

Experimental Results from the
Design Institute for
Physical Property Data
I: Phase Equilibria

1985



Experimental Results from the Design Institute for Physical Property Data I: Phase Equilibria

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FOREWORD

Valuable data on phase equilibria of industrially important systems have been gathered to date under the auspices of the Mixture Properties Project (Project 805) of the AIChE Design Institute for Physical Property Data (DIPPR). Reports on the experimental procedures and the data gathered on forty systems are presented in this volume. These systems were selected for study by DIPPR mainly because the data are needed either for industrial design or for filling gaps in the binary-interaction matrices of generalized correlations.

The systems studied reflect the wide interests of the member organizations. In spite of the variety, all companies have common interests among which are pollution abatement and energy savings. The binary system water/acetic acid was considered so important by eight companies that a separate project (Project 804) and Steering Committee were devoted to its study.

This Symposium is the result of the efforts of the Steering Committee members for these two projects. Their contributions in proposing systems to study, coordinating the research, and reviewing the data and correlations is acknowledged herein. The contributions of those listed below are greatly appreciated.

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**Summary of Data Reported
In the First AIChE Symposium Series on DIPPR Experimental Data**

Year	Project	Investigators	Systems
1980	804	J. R. Freeman and G. M. Wilson (Wiltec Research Co.)	Acetic Acid + Water
1980	804	J. R. Freeman and G. M. Wilson (Wiltec Research Co.)	Acetic Acid + Water
1980	805/80A	P. C. Gillespie, J. R. Cunningham and G. M. Wilson (Wiltec Research Co.)	Ethylene Oxide + Water
1980	805/80A	P. C. Gillespie, R. Cunningham and G. M. Wilson (Wiltec Research Co.)	Hydrogen Fluoride + Hydrogen Chloride
1980	805/80A	P. C. Gillespie, J. R. Cunningham and G. M. Wilson (Wiltec Research Co.)	Hydrogen Chloride + Vinyl Chloride Hydrogen Chloride + Phosgene
1980	805/80A	P. C. Gillespie, J. R. Cunningham and G. M. Wilson (Wiltec Research Co.)	Vinyl Chloride + Acetone Vinyl Chloride + n-Hexane Vinyl Chloride + Water
1981	805/81B	David H. Krevor, Stefan O. Maixner and John M. Prausnitz (University of California, Berkeley)	Aniline + m-Cresol Ethyl Propionate + Propanoic Acid
1981	805/81C	Ronald W. Rousseau (NC State University)	Methanol + Methyl Mercaptan
1981	805/81D	Edwin J. Kolodziej, Zhang-Li Jin, Robert A. Greenkorn and Kwang-Chu Chao (Purdue University)	Propylene Oxide + 1,2-Dichloropropane Propylene Oxide + t-Butanol
1981	805/81D	Hwayong Kim, Ho-Mu Lin and Kwang-Chu Chao (Purdue University)	Carbon Dioxide + Phenyl Octane Carbon Dioxide + 1-Hexadecene
1981	805/81D	Zhang-Li Jin, Ho-Mu Lin and Kwang-Chu Chao (Purdue University)	Propylene + Propylene Oxide
1981	805/81D	Hwayong Kim, Ho-Mu Lin and Kwang-Chu Chao (Purdue University)	Carbon Dioxide + n-Propylcyclohexane Carbon Dioxide + n-Octadecane
1982	805/82B	G. Radnai, S. Bottini, P. Rasmussen and A. Fredenslund (Technical University of Denmark, Denmark)	Propyl Bromide + Toluene + p-Xylene + Propyl Acetate + Ethyl Propionate + Acetic Acid + Propionic Acid + Ethanol + 1-Propanol Methanol + Propyl Bromide + Butyl Bromide

