

The Densities and Compression Isotherms of Formic Acid-, Acetic Acid-, Propionic Acid-, and Isobutyric Acid-Water Mixtures

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The densities and compressions of formic acid-, acetic acid-, propionic acid-, and isobutyric acid-water mixtures were measured at pressures that were multiples of 500 atmospheres up to 2500 atmospheres at the three temperatures 25°C, 40°C, and 55°C. The mixtures have maximum density and minimum compression values at different compositions. As the pressure increases, the minimum compression and the maximum density shift to a composition containing more carboxylic acid, but the effect of temperature is the reverse. Values of the constants *B* and *C* of Tait's equation, the compressibilities at one atmosphere, and the excess compressibilities and excess molar volumes of the carboxylic acid-water mixtures were calculated. The values are compared with corresponding values for mixtures of water and other organic solvents. The effect of hydrogen bonding on the compression of liquids is discussed.

Only a few papers have been published on the compressions of carboxylic acids and their aqueous mixtures. Lanman and Mair¹ measured the compressions of acetic acid and three of its mixtures with water at pressures of 100–200 Mbar at 25°C, and Gibson² the compressions of acetic acid-water mixtures at 1000 bar at 25°C. Andersson³ determined the compressibility of formic acid at one atmosphere and 22.4°C, and Lutskii and Solońko⁴ the adiabatic compressibilities of ten carboxylic acids at one atmosphere and 20–150°C. In this work, the compressions of carboxylic acids and their mixtures with water were measured at several pressures from 1 to 2500 atmospheres at 25°C, 40°C, and 55°C.

EXPERIMENTAL

Formic acid (Merck, *puriss.*) was purified by crystallizing it five times from the melt. The melting point of the product was 7.8°C and its water content 0.5 wt. % as determined by Karl Fisher titration. Acetic acid (Fluka, *puriss.*) was dried by adding an amount of

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acetic anhydride equivalent to the water present and boiling the mixture for 24 h, after which the product was recrystallized twice from the melt. The purity of the product was controlled by NMR spectrometry. As determined by Karl Fisher titration, the water content was 0.005 wt %. The melting point was 16.6°C. Propionic acid (Fluka, *puriss.*) was boiled with a small quantity of potassium permanganate,⁶ distilled and crystallized two times from the melt. The water content of the product was found by Karl Fisher titration to be 0.06 %. The melting point was -22.2°C. As determined by GLC, using a Porapak Q column, 50 cm long, the acid was 99.9 % pure. Isobutyric acid (Fluka, *puriss.*) was used as received. Its water content determined by Karl Fisher titration was 0.02 %, and it was found 99.8 % pure by GLC, using the Porapak Q column.

A Heise bourdon pressure gauge was calibrated before use with calibrated weights.⁸ The compression measurements at 25°C were performed, as described earlier, in the apparatus shown in Fig. 1.⁷ For the density measurements at 40°C and 55°C, the piezo-

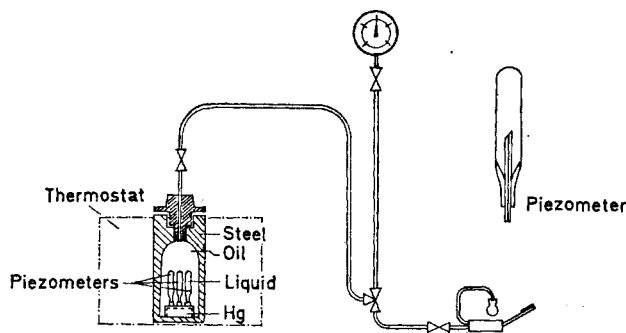


Fig. 1. The apparatus.

meters were held at the temperature in question for 20 min, cooled and weighed before and after filling them with solution. The compressions were measured in the same manner as at 25°C. The pressure cylinder and the oil to be added were held at a temperature slightly below the chosen temperature until the piezometers were put into the vessel in the pressure cylinder. The capillary ends of the three piezometers were placed in mercury, and the cylinder was filled with oil and closed, after which the pressure was increased slowly. The pressure in question was held for 1 h, after which it was decreased slowly. The piezometers were taken away and held at the temperature in question for 20 min. The piezometers were then cleaned externally with acetone, cooled and weighed.

The isothermal compressions of formic acid-water mixtures at 25°C were measured at pressures that were multiples of 500 atmospheres up to 2000 atmospheres. When an attempt was made to measure the compression of pure formic acid at 2500 atm at 25°C, the pressure vessel exploded and the piston was broken. Because of this, formic acid-water mixtures were not studied at 40°C and 55°C. Owing to the high melting point of acetic acid, the compressions of the acid were measured only up to 1000 atm at 25°C. The compressions at 40°C and 55°C were measured over the whole pressure range. The compressions of the propionic acid-water mixtures were measured up to 2500 atm at all three temperature. As isobutyric acid is only slightly soluble in water, only the compression values of the mixtures containing 0-20 and 80-100 % acid could be measured over the chosen ranges of pressure and temperature.

The compressions of the mixtures were calculated as before.⁷ The densities of mercury were taken to be 13.5335 g/ml at 25°C, 13.4967 g/ml at 40°C, and 13.4601 g/ml at 55°C.⁸ The compression values of mercury and glass were read from Andersson's tables.³ The values of the constant B in the integrated form of Tait's equation were determined

$$k = C \log_{10} \frac{B+p}{B+p^0} \quad (1)$$

by iteration on an IBM 360/30 computer, using the method of least squares, and the values of constant C were calculated from the obtained values of B by eqn. (2).⁸

$$C = \frac{\sum_i k_i \log \frac{B+p_i}{B+1}}{\sum_i \left(\log \frac{B+p_i}{B+1} \right)^2} \quad (2)$$

