probe at the heart of its composition, and to lay open—as on the operating table—the components in a way which accurately discloses their identity, API Research Project 6 has had this one well-selected representative petroleum under exhaustive examination continuously since 1928. To learn how different petroleums vary in composition, the project some years ago completed a long, but less exhaustive, analysis of the hydrocarbons in the gasoline fraction of seven different, carefully selected, representative petroleums. These latter data permit translating the extensive results obtained on the project's one representative petroleum to other petroleums on which only a few key points of data need be known or obtained. The exhaustive fractionation, although very costly, fortunately needs doing only once, and is of such a fundamental nature as to be particularly well suited to cooperative action by the entire industry.

A detailed description of the petroleum under investigation and the fractionating processes used is given by Rossini, Mair, and Streiff (*1*). A complete list of the publications of API Research Project 6 is obtainable on request.

LITERATURE CITED

(1) Rossini, F. D., Mair, B. J., Streiff, A. J., "Hydrocarbons from Petroleum," Reinhold, New York, 1953.

Received for review June 17, 1957. Accepted October 25, 1957. Report prepared under American Petroleum Institute Research Project 6.

Viscosity of Aqueous Solutions of Phosphoric Acid at 25° C.

O. W. EDWARDS and E. O. HUFFMAN
Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Ala.

Rapid growth in the industrial use of phosphoric acid has developed a widespread need for reliable information on the viscosity of its aqueous solutions. Important in the engineering design of equipment for handling phosphoric acid, viscosity must be considered also in laboratory studies of some of the other physicochemical properties of the acid.

Viscosity data from several sources (*10, 12, 13, 15*) were correlated and smoothed by graphical methods in 1946 to yield a compilation (*14*) that covered wide ranges of concentration and temperature. Error in the values for 25° C. was estimated as ±10%. Appearing also in 1946, a new set of measurements (*9*) was more precise but unfortunately covered only the concentration range below 12% of phosphoric acid.

An immediate need in connection with theoretical calculations relating to diffusion of phosphoric acid solutions prompted a remeasurement of viscosities at 25° C. over the concentration range 2 to 89% of phosphoric acid (0.21 to 85 molal).

VISCOSITY MEASUREMENTS

A series of 15 solutions, ranging from 0.21 to 6.93 molal, was prepared from reagent grade phosphoric acid and distilled water. Another series of 10 solutions, ranging from 9.89 to 84.77 molal, was prepared from triply crystallized phosphoric acid hemihydrate and conductance water. The difference in purity of the two sources of acid was quite small. At high concentrations, small amounts of phosphates other than orthophosphate were present. In the most concentrated solution, 0.3% of the total phosphorus was in nonortho forms.

The densities of the solutions at 25° C. were determined by means of 25-ml. pycnometers of the modified Gay-Lussac type. Each density was determined in duplicate, the weights being corrected for the buoyancy of air. Duplicates agreed to within 1 part in 10,000. Concentrations were taken from tables of densities (*7*).

Viscosities were determined by means of Cannon-Fenske viscometers (*4–6, 11*), which were calibrated with water or with solutions of sucrose (*2*). The viscosity of water at 25° C. was calculated (*8*) from the reliable value at 20° C. (*16*).

The measurements were made according to the standard procedure in a water bath and with the usual precautions (*1, 5*). Efflux times were measured by means of an electric timer that was read to 0.01 second. The temperature of the bath was held at 25° ± 0.005° C. Samples of solutions in the first series were filtered under slight pressure through fritted glass before they were charged to the viscometers.

Each measurement was made at least three times, usually with the same charge. Replicates agreed within 0.1%. Viscosities were corrected for kinetic energy losses by means of a conventional formula (*5*) in which the kinetic energy coefficient was taken as 0.56 (*3*), because the openings of the capillaries of the Cannon-Fenske instruments are trumpet-shaped (*5*).

The corrected viscosities are shown in Table I. At concentrations up to 6.93 molal, corresponding measurements with different viscometers agree closely, except those for 3.51 and 4.97 molal solutions. At concentrations above 6.93 molal, the results from the different viscometers agree less closely. The greater deviations among the more concentrated solutions may reflect changes in composition as a result of hygroscopicity. The viscosities of solutions more concentrated than 1 molal are from 0.7 to 2.0% higher than those reported in the 1946 compilation (*14*). The new viscosity values are in excellent agreement with those of Drucker (*9*) in the range of overlap (up to 1.4 molal).

The accuracy of the results depends upon the accuracy of the calibration, which, in turn, is limited by uncertainties in efflux times and in the viscosities of the standard liquids. These uncertainties are small, however, and the accuracy probably is of the same order as the precision.

Secondary values of viscosity are shown in Table II at integral values of concentration in weight per cent.

Table I. Viscosities of Phosphoric Acid Solutions at 25° C.