Year	Project	Investigators	Systems
1982	805/82B	Jurgen Gmehling (University of Dortmund, Federal Republic of Germany)	Ethanol + Dibutyl Ether Styrene + Aniline Toluene + o-Methylaniline
1982	805/82C	Fu-Juan Hsu, Jason M. Lazar Caroline E. Engelhardt, Marcia B. Tapper, Carolyn S. Birnbaum David Zudkevitch and Vojtech Fried (Brooklyn College, City University of New York)	n-Butanal + Toluene
1982	805/82C	Marcia B. Tapper, Caroline E. Engelhardt, Jason M. Lazar, Barry A. Schechter and Vojtech Fried (Brooklyn College, City University of New York)	n-Butanal + Water
1982	805/82C	Marcia B. Tapper, Jason M Lazar, Caroline E. Engelhardt, Barry A. Schechter and Vojtech Fried (Brooklyn College, City University of New York)	Water + Dibutyl Ether
1982	805/82D	Hwayong King, Ho-Mu Lin and Kwang-Chu Chao (Purdue University)	Propane + n-Butyraldehyde
1982	805/82D	Hwayong Kim, Cuong M. Dinh, William A. Leet, Ho-Mu Lin and Kwang-Chu Chao (Purdue University)	Carbond Dioxide + Diethylamine + Water
1982	805/82D	Zhang-Li Jin, Ho-Mu Lin Robert A. Greenkorn and Kwang-Chu Chao (Purdue University)	Methylene Chloride + Ethanol
1982	805/82D	Zhang-Li Jin, Ho-Mu Lin, Robert A. Greenkorn and Kwang-Chu Chao (Purdue University)	t-Butyl Methyl Ether + n-Hexane t-Butyl Methyl Ether + Benzene
1982	805/82D	Zhang-Li Jin, Ho-Mu Lin, Robert A. Greenkorn and Kwang-Chu Chao (Purdue University)	Propylene Oxide + Methyl Acetate

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HIGH TEMPERATURE PVT PROPERTIES OF ACETIC ACID/WATER MIXTURES

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PVT measurements of acetic acid/water mixtures in the vapor region have been measured at the four isotherms, 100, 140, 190, and 230° C. An Inconel-600 cell was used for the two high temperature measurements and a glass cell was used for the two low temperature measurements.

A modified Van der Waals equation of state was used to calculate fugacity coefficients and vapor phase compressibility factors. Strong deviations from ideal behavior were observed due to the formation of acetic acid dimers in the vapor phase. Derived dimerization constants are in good agreement with literature values when physical interactions are calculated from an equation-of-state based on monomer properties similar to methyl formate and dimer properties similar to p-xylene. No chemical interaction was found between water and acetic acid in the vapor phase.

This work is part of an on-going research effort supported by DIPPR to collect and measure physical property data.

Acetic acid and water are encountered in many industrial process streams at elevated temperatures and pressures. Adequate correlations for predicting the properties of these streams require a knowledge of the PVT behavior of these components. In particular, the PVT behavior of this system is required in order to thermodynamically correlate the vapor-liquid equilibrium behavior of mixtures containing both acetic acid and water. At saturated conditions, acetic acid strongly dimerizes in the vapor phase. This effect has been studied by a number of investigators at low pressures as follows:

<u>Authors</u>	<u>Temp. Range, °C</u>	<u>Pressure Range, psia</u>
Barton & Hsu (1)	50 to 125	0.6 to 13.5
Fenton & Garner (2)	185 to 230	2.3 to 5.6
Johnson & Nash (3)	80 to 200	3.3 to 21.9
Levy et al (4)	90 to 120	7.2 to 12.9
McDougall (5)	25 to 40	0.1 to 0.5
Nerst and Von Wartenberg (6)	40 to 200	7.7 to 29
Ritter & Simmons (7)	50 to 207	0.85 to 15.7
Taylor (8)	50 to 150	0.25 to 2.0

All of these authors have concentrated on measuring data at low pressures in order to avoid nonideality corrections necessary at higher pressures in calculating the true thermodynamic equilibrium constant. Unfortunately, these low-pressure data do not cover commercial conditions of interest which may involve saturation pressures as high as 200 psia (1379 kPa) and perhaps even higher. Questions not answered by the low pressure data include the following:

1. What corrections must be applied at high pressures to correct for non-ideal behavior besides vapor phase dimerization?
2. Does acetic acid interact at high pressure to form associated complexes with other vapor components such as water?

In order to answer these questions, PVT measurements have been made on acetic acid/water mixtures at temperatures from 100°C to 230°C (373 K to 503 K) and at pressures up to saturation conditions. The measurement apparatus and results of this study are given in subsequent sections of this paper.

