point in Table III, the largest deviation between experimental and calculated values is about 10%.

Both systems exhibit positive azeotropes whose compositions vary strongly with temperature, *n*-decane concentration increasing with temperature.

Nomenclature

A_{ij}, A_{ji} = Wilson equation parameters
a_i = Wilson equation parameter
b_i = Wilson equation parameter

$$D = \text{Herington parameter} = 100 \times \frac{\int_0^1 \frac{\gamma_1}{\gamma_2}\, dx_1}{\int_0^1 \left|\frac{\gamma_1}{\gamma_2}\right| dx_1}$$

J = Herington parameter = $150\ |\theta|/T\text{min}$
ln = natural logarithm
P_v = vapor pressure of pure component, atm
T = temperature, K
T_{min} = lowest measured boiling point of the system, K
X_i = mole fraction in the liquid of component *i*
Y_i = mole fraction in the vapor of component *i*
γ_i = activity coefficient of component *i*
θ = range of boiling points of the system, °C

Subscripts

i, j = component number
1, 2 = component number. 1 is always *n*-decane

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Vinyl Chloride Gas Compressibility and Solubility in Water and Aqueous Potassium Laurate Solutions

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Volumetric properties of vinyl chloride gas are reported for temperatures from 0° to 75°C and for pressures from atmospheric to the saturation pressures. Solubilities in water are also reported for the same temperature range and pressures up to 6 atm. Solubilities of vinyl chloride in aqueous solutions of potassium laurate for concentrations up to 15 g/l. are reported and compared with those in water. A new solubility apparatus useful for moderate pressures and incorporating a solvent cell with an externally operated magnetic flow control valve is described.

A knowledge of vinyl chloride volumetric properties and solubilities in water and aqueous surfactant solutions is useful when dealing with polymerization reactions of this monomer in aqueous emulsions or suspensions. Although vinyl chloride is condensable at relatively low pressures, neither gas compressibilities nor any concerted study of solubilities in water or surfactant solutions (to the authors' knowledge) has heretofore appeared in the literature.

Some vinyl chloride properties can be found in the monograph edited by Leonard (*7*) as well as an earlier publication edited by Blout et al. (*1*). These properties included vapor pressures, calculated critical properties, and saturated vapor densities.

In this work the vinyl chloride gas density was measured at 0°C and atmospheric pressure with an Anton Paar (Austria) vibrating reed densitometer and was 2.86 g/l. This density was extrapolated to other temperatures as required in the compressibility determinations. Accurate density measurements at 25°, 50°, and 75°C were unsuccessful apparently because of some chemical reaction of the gas occurring in the densitometer at the higher temperatures.

Compressibilities were measured with an accurately calibrated piston-type volumetric pump as a volume regulator in conjunction with a pressure transducer and an appropriate charging and evacuation system. The compressibility apparatus was submerged in a constant temperature bath so that once charged, direct readings of pressure and volume could be obtained at constant temperature.

Solubilities in water at atmospheric pressure were measured by a continuous solvent flow apparatus formerly described by Hayduk and Cheng (*5*) and Hayduk and Buckley (*4*). Solubilities above atmospheric pressure were obtained by means of a new apparatus by use of the volume measuring system of the compressibility apparatus in conjunction with a solvent saturation tube. A known volume of deaerated solvent initially confined in a cell was saturated by passing it dropwise over a packing in the tube. The total volume of dissolved gas required to saturate the solvent was measured at constant pressure with the calibrated volumetric pump. When operated at atmospheric pressure, this new apparatus gave nearly equivalent results to those obtained by means of the continuous solvent flow apparatus. Consequently, it was assumed that the apparatus would also give reliable results at elevated pressures.

Solubilities of vinyl chloride in potassium laurate solutions were measured with the same solubility equipment as that used for water with little added difficulty. The low solubility of potassium laurate in water at lower temperatures limited the possible surfactant concentrations for these measurements. It was possible to estimate the ex-

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tent of "solubilization" or increase in vinyl chloride solubility resulting from the presence of the dissolved surfactant in the solution.

