

TABLE II. VISCOSITY OF NITROGEN DIOXIDE IN THE LIQUID PHASE

Pressure, Lb./Sq. Inch Abs. Bubble Point	Temperature, ° F.							
	40	70	100	130	160	190	220	250
	Bubble Point Pressure, Pounds per Square Inch Absolute							
	14.8	30.7	60.0	111.2	196.4	332.8	543.9	864.1
	Viscosity, Micropoises							
	4990	4182	3420	2784	2235	1752	1325	924
200	5021	4155	3441	2800	2250	1753	1350	948
400	5055	4180	3470	2820	2281	1804	1420	948
600	5090	4208	3495	2840	2310	1850	1482	1028
800	5121	4232	3520	2861	2334	1896	1539	1100
1000	5150	4260	3544	2880	2355	1939	1599	1179
1250	5190	4297	3566	2906	2380	1975	1646	1252
1500	5230	4330	3587	2929	2400	2010	1686	1319
1750	5270	4366	3608	2949	2420	2040	1720	1370
2000	5310	4400	3628	2965	2440	2063	1742	1400
2250	5345	4433	3649	2990	2459	2080	1764	1430
2500	5382	4470	3670	3010	2480	2098	1785	1444
2750	5422	4502	3691	3024	2496	2110	1800	1470
3000	5465	4535	3713	3042	2510	2127	1822	1510
3500	..	4593	3753	3070	2540	2151	1850	1532
4000	..	4655	3792	3095	2568	2183	1880	1555
4500	..	4714	3830	3118	2600	2200	1900	1579
5000	..	4782	3869	3145	2625	2229	1900	1579

showed a standard deviation of 90 micropoises and an average deviation of 4 micropoises, taking into account the sign of the difference. There is only a relatively small change in viscosity with pressure in comparison to the behavior of paraffin hydrocarbons (9-12). An initial set of data was obtained at 100° F. The instrument was then disassembled, a new, four-stage, centrifugal, circulating pump was installed, and the rest of the measurements were made. The results of these measurements are shown in Table I along with interpolated curves for intermediate temperatures.

Smoothed values of the viscosity as a function of pressure for each of the temperatures investigated are recorded in Table II. It is believed that the calibrations were made with sufficient care and the data presented in Figure 1 were of such reproducibility that the standard error of the smoothed values recorded in the table is estimated to be 90 micropoises.

The effect of temperature upon the viscosity of nitrogen dioxide is presented in Figure 2. The measurements of Thorpe and Rodger (16) were included. Satisfactory agreement between the two sets of measurements was realized.

ACKNOWLEDGMENT

The laboratory work was supported by the Office of Naval Research. G. N. Richter was a recipient of a fellowship from the Dow Chemical Co. L. T. Carmichael assisted with the opera-

tion of the apparatus. Olga Strandvold contributed to the assembly of the manuscript. The assistance of W. N. Lacey in its review is acknowledged.

NOMENCLATURE

- A = dimensional coefficient of Equation 1
 B = dimensional coefficient of Equation 1
 η = absolute viscosity, micropoises
 σ_B = specific weight of ball, pounds per cubic foot
 σ_f = specific weight of fluid, pounds per cubic foot
 θ = roll time of ball, seconds

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RECEIVED for review March 28, 1953.

ACCEPTED May 22, 1953.

Distribution of Formic Acid between Water and Methyl Isobutyl Ketone

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PURIFICATION and separation of organic acids by physical means such as extraction rather than distillation or other methods has stimulated interest in solubility relations and distribution of organic compounds between water and immiscible organic solvents. However, in order to better predict the distribution behaviors of certain specific compounds, it is helpful to know how members of a homologous series react in a given water-organic solvent system. Then, generalized rules can be

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formulated to aid in predicting behaviors of other compounds in these same solvent systems.

The objective of this work was to study the distribution coefficient in dilute solutions of formic acid between the immiscible solvents water and methyl isobutyl ketone; the latter is a good solvent for many organic compounds and plastics. The distribution ratio of formic acid was then compared with that of acetic acid and propionic acid which are the next higher members of the saturated carboxylic acid series.