MEASUREMENT APPARATUS

The problem of measuring PVT data on acetic/water mixtures at high temperatures and pressures is complicated by the fact that these mixtures seriously corrode most metals and alloys. This one fact probably explains why no one has previously measured high-pressure PVT data on this system. Glass equipment which does not corrode can be used at low pressures, so this explains the existence of several studies done at low pressures. Zirconium was initially considered as the construction material for this project because of its resistance to corrosion by acetic acid, but because of its mechanical properties it would not withstand high pressures. Its use would therefore have required the fabrication of a zirconium liner to go inside a higher strength material such as stainless steel. The cost of such construction would have exceeded the funds budgeted for the entire project, so a cell was constructed of Inconel-600 instead. Inconel-600 does corrode when exposed to liquid mixtures of acetic acid and water, but only minor corrosion appears to occur when exposed to vapor mixtures.

The apparatus used for these measurements is shown schematically in Figure 1. It consists of a 12-liter (0.012m^3) Inconel cell which was rocked manually in order to achieve mixing and thermal equilibrium. Temperature gradients were also reduced by conduction along the heavy cell wall which was insulated from the ambient air.

In actual operation, the cell was first evacuated by means of the cell evacuation system shown in Figure 1. This was done at the desired temperature of measurement in order to remove the last traces of water and acetic acid from a previous run. After evacuation, accurately measured volume increments of acetic acid/water mixture were displaced into the cell by means of the Ruska-type hand pump readable to $\pm 0.01\text{cc}$ (10^{-8}m^3). After each increment, the cell was rocked and the temperature was adjusted back to the desired isothermal condition. When this temperature had equilibrated, then the pressure in the cell was measured by means of the calibrated precision pressure gauge shown in Figure 1. The distillation of part of the cell charge into the line connected to the pressure gauge was avoided by initially filling the line and Bourdon tube of the gauge with liquid water. A given run was terminated when sequential increments of

mixture produced very little change in pressure; thus indicating condensation in the cell.

PVT measurements were successfully made in the Inconel-600 cell shown in Figure 1 at 190°C (463 K) and 230°C (503 K), but when measurements were attempted at 140°C (413 K) it was found that data on pure water did not agree with literature data. This was interpreted to be due to corrosion which probably changed the surface characteristics of the cell. PVT measurements on pure water at 230°C (503 K) and 190°C (463 K) appear to agree with literature data, so this change occurred after these measurements were made. Because of this problem, the measurements at 100°C (373 K) and 140°C (413 K) were measured in a glass cell submerged in an oil bath. For this purpose, a heavy-walled 26.5-liter (0.0265m^3) carbuoy was used. Also the precision pressure gauge was replaced with a heated mercury null manometer connected to a ballast tank. For pressure readings, the pressure in the ballast tank was adjusted so that only a small differential existed on the null manometer; this differential was then added to a separate manometer reading of the pressure in the ballast tank. Corrosion of the mercury in the null manometer was not a problem when the vapors were removed between isotherms in order to avoid long-term contact with the mercury.

Reagent grade acetic acid containing less than 0.1 wt% water, and distilled water were used as chemicals for preparation of the acetic-acid/water mixtures used in this study. The estimated accuracy of measured data is as follows:

Property	Accuracy	
	100°C & 140°C (373 K & 413 K)	190°C & 230°C (463 K & 503 K)
	Data	Data
Temperature	$\pm 0.1^\circ\text{C}$	$\pm 0.5^\circ\text{C}$
Pressure	$\pm 0.1\%$	$\pm 0.2\%$
Volume	$\pm 0.05\%$	$\pm 0.05\%$
Composition	$\pm 0.03\text{ wt}\%$	$\pm 0.03\text{ wt}\%$

MEASUREMENT RESULTS

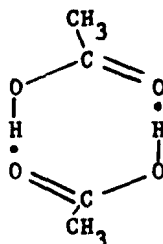
Tables 1, 2, 3, and 4 summarize the measured PVT data at 100, 140, 190, and 230°C (373, 413, 463, and 503 K) respectively. Each of these tables summarize data on

isotherms at 10, 30, 50, 70, 90, and 100 wt% acetic acid. In addition, Tables 1 and 4 contain data on pure water to show the reliability of the measurements at known conditions. Comparisons with the ASME Steam Tables (9) show that these data agree to an average scatter of about $\pm 0.7\%$. Calculated data in Tables 1 to 4 are discussed in the correlation section of this paper. The measured data in Tables 1 to 4 are plotted in Figures 2 to 5. Some features which can be seen in these plots are the following.

