expansion upon mixing, the molecular group which is displaced contains molecules in some association. This is consistent with the fact that the more polar nitromethane is more likely to dimerize than nitroethane. The moderate amount of nonideality is consistent with the conclusion based on density data (*6*) that these binary solutions are nearly ideal.

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P-V-T-X Properties of Associated Vapors of Formic and Acetic Acids

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The *P-V-T-X* properties of the associated vapors of acetic and formic acids and their mixtures were measured over the range of 50° to 125° C. and 30 to 700 mm. of Hg. The presence of clusters of more than two molecules is strongly suggested in the pure acids and mixtures. The data were interpreted in terms of an ideal gas association theory. Dimerization constants and heat of association are presented for the pure and crossdimer formations.

CARBOXYLIC ACID VAPORS have long been known to deviate appreciably from ideal gas behavior (*6, 18*), the indications being that the prime contribution to nonideality is the formation of low-order molecular clusters. Several investigations (*2, 5, 8, 9, 11*) have shown that intermolecular hydrogen bonding is responsible for the formation of relatively stable clusters of molecules which thus cause a trend in the apparent molecular weight as a function of both temperature and pressure.

This work was an experimental study of the volumetric properties of the mixtures of the first two members of the carboxylic acid homologous series. Comprehensive experimental data for the pure acids were available in the literature (*1, 2, 3, 5, 6, 7, 11, 12, 15, 16, 18, 21*); however, data for the mixtures of these acids appear to be lacking. As a check on the reliability of the apparatus used by the authors, pure component *P-V-T* data were also measured and compared with data from the literature.

EXPERIMENTAL

Materials. Formic acid was supplied by the British Drug Houses, Poole, England, as 98% minimum formic acid, the balance being less than 0.01% impurities other than water. This acid was purified by a method suggested by Winstein and Marshall (*23*). The refractive index of the purified acid, 1.3710, compares favorably with values of 1.3710 (*1*) and 1.3714 (*10*), all at 20° C. The density of the acid at 20° C. was 1.2209, which compares with 1.2206 (*3*) and 1.2201 (*8*). These data indicate a purity of at least 99.9% formic acid. Formic acid is readily decomposed at high temperatures; however, in the temperature range of this investigation data from the literature (*1, 3, 13*) indicate that this should produce a negligible effect.

Acetic acid was supplied by the J. T. Baker Chemical Co., Phillipsburg, N. J., with a guranteed purity of 99.9%. Further tests of purity performed in this laboratory confirmed this figure. The index of refraction was 1.3720, in excellent agreement with the value of 1.3721 at 20° C. reported in the literature (*10*). No further purification of this acid was attempted.

Equipment. The compressibility data of this research were obtained by vapor density measurements at various temperatures and compositions. The equipment is schematically represented in Figure 1. The procedure consisted essentially of filling an evacuated bulb of known internal volume with the gas mixture under measurable conditions of temperature and pressure. A similar technique was employed by Roper (*20*) in determining compressibility data for pure hydrocarbon gases.

The determination of the specific volume of the gas required knowing the internal volume of the sample bulb at the experimental temperature and knowing the mass of the contained gas. The internal volume of the bulb (nominal volume of 0.5 liter) was determined at room temperature by weighing the amount of distilled water it contained. The determination was repeated several times with a maximum volume deviation of 0.004%. Volume expansion of the Pyrex glass bulb with temperature was calculated using the coefficient of expansion of No. 7740 Pyrex glass supplied by the Corning Glass Works (*4*). No correction was applied for expansion or contraction of the bulb due to pressure, since the entire range of this investigation was less than 1 atm. Mass determinations were made by difference weighings on a Mettler micrometer balance. The maximum over-all deviation in the determination of the specific volume is estimated to be 0.3%.

The effect of the adsorption of the acid on the walls of the flask was not examined in this investigation. It was, however, shown by Coolidge (*3*) for formic acid that at temperatures above 40° C. the correction for wall adsorption was negligible. A similar effect was discussed by Nicholls (*17*) for acetic acid and adsorption was calculated to introduce an error of less than 0.07% in the measurements of P-V-T data for the temperature range of 50° to 125° C.

At steady state there was no perceptible temperature gradient within the controlled temperature bath. The temperature was controlled by means of a proportional controller with a thermistor sensor. The actual bath temperatures were measured by means of an iron-constantan thermocouple previously calibrated against a mercury-in-glass thermometer certified by the National Bureau of Standards. The reported temperatures are accurate to within 0.05 ° C.