Experimental

Vinyl chloride, of the polymerization grade and having a minimum specified purity of 99.9%, was purchased from Matheson of Canada. It was used directly without removing traces of inhibitor added for stabilization. Potassium laurate having a specified purity of 95–98% was purchased from K and K Laboratories, Plainview, N.Y. This soap was considered sufficiently pure for determining the solubilizing effect for vinyl chloride in aqueous solutions. Distilled water was used as a solvent and for the preparation of the soap solutions. Soap solutions were prepared in 1000-ml volumetric flasks by partially immersing the flasks containing weighed portions of soap and distilled water in a constant temperature bath. The potassium laurate solubility was too low at the lower temperatures to permit preparation of the complete range of soap concentrations from 0.1 to 15.0 g/l. At 25°C the limit of solubility was 1 g/l., and only at 50° and 75°C was the soap soluble to 15.0 g/l.

The vinyl chloride gas density was determined at 0°C with an Anton Paar (Austria) Model DMA 02C digital precision density meter. The instrument utilizes a vibrating reed, the frequency of which is closely related to the density of the fluid in which the reed is immersed. The instrument requires calibration with two fluids of accurately known density, usually dried air and distilled water. The calibration constant (A) is obtained from the fluid densities and corresponding vibration frequencies:

$$\rho_1 - \rho_2 = \frac{1}{A}(T_1^2 - T_2^2) \qquad (1)$$

The instrument is capable of providing densities to at least four-figure accuracy if the cell temperature is controlled to ±0.001°C. For calibration purposes, densities of dry air and deaerated water were obtained from Weast (*11*) and Perry et al. (*9*), respectively. Density measurements for vinyl chloride were somewhat nonreproducible at 25°C and increasingly so at 50° and 75°C in spite of all precautions to ensure purity in the densitometer cell. Because reproducible density measurements could be readily obtained at all temperatures with other gases such as carbon dioxide, methane, and propane, it was assumed that vinyl chloride reacted sufficiently in the densitometer to cause density changes at the higher temperatures.

The compressibility apparatus consisted essentially of a calibrated 100-ml volumetric pump (Ruska Instrument Corp.) equipped with a vernier readable to 0.01 ml, connected to an absolute pressure transducer (Statham Model PA 822). The latter employed a strain gauge incorporated on a metal diaphragm whose displacement was specified to be a maximum of 0.00015 cm^3. A Statham (Model SC1001) meter was used to convert the millivolt output to pressures in psia. The combination was calibrated daily with a precalibrated Heise gauge for the range required. For the determination of compressibility by the direct volume-pressure method, it is essential to have an accurate knowledge of the total volume of the gas-containing system, as well as an accurate measure of the imposed change in volume. The dead volume at the end of the volumetric pump, inside the pressure transducer, the high-pressure valves, and interconnecting tubing were accurately measured by mercury displacement as 32.0 ml, giving a possible total initial charge volume of 132.0 ml. It was hence possible to make an approximately fourfold reduction in the system volume.

In preparation for compressibility measurements, vinyl chloride gas was purged directly from a cylinder through the high-pressure valve and ⅛-in. tubing, the volumetric pump and transducer, and then vented through a second valve. The volumetric pump was slowly opened to completely fill the chamber, after which the outlet and inlet valves were closed. The pressure was adjusted to 1 standard atm pressure by either venting some gas or depressing the volumetric pump as the temperature reached steady state. The functional parts of the apparatus were completely submerged in a constant temperature (±0.02°C) bath filled with an aqueous–ethylene glycol solution. The barrel of the volumetric pump, the pressure transducer (excepting the electrical connector), the valves, and interconnection tubing were all immersed. Hence, it was ensured that all portions of the equipment containing the sample were at the bath temperature.

After the initial volume reading was taken, the gas volume was reduced by about 20 ml. The apparatus was then allowed to equilibrate after which the corresponding pressure was taken. This procedure was repeated a number of times until a pressure of about 3 atm or the saturation pressure was reached. The reverse procedure was also followed by an incremental reduction in pressure to ensure that the pressure-volume readings were identical to those obtained for increasing pressures. To obtain compressibilities above 3 atm, the apparatus was initially charged at a pressure of 3 atm. Otherwise, an identical procedure was followed.