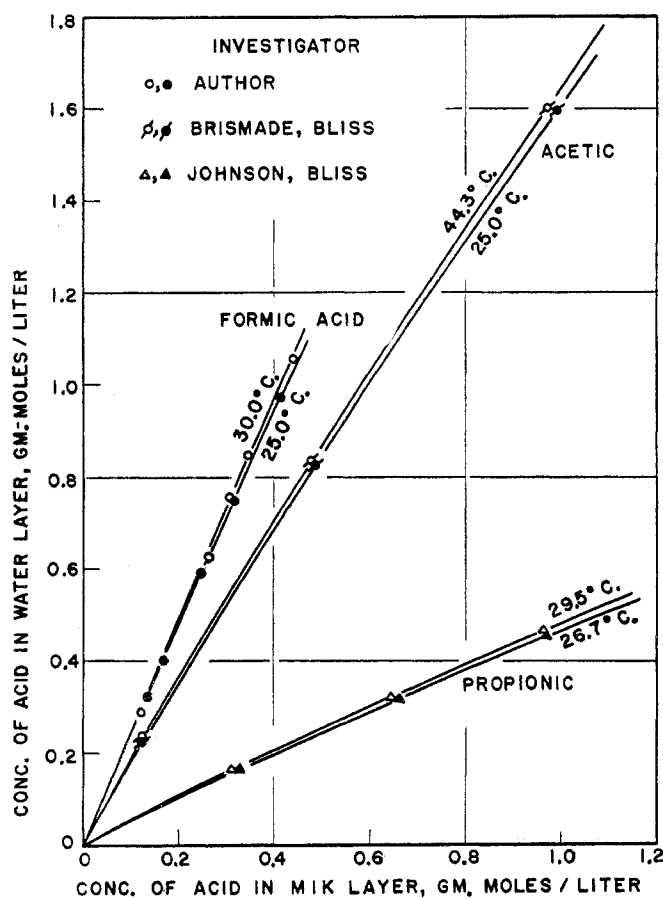


Figure 1. Distribution Data for Water-Organic Acid-Methyl Isobutyl Ketone

TABLE I. EQUILIBRIUM DATA FOR WATER-FORMIC ACID-METHYL ISOBUTYL KETONE

Temp., °C.	Formic Acid in Solvent Layer, G. Moles/Liter		Distribution Ratio, $K = C_K/C_W$
	C_W , water	C_K , ketone	
25.0 ± 0.5	0.321	0.1337	0.416
	0.398	0.1680	0.422
	0.590	0.2445	0.415
	0.748	0.314	0.420
	0.970	0.413	0.426
30.0 ± 0.5	0.289	0.1198	0.415
	0.624	0.260	0.417
	0.766	0.306	0.405
	0.844	0.342	0.405
	1.054	0.436	0.414

EXPERIMENTAL

About 75 ml. of methyl isobutyl ketone, 75 ml. of distilled water, and suitable amounts of formic acid were added to 250-ml. Erlenmeyer flasks. The flask was suspended in a constant temperature bath held at $25.0^\circ \pm 0.5^\circ$ or $30.0^\circ \pm 0.5^\circ$ C. The contents of the flask were vigorously mixed by an air-driven glass stirrer for $1\frac{1}{2}$ hours and the temperature was checked periodically by a thermometer immersed in the flask. After stirring and with the flask in the bath, the contents were allowed to settle for 15 minutes and then 10-ml. samples of each phase were pipetted into separate flasks for analyses.

The amount of formic acid in the water layer was determined by acid-base titration using 0.1 N carbonate-free sodium hydroxide with phenolphthalein as an indicator. The formic acid in the ketone phase was determined by first adding 20 ml. of ethyl alcohol and then titrating with base. End point blanks were determined on both the water and ketone phases.

The methyl isobutyl ketone used was technical grade and was obtained from Carbide and Carbon Chemicals Corp. and the formic acid was Baker's A.C.S. reagent grade.

The experimental data obtained are given in Table I.

DISCUSSION

The concentration of formic acid in the water layer is plotted against the concentration of formic acid in the methyl isobutyl ketone layer in Figure 1. The plot shows that the distribution coefficient greatly favors the water layer by a factor of about 2.4 to 1. For purposes of comparison the acetic acid data of Brismade and Bliss (1) and the propionic acid data of Johnson and Bliss (2) are plotted on the same graph. This shows that as the number of carbon atoms is increased in the homologous carboxylic acid series, the distribution ratio shifts from favoring the water layer toward favoring the methyl isobutyl ketone layer. This change in distribution ratio is to be expected because as the molecular weight of the acid is increased, the solubility of the acid in water generally decreases.

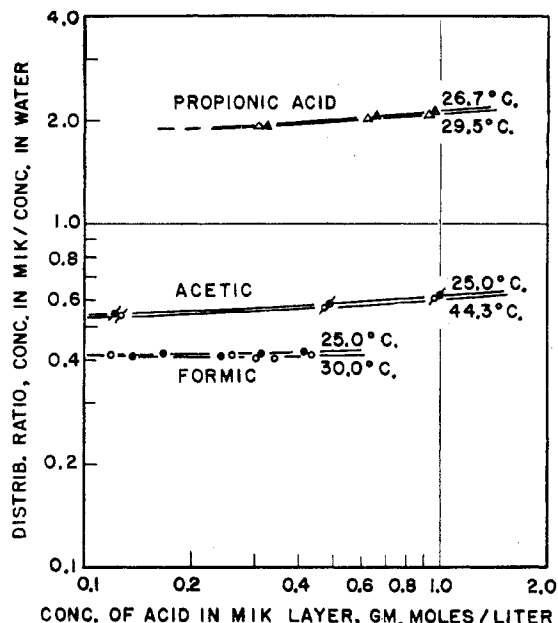


Figure 2. Comparison of Distribution Coefficients

The same data are plotted as the distribution ratio versus the concentration of the acid in the ketone layer in Figure 2. The graph shows that the distribution ratio for all three acids is fairly constant and independent of concentration below a concentration in the ketone layer of about 0.5 gram moles acid per liter.

Increasing the temperature in the case of all three acids tends to shift the distribution slightly toward favoring the water layer. This may mean that as the temperature is increased the activity of the acids in the water increases, the activity in the ketone layer decreases, or a combination of both phenomena occur.

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RECEIVED for review December 22, 1952.

ACCEPTED March 13, 1953.