The gas pressure was transmitted to an absolute manometer by means of a metal diaphragm sensing device. The sensor was designed specifically for this research project, to permit measurements with the entire gas sample at the uniform temperature of the bath. It also avoided any contact of the sample with the mercury of the absolute manometer. Operation of the sensor consists essentially of adjusting a reference gas pressure, in this case dried air, until there is no deflection of the diaphragm as indicated by just making or breaking the electrical circuit. In practice the unit is balanced at atmospheric pressure and the temperature of the bath by means of the adjustable contact. Then any pressure encountered in the experiment, at this temperature, is transmitted to the absolute manometer by the nulling operation mentioned above.

The sensitivity of the 0.001-inch thick stainless steel 347 diaphragm was determined to be ±0.05 mm. of Hg. Other parts of the sensor were constructed of stainless steel 316 and Teflon. The unit is illustrated in Figure 2.

RESULTS AND DISCUSSION

The actual P-V-T measurements were carried out on mixtures of approximately 20, 40, 60, and 80 weight % formic acid. The data were then interpolated to intervals of 10 weight % formic acid. Complete data for six temperatures between 50° and 125° C. and for interpolated compositions in intervals of 10 weight % formic acid are available from the National Auxiliary Publications Service. A sample is presented in Table I. A total of 244 sets of P-V-T-X experimental measurements were made over the range of this investigation.

The P-V-T data of pure acids obtained in this work were compared with those of Coolidge (*3*) and Kottick (*14*) on formic acid and those of Nicholls (*17*) on acetic acid. Over the entire range of this investigation the agreement of the data is within 1%. Although no data had been obtained previous to this work for mixtures of the two acids, it is believed that the accuracy is of the same order of magnitude as for the pure components.

The association constant of dimerization is defined by

$$K = \frac{P_{\text{dimer}}}{(P_{\text{monomer}})^2}$$

where P_{dimer} and P_{monomer} are the partial pressures of the dimer and monomer, respectively. The K values were determined using an ideal gas association theory as described by Johnson and Nash (*12*) and Ritter and Simons (*19*). According to this theory the K values should be independent of the total sample pressure. The true constants were obtained by extrapolating the data to zero pressure where the gas is considered to be ideal, in a manner similar to that of Ritter and Simons (*19*). These extrapolated

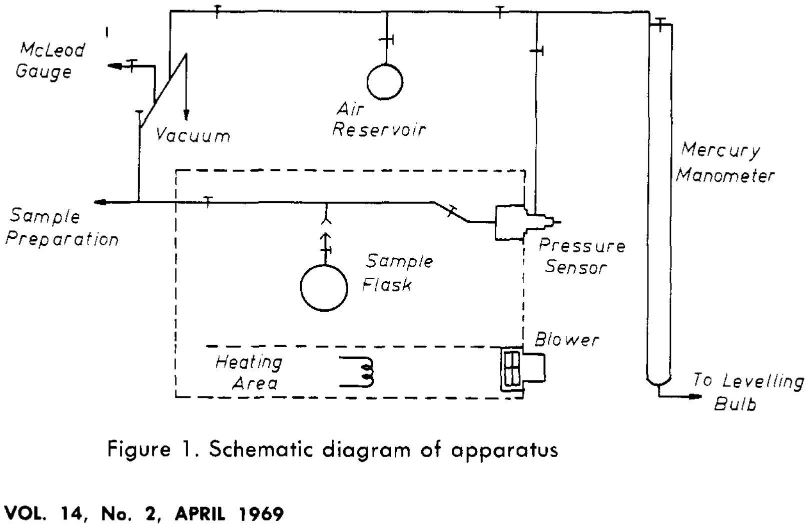

Figure 1. Schematic diagram of apparatus

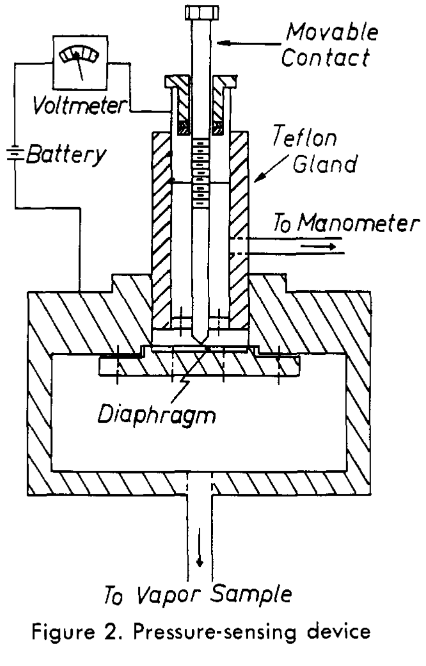

Figure 2. Pressure-sensing device

Table I. P-V-T-X Data of Mixtures of Acetic and Formic Acids[a]