The apparatus for solubility measurements at atmospheric pressure was similar to that described previously (*4, 5*) with some variation allowing for the particular range of solubilities measured. Gas and solution burets were of 5-ml capacity, graduated in 0.02-ml divisions. Deaerated solvent was charged into the apparatus by means of a 5-ml gas-tight Hamilton syringe in conjunction with a ⅕-rpm Harvard apparatus syringe pump. Most measurements took about 90 min after initial purging of the apparatus. An accurate infusion rate for the syringe pump was determined by weighing the quantity of distilled water discharged in a certain time. The degassing apparatus consisted of an evacuated leveling bottle used for the first stage of deaeration and a glass tube about 1 cm in diameter and 100 cm in length and containing a 1-mm capillary sealed in the side of it for the second stage.

After an initial period of slow boiling under vacuum for about 30 min, the solvent was permitted to flow from the bottle through the capillary into the evacuated tube. The solvent sprayed into the tube, yielding an excellent opportunity for deaeration, and was accumulated at the bottom of the tube. To prevent excessive vaporization, the vacuum was measured by a vacuum gauge and controlled by a clamp in the vacuum line. Care was taken to minimize the evaporation loss of water during the deaeration of soap solutions. A cold trap used in conjunction with the vacuum deaeration tube collected only about 2–3 ml of condensate from about 200 ml of solution. Hence, the change in soap concentration as a result of deaeration was considered small. The carryover of froth during deaeration was likewise minimal. Because of the two-stage deaeration process utilized, however, deaeration was still considered to be complete.

Solubilities in water could not be measured at exactly 0°C because of freezing. Instead the aqueous–ethylene glycol coolant temperature was maintained at 0°C at the inlet to the solubility apparatus while the outlet temperature was no greater than about 0.4°C, yielding an average temperature in the apparatus of 0.2°C. Because of the circulating system employed, the average temperature could be readily controlled to ±0.1°C.

A diagram of the new solubility apparatus used at pressures above atmospheric and up to 6 atm is shown in Figure 1. A pyrex glass high-pressure chromatography column (from O. H. Johns Glass Co.) 1.2 cm i.d., 75 cm long, and specified to withstand pressures to 15 atm was used as the absorption tube. The glass solvent cell which fitted into the absorption tube contained a magnetically operated glass valve at the lower end as well as pieces of capillary glass at either end. The purpose of the small bore tubing was to prevent partial saturation of the deaerated solvent prior to the actual experiment. The lower capillary tube was drawn to a needle point to give a very low solvent flow rate through it. The total volume of solvent in the cell of approximately 10 ml could be drained in about 20 min with the magnetic flow valve open. To permit a further control of the solvent, an on-off cycle controller was connected to the energizing solenoid which then made it possible to keep the valve open only for a preset fraction of the time. A packing of 3-mm glass helices was placed in the absorption tube to a depth of about 25 cm to permit saturation of the solvent. The packing was initially wetted with solvent to provide enough solvent vapor to saturate the gas with vapor during the initial equilibration period.

Prior to the solubility measurement, the solvent cell was filled, carefully purged with several volumes of deaerated solvent which had been heated (or cooled) to approximately the temperature of the experiment, and then placed inside the absorption tube. After vinyl chloride gas had been flushed through the absorption tube to remove residual air, a small volume of gas (about 50 ml) was confined in the solubility apparatus at the required pressure. An equilibration period of at least an hour was required to achieve temperature equilibrium particularly for the solvent in the cell, as well as to ensure saturation of the gas with solvent vapor. The experiment was started when no further changes in pressure, as sensed by the pressure transducer, occurred. The solenoid timer was set so that the total solvent efflux time was about 3 hr. After the initial position of the volumetric pump was taken, continual adjustments to the gas volume were made as small pressure changes were observed; hence, the solubilities were measured at essentially constant pressure. The final gas volume was taken after all the solvent had emptied from the cell. The original volume of solvent along with the volume of vapor-free gas required to keep the pressure constant permitted calculation of the solubility.

