The two equations agree within 0.001 weight % over practically the entire experimental range of temperature. However, the third order equation gave a better (statistically significant) fit of the data. It was probable that the use of still higher terms also would have permitted a significantly better fit of the data.

The reproducibility of the analyses was such that the standard deviation of an average was 0.0028 weight % unit, the probable (50% confidence) error of a single value was 0.0019 weight % unit. For 95% confidence, the value was 0.0055 weight % unit. Based upon a solubility of 0.173 weight %, the value applicable from about 10° to 25°C., these figures represent, respectively, 1.1 and 3.2% for 50 and 95% confidence.

From the third-order equation, the minimum solubility is 0.172 weight % benzene at 16.80°C. From 10° to 25°C. the solubility is constant within 0.173 ± 0.001 weight %, or within ±0.6% of the average value.

ACKNOWLEDGMENT

The statistical analysis was carried out by J. S. Hunter of the Institute of Statistics.

This work was supported by the United States Atomic Energy Commission under Contract No. AT-(40-1)-1320. The paper is a condensation of Progress Report No. 5 (*2*).

LITERATURE CITED

(1) Andrew, L. J., Keefer, R. M., *J. Am. Chem. Soc.* **71**, 3644 (1959).
(2) Arnold, D. S., Plank, C. A., Erickson, E. E., Pike, F. P., **ORO-156**, "Solubility of Benzene in Water," Tech. Inform. Division, U. S. Atomic Energy Comm., Oak Ridge, Tenn., 1954.
(3) Barbaudy, J., *J. chim. phys.* **23**, 289 (1926).
(4) Bohon, R. L., Claussen, W. F., *J. Am. Chem. Soc.* **73**, 1571 (1951).
(5) Booth, H. S., Everson, H. E., *Ind. Eng. Chem.* **40**, 1491 (1948); **41**, 2627 (1949).
(6) Brady, A. P., Huff, H., *J. Phys. Chem.* **62**, 644 (1958).
(7) Durand, R., *Compt. rend.* **223**, 898–900 (1946).
(8) Groschuff, E., *Z. Elektrochem.* **17**, 348 (1911).
(9) Gross, P. M., Saylor, J. H., *J. Am. Chem. Soc.* **53**, 1744 (1931).
(10) Hantzsch, A., Sebaldt, F., *Z. physik. Chem.* **30**, 295 (1899).
(11) Hayashi, M., Sasaki, T., *Bull. Chem. Soc. Japan* **29**, 857–9 (1956).
(12) Herz, W., *Ber.* **31**, 2669 (1898).
(13) Hill, A. E., *J. Am. Chem. Soc.* **44**, 1163 (1922).
(14) Horiba, S., *Mem. Coll. Eng., Kyoto Imp. Univ.* **1**, 49 (1914).
(15) Jaeger, A., *Brennstoff Chem.* **4**, 259 (1923).
(16) McDevit, W. F., Long, F. A., *J. Am. Chem. Soc.* **74**, 1773 (1952).
(17) Milligan, L. H., *J. Phys. Chem.* **28**, 494 (1924).
(18) Moore, B., Roaf, H. E., *Proc. Roy. Soc. (London)* **77B**, 86 (1905).
(19) Niini, A., *Suomen Kemistilehti* **11A**, 19 (1938).
(20) Paul, M. A., *J. Am. Chem. Soc.* **74**, 5274 (1952).
(21) Richards, T. W., Carver, E. K., Schumb, W. C., *Ibid.*, **41**, 2019 (1919).
(22) Saylor, J. H., Stuckey, J. M., Gross, P. M., *Ibid.*, **60**, 373 (1938).
(23) Saylor, J. H., Whitten, A. I., Claiborn, I., Gross, P. M., *Ibid.*, **74**, 1778 (1952).
(24) Seidell, A., "Solubilities of Organic Compounds," 3rd ed., vol. II, Van Nostrand, New York, 1941.
(25) Stearns, R. S., Oppenheimer, H., Simon, E., Harkins, W. D., *J. Chem. Phys.* **15**, 496 (1947).
(26) Uspenskii, S. P., *Neftyanoe Khoz.* **17**, 713 (1929).
(27) Vermillion, H. E., Ph.D. thesis, 1939, Duke University, Durham, North Carolina.