Concentration of H_3PO_4, Molality	Viscosity, Centipoises, as Determined with Indicated Viscometer[a]						Difference between Viscometers, %[b]
	E	*A*	*B*	A_1	B_1	*C*	
0.21	0.939						
0.39	0.979						
0.77	1.075						
1.22	1.189	1.191	1.193				+0.17
1.66	1.310	1.305	1.306				+0.08
2.17		1.457	1.457				0.00
2.69		1.620	1.620				0.00
3.15		1.785	1.787				+0.11
3.57		1.962	1.947				−0.77
4.27		2.204	2.203				−0.05
5.04		2.530	2.511				−0.76
5.66		2.846	2.837				−0.32
6.18			3.033				
6.56			3.198				
6.93			3.378				
9.892				4.922	4.882		−0.82
15.01				7.942	7.930		−0.15
20.05				11.39	11.24	11.34	+0.89
25.05					14.85	14.91	+0.40
30.03					18.75	18.85	+0.53
35.06					22.92	22.93	+0.04
40.52					27.42	27.06	−1.31
49.97					35.12	35.26	+0.40
64.84					46.41	46.19	−0.47
84.77					59.60	59.92	+0.54

[a] Viscometer constants, centistokes/sec.
E, 0.0012090, determined with water.
A, 0.0022591, determined with water.
B, 0.0040075, determined with water.
A_1, 0.0037484, determined with water.
B_1, 0.015031, determined with sucrose solutions.
C, 0.038014, determined with sucrose solutions.

[b] $(B - A)100/B$; or $(B_1 - A_1)100/B_1$; or $(C - B_1)100/B_1$.

Table II. Viscosities of Phosphoric Acid Solutions at Integral Values of Concentration

(From Equations 1 to 3, 25° C.)

H_3PO_4, %	Viscosity, Centipoises	H_3PO_4, %	Viscosity, Centipoises
0	0.8902	45	4.094
5	1.015	50	5.090
10	1.166	55	6.378
15	1.350	60	8.105
20	1.576	65	10.48
25	1.879	70	13.90
30	2.254	75	19.08
35	2.728	80	27.60
40	3.329		

EMPIRICAL EQUATIONS

Empirical equations covering the concentration range 0.2 to 50 molal were fitted to the observed viscosities by the method of least squares.

$$\eta = \eta_w + 0.22330m + 0.017841m^2 \quad (m = 0.2 \text{ to } 2.7) \qquad (1)$$

$$\eta = \eta_w + 0.20566m + 0.0275378m^2 - 0.000744285m^3 \quad (m = 2.69 \text{ to } 9.9) \qquad (2)$$

$$\log (\eta - \eta_w) = 1.334646 \log m - 0.723152 \quad (m = 9.89 \text{ to } 50) \qquad (3)$$

where

η = viscosity of phosphoric acid solution, centipoises
η_w = viscosity of water at 25° C. (0.8902 centipoise)
m = molality of phosphoric acid solution

The average deviation of experimental viscosities from Equation 1 is ± 0.15%, and the maximum is 0.34%. The average deviation of measured viscosities from Equation 2 is ± 0.31%, and the maximum is 1.28%. The average deviation of experimental viscosities from Equation 3 is ±0.77%, and the maximum, 1.75%, occurs at 50 molal. The viscosities at the two concentrations above the range of Equation 3 are lower than those calculated from the equation by 8 and 17%, respectively.

LITERATURE CITED

(1) Am. Soc. Testing Materials, Philadelphia, Pa., "ASTM Standards," 1953 Supplement, Part 5, pp. 49–59.
(2) Bates, F. J., others, "Polarimetry, Saccharimetry, and the Sugars," Natl. Bur. Standards, Circ. 440 (1942).
(3) Bingham, E. C., Thompson, T. R., *J. Rheol.* **1**, 418 (1930).
(4) Cannon, M. R., *Ind. Eng. Chem., Anal. Ed.* **16**, 708 (1944).
(5) Cannon, M. R., Fenske, M. R., *Ibid.*, **10**, 297 (1938).
(6) *Ibid.*, **13**, 299 (1941).
(7) Christensen, J. H., Reed, R. B., *Ind. Eng. Chem.* **47**, 1277 (1955).
(8) Coe, J. R., Jr., Godfrey, T. B., *J. Appl. Phys.* **15**, 625 (1944).
(9) Drucker, C., *Arkiv Kemi, Mineral. Geol.* **A22**, No. 21 (1946).
(10) Durgin, C. B., Lum, J. H., Malowan, J. E., *Trans. Am. Inst. Chem. Engrs.* **33**, 643 (1937).
(11) Geist, J. M., Cannon, M. R., *Ind. Eng. Chem., Anal. Ed.* **18**, 611 (1946).
(12) Kasbekar, G. S., *J. Univ. Bombay* **9**, Part 3, 55 (1940).
(13) Litvinov, N. D., Kryukov, T. A., Kurochkina, E. A., *J. Appl. Chem. (U. S. S. R.)* **7**, 1121 (1934).
(14) Monsanto Chemical Co., St. Louis, Mo., "Phosphoric Acid, Its Physical and Chemical Properties," Tech. Bull. P-26 (1946).
(15) Reyher, R., *Z. physik. Chem.* **2**, 744 (1888).
(16) Swindells, J. F., Coe, J. R., Jr., Godfrey, T. B., *J. Research Natl. Bur. Standards* **48**, 1 (1952).

Received for review March 4, 1957. Accepted May 22, 1957.