Results and Discussion

The vinyl chloride vapor density obtained at 0°C and atmospheric pressure of 2.86 g/l. yielded a compressibility factor of 0.975. Compressibilities for the higher temperatures and atmospheric pressure were calculated with the Pitzer correlation for fluid volumetric properties as recently extended by Lu et al. (*8*):

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{2}$$

In Equation 2 both compressibility terms were correlated as functions of P_r and T_r, and the acentric factor was determined from vapor-pressure data. The vapor compressibilities calculated for atmospheric pressure and 0°, 25°, 50°, and 75°C, were, respectively, 0.974, 0.981, 0.985, and 0.988. The compressibility calculated for 0°C is nearly identical to the experimental value; hence, only minimal errors are expected from the use of Equation 2 for determining compressibilities at atmospheric pressure. Compressibilities at higher pressures were calculated from experimental volume measurements by:

$$Z = \frac{Z_i P(V_i - V)}{P_i V_i} \tag{3}$$

The vinyl chloride vapor compressibilities are listed in Table I and graphically represented in Figure 2. It was

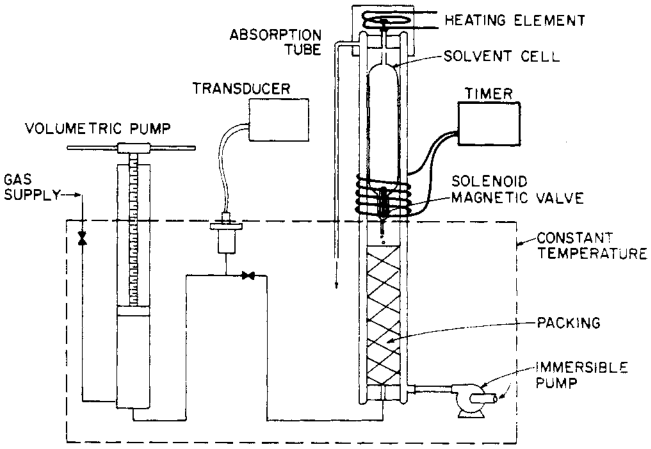

Figure 1. Solubility apparatus for moderate pressures

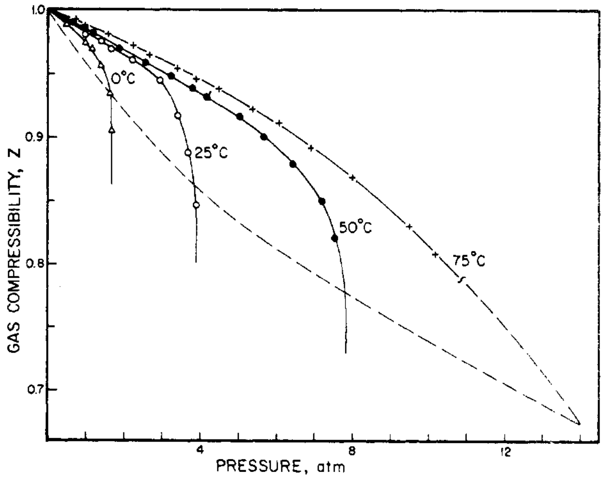

Figure 2. Compressibility factors for vinyl chloride

Table I. Vinyl Chloride Gas Compressibility

Press, atm	Z	Press, atm	Z	Press, atm	Z
0°C		50°C		75°C	
0.52	0.988				
1.00	0.974	0.68	0.990	0.68	0.992
1.18	0.969	1.00	0.985	1.00	0.988
1.41	0.956	1.22	0.983	1.59	0.981
1.65	0.933	1.88	0.969	2.26	0.972
1.71	0.905	2.57	0.958	2.71	0.965
		3.26	0.948	3.41	0.954
25°C		3.80	0.938	3.90	0.946
1.00	0.981	4.14	0.932	4.42	0.939
1.43	0.975	5.06	0.916	5.40	0.922
1.67	0.969	5.67	0.900	6.07	0.911
2.27	0.961	6.43	0.879	6.91	0.892
2.95	0.945	7.22	0.850	8.02	0.869
3.41	0.916	7.55	0.820	9.49	0.830
3.65	0.888	7.97	0.700	10.20	0.808
3.90	0.846				