Received for review July 1, 1957. Accepted November 12, 1957.

Distribution Coefficients of Fatty Acids between Water and Methyl Isobutyl Ketone

E. BAK[1] **and C. J. GEANKOPLIS**
Chemical Engineering Department, The Ohio State University, Columbus, Ohio

It is often desirable to predict the distribution coefficient of organic compounds in a given immiscible water-organic solvent system. To do this it is helpful to know how members of a homologous series react in such a system. With such data it may be possible to develop generalized correlations to help predict these phenomena. Previous studies (*1–4*) have been made with formic and acetic acids in the water-methyl isobutyl ketone solvent system at 25.0°C. and some experimental distribution coefficient data have been obtained.

In this work additional experimental distribution data were obtained in the very dilute region for the above two acids in the same solvents and data were also obtained for the higher members—propionic, *n*-butyric, *n*-valeric, and *n*-caproic—of the fatty acid series. Data were obtained primarily in the dilute region to allow the distribution coefficient, K, at infinite dilution to be determined.

EXPERIMENTAL

The equilibrium determinations were performed in glass-stoppered flasks totally immersed in a constant temperature bath and agitated by magnetic stirrers. The flasks were sealed on the outside by rubber stalls. After agitation and settling, a sample of each phase was removed with a pipet and analyzed for acid content by titration with standard sodium hydroxide solution using phenolphthalein as an indicator. In the ketone phase, alcohol was added before titration to make the phases miscible. Each acid was equilibrated separately in the flask. The data are given in Table I. The source and purity of the acids used are: formic, reagent grade, > 99.6% purity, Baker's; acetic, reagent grade, > 99.7% purity, Eastman; propionic, boiling point 140–2°C., Eastman; *n*-butyric, boiling point 161–3°C., Matheson; *n*-valeric, boiling point 184–7°C., Eastman; *n*-caproic, boiling point 203–5°C., Matheson.

RESULTS AND DISCUSSION

To determine the distribution coefficient at infinite dilution for formic acid, the concentration in the water phase was plotted against the equilibrium concentration in the ketone phase, and a smooth curve was drawn through the data. Then the slope or K value was determined at the origin. As a check, the experimental K values were plotted against the concentration in the ketone phase and the extrapolated value at zero concentration was determined. This was done for each acid (Table I). The plots showed that the K val-

---

[1] Present address, Diamond Alkali Co., Painesville, Ohio.

ues increased with increasing concentration. The few data points of Vogt (*4*) for formic and Brismade (*1*) for acetic acid in dilute solution are similar to the data in Table I. The plots of the concentration in the water *vs.* that in the ketone for all acids showed a slight curvature.

A plot of the *K* value of the acid at infinite dilution *vs.* the number of carbon atoms in the acid is shown in Figure 1 on semilog paper. With the exception of formic acid, a straight line can be drawn through the data for the homologous series from acetic to caproic acid. Data for higher acids might possibly fall on a continuation of this line. If additional data for other systems show similar trends, this could be useful to estimate K values or fill in missing data in a homologous series of solutes in different solvent systems.

If the separation factor is defined as the *K* of one acid over the *K* of the next lower acid in the series, it is seen that this factor has an average value of about 3.5 in going from caproic to acetic acid. Hence, fractional solvent extraction could be used to separate a mixture of these acids.

LITERATURE CITED

(1) Brismade, D. S., Bliss, H., *Trans. Am. Inst. Chem. Engrs.* **39,** 679 (1943).
(2) Scheibel, E. G., Karr, A. E., *Ind. Eng. Chem.* **42,** 1048 (1950).
(3) Sherwood, T. K., Evans, J. E., Longcor, J. V. A., *Ibid.*, **31,** 1144 (1939).
(4) Vogt, H. J., Geankoplis, C. J., *Ibid.*, **45,** 2119 (1953).

