Duedall by as much as 0.18 × 10^{-6} bar^{-1} at 2 °C and 0.13 *m*. The difference in $\Delta\beta$, if integrated over the pressure range at 2 °C and 0.13 *m*, would indicate that the density of Duedall is ~150 × 10^{-6} g cm^{-3} higher than our value at 900 bar. Since our density is only 23 × 10^{-6} g cm^{-3} higher than that of Chen, Emmet, and Millero, which is well within the combined precision of these two studies, we suspect that the work of Duedall may have been subjected to some systematic error for $MgCl_2$ solutions.

The agreement of our $\Delta\beta$ data for Na_2SO_4 and $MgSO_4$ with the data of Duedall is well within the combined precision of the two studies. The good agreement substantiates the validity of our sound-derived equations and suggests that the direct density measurement of Chen, Emmet, and Millero (*2*) for $MgSO_4$ may be too low.

In summary, we have presented what we feel are the best available high-pressure properties for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ solutions from 0 to 1000 bar, 0 to 40 °C, and 0 to 1 *m*.

Acknowledgment

Chen-Tung A. Chen acknowledges the support of the Oregon State University Computer Center and the School of Oceanography for data analysis.

Literature Cited

(1) Emmet, R. T. Ph.D. Dissertation, University of Miami, Miami, FL, 1973.
(2) Chen, C. T.; Emmet, R. T.; Millero, F. J. *J. Chem. Eng. Data* **1977**, *22*, 201.
(3) Chen, C. T.; Millero, F. J. *Deep-Sea Res.* **1976**, *23*, 595.
(4) Millero, F. J.; Knox, J. H.; Emmet, R. J. *J. Solution Chem.* **1972**, *1*, 173.
(5) Chen, C. T.; Chen, L. S.; Millero, F. J. *J. Acoust. Soc. Am.* **1978**, *63*, 1795.
(6) Chen, C. T.; Chen, J. H.; Millero, F. J. *J. Chem. Eng. Data*, in press.
(7) Chen, C. T. Ph.D. Dissertation, University of Miami, Miami, FL, 1977.
(8) Chen, C. T.; Millero, F. J. *J. Mar. Res.* **1978**, *36*, 657.
(9) Desnoyers, J. E.; de Visser, C.; Perron, G.; Picker, P. *J. Solution Chem.* **1976**, *5*, 605.
(10) Millero, F. J.; Perron, G.; Desnoyers, J. E. *J. Geophys. Res.* **1973**, *78*, 4499.
(11) Perron, G.; Desnoyers, J. E.; Millero, F. J. *Can. J. Chem.* **1974**, *52*, 3738.
(12) Chen, C. T.; Fine, R. A.; Millero, F. J. *J. Chem. Phys.* **1977**, *66*, 2142.
(13) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97.
(14) Freund, E. "Mathematical Statistics"; Prentice-Hall: Englewood Cliffs, NJ, 1962.
(15) Ellis, A. J. *J. Chem. Soc. A* **1966**, 1579.
(16) Gorbachev, S. V.; Kondratev, V. P.; Androsov, V. E. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1974**, *48*, 1581.
(17) Polyakov, E. A. *Prikl. Geofiz.* **1965**, *41*, 163 (in Russian).
(18) Millero, F. J.; Ward, G. K.; Lepple, F. K.; Hoff, E. V. *J. Phys. Chem.* **1974**, *78*, 1636.
(19) Duedall, I. W. Ph.D. Dissertation, Dalhousie University, Halifax, Nova Scotia, Canada, 1973.
(20) Rowe, A. M., Jr.; Chou, J. C. S. *J. Chem. Eng. Data* **1970**, *15*, 61.
(21) Fox, F. E.; Marion, T. M. *J. Acoust. Soc. Am.* **1953**, *25*, 661.
(22) Hayward, A. T. J. *Nature* (*London*) **1969**, *221*, 1047.
(23) Millero, F. J.; Ward, G. K.; Chetirkin, P. V. *J. Acoust. Soc. Am.* **1977**, *61*, 1492.
(24) Stuehr, J.; Yeager, E. "Physical Acoustics"; Academic Press: New York, 1965; Vol. II, Part A.

Received for review August 21, 1980. Accepted March 16, 1981. We acknowledge the support of the Office of Naval Research (N00014-75-C-0173) and the Oceanographic Branch of the National Science Foundation (OCE73-00351-A01) for this study.