1. There is significant deviation of the Z-factor from unity at high concentrations of acetic acid, presumably due to dimerization of acetic acid.
2. At low concentrations of acetic acid the deviation from unity is smaller, but still significant. This means that a predicting model must account for both chemical and physical interactions.
3. At high acetic acid concentrations the Z-factor curves out at higher pressures. This effect is presumably due to the dimerization effect.

THERMODYNAMIC CORRELATION OF DATA

Acetic acid forms a fairly significant amount of hydrogen bonded dimer which is in chemical equilibrium with the monomer. The equilibration rate is probably comparable to the rate of equilibration of vapor and liquid phases, so for practical purposes it can be assumed to be in equilibrium at all times. This occurs because the energy of formation is about 15 kcal, and the activation energy is either zero or very low. The actual structure of the dimer can be considered to be analogous to a six-membered ring such as benzene. The following is a schematic representation of the molecule.



The ring of this molecule presumably

contributes to its stability even though other compounds involving hydrogen bonds are usually not stable. Acetic acid vapors show evidence of strong dimerization; thus, at saturation, the partial pressure of dimer and monomer in the vapor consist of about 67% dimer and 33% monomer.

In order to model the behavior of acetic acid in multicomponent mixtures it is necessary to model the chemical equilibrium between monomer and dimer by a method which accounts for both chemical and physical interactions. When this is done, the association constant is written in terms of fugacities instead of partial pressures as follows;

$$k_D = \frac{f_D}{f_m^2} \quad (1)$$

The fugacities can be written in terms of partial pressure and fugacity coefficients as follows:

$$f = p\phi \quad (2)$$

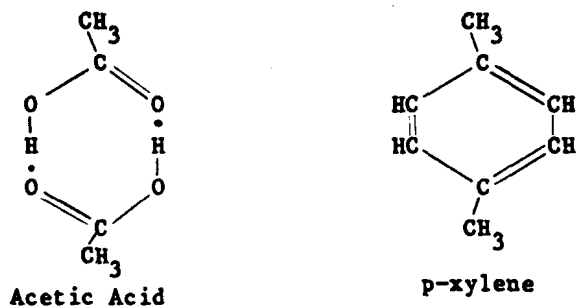
When $p\phi$ is substituted for fugacity, then Equation (1) becomes as follows:

$$k_D = \frac{p_D \phi_D}{p \phi_m^2} = \left(\frac{p_D}{p_m^2} \frac{\phi_D}{\phi_m^2} \right) \quad (3)$$

This equation shows that when the fugacity coefficients are unity, such as an ideal gas, then the equation for k_D reduces to partial pressures only; but in general a correction term calculated as ϕ_D/ϕ_m^2 must be applied. In order to calculate these fugacity coefficients, one must use an equation of state which accounts for physical interactions between all molecular species present in the gas phase. In this case the molecules present are acetic acid monomer, acetic acid dimer, and water. The derivation of physical interaction parameters for water is not difficult because its behavior can be correlated in terms of physical interactions. But in the case of acetic acid, its properties represent the combined result of both chemical and physical interactions; and one cannot separate them without some ambiguity. This ambiguity occurs because one cannot directly measure the properties of the

monomer or dimer as pure compounds in order to obtain modeling information normally used for calculating vapor phase nonidealities. For this reason, one must make assumptions regarding the properties of the monomer and dimer which will allow the estimation of the pure-component parameters of these compounds.

The properties of the dimer are probably close to the properties of para-xylene which involves a similar ring structure as follows:



The ring structure of the dimer would not be expected to exhibit hydrogen bonding character because the hydrogen bonds are tied up in forming the dimer. If the liquid phase is primarily dimer (which seems to be the case), then the vapor pressure of the dimer can be calculated from the partial pressure of the dimer over pure liquid acetic acid. The following is a comparison of the dimer vapor pressure calculated by this method versus the vapor pressure of para-xylene.

Temp °C	RAc Vapor Press. mmHg	Mole Fraction of Dimer	Pressure, mmHg	
			Dimer Par.	p-xylene Vapor Press.
120	804	0.575	462	452
140	1432	0.535	766	800
170	3035	0.490	1487	1661

These vapor pressures are close enough that it seems reasonable to use the properties of p-xylene to model the properties of the dimer.