The obtained values of B and C were substituted in Tait's equation⁷

$$\beta = - \frac{(\partial V / \partial p)_T}{V^0} = \frac{C}{2.3026 (B+p)} \quad (3)$$

to evaluate the compressibility β . The excess volume compressibilities were calculated from the resulting values of the compressibility β , using the equation

$$\beta_{\phi^E} = \beta^M - \phi_1 \beta_1^0 - \phi_2 \beta_2^0 \quad (4)$$

in which the ϕ 's are the volume fractions of the components in the mixture,⁹ the superscript E denotes an excess quantity, M denotes the mixture, and o the pure component, and the subscripts 1 and 2 denote the two components of the mixture. The densities of the different mixtures were calculated from the compression values and were used to determine the parameters of the equation

$$\delta = \delta_{25}^c + a(t-25) + b(t-25)^2 \quad (5)$$

where t is the temperature ($^{\circ}\text{C}$), and a and b are constants. Coefficients of expansion were calculated from eqn. (6).¹⁰

$$\alpha = - \frac{1}{\delta} \left(\frac{\partial \delta}{\partial t} \right)_p \quad (6)$$

and thermal coefficients of pressure by substituting the values of α and β in the equation

$$\gamma = \left(\frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\beta} \quad (7)$$

The intrinsic pressure of a mixture

$$\pi = \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p = \pi_a + \pi_r \quad (8)$$

its attraction component

$$\pi_a = T \left(\frac{\partial p}{\partial T} \right)_V + B \quad (9)$$

and repulsion component

$$\pi_r = -(B+p) \quad (10)$$

were calculated as described by Gibson^{11,12} and Adams and Laidler.¹³

The compression values of the mixtures were calculated from a large number of compression values determined at increments of 10 wt % by graphical interpolation, and the values for the pure acids by extrapolation as before.⁷ Power series were fitted to the density values on an Elliot 760 computer, and from these equations, densities of the mixtures were recalculated at increments of 10 wt %.

The compression values of Pyrex glass and mercury that were used in this work, compression values calculated in this work, and Bridgman's compression values for pure water are shown in Table 1. Isothermal compressibility values of carboxylic acids interpolated and calculated from the data of Luts'kii and Soloňko⁴ and those obtained in this work are shown in Table 2. Considering the different methods of measurement, the

Table 1. The compression values $k_w(K)$ of water, determined in this study, and those $k_w(B)$ interpolated from the values given by Bridgman,³ the compressions of Pyrex glass (k_g) and mercury (k_{Hg}).³

| Pressure, atm | 10 ³ k | | | | | | | | | | | |
|------------------|-------------------|----------|-------|----------|----------|----------|-------|----------|----------|----------|-------|----------|
| | 25°C | | | | 40°C | | | | 55°C | | | |
| | $k_w(K)$ | $k_w(B)$ | k_g | k_{Hg} | $k_w(K)$ | $k_w(B)$ | k_g | k_{Hg} | $k_w(K)$ | $k_w(B)$ | k_g | k_{Hg} |
| 500 | 21.3 | 21.3 | 1.53 | 2.01 | 20.6 | 20.6 | 1.54 | 2.08 | 20.6 | 20.4 | 1.56 | 2.11 |
| 1000 | 39.4 | 39.3 | 3.08 | 4.01 | 38.5 | 38.4 | 3.09 | 4.07 | 38.4 | 38.0 | 3.10 | 4.15 |
| 1500 | 55.5 | 55.3 | 4.63 | 5.95 | 54.2 | 54.2 | 4.64 | 6.05 | 54.2 | 53.7 | 4.66 | 6.17 |
| 2000 | 69.8 | 69.9 | 6.17 | 7.86 | 68.4 | 68.5 | 6.19 | 8.00 | 68.3 | 68.0 | 6.23 | 8.16 |
| 2500 | 82.9 | 82.6 | 7.71 | 9.75 | 81.1 | 81.1 | 7.75 | 9.93 | 80.9 | 80.6 | 7.79 | 10.04 |

Table 2. Isothermal compressibility values of carboxylic acid – water mixtures at 1 atm.

| Acid | 25°C | | 40°C | | 55°C | |
|------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| | 10 ⁶ β | 10 ⁶ β | 10 ⁶ β | 10 ⁶ β | 10 ⁶ β | 10 ⁶ β |
| | This study | Lutskii ⁴ | This study | Lutskii ⁴ | This study | Lutskii ⁴ |
| Formic | 65.6 | 61.6 | | 68.0 | | 75.0 |
| Acetic | 93.0 | 95.8 | 102.6 | 105.7 | 115.0 | 117.5 |
| Propionic | 94.2 | 95.4 | 104.5 | 105.9 | 115.4 | 117.7 |
| Isobutyric | 104.4 | | 111.9 | | 123.8 | |

Table 3. Formic acid – water mixtures at 25°C. x_1 = mole fraction of water, k_{1000} = isothermal compression at 1000 atm, B and C = constants of Tait's equation, β = isothermic compressibility at 1 atm, β^E = excess volume compressibility, δ = density at 1 atm, and V^E = excess molar volume.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | 10 ⁶ β atm ⁻¹ | 10 ⁶ β^E atm ⁻¹ | δ g/ml | V^E ml/mol |
|-------------------------|--------|------------|-------------------|--------|----------------------------------------------|------------------------------------------------|------------------|-----------------|
| 100 | 1.0000 | 0.0394 | 2891 | 0.3061 | 45.97 | 0.00 | 0.9971 | 0.00 |
| 90 | 0.9583 | 0.0383 | 2857 | 0.2943 | 44.72 | -2.89 | 1.0215 | -0.12 |
| 80 | 0.9109 | 0.0378 | 2786 | 0.2847 | 44.36 | -4.96 | 1.0458 | -0.22 |
| 70 | 0.8563 | 0.0379 | 2705 | 0.2779 | 44.60 | -6.48 | 1.0692 | -0.31 |
| 60 | 0.7930 | 0.0384 | 2490 | 0.2623 | 45.73 | -7.18 | 1.0913 | -0.36 |
| 50 | 0.7187 | 0.0392 | 2323 | 0.2524 | 47.17 | -7.65 | 1.1143 | -0.41 |
| 40 | 0.6301 | 0.0402 | 2180 | 0.2448 | 48.74 | -8.06 | 1.1371 | -0.46 |
| 30 | 0.5226 | 0.0417 | 2045 | 0.2416 | 51.28 | -7.59 | 1.1586 | -0.46 |
| 20 | 0.3898 | 0.0437 | 1850 | 0.2315 | 54.32 | -6.69 | 1.1791 | -0.41 |
| 10 | 0.2211 | 0.0463 | 1629 | 0.2236 | 59.58 | -3.67 | 1.1988 | -0.31 |
| 0 | 0.0000 | 0.0500 | 1467 ^a | 0.2217 | 65.59 | 0.00 | 1.2136 | 0.00 |