Weight Per Cent Formic Acid

0%		20%		40%		60%		80%		100%	
P, mm. Hg	*V*, l./mole	*P*, mm. Hg	*V*, l./mole	*P*, mm. Hg	*V*, l./mole	*P*, mm. Hg	*V*, l./mole	*P*, mm. Hg	*V*, l./mole	*P*, mm. Hg	*V*, l./mole
125.43° C.											
548.09	30.00	566.00	29.74	582.25	29.55	597.25	29.53	610.90	29.69	620.18	30.00
349.15	50.00	362.83	49.49	372.21	49.21	381.99	49.21	391.87	49.49	394.30	50.00
259.40	70.00	268.27	69.28	275.22	68.90	282.92	68.90	290.82	69.28	292.80	70.00
208.55	90.00	195.25	98.98	199.71	98.42	225.83	88.58	231.74	89.08	213.95	100.00
161.63	120.00	165.91	118.77	169.66	118.11	174.28	118.11	194.37	108.87	158.42	140.00
106.30	190.00	127.82	158.36	130.66	157.48	134.13	157.48	137.01	158.36	119.21	190.00
110.00° C.											
486.61	30.00	505.30	29.74	521.70	29.55	536.20	29.53	548.10	29.69	557.65	30.00
377.13	40.00	391.10	39.65	403.75	39.40	415.10	39.37	424.80	39.59	432.82	40.00
263.33	60.00	272.90	59.47	282.05	59.10	290.10	59.05	297.02	59.38	302.80	60.00
204.10	80.00	211.30	79.30	218.25	78.80	224.65	78.74	207.65	89.07	211.87	90.00
153.92	110.00	159.35	109.03	164.68	108.35	169.53	108.26	150.17	126.66	153.25	130.00
99.50	180.00	103.03	178.42	106.49	177.30	109.68	117.16	112.45	178.15	100.44	210.00
95.40° C.											
346.29	40.00	358.80	39.65	302.10	49.20	310.00	49.20	315.90	49.47	388.30	40.00
283.20	50.00	292.80	49.47	257.40	59.04	263.03	59.04	267.80	59.37	318.26	50.00
185.40	80.00	216.30	69.26	197.70	78.72	229.06	68.88	233.40	69.26	235.79	70.00
128.64	120.00	156.60	98.95	137.20	118.07	166.02	98.39	169.60	98.95	171.57	100.00
89.26	180.00	115.75	138.53	105.75	157.43	106.65	157.43	143.90	118.74	101.60	180.00
64.80° C.											
109.50	110.00	112.37	109.03	115.29	108.20	118.21	108.20	121.04	108.81	147.18	90.00
82.18	150.00	84.50	148.68	86.85	147.55	89.21	147.55	91.31	148.38	105.82	130.00
43.27	300.00	44.74	296.75	46.15	295.10	47.49	295.09	48.57	296.75	58.85	250.00
49.96° C.											
56.80	200.00	76.10	148.68	69.19	167.20	70.52	167.20	71.74	168.14	118.71	100.00
46.07	250.00	58.12	198.24	48.26	245.88	59.25	245.88	50.20	247.26	81.81	150.00
33.59	350.00	34.47	346.67	35.29	344.23	36.09	344.22	36.77	346.16	43.29	300.00

[a] Interpolated values based on experimental data.

equilibrium constants are then correlated by the following equations for the pure acids:

$$\text{Formic.}\quad \mathrm{Log}_{10} K_F = \frac{3037}{T} - 7.735$$

$$\text{Acetic.}\quad \mathrm{Log}_{10} K_A = \frac{3225}{T} - 7.695$$

For the gas mixtures, the volumetric behavior is again characterized by the association of molecules. The two acids give large negative excess volumes of mixing. It is then evident that there is a great tendency to form crossdimer molecules composed of a monomer of acetic acid coupled with a monomer of formic acid. For a mixture of 10% formic acid at 50° C. and 100 mm. of Hg pressure about 80% of the formic acid present is in the crossdimer state, about 5% is in the pure dimer state, and the remaining 15% would be monomer. A 50% formic acid mixture at 50° C. and 40 mm. of Hg pressure has 40% of the formic acid present in the crossdimer form, 31% in the pure dimer form, and 27% as monomer. This same mixture at 110 mm. of Hg pressure, however, has 50% of the formic acid as crossdimer, 34% as pure formic dimer, and 16% as monomer. This much larger increase in formic monomers going to crossdimer than to pure dimer is indicative of the greater tendency of acetic acid to form polymers than of formic acid under the same conditions.