Ritter and Simmons (7) have postulated the formation of trimers and tetramers in the vapor phase of pure acetic acid. We think this is very unlikely because the high concentration of dimer in the vapor phase indicates a high concentration of dimer in the liquid phase; thus the concentration of trimer or tetramer in the liquid phase would be expected to be small. This combined with a much lower volatility of the trimer or

tetramer suggests that the concentration of these species in the vapor phase must be very small. For example, at 120°C (393 K) the vapor pressure of pure tetramer would probably be less than the vapor pressure of pure n-hexadecane, which has the same number of atoms excluding hydrogen. At this temperature the vapor pressure of n-hexadecane is about 2 mmHg (0.27 kPa) while Potter et al. (7) postulated a tetramer partial pressure of about 93 mmHg (12.4 kPa) over pure acetic acid at 120°C (393 K). This is unreasonably high compared with 2 mmHg (0.27 kPa), and the effects attributed to trimer or tetramer formation are probably due to the usual vapor phase nonidealities caused by physical interactions between the molecules.

Since the effect of hydrogen bonding is accounted for by the formation of dimer, the monomer also loses its hydrogen bonding characteristics; thus its properties should be a lot like methyl formate which has the same formula without any hydrogen bonding effect. Methyl formate thus seems to be a logical choice for modeling the properties of the monomer.

With these assumptions, one can derive equation-of-state modeling parameters of the monomer, the dimer, and for water. These parameters can then be used to calculate fugacity coefficients in a generalized fashion which will allow for the addition of other components in process streams. The equation of state chosen for these modeling calculations is a modified Van der Waals equation given by Wilson and Weiner (10). It was chosen because of its favorable characteristics found in fitting the properties of water, but any other equation-of-state which will reliably predict these properties could also be used. The equation-of-state is as follows:

$$\frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V} - b} - \frac{\sum_i \sum_k x_i x_k \frac{S_{ik}}{(\bar{V} + S - b)^2} (A_{ik}/RT)}{\quad} \quad (4)$$

$$b = \sum_i x_i b_i$$

$$S = \sum_i x_i S_i$$

This equation reduces to the form of the Van der Waals equation when S equals b. The parameters S_i and A_{ij}/RT have been assumed to be temperature dependent as follows:

$$\ln(S_j/b_j) = C_j \left(\frac{T_{c_j}}{T} \right) \quad (5)$$

$$S_j A_{jj}/RT = \alpha + \beta \left(\frac{T_{c_j}}{T} \right) + \gamma \left(\frac{T_{c_j}}{T} \right)^2 + \delta \left(\frac{T_{c_j}}{T} \right)^3 + \sigma \left(\frac{T_{c_j}}{T} \right)^4 \quad (6)$$

The energy parameters A_{jk} are calculated from A_{jj} and A_{kk} as follows:

$$A_{jk} = k_{jk} \left(\frac{A_{jj} + A_{kk}}{2} \right) \quad (7)$$

k_{jk} is a mixture parameter with a numerical value close to unity. Fugacity coefficients are calculated from this equation-of-state by means of the following equation:

$$\begin{aligned} \ln \phi_k = & -\ln Z + \frac{b_k \sum_i n_i}{v - \sum_j n_j b_j} \\ & - \frac{2S_k \sum_i n_i S_i (A_{ik}/RT)}{v + \sum_j n_j (S_j - b_j)} \\ & + \ln \left(\frac{v}{v - \sum_j n_j b_j} \right) \\ & + \frac{(S_k - b_k) \sum_i \sum_j n_i S_i n_j S_j (A_{ij}/RT)}{[v + \sum_j n_j (S_j - b_j)]^2} \end{aligned} \quad (8)$$

The parameters used in this equation were obtained by fitting the saturated liquid and vapor properties of water, methyl formate, and p-xylene. The resulting parameters are given in Table 5, and comparisons between literature and calculated values are given in Tables 6, 7, and 8. Table 5 shows that the critical temperature and acentric factor of the monomer and dimer are slightly different than the values for methyl formate and p-xylene. These adjustments were made in order to fit the saturation properties of acetic acid using Equation (4) for both phases while accounting for chemical equilibrium. In retrospect, this probably was not necessary; and the parameters for methyl formate and p-xylene probably could have been used directly without any changes.