^a Values at 22.4°C reported by Andersson³ are: $B = 1493$, $C = 0.2119$.

differences are not great. The compression values of the carboxylic acid-water mixtures at 1000 atm and the densities at 1 atm are presented in Tables 3-12. In addition, these tables contain values of the constants B and C of Tait's equation, with the aid of which compression values at different pressures can be calculated. The mean difference between the experimental and calculated compression values at 25°C is ± 0.0001 , or the same as the uncertainty of a compression measurement. The accuracies of the values at 40°C and 55°C are somewhat poorer; the mean differences between the experimental and calculated compression values at these temperatures are ± 0.003 . The compressibilities of the mixtures at 1 atm, the excess molar volume compressibilities, and the excess molar volumes are presented in Tables 3-12.

Table 4. Acetic acid-water mixtures at 25°C.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | $10^6 \beta$ atm ⁻¹ | $10^6 \beta^E$ atm ⁻¹ | δ g/ml | V^E ml/mol |
|-------------------------|--------|------------|------------|--------|-----------------------------------|-------------------------------------|------------------|-----------------|
| 100 | 1.0000 | 0.0394 | 2900 | 0.3065 | 45.88 | 0.00 | 0.9971 | 0.00 |
| 90 | 0.9677 | 0.0380 | 2858 | 0.2920 | 44.35 | - 6.05 | 1.0104 | -0.18 |
| 80 | 0.9302 | 0.0372 | 2700 | 0.2724 | 43.79 | -11.16 | 1.0233 | -0.36 |
| 70 | 0.8861 | 0.0375 | 2486 | 0.2557 | 44.64 | -14.92 | 1.0350 | -0.53 |
| 60 | 0.8333 | 0.0384 | 2255 | 0.2411 | 46.40 | -17.80 | 1.0450 | -0.71 |
| 50 | 0.7692 | 0.0398 | 1984 | 0.2251 | 49.24 | -19.65 | 1.0530 | -0.96 |
| 40 | 0.6896 | 0.0420 | 1752 | 0.2144 | 53.11 | -20.50 | 1.0596 | -1.01 |
| 30 | 0.5882 | 0.0446 | 1560 | 0.2076 | 57.75 | -20.63 | 1.0633 | -1.11 |
| 20 | 0.4545 | 0.0484 | 1365 | 0.2029 | 64.50 | -18.70 | 1.0645 | -1.14 |
| 10 | 0.2703 | 0.0536 | 1170 | 0.2002 | 74.24 | -13.81 | 1.0602 | -0.95 |
| 0 | 0.0000 | 0.0643 | 1000 | 0.2143 | 92.96 | 0.00 | 1.0434 | 0.00 |

Hayward¹⁴ stated that the so-called Tait's equation was not proposed by Tait, as is generally believed, and that the so-called "secant modulus" equation corresponds better to the one originally presented by Tait, and also represents compression values better. The results obtained in this work satisfy better the integrated form of Tait's equation, and therefore this form has been fitted to the compression values (Tables 3-12).

Table 5. Acetic acid-water mixtures at 40°C.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | $10^6 \beta$ atm ⁻¹ | $10^6 \beta^E$ atm ⁻¹ | δ g/ml | V^E ml/mol |
|-------------------------|--------|------------|------------|--------|-----------------------------------|-------------------------------------|------------------|-----------------|
| 100 | 1.0000 | 0.0385 | 3028 | 0.3108 | 44.55 | 0.00 | 0.9923 | 0.00 |
| 90 | 0.9677 | 0.0379 | 3053 | 0.3085 | 43.87 | - 6.24 | 1.0040 | -0.16 |
| 80 | 0.9302 | 0.0379 | 2931 | 0.2977 | 44.09 | -11.75 | 1.0154 | -0.33 |
| 70 | 0.8861 | 0.0386 | 2723 | 0.2846 | 45.37 | -16.03 | 1.0253 | -0.50 |
| 60 | 0.8333 | 0.0399 | 2421 | 0.2668 | 47.84 | -19.44 | 1.0338 | -0.67 |
| 50 | 0.7692 | 0.0419 | 2139 | 0.2522 | 51.17 | -21.73 | 1.0410 | -0.84 |
| 40 | 0.6896 | 0.0444 | 1914 | 0.2432 | 55.16 | -23.71 | 1.0461 | -0.99 |
| 30 | 0.5882 | 0.0475 | 1677 | 0.2341 | 60.57 | -24.02 | 1.0491 | -1.10 |
| 20 | 0.4545 | 0.0516 | 1447 | 0.2266 | 67.97 | -22.51 | 1.0491 | -1.13 |
| 10 | 0.2703 | 0.0576 | 1219 | 0.2218 | 78.96 | -17.54 | 1.0444 | -0.98 |
| 0 | 0.0000 | 0.0691 | 908 | 0.2147 | 102.55 | 0.00 | 1.0265 | 0.00 |