Table II. Solubility of Vinyl Chloride in Water

Temp		Total press, atm				
		1.00[a]		1.36[b]	3.06[b]	6.12[b]
0.2°C	L	2.66		2.15	...	...
(10^4)	x	21.7		24.3	...	...
	H	457		558	...	...
25°C	L	1.07		...	0.868	...
(10^4)	x	7.79		...	20.6	...
	H	1284		...	1472	...
50°C	L	0.602	0.589[b]	...	0.543	0.473
(10^4)	x	3.68	3.60	...	11.5	22.1
	H	2384	2440	...	2560	2720
75°C	L	0.361		...	0.340	0.349
(10^4)	x	1.46		...	6.12	14.3
	H	4250		...	4380	4030

[a] Solubility apparatus for atmospheric pressure. [b] Solubility apparatus for pressures above atmospheric.

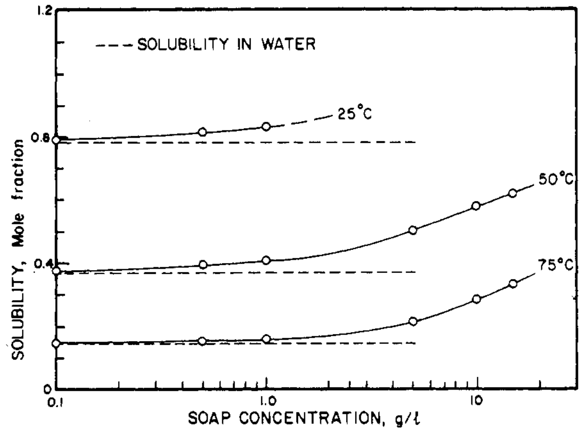

Figure 4. Vinyl chloride solubilities in potassium laurate solutions at atmospheric pressure

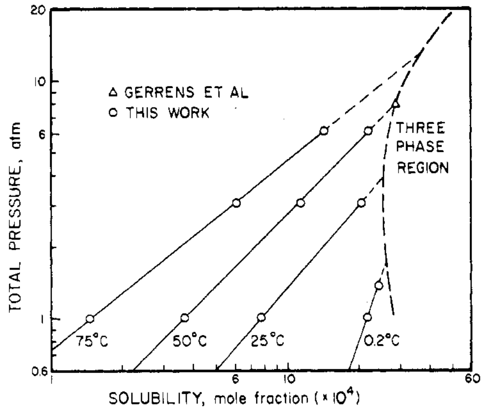

Figure 3. Vinyl chloride solubilities in water

possible to estimate the compressibilities of saturated vapor based on the compressibilities of super-heated vapor and vinyl chloride vapor pressure. This line is also shown in Figure 2.

Vinyl chloride solubilities expressed as Ostwald coefficients were calculated from the measured volume of vapor-free gas required to saturate the corresponding solvent volume by means of:

$$L = \frac{v_G{}^1 P}{v_L\left\{P - P_1^\circ(1 - x)\right\}} \tag{4}$$

The same equation was used to calculate the solubility for both devices since in both cases an incremental volume of vapor-free gas was measured. For the apparatus used at higher pressures, v_L corresponded to the volume of solvent in the solvent cell. Raoult's law was used to determine the solvent partial pressure; as a result, an iterative procedure was required to calculate the Ostwald coefficient based on estimated values of x. The corresponding mole fraction solubility, with due consideration to the gas compressibility, was calculated from:

$$x = \frac{\dfrac{pL}{PV_G}}{\dfrac{pL}{PV_G} + \dfrac{1}{V_L}} = \frac{\dfrac{pL}{ZRT}}{\dfrac{pL}{ZRT} + \dfrac{1}{V_L}} \tag{5}$$

The solubility results are given in Table II. A comparison of solubility measurements was made for the two solubility devices at atmospheric pressure and 50°C. A slightly lower solubility for the higher pressure apparatus of an average of about 2% may indicate incomplete saturation of the liquid in that apparatus. It is therefore considered possible that the solubilities obtained with the higher pressure apparatus are too low by that amount. This small possible uncertainty, however, would not seriously influence the observed effects of pressure and soap content on the solubilities.