Equations (4) and (8) were used to

calculate the vapor-phase compressibility factor and fugacity coefficients to be substituted into Equation (3). This involved an iterative procedure because the fugacity coefficients depend on the monomer-dimer ratio which depends on the pressure equilibrium constant which depends on the fugacity coefficients. The pressure-equilibrium constant was calculated from k_D as follows:

$$k_P = k_D \left(\frac{\phi_m^2}{\phi_D} \right) = \frac{P_D}{P_m^2} \quad (9)$$

At a given pressure, temperature, and composition of acetic acid/water mixtures, the partial pressures of monomer and dimer were calculated from k_P based on the following derivation. At equilibrium, the concentration of acetic acid in the vapor is related to the partial pressures of monomer and dimer in the vapor as follows:

$$y_A = \frac{n_m + 2n_D}{n_m + 2n_D + \sum_{i \neq m,D} n_i} \quad (10)$$

$$n_i = \frac{P_i}{P} (n_m + n_D + \sum_{i \neq m,D} n_i) \quad (11)$$

Substitution of Equation (11) into Equation (10) for each component gives the following:

$$y_A = \frac{P_m + 2P_D}{P_m + 2P_D + \sum_{i \neq m,D} P_i} \quad (12)$$

Since $P = P_m + P_D + \sum_{i \neq m,D} P_i$, this can also be written as follows:

$$y_A = \frac{P_m + 2P_D}{P + P_D} \quad (13)$$

When P_D is substituted from Equation (9), this becomes as follows:

$$y_A = \frac{P_m + 2k_P P_m^2}{P + k_P P_m^2} \quad (14)$$

This is a quadratic equation in P which can be solved in terms of y_A , P_m , and k_P as follows:

$$P_m = \frac{2Py_A}{1 + \sqrt{1 + 4k_P(2-y_A)Py_A}} \quad (15)$$

From these equations, the iterative calculation procedure used to find P_m and P_D was as follows:

1. Assume ϕ_m and $\phi_D = 1$
2. Calculate k_p from Equation (9)
3. Calculate P_m from Equation (15)
4. Calculate P_D from Equation (9)
5. Calculate $P_{i=m,D}$ from the following equation

$$P_{i=m,D} = y_i (P + P_D)$$
6. Calculate $y_i = P_i/P$
7. Calculate Z and ϕ_i from Equations (4) and (8)
8. Test for convergence; if not converged return to (2) above.

Equation (4) gives the vapor-phase compressibility factor when considering all of the species present in the vapor-phase. The measured Z -factors in Tables 1 to 4 ignore any dimerization because monomer and dimer are both counted as monomer. To account for this, Equation (4) has to be multiplied by the mole ratio of (moles with dimer)/(moles without dimer):

$$Z^* = \frac{n_m + n_D + \sum_{i=m,D} n_i}{n_m + 2n_D + \sum_{i=m,D} n_i} Z \quad (16)$$

where Z^* = ignores dimerization

Z = value from Equation (4)

In terms of partial pressures, this reduces to the following:

$$Z^* = \left(\frac{P}{P + P_D} \right) Z \quad (17)$$

Calculated Z -factors in Tables 1 to 4 are based on the 8-step procedure given above with Z^* calculated from Equation (17).

The only information not given in the calculation procedure above is the thermodynamic association constant between

acetic acid monomer and dimer which only depends on temperature. Thus a good test of the model is to see if all of the measured PVT data in Tables 1 to 4 can be correlated in terms of a single association constant at each temperature. If they can, then this means that the assumed nonideality corrections are adequate; and that no other chemical association occurs. An examination of calculated versus measured data in Tables 1 to 4 shows that all compositions are about equally represented, with each set correlated almost within the accuracy of the measured data. The association constant used to correlate each set is given at the end of each table. This result indicates that if any chemical association exists between acetic acid and water it must be small enough to have no significant effect on the measured Z -factor data.

Some of the measured Z -factors on isotherms in Table 1 to 4 drop off at the higher pressures compared with calculated values. This phenomenon is similar to behavior found by Ritter and Simmons (7) which they interpreted to be due to formation of trimer and tetramer. A more likely explanation is that the acetic acid tends to form multiple absorption layers on the surfaces of the PVT cell at conditions near saturation. This drop-off only occurs in Tables 1 to 4 at conditions very close to saturation, and minor temperature gradients or trace impurities could also be affecting the data in this region. Except for this region, the data appear to be correlated quite accurately. This indicates that the assumed method for calculating vapor-phase nonidealities also appears to be adequate.