Table 6. Acetic acid-water mixtures at 55°C.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | $10^6\beta$ atm ⁻¹ | $10^6\beta^E$ atm ⁻¹ | δ g/ml | ν^E ml/mol |
|-------------------------|--------|------------|------------|--------|----------------------------------|------------------------------------|------------------|-------------------|
| 100 | 1.0000 | 0.0384 | 2946 | 0.3035 | 44.72 | 0.00 | 0.9860 | 0.00 |
| 90 | 0.9677 | 0.0384 | 2959 | 0.3044 | 44.66 | - 6.81 | 0.9961 | - 0.15 |
| 80 | 0.9302 | 0.0389 | 2792 | 0.2938 | 45.68 | -12.84 | 1.0061 | - 0.32 |
| 70 | 0.8861 | 0.0402 | 2521 | 0.2775 | 47.77 | -17.37 | 1.0150 | - 0.49 |
| 60 | 0.8333 | 0.0420 | 2226 | 0.2606 | 50.82 | -21.62 | 1.0225 | - 0.67 |
| 50 | 0.7692 | 0.0441 | 2015 | 0.2524 | 54.36 | -24.71 | 1.0282 | - 0.82 |
| 40 | 0.6896 | 0.0468 | 1825 | 0.2472 | 58.77 | -27.72 | 1.0233 | - 0.97 |
| 30 | 0.5882 | 0.0505 | 1656 | 0.2456 | 64.36 | -28.88 | 1.0347 | - 1.10 |
| 20 | 0.4545 | 0.0555 | 1353 | 0.2298 | 73.70 | -26.98 | 1.0340 | - 1.15 |
| 10 | 0.2703 | 0.0626 | 983 | 0.2044 | 90.21 | -17.47 | 1.0275 | - 0.96 |
| 0 | 0.0000 | 0.0747 | 796 | 0.2111 | 115.01 | 0.00 | 1.0095 | 0.00 |

Table 7. Propionic acid-water mixtures at 25°C.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | $10^6\beta$ atm ⁻¹ | $10^6\beta^E$ atm ⁻¹ | δ g/ml | ν^E ml/mol |
|-------------------------|--------|------------|------------|--------|----------------------------------|------------------------------------|------------------|-------------------|
| 100 | 1.0000 | 0.0394 | 2899 | 0.3069 | 45.95 | 0.00 | 0.9971 | 0.00 |
| 90 | 0.9737 | 0.0378 | 3031 | 0.3054 | 43.73 | - 7.08 | 1.0053 | - 0.17 |
| 80 | 0.9427 | 0.0373 | 2931 | 0.2931 | 43.38 | -12.38 | 1.0121 | - 0.36 |
| 70 | 0.9056 | 0.0380 | 2665 | 0.2746 | 44.73 | -15.78 | 1.0173 | - 0.53 |
| 60 | 0.8605 | 0.0396 | 2319 | 0.2542 | 47.57 | -17.78 | 1.0204 | - 0.69 |
| 50 | 0.8044 | 0.0415 | 2062 | 0.2416 | 50.85 | -19.33 | 1.0220 | - 0.85 |
| 40 | 0.7327 | 0.0438 | 1825 | 0.2313 | 55.00 | -20.00 | 1.0220 | - 0.99 |
| 30 | 0.6380 | 0.0470 | 1562 | 0.2190 | 60.85 | -18.95 | 1.0195 | - 1.10 |
| 20 | 0.5069 | 0.0508 | 1380 | 0.2148 | 67.54 | -17.06 | 1.0148 | - 1.15 |
| 10 | 0.3136 | 0.0557 | 1176 | 0.2092 | 77.18 | -12.22 | 1.0055 | - 0.95 |
| 0 | 0.0000 | 0.0644 | 961 | 0.2086 | 94.18 | 0.00 | 0.9878 | 0.00 |

Table 8. Propionic acid-water mixtures at 40°C.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | $10^6\beta$ atm ⁻¹ | $10^6\beta^E$ atm ⁻¹ | δ g/ml | ν^E ml/mol |
|-------------------------|--------|------------|------------|--------|----------------------------------|------------------------------------|------------------|-------------------|
| 100 | 1.0000 | 0.0285 | 3028 | 0.3108 | 44.55 | 0.00 | 0.9923 | 0.00 |
| 90 | 0.9737 | 0.0375 | 3204 | 0.3186 | 43.16 | - 7.43 | 0.9988 | - 0.17 |
| 80 | 0.9427 | 0.0379 | 2997 | 0.3033 | 43.93 | -12.69 | 1.0041 | - 0.34 |
| 70 | 0.9056 | 0.0392 | 2638 | 0.2808 | 46.20 | -16.46 | 1.0076 | - 0.51 |
| 60 | 0.8605 | 0.0411 | 2230 | 0.2558 | 49.79 | -18.88 | 1.0093 | - 0.66 |
| 50 | 0.8044 | 0.0434 | 1869 | 0.2342 | 54.37 | -20.37 | 1.0098 | - 0.81 |
| 40 | 0.7327 | 0.0462 | 1531 | 0.2134 | 60.47 | -20.17 | 1.0087 | - 0.96 |
| 30 | 0.6380 | 0.0496 | 1271 | 0.1987 | 67.82 | -18.81 | 1.0057 | - 1.09 |
| 20 | 0.5069 | 0.0541 | 1061 | 0.1889 | 77.23 | -15.36 | 1.0002 | - 1.14 |
| 10 | 0.3136 | 0.0601 | 896 | 0.1858 | 89.93 | - 8.99 | 0.9899 | - 0.95 |
| 0 | 0.0000 | 0.0696 | 869 | 0.2094 | 104.49 | 0.00 | 0.9717 | 0.00 |