Solubilities of Vinyl Chloride and Vinylidene Chloride in Water

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A review of the published data for the solubilities of vinyl chloride and vinylidene chloride in water is presented, and data from new experiments are offered. A consensus existed among the vinyl chloride data sources. Our new data agreed with the majority position. The solubility of vinyl chloride in water was found to be nearly constant at 0.95 wt % over the range 15–85 °C. Little vinylidene chloride data have been published, and no consensus existed. Our data showed the solubility of vinylidene chloride in water to be nearly constant at 0.25 wt % over the range 15–90 °C.

Introduction

The solubilities of vinyl chloride and vinylidene chloride in water are valuable data for understanding any process which involves water and either of these monomers. They are especially important for the polymerization and finishing of homopolymers or copolymers of these monomers. The purpose of this paper is to provide this valuable solubility information in one place.

Vinyl Chloride. A Review

Six sources of vinyl chloride solubility data were found. Gerrens et al. (*1*) reported the solubility of vinyl chloride in water to be 1 g/100 mL, or 1.0 wt %, at 50 °C. The value was given without explanation or reference.

Hayduk and Laudie (*2*) reported extensive studies of the vinyl chloride–water system. Their solubility experiments were performed over a wide range of temperatures. Although they did not directly measure the solubility of vinyl chloride in water at the vapor pressure of vinyl chloride, they were able to extrapolate. They started with a known volume and partial pressure of vinyl chloride in a thermostatted bomb. They introduced a known amount of water to the bomb and adjusted the volume of the bomb to maintain the starting pressure. The vinyl chloride lost from the vapor phase was assumed to have dissolved in water. At 0.2, 25, 50, and 75 °C, they performed experiments at two or more vinyl chloride partial pressures. These data were then extrapolated to the vapor pressure of vinyl chloride by using a general form of Henry's law, eq 1,

$$P = H'C^{k} \tag{1}$$

where *P* is the partial pressure (or vapor pressure) of vinyl chloride, *H'* is a solubility coefficient which is exactly the Henry's law coefficient when *k* = 1, *C* is the concentration of vinyl chloride in the water, and *k* is an adjustable parameter. Restatement of their data gives the solubility of vinyl chloride in water as 0.90 wt % at 0.2 °C, 0.87 wt % at 25 °C, 1.01 wt % at 50 °C, and 1.28 wt % at 75 °C.

Berens (*3*) reported the solubility of vinyl chloride in water at 30 and 50 °C. He determined the solubility of vinyl chloride by measuring the pressure at apparent equilibrium in a stirred,

0021-9568/81/1726-0274$01.25/0

thermostatted bomb of known volume containing weighed amounts of water and vinyl chloride. Any vinyl chloride not accounted in the vapor phase was assumed to have dissolved in the water. Berens reported the equilibrium concentration of vinyl chloride in water at several partial pressures for both temperatures. He reported directly the solubility at 30 °C. We have extrapolated his data to obtain the solubility at 50 °C. His results for the solubility of vinyl chloride in water are 0.83 wt % at 30 °C and 1.04 wt % at 50 °C.

One secondary reference (*4*) reported that at 25 °C 0.11 g of vinyl chloride dissolves in 100 g of water, or 0.11 wt %.

Nilsson et al. (*5*) conducted vinyl chloride solubility experiments between 15 and 60 °C. They injected measured amounts of vinyl chloride into a bomb containing only a known amount of water. They measured the equilibrium partial pressure within the bomb and calculated the amount of vinyl chloride which had not dissolved. This gave them the amount of vinyl chloride which had dissolved, and they were able to describe partition coefficients. They did not report the results of specific experiments, but, rather, stated that eq 2 (a form of Henry's

$$S = 8.8 \times 10^{-3}(P/P_0) \qquad (2)$$

law) holds from 15 to 60 °C, where S is the concentration of vinyl chloride dissolved in water (g of VCM/g of H_2O) in equilibrium with a partial pressure of vinyl chloride P when the vapor pressure is P_0. By setting $P = P_0$ and adjusting the units of solubility, they determined the solubility of vinyl chloride in water to be constant at 0.87 wt % from 15 to 60 °C.