Received for review September 17, 1957. Accepted January 20, 1958.

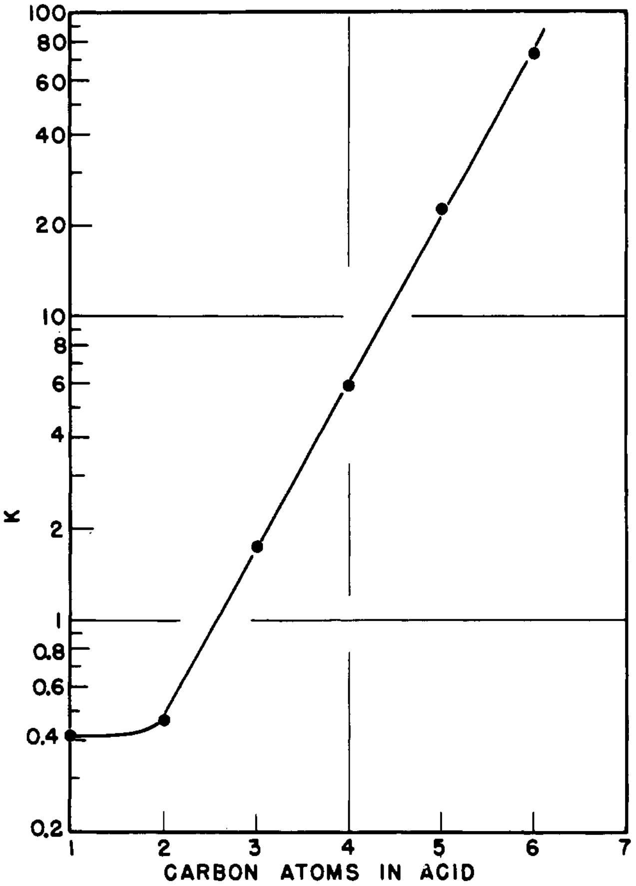

Figure 1. Distribution coefficient, *K*, at infinite dilution *vs.* number of carbon atoms in acid

Table I. Distribution Coefficient of Organic Acids between Water and Methyl Isobutyl Ketone at 25.0° C.

(Each acid equilibrated separately)

Concn. of Acid in Phases at Equil., Gram Moles/Liter Ketone, C_K	Concn. of Acid in Phases at Equil., Gram Moles/Liter Water, C_W	Distribn. Coeffic., $K = C_K/C_W$
Formic acid (*K* inf. diln. = 0.413)		
0.0717	0.1700	0.422
0.1270	0.3042	0.418
0.1960	0.464	0.423
0.2600	0.593	0.439
0.380	0.884	0.430
0.515	1.188	0.433
0.756	1.718	0.440
1.209	2.678	0.452
Acetic acid (*K* inf. diln. = 0.463)		
0.0556	0.01180	0.471
0.1692	0.3462	0.489
0.2260	0.456	0.496
0.3346	0.655	0.510
0.446	0.860	0.519
0.686	1.240	0.553
1.175	1.946	0.604
1.885	2.870	0.657
Propionic acid (*K* inf. diln. = 1.76)		
0.0833	0.0465	1.791
0.1905	0.1034	1.841
0.337	0.1767	1.909
0.498	0.2565	1.940
0.825	0.406	2.033
1.265	0.581	2.177
n-Butyric acid (*K* inf. diln. = 5.91)		
0.1848	0.0303	6.10
0.3615	0.0570	6.34
0.3623	0.0560	6.46
0.519	0.0803	6.46
0.690	0.1031	6.70
0.848	0.1252	6.78
1.103	0.1559	7.08
n-Valeric acid (*K* inf. diln. = 22.9)		
0.481	0.01978	24.32
0.631	0.02553	24.76
0.774	0.03044	25.40
0.909	0.0358	25.43
n-Caproic acid (*K* inf. diln. = 72.3)		
0.417	0.00553	75.5
0.550	0.00703	78.2
0.656	0.00835	78.6
0.792	0.00985	80.4
0.905	0.01125	80.4