Table 9. Propionic acid – water mixtures at 55°C.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | $10^6\beta$ atm ⁻¹ | $10^6\beta^E$ atm ⁻¹ | δ g/ml | V^E ml/mol |
|-------------------------|--------|------------|------------|--------|----------------------------------|------------------------------------|------------------|-----------------|
| 100 | 1.0000 | 0.0384 | 2964 | 0.3049 | 44.65 | 0.00 | 0.9860 | 0.00 |
| 90 | 0.9737 | 0.0382 | 3051 | 0.3118 | 44.36 | - 7.42 | 0.9912 | - 0.17 |
| 80 | 0.9427 | 0.0399 | 2788 | 0.2944 | 45.66 | - 13.24 | 0.9951 | - 0.33 |
| 70 | 0.9056 | 0.0403 | 2487 | 0.2771 | 48.31 | - 17.64 | 0.9971 | - 0.49 |
| 60 | 0.8605 | 0.0430 | 2146 | 0.2600 | 52.59 | - 20.52 | 0.9981 | - 0.65 |
| 50 | 0.8044 | 0.0459 | 1889 | 0.2494 | 57.31 | - 22.87 | 0.9976 | - 0.81 |
| 40 | 0.7327 | 0.0492 | 1732 | 0.2473 | 61.96 | - 25.28 | 0.9951 | - 0.95 |
| 30 | 0.6380 | 0.0533 | 1344 | 0.2209 | 71.33 | - 22.98 | 0.9915 | - 1.08 |
| 20 | 0.5069 | 0.0580 | 1167 | 0.2162 | 80.39 | - 20.95 | 0.9852 | - 1.14 |
| 10 | 0.3136 | 0.0643 | 1035 | 0.2186 | 91.64 | - 16.72 | 0.9744 | - 0.96 |
| 0 | 0.0000 | 0.0748 | 797 | 0.2120 | 115.38 | 0.00 | 0.9556 | 0.00 |

Table 10. Isobutyric acid – water mixtures at 25°C.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | $10^6\beta$ atm ⁻¹ | $10^6\beta^E$ atm ⁻¹ | δ g/ml | V^E ml/mol |
|-------------------------|--------|------------|------------|--------|----------------------------------|------------------------------------|------------------|-----------------|
| 100 | 1.0000 | 0.0394 | 2891 | 0.3061 | 45.97 | 0.00 | 0.9971 | 0.00 |
| 90 | 0.9778 | 0.0379 | 2939 | 0.2990 | 44.17 | - 7.94 | 1.0005 | - 0.18 |
| 80 | 0.9514 | 0.0387 | 2592 | 0.2747 | 46.01 | - 12.17 | 1.0003 | - 0.31 |
| 20 | 0.5501 | 0.0566 | 1109 | 0.2002 | 78.33 | - 14.88 | 0.9709 | - 0.94 |
| 10 | 0.3521 | 0.0610 | 959 | 0.1955 | 88.44 | - 10.39 | 0.9599 | - 0.82 |
| 0 | 0.0000 | 0.0684 | 804 | 0.1935 | 104.39 | 0.00 | 0.9430 | 0.00 |

Table 11. Isobutyric acid – water mixtures at 40°C.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | $10^6\beta$ atm ⁻¹ | $10^6\beta^E$ atm ⁻¹ | δ g/ml | V^E ml/mol |
|-------------------------|--------|------------|------------|--------|----------------------------------|------------------------------------|------------------|-----------------|
| 100 | 1.0000 | 0.0385 | 3075 | 0.3150 | 44.47 | 0.00 | 0.9923 | 0.00 |
| 90 | 0.9778 | 0.0381 | 3037 | 0.3072 | 43.91 | - 7.71 | 0.9940 | - 0.17 |
| 80 | 0.9514 | 0.0395 | 2605 | 0.2798 | 46.63 | - 12.05 | 0.9925 | - 0.30 |
| 20 | 0.5501 | 0.0586 | 1097 | 0.2088 | 82.59 | - 16.50 | 0.9576 | - 0.96 |
| 10 | 0.3521 | 0.0639 | 936 | 0.2037 | 94.41 | - 11.11 | 0.9454 | - 0.82 |
| 0 | 0.0000 | 0.0719 | 784 | 0.2022 | 111.86 | 0.00 | 0.9279 | 0.00 |

Table 12. Isobutyric acid – water mixtures at 55°C.

| H ₂ O wt% | x_1 | k_{1000} | B atm | C | $10^6\beta$ atm ⁻¹ | $10^6\beta^E$ atm ⁻¹ | δ g/ml | V^E ml/mol |
|-------------------------|--------|------------|------------|--------|----------------------------------|------------------------------------|------------------|-----------------|
| 100 | 1.0000 | 0.0384 | 3002 | 0.3083 | 44.59 | 0.00 | 0.9860 | 0.00 |
| 90 | 0.9778 | 0.0382 | 2829 | 0.2929 | 44.95 | - 8.12 | 0.9865 | - 0.17 |
| 80 | 0.9514 | 0.0406 | 2377 | 0.2672 | 48.80 | - 12.63 | 0.9834 | - 0.29 |
| 20 | 0.5501 | 0.0623 | 1033 | 0.2121 | 89.08 | - 19.85 | 0.9441 | - 0.95 |
| 10 | 0.3521 | 0.0685 | 854 | 0.2045 | 103.87 | - 12.56 | 0.9307 | - 0.83 |
| 0 | 0.0000 | 0.0772 | 718 | 0.2050 | 123.82 | 0.00 | 0.9126 | 0.00 |

RESULTS AND DISCUSSION

A. The structure of water. Many model structures have been proposed for liquid water.¹⁵ Most likely, many structures exist simultaneously in liquid water, and hence no exact picture of the structure can be given.¹⁵ According to Ginell,¹⁶ there are both large and small particles in an associating liquid. Corresponding to these, there are holes surrounded by molecules and holes enclosed by clusters. The increase of the free hole volume with rising temperature arises partly from a decrease in the degree of association, whereupon the cluster holes become free holes. According to Ginell, an increase in pressure reduces the average molecular weights of the associated aggregates, and the decrease in volume arises mostly from the decrease in the free hole volume.