Recently, Patel et al. (*6*) measured the partition of vinyl chloride between water and the vapor phase. They performed experiments at several vinyl chloride partial pressures at each of several temperatures between 25 and 85 °C. They added water to a bomb and evacuated the air from the headspace. Next, a known amount of vinyl chloride was added to the bomb. After equilibrium was reached in a thermostatted environment, the pressure in the bomb was measured. The vapor phase of the bomb was sampled, and the concentration of vinyl chloride was determined chromatographically. This served as a check on the pressure measurement. Finally, the water phase of the bomb was sampled, and the concentration of vinyl chloride was determined chromatographically. Experiments at several partial pressures at each temperature demonstrated that Henry's law was obeyed. We have extrapolated their data to the vapor pressure of vinyl chloride at 25, 55, 65, 75, and 85 °C and found the solubility of vinyl chloride in water to be 0.87, 1.21, 1.22, 1.16, and 1.06 wt %, respectively.

Thus, solubility data for vinyl chloride are available over a wide temperature range, and there is a good consensus among the various works. It is interesting that such good agreement resulted since, with the exception of one experiment by Berens (*3*), the solubility has been extrapolated from lower pressure experiments. Yet, the various authors disagree on the dependency of the solubility coefficient on the partial pressure of vinyl chloride. Hayduk (*2*) showed that Henry's law is obeyed at 50 °C, but not at 0, 25, or 75 °C. Berens (*3*) showed that Henry's law is obeyed at 30 °C but not at 50 °C. Nilsson (*5*) did not offer specific data, but did claim that Henry's law is obeyed from 15 to 60 °C. Patel (*6*) showed that Henry's law is obeyed from 25 to 85 °C. However, since the extrapolations to the vapor pressure are small for the data of these four sources, their consensus will be used as a validation test for the experiments to be described herein. The report by Hardie (*4*) is discarded.

Vinylidene Chloride. A Review

Five sources of vinylidene chloride solubility data were found.

Weiner (*7*) limited his study to 25 °C. He found the solubility of vinylidene chloride in water to be 0.64 wt %. The experimental technique involved adding small known amounts of vinylidene chloride vapor to a closed vessel containing a known amount of water and headspace. The pressure in the vessel was monitored after each increment. When a constant pressure was reached, the amount of added vinylidene chloride was adjusted for the headspace volume, and the remainder was assumed to have dissolved in the water.

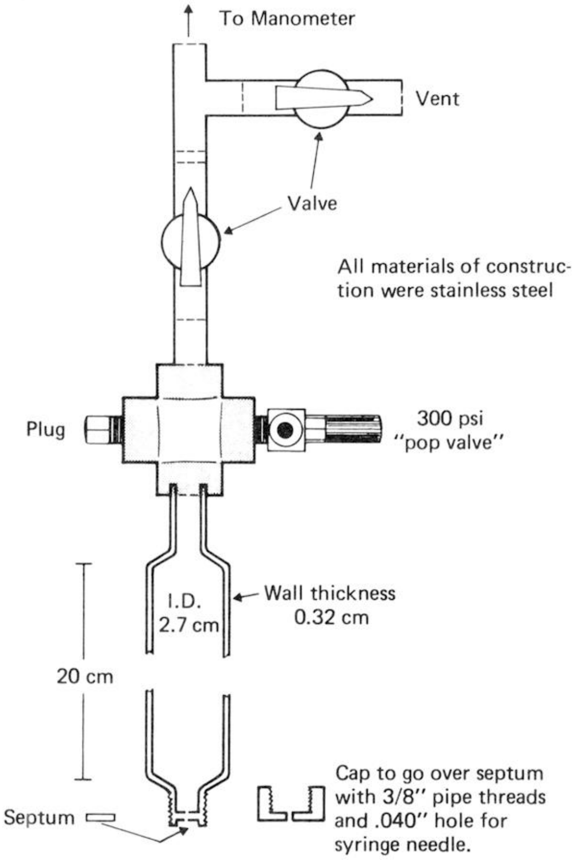

Figure 1. Cutaway view of the solubility bomb.

Jaeger and Stringer (*8*) studied the solubility of vinylidene chloride in water from 4 to 25 °C. Their experimental methods were not published; however, their solubility at 25 °C, 0.25 wt %, was much less than Weiner's value. At 4 and 16 °C, they found the solubility to be 0.35 and 0.30 wt %, respectively.