For the determination of the equilibrium constants of crossdimerization, the ideal gas association theory is again used. Now there are five components in the gas which must be represented: the two species of acid monomer, the two species of acid dimer, and the crossdimer molecules. In addition, the assumption is made that the dimerization constant for each pure acid remains the same in the mixtures of acids at the same temperature. Since K'_A and K'_F, the equilibrium constants before extrapolating to zero pressure, are pressure-dependent, it is necessary to employ a value of these constants which is calculated at the same temperature and pressure of the mixture. This is accomplished by numerically curve-fitting the values of K'_A and K'_F against pressure at each temperature by means of a fourth-order polynomial in pressure. The values at the pressures of mixture are then recalculated from this least squares curve fitting.

Like the pure acid equilibrium constants, the crossdimer equilibrium constant, K'_{AF}, is also a function of pressure. Figure 3 shows the extrapolation of K'_{AF} to zero pressure. The extrapolated values of K_{AF} appear to be independent of concentration within the limits of error involved in the extrapolation. A plot of K_{AF} against $1/T$ gives a straight line, as shown in Figure 4. The line can be represented by the following equation:

$$\mathrm{Log}_{10} K_{AF} = \frac{3193}{T} - 7.475$$

From the slope of this line the heat of association of crossdimerization is −14.6 kcal. per mole. As expected, this value is intermediate of those calculated for the association of pure formic and acetic acids, −13.9 and −14.8 kcal. per mole, respectively.

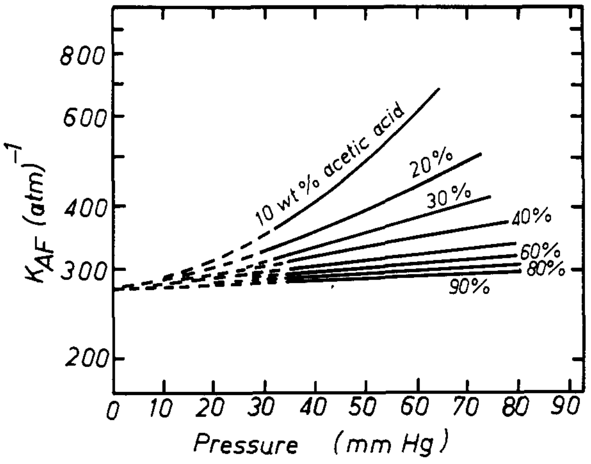

Figure 3. Variation of K_{AF} at 50° C.

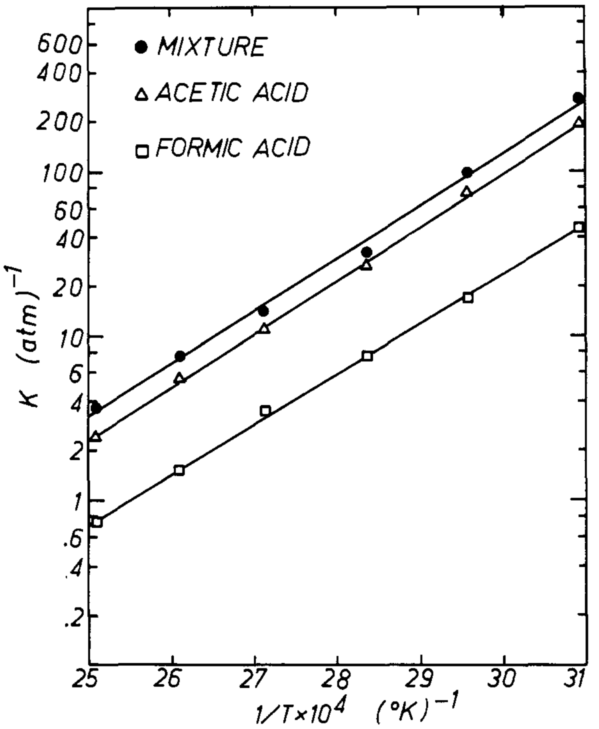

Figure 4. Temperature dependence of K

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