Water has its maximum density at about 4°C, but the compression of water is a minimum between 40 and 55°C, according to the results obtained in this work (Fig. 2). Smith and Lawson¹⁷ stated that the compression is a minimum at 45°C. Thus the ability of the structure of water to withstand compression is not greatest when the density is a maximum. It has been reported that the free volume of the particles¹⁶ has to increase, so that the small particles can enter the holes formed by the big particles as effectively as possible, in order that the structure can withstand compression. An increase in pressure shifts the compression minimum to a higher temperature.¹⁷ It has recently been observed that also other characteristics of water change greatly in the range between 40 and 50°C.¹⁵ Nývlt and Erdős¹⁰ found that the logarithm of the adiabatic compressibility of water is a linear function of temperature up to 35°C, above which point the slope of the line changes.

B. The compressibility of carboxylic acid-water mixtures. Relatively strong attractive forces act between molecules of formic acid, which are associated mainly into chains.¹⁸ Because of the dense structure of the pure acid, its com-

Table 13. Mol fractions of water, X_{H_2O} , in carboxylic acid-water mixtures at which compressions, densities, excess volume compressibilities, and excess molar volumes have extreme values at a pressure of one atmosphere.

| Temperature | Acid | Compression min. | Density max. | β_ϕ^E max. | γ^E max. |
|-------------|----------------------------------------|------------------|--------------|---------------------|-----------------|
| 25°C | HCOOH | 0.89 | | 0.61 | 0.59 |
| | CH ₃ COOH | 0.92 | 0.49 | 0.62 | 0.50 |
| | CH ₃ CH ₂ COOH | 0.94 | 0.77 | 0.76 | 0.57 |
| | (CH ₃) ₂ CHCOOH | 0.98 | 0.96 | 0.55 | 0.50 |
| 40°C | HCOOH | | | | |
| | CH ₃ COOH | 0.95 | 0.52 | 0.63 | 0.51 |
| | CH ₃ CH ₂ COOH | 0.97 | 0.82 | 0.78 | 0.57 |
| | (CH ₃) ₂ CHCOOH | 0.99 | 0.97 | 0.63 | 0.50 |
| 55°C | HCOOH | | | | |
| | CH ₃ COOH | 0.98 | 0.55 | 0.60 | 0.50 |
| | CH ₃ CH ₂ COOH | 0.98 | 0.85 | 0.73 | 0.55 |
| | (CH ₃) ₂ CHCOOH | 0.99 | 0.98 | 0.66 | 0.50 |

pression is relatively low.⁷ The next homologs of the series are associated mainly to dimers.¹⁹ As the attractive forces between dimers are small, the compression of acetic and higher acids is correspondingly greater than that of formic acid. The compressions of acetic and propionic acids are only slightly smaller than the compression of benzene.^{12,20} The compression of isobutyric acid is somewhat larger than that of benzene. The compressions of all carboxylic acids increase with temperature. The compression values obtained in this study are shown in Tables 3–12. The calculated compressibilities at 1 atm can be compared with those interpolated from the values of Lutskii and Sołóńko in Table 2.⁴

As has been noted before,⁷ the compression minima and density maxima of the carboxylic acid–water mixtures are in different composition ranges (Table 13). Some investigators have tried to clarify the reasons for the minimum compressions of aqueous mixtures. Gibson²¹ found that a small addition of methanol or resorcinol first increases the degree of association of water in the mixture, and reduces the compression. Because organic compounds are usually more compressible than water, the compression increases finally when more organic compound is added to water. Consequently, the compression is a minimum at a certain composition.

Jacobson²² determined the adiabatic compressibilities of mixtures of water and organic solvents, and came to the conclusion that some of the hydrogen bonds are broken when an organic solvent is added to water. The water molecules become more tightly packed, and the result is a reduction of the compression to a minimum value. From mostly kinetic and thermodynamic data, Hyne²³ concluded that the results of many investigators show that the addition of another component at first “buttresses” the structure of water.

Table 14. Mol fractions of water in alcohol–water mixtures, the compression of which is a minimum at 25°C and 1000 atm.²⁴

| Alcohol | Methanol | Ethanol | Propanol | Acetone |
|-----------------------|----------|---------|----------|---------|
| Mol fraction of water | 0.875 | 0.91 | 0.94 | 0.94 |

The compression minima in carboxylic acid–water mixtures shift to mixtures containing increasing proportions of water in the order formic acid, acetic acid, propionic acid, and isobutyric acid (Table 13 and Fig. 3). The compression curve for mixtures of water and isobutyric acid has its minimum at the lowest water content, but the minimum is almost as deep as that in the curve for formic acid–water mixtures.

The maximum densities of carboxylic acid–water mixtures, except formic acid–water mixtures, shift to compositions containing more water in the same order as the compression minima, *viz.* acetic acid, propionic acid, and isobutyric acid (Fig. 4).

With increasing pressure, the mixtures of minimum compression and also maximum density contain more carboxylic acid (Figs. 5 and 6). When the temperature rises, the compression minima and the density maxima shift to

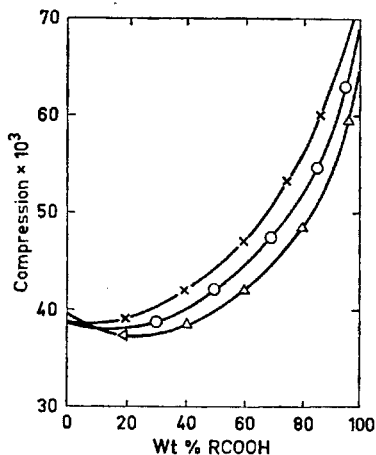


Fig. 2. Compressions of acetic acid-water mixtures. Δ , values of 10^3k at 1000 atm and 25°C. \circ , values of 10^3k at 1000 atm and 40°C. \times , values of 10^3k at 1000 atm and 55°C.