Since the equation-of-state parameters given in Table 5 are based on other data, the end product of the measurements given in Tables 1 to 4 is the dimerization constant given at the end of each table for each temperature studied. These results are as follows:

Temp. °C	(K)	Dimerization Constant, (mm Hg) ⁻¹		(kPa) ⁻¹
100	(373)	1.005	X 10 ⁻²	(7.54 X 10 ⁻²)
140	(413)	1.538	X 10 ⁻³	(1.154 X 10 ⁻²)
190	(463)	2.71	X 10 ⁻⁴	(2.03 X 10 ⁻³)
230	(503)	9.44	X 10 ⁻⁵	(7.08 X 10 ⁻⁴)

These values are plotted in Figure 6 as $\log k_f$ versus $1/T^\circ K$. This plot also shows literature values which have been derived from low-pressure measurements. At $100^\circ C$ (373 K) and $140^\circ C$ (413 K), the values derived from Tables 1 and 2 are slightly lower than the values determined by Taylor (8) or Barton and Hsu (1). At $190^\circ C$ (463 K) and $230^\circ C$ (503 K), the values derived from Tables 3 and 4 are slightly higher than a straight line extrapolation of either Taylor's or Barton and Hsu's data. The DECHEMA (11) values are not experimental points, but are points calculated from their correlation of literature data. Their values appear to follow the values of Barton very closely. A straight line can be drawn through either Taylor's or Barton and Hsu's data, but if one believes data around $50^\circ C$ (323 K) one would have to draw a curve through the new data points. This has been done as is shown in Figure 6. The equation which fits this curve is as follows:

$$\ln(k_f) = -16.637 + \frac{1457.7}{T^\circ K} + \frac{1132000}{(T^\circ K)^2} \quad (18)$$

where k_f is in mm Hg⁻¹

The heat of dimerization from this equation is given as follows:

$$\Delta H = -2896 - \frac{4499000}{T} \quad (19)$$

where ΔH is given in calories/mole with T in degrees Kelvin. At $100^\circ C$ (393 K), this compares with values from Taylor's or Barton and Hsu's data as follows:

Source	Calories/mole
Wiltec	14,953
Taylor (8)	15,270
Barton & Hsu (1)	14,755

Curiously, this new value is very close to the average of the other two values of 15,013 calories/mole; however, the Barton and Hsu equation for the dimerization constant probably represents the best straight line through the new data in consideration of the data at low temperatures. This is also in close agreement with the DECHEMA

correlations, so it could also be used as a "best" straight-line fit to the new data.

The dimerization constant given in Equation (18) can be used to calculate the mole fraction of dimer in the vapor from pure acetic acid at saturated conditions. The results of this calculation are shown in Figure 7 where the dimer mole fraction varies from about 0.9 at $0^\circ C$ (273 K) to about 0.4 at $230^\circ C$ (503 K). The curve is based on extrapolated dimerization constants below $25^\circ C$ (298 K) and above $230^\circ C$ (503 K).

CONCLUSIONS

Measured PVT data on acetic acid/water mixtures at high temperatures and pressures show strong deviations from ideal behavior as a result of vapor-phase association of acetic acid and of physical interactions between the various molecular species in the vapor phase. When the effects of physical interactions are calculated from an equation-of-state based on monomer properties similar to methyl formate and dimer properties similar to p-xylene, then derived dimerization constants are in good agreement with values currently accepted to be reliable in the literature. This means that any chemical association between water and acetic acid is negligible, and that the vapor phase nonideality is predictable from intuitive considerations regarding the physical properties of monomer and dimer.

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NOTATION

- A Energy parameter analogous to Van der Waals A
- b Molecular volume parameter analogous to Van der Waals b
- C A constant
- f Fugacity
- H Heat of dimerization

k	Association constant or mixture parameter
n	Moles
p	Partial pressure
P	Pressure
R	Gas constant
S	Symmetry parameter from the empirical Van Laar equation
T	Temperature
V	Volume
x	Liquid phase mole fraction
y	Vapor phase mole fraction
Z	Compressibility factor or ratio

Greek Symbols

α	A constant or Relative volatility
β	A constant
γ	A constant or activity coefficient
ϕ	Fugacity coefficient
ω	Acentric factor
Σ	Summation
δ	A constant
σ	A constant

Superscripts

o	Pure component property
-	Molar quantity
*	Ignores dimerization

Subscripts

c	Critical property
D	Dimer
i, j, k	Component numbers
m	Monomer

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