Three secondary references reported the solubility of vinylidene chloride in water. They neither disclosed the original reference nor described the experimental procedures. The first reference (*9*) reported the solubility to be 0.01 wt % at 25 °C. The second reference (*10*) reported the solubility to be 0.021 wt % at 25 °C. The third reference (*11*) reported the solubility to be 0.04 wt % at 20 °C.

With only one exception, the available data were taken near room temperature. The values at 25 °C range from 0.01 to 0.64 wt %. The need for new experimental data was apparent.

New Experiment

The solubilities of vinyl chloride and vinylidene chloride in water were determined directly with the following simple method.

(1) Approximately 60 mL each of deaerated, distilled water and vinyl chloride or vinylidene chloride were placed in a stainless steel bomb (see Figure 1). The vinylidene chloride in these experiments usually contained MEHQ (the monomethyl ether of hydroquinone). This was necessary since autopolymerization is expected when this inhibitor is absent. Experimentally, the presence of MEHQ did not affect the solubility.

(2) The bomb was closed, and the headspace was briefly evacuated to remove air.

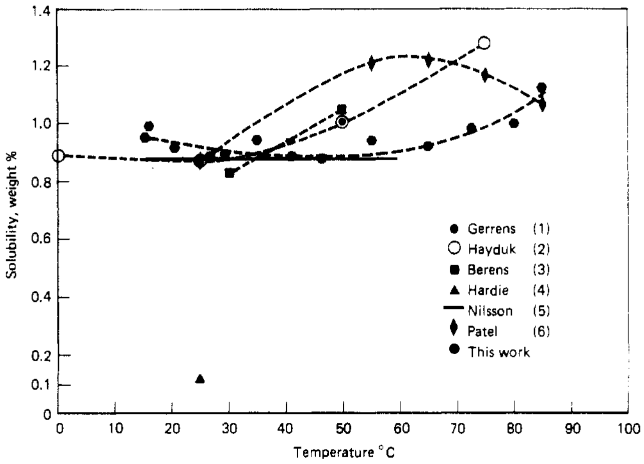

Figure 2. Solubility of vinyl chloride in water.

Table I. Solubility of Vinyl Chloride in Water (This Work)

temp, °C	solubility, wt %	temp, °C	solubility, wt %	temp, °C	solubility, wt %
15	0.95	29.5	0.89	55	0.95
16	0.995	35	0.94	65	0.92
20.5	0.915	41	0.89	72.5	0.98
26	0.88	46.5	0.88	80	1.00
				85	1.12

(3) The bomb was placed into a thermostatted bath and mechanically shaken for periods of 6–24 h.

(4) The bomb was lifted from the bath, and the water phase was sampled immediately by inserting a gas-sampling syringe through the septum.

(5) The water sample was immediately injected through a septum into a measured aliquot of DMAC (dimethylacetamide). For the vinyl chloride experiments, 0.25 mL of water solution was sampled and injected into 99.75 mL of DMAC to achieve a 1:400 dilution. For the vinylidene chloride experiments, 0.25 mL of water solution was sampled and injected into 24.75 mL of DMAC to achieve a 1:100 dilution.

(6) The DMAC solutions were analyzed with a gas chromatographic technique. Five microliters of DMAC solution was injected into a 6-ft glass column packed with Chromosorb 103 80/100M. The column temperature was 90 °C for vinyl chloride and 110 °C for vinylidene chloride. A flame ionization detector was used. Helium was the carrier gas. Standard vinyl chloride/DMAC solutions were prepared every 1 or 2 days. Standard vinylidene chloride/DMAC solutions were used no longer than 3 days. Relative peak heights were used to calculate the amounts of vinyl chloride or vinylidene chloride in the samples.

These experiments required several safety precautions. Since vinyl chloride and vinylidene chloride are potentially hazardous, they were used in a well-ventilated fume hood with spark-proof electrical equipment. Goggles and gloves were worn during all handling procedures. Since vinyl chloride and vinylidene chloride have high vapor pressures in the temperature ranges of these experiments, the experimental bomb was equipped with a 300 psi pressure relief valve which was pointed toward the rear of the hood. Special caution was used when handling DMAC since it is toxic by topical application.