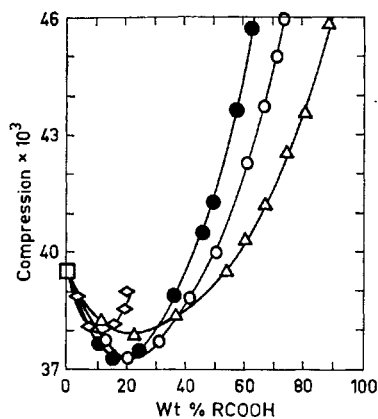


Fig. 3. Compressions of carboxylic acid-water mixtures at 1000 atm and 25°C. Δ , values of 10^3k at 1000 atm and 25°C for formic acid-water mixtures. \circ , values of 10^3k at 1000 atm and 25°C for acetic acid-water mixtures. \bullet , values of 10^3k at 1000 atm and 25°C for propionic acid-water mixtures. \diamond , values of 10^3k at 1000 atm and 25°C for isobutyric acid-water mixtures.

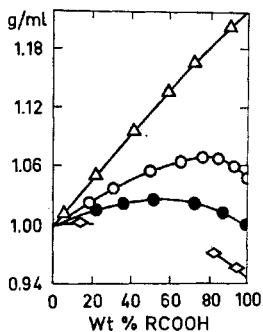


Fig. 4. Densities of carboxylic acid-water mixtures at 1 atm and 25°C. Δ , formic acid-water mixtures. \circ , acetic acid-water mixtures. \bullet , propionic acid-water mixtures. \diamond , isobutyric acid-water mixtures.

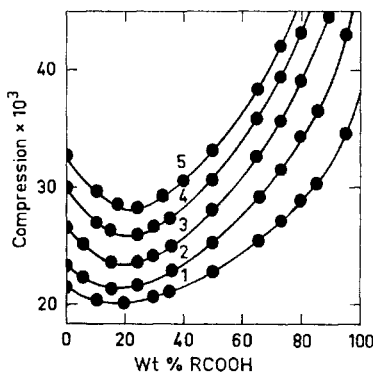


Fig. 5. Compressions of propionic acid-water mixtures. 1. Values of 10^3k at 500 atm and 25°C. 2. Values of 10^3k-16 at 1000 atm and 25°C. 3. Values of 10^3k-29 at 1500 atm and 25°C. 4. Values of 10^3k-40 at 2000 atm and 25°C. 5. Values of 10^3k-50 at 2500 atm and 25°C.

carboxylic acid–water mixtures that contain more water (Tables 3–12 and Fig. 2). The compression minimum becomes shallower with rising temperature. Thus temperature seems to have an effect opposite to that of pressure on the location and depth of the compression minimum.

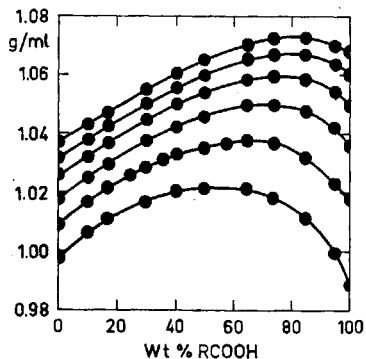


Fig. 6. Densities of propionic acid–water mixtures. 1. Values of δ at 1 atm and 25°C. 2. Values of $\delta - 0.01$ at 500 atm and 25°C. 3. Values of $\delta - 0.02$ at 1000 atm and 25°C. 4. Values of $\delta - 0.03$ at 1500 atm and 25°C. 5. Values of $\delta - 0.04$ at 2000 atm and 25°C. 6. Values of $\delta - 0.05$ at 2500 atm and 25°C.

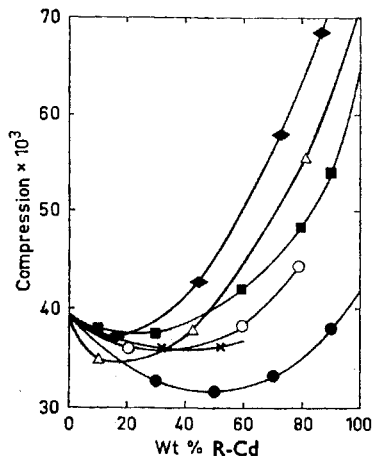


Fig. 7. Compressions of aprotic solvent–water mixtures, acetic acid–water mixtures, and ethanol–water mixtures. \blacklozenge , values of 10^3k for acetone–water mixtures at 1000 atm and 25°C. Data of Newitt.²⁴ \circ , values of $10^3k - 5.8$ for dioxane–water mixtures at 1144 atm and 25°C. Data of Korpela.⁹ \bullet , values of 10^3k for *N*-methylpyrrolidone–water mixtures at 1000 atm and 25°C. Data of Korpela.⁷ \times , values of 10^3k for dimethyl sulphoxide–water mixtures at 1000 atm and 55°C. Unpublished data of the present writer. \blacksquare , values of 10^3k for acetic acid–water mixtures at 1000 atm and 25°C (Table 4). \triangle , values of $10^3k - 2.2$ for ethanol–water mixtures. Data of Stutchbury.²⁵

Minimum compressions and maximum densities were analyzed above. They could be analyzed also by studying the deviations from the ideal values for the mixtures. Isothermal compressibility is generally considered to be highly dependent on the volume of the compressible liquid. So Hamann⁹ believes that the excess compressibilities expressed in terms of volume fractions of the components describe the behavior of liquids best. Excess compressibility values and also the excess molar volumes for carboxylic acid–water mixtures are presented in Tables 3–12. In Table 13 are given the minimum values of the quantities β^E and V^E . Like the extreme compression and density values, the extreme values of the excess molecular quantities occur in different com-

position ranges, although the differences between the extreme values are not great. The effects of pressure and temperatures are small, and the values of β^E are not accurate enough for an evaluation of these effects. Compressibility values calculated from the constants B and C of the so-called Tait's equation were used to calculate the values of β^E . It is not, however, possible to calculate accurate values of constants B and C from compression values measured to four decimals, as the values of the constants for water (Tables 3–12) show.