The effect of pressure on vinyl chloride solubilities in water is illustrated in Figure 3. The solubility at 50°C and the saturation pressure as reported by Gerrens et al. (*3*) appear consistent with the results reported here. Similar linear extrapolations to the saturation pressure for the other temperatures indicate the probable limit of the three-phase region. The temperature effect of vinyl chloride solubilities in water, along with those of a number of other gases, has been considered in a recent publication (*6*).

Solubilities of vinyl chloride in aqueous potassium laurate solutions of concentrations increasing from 0.1 to 15.0 g/l. are listed in Table III. True three-component mole fraction solubilities are indicated, although the correction for the presence of soap in the water solution was small. The density of the soap solution increased by a maximum of only 1 part in 1000 (at 75°C) when compared with that for pure water for an increase in soap content from 0 to 15.0 g/l. Solubilization has been associated with the formation of soap micelles within which the additional solubilized material dissolves as discussed by Garrett (*2*).

In Table III are shown the percentage increases in solubility for vinyl chloride in potassium laurate solutions when compared with those in pure water. The effect of solubilization is greatest at 75°C at which temperature, for a soap concentration of 15.0 g/l., the solubility is enhanced by about 120%. The effect of pressure on the extent of solubilization is not expected to change significantly with a moderate increase in pressure. This is supported by the fact that at 50°C for soap concentrations of 1.0 g/l., the increase is 11.0, 11.2, and 11.3% for atmospheric pressure and pressures of 3 and 6 atm, respectively, whereas for concentrations of 10.0 g/l., the increase is 57.0, 59.1, and 55.2%, respectively. The effect

Table III. Solubilities of Vinyl Chloride in Aqueous Potassium Laurate Solutions

	Potassium laurate		Temp, °C		
Press	Concn, g/l.		25	50	75
Atmospheric	0.1	L	1.09	0.612	0.363
		$(10^4)\,x$	7.92 (1.7)[a]	3.77 (2.4)	1.47 (0.4)
	0.5	L	1.12	0.637	0.376
		$(10^4)\,x$	8.15 (4.6)	3.94 (5.8)	1.52 (4.0)
	1.0	L	1.14	0.667	0.387
		$(10^4)\,x$	8.30 (6.5)	4.08 (11.0)	1.56 (6.9)
	5.0	L	...	0.811	0.515
		$(10^4)\,x$	...	4.99 (35.3)	2.09 (43.2)
	10.0	L	...	0.935	0.698
		$(10^4)\,x$	...	5.78 (57.0)	2.80 (91.8)
	15.0	L	...	0.989	0.792
		$(10^4)\,x$	...	6.15 (67.1)	3.29 (125)
3.06 atm	1.0	L	...	0.610	...
		$(10^4)\,x$	...	12.9 (11.2)	...
	10.0	L	...	0.859	...
		$(10^4)\,x$	...	18.3 (59.1)	...
6.12 atm	1.0	L	...	0.530	...
		$(10^4)\,x$	...	24.6 (11.3)	...
	10.0	L	...	0.732	...
		$(10^4)\,x$		34.3 (55.2)	...

[a] Values in brackets indicate percentage increase in solubility compared with that in water.

of solubilization is graphically illustrated in Figure 4 in which the solubilities are shown to increase markedly above soap concentrations of 1 g/l. This type of change in solubility behavior has been used by Ross and Hudson (*10*) to estimate the critical micelle concentration. Critical micelle concentrations are, however, more commonly determined from surface tension measurements.

Nomenclature

A = calibration constant in Equation 1
H = Henry's law constant, atm/mole fraction
L = Ostwald coefficient, volume gas, cm^3/volume solvent, cm^3
P = total pressure of experiment, atm
$P_1{}^\circ$ = solvent vapor pressure, atm
p = gas partial pressure, atm
P_r = reduced pressure
T = vibration frequency, cycles/sec
T_r = reduced temperature
$v_G{}^1$ = volume of vapor-free gas, cm^3
v_L = volume of solvent, cm^3
V_G = gas molar volume at P, cm^3/g mol
V_L = liquid molar volume, cm^3/g mol
V = volume of compressed gas, cm^3
x = gas solubility, mole fraction
Z = gas compressibility factor $\left(\frac{PV}{nRT}\right)$
ω = Pitzer acentric factor
ρ = fluid density, g/cm^3

Subscript

i = initial conditions

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