Data and Discussion

The measured solubility of vinyl chloride in water is shown in Table I and Figure 2. The precision of the data with three or more trials at each temperature is about 5 relative percent. There was no systematic variation of the data as a function of equilibrating time over the experimental range, 6–24 h. In fact, in some cases a second or third temperature was tested with the same charge of vinyl chloride and water, and those data with effective equilibrating times up to 72 h showed no systematic difference from data gathered at the same temperature with a shorter equilibrating time. These data agree with the literature concensus as much as the consensus values agree with each other. Hence, we consider the technique validated.

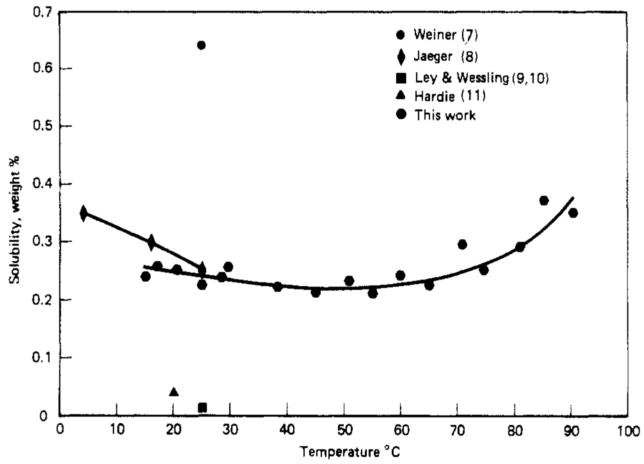

Figure 3. Solubility of vinylidene chloride in water.

Table II. Solubility of Vinylidene Chloride in Water (This Work)

temp, °C	solubility, wt %	temp, °C	solubility, wt %	temp, °C	solubility, wt %
15	0.24	38.5	0.22	71	0.295
17	0.255	45	0.21	74.5	0.25
20.5	0.25	51	0.23	81	0.295
25	0.225	55	0.21	85.5	0.37
28.5	0.24	60	0.24	90.5	0.35
29.5	0.255	65	0.225		

Table II and Figure 3 show the measured solubility of vinylidene chloride in water. The precision of the data with three or more trials at each temperature is about 11 relative percent. There was no systematic variation of the data as a fuunction of equilibrating time. These data are in good agreement with the data of Jaeger and Stringer (*8*). The vinylidene chloride solubility data of all other sources seem to be incorrect.

Summary

These experiments agree with the majority of the available data for the solubility of vinyl chloride in water. The solubility of vinyl chloride in water is nearly constant at 0.95 wt % over the range 15–85 °C. These experiments indicate that nearly all of the available data for the solubility of vinylidene chloride in water are incorrect. The solubility of vinylidene chloride in water is nearly constant at 0.25 wt % over the range 15–90 °C.

Literature Cited

(1) Gerrens, H.; Fink, W.; Köhnlein, E. *J. Polym. Sci., Sect. C* **1967**, *16*, 2781.
(2) Hayduk, W.; Laudie, H. *J. Chem. Eng. Data* **1974**, *19*, 253.
(3) Berens, A. R. *Polym. Prep.* **1974**, *15* (2), 197.
(4) Hardie, D. W. F. In "Kirk-Othmer Encyclopedia of Chemical Technology"; Wiley: New York, 1964; 2nd ed, Vol. 5, p 171.
(5) Nilsson, H.; Silvegren, C.; Tornell, B. *Eur. Polym. J.* **1978**, *14*, 737.
(6) Patel, C. B.; Grandin, R. E.; Gupta, R.; Phillips, E. M.; Reynolds, C. E.; Chan, R. K. S. *Polym. J.* **1979**, *11*, 43.
(7) Weiner, H. *J. Polym. Sci.* **1951**, *7* (1), 1.
(8) Jaeger, J.; Stringer, W. In "Vinylidene Chloride Monomer"; Dow Chemical U.S.A. Circular, 1972; No. 102-232-72.
(9) Ley, G. J. M.; Hummel, D. O.; Schneider, C. *Adv. Chem. Ser.* **1967**, *No. 66*, 191.
(10) Wessling, R. A.; Edwards, F. G. In "Encyclopedia of Polymer Science and Technology"; Wiley: New York, 1971; Vol. 14, p 542.
(11) Hardie, D. W. F. In "Kirk-Othmer Encyclopedia of Chemical Technology"; Wiley: New York, 1964; 2nd ed, Vol. 5, p 178.

Received for review August 25, 1980. Accepted March 13, 1981.