C. The compressibilities of mixtures of water and other organic compounds. Newitt²⁴ measured the compressions of water–alcohol and water–acetone mixtures, and noted that the positions and forms of the minima differ for these systems. Mixture compositions corresponding to minimum compressions are presented in Table 14. The steric effects of the substituents of an organic compound can be seen in the compression values for aqueous mixtures of isopropyl alcohol and tertiary butyl alcohol, presented by Stutchbury.²⁵

The compressions of mixtures of water and polar aprotic solvents vary greatly. Fig. 7 shows compression values for aqueous mixtures of dioxane,⁶ *N*-methylpyrrolidone,⁷ and acetone,²⁴ and for aqueous mixtures of the protic solvents acetic acid and ethanol at 25°C.²⁵ Also compression values of dimethyl sulfoxide–water mixtures at 55°C, determined by this writer, are given. It will be noted that the locations of the compression minimum differ in the aprotic solvent–water mixtures from those in the protic solvent–water mixtures.

D. The constants of Tait's equation. Attempts have been made to determine the meaning of the constants B and C of Tait's equation. Neece and Squire²⁶ derived expressions for the constants by means of the constants of the so-called Percus–Yevick and Mie equations. Constant B was found to change more than constant C when the temperature was changed, and to vary to a different extent with different substances. Constant B is determined by both attractive and repulsive forces between the molecules in a solvent mixture.

Ginell¹⁶ thought that the constant B represents the so-called excluded volume of the large molecular associates, into which the small particles cannot penetrate until the temperature expands the volume of these associates. Then B begins to decrease, becomes negative at a certain temperature, and assumes the value $-p$ at the so-called critical point. Constant C was concluded by Ginell to be a measure of the volume change of the holes in the liquid.

Gibson^{11,12} proposed that constant B , or more accurately the quantity $-(B+p)$, represents the repulsive forces π_r between molecules. Furthermore, he evaluated the quantity π_a , which is a measure of the attractive forces in the liquid. The sum of these π ($=\pi_a+\pi_r$) is the internal pressure of the liquid. He studied the variation of this quantity with pressure, temperature and molar volume. Gibson found that the plot of the internal pressure π of liquid water against the molar volume is a curve whose slope is negative at low temperatures and becomes positive when the temperature rises. Furthermore, the internal pressure increases with temperature. The same observations were made in this work. The slope of the plot of the internal pressure against molar volume changed between 40 and 55°C. The values of the internal pressure obtained for the pure carboxylic acids are not accurate enough for any reliable conclusions.

The data for the carboxylic acid – water mixtures show that the value of π is somewhat greater in the mixtures containing 80 % water than in water, and is a maximum in mixtures containing 40 – 60 % water. The internal pressure must hence be related to the deviations of the mixtures from the ideal behavior, because also β^E deviates most from the ideal value in the composition ranges mentioned (Table 13). The repulsive pressure $-(B+p)$ of pure water has an extreme value between 40 and 55°C, and, moreover, in carboxylic acid – water mixtures, the extreme value is in the same composition range as the minimum compression, although the compositions are not identical.

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REFERENCES

1. Lanman, E. H. and Mair, B. J. *J. Am. Chem. Soc.* **56** (1934) 390.
2. Gibson, R. E. *J. Am. Chem. Soc.* **57** (1935) 284.
3. Andersson, G. R. *Arkiv Kemi* **20** (1963) 513.
4. Lutskii, A. E., and Soloňko, V. N. *Zh. Fiz. Khim.* **38** (1964) 1421.
5. Bousfield, W. R. and Lowry, T. M. *J. Chem. Soc.* **99** (1911) 1432.
6. Korpela, J. and Koskikallio, J. *Suomen Kemistilehti B* **39** (1966) 165.
7. Korpela, J. and Virtanen, P. O. I. *Suomen Kemistilehti B* **40** (1967) 316.
8. Lange, N. A. *Handbook of Chemistry*, McGraw, New York 1961, p. 1188.
9. Hamann, S. D. *Physico-Chemical Effects of Pressure*, Butterworths, London 1957.
10. Nývlt, J. und Erdős, E. *Coll. Czech. Chem. Commun.* **26** (1961) 485, 500.
11. Gibson, R. E. and Kincaid, J. F. *J. Am. Chem. Soc.* **60** (1938) 511.
12. Gibson, R. E. and Loeffler, O. H. *J. Am. Chem. Soc.* **61** (1939) 2515, 2877; **63** (1941) 898.
13. Adams, W. A. and Laidler, K. J. *Can. J. Chem.* **45** (1967) 123.
14. Hayward, A. T. *J. Brit. J. Appl. Phys.* **18** (1967) 965.
15. Scott, A. F. *Survey of Progress in Chemistry*, Academic, New York 1968, Vol. 4, pp. 1 – 43.
16. Ginell, R. *J. Chem. Phys.* **34** (1961) 1249, 2174; **35** (1961) 1776.
17. Smith, A. H. and Lawson, A. W. *J. Chem. Phys.* **22** (1954) 351.
18. Chapman, D. *J. Chem. Soc.* **1956** 225.
19. Reeves, L. W. *Trans. Faraday Soc.* **55** (1959) 1684.
20. Cutler, W. G., McMickle, R. H., Webb, W. and Schiessler, R. W. *J. Chem. Phys.* **29** (1958) 727.
21. Gibson, R. E. *J. Am. Chem. Soc.* **57** (1935) 1551.
22. Jacobson, E. *Arkiv Kemi* **11** (1950) 177.
23. Hyne, J. B. *Discussions Faraday Soc.* **43** (1967) 144.
24. Newitt, D. M. and Weale, K. E. *J. Chem. Soc.* **1951** 3092.
25. Stutchbury, J. E. *Australian J. Chem.* **9** (1956) 536.
26. Neece, G. A. and Squire, D. R. *J. Phys. Chem.* **72** (1968) 128.

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