# Liquid-Vapor Equilibrium Studies By Use of Excess Properties
# IV. Water-Ethylene Chlorohydrin System

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**The liquid-vapor equilibrium in the water–ethylene chlorohydrin system was studied at 100-mm Hg pressure, and the dependence on pressure of the water content of the azeotrope was determined by relative volatility measurements. The data obtained were thermodynamically consistent and may be correlated by use of the Wilson equations. The dependence of the composition of the azeotrope on pressure may be predicted also by use of the Margules equations with temperature-dependent parameters computed from heats of mixing.**

The data reported in the literature on the vapor-liquid equilibria of the water–ethylene chlorohydrin system contain incongruities such as different compositions of the azeotrope formed at the same pressure (*8–10*), or constant composition of the azeotrope formed at different pressures in the range of 200–760 mm Hg (*1*). There are also significant differences between the vapor pressures reported in the literature for ethylene chlorohydrin (*8, 10, 11*); as a consequence, the selection of thermodynamically consistent data is difficult, with the deviations of the Redlich-Kister consistency test,

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} \cdot dx_1 = 0 \qquad (1)$$

where the activity coefficients are computed from compositions of the phases in equilibrium and vapor pressures,

$$\gamma_i = \frac{P \cdot y_i}{P_i \cdot x_i} \qquad (2)$$

being highly dependent on the vapor pressures used. Regardless of the vapor pressures used for this purpose, the equilibrium data indicating constant azeotropic composition in the pressure range of 200–760 mm Hg (*1*) show large thermodynamic inconsistency.

To obtain reliable isobaric vapor-liquid equilibrium data in the water–ethylene chlorohydrin system for pressures of 100–760 mm Hg, first the vapor pressures of highly pure (99.9%) ethylene chlorohydrin were measured from 20° to 140°C. The influence of lower boiling thermal decomposition products formed during boiling above 80°C and detected by gas-liquid chromatography was avoided by use of a dynamic ebulliometer.

The vapor pressures of ethylene chlorohydrin are reported in Table I and are close to those determined by Komarov (*10*) and listed by Perry (*11*).

The vapor pressures were correlated with the least-squares method by use of the Antoine equation:

$$\log P_i = A_i - \frac{B_i}{C_i + t} \qquad (3)$$

Two sets of constants were used in the ranges of 50–90°C and 90–140°C, respectively, which are reported together with the constants used for water-vapor pressures in Table II.

The vapor-liquid equilibrium of the water–ethylene chlorohydrin system was studied by use of the recirculation still described in detail previously (*3*) and shown in Figure 1. The reboiler (a) is electrically heated and provided with the magnetic stirrer (m). The mixture of vapor and liquid rising through the Cottrell pump (b) separates below the baffle (S) provided with the precision thermometer (t). The vapors lift the tube (t), and the liquid returns to the reboiler (a) through the joint (e) and the truncated valve ($R_1$) which enables sampling without stopping the recycle. The upper part of the still was also heated to avoid changes in vapor compositions owing to thermal losses. The vapors are condensed in (c), and the condensate returns to the reboiler (a) through joint (r) and valve ($R_2$).

Operating at low pressures, the still was connected to a dynamic manostate, and at normal pressure it was connected to the dilatation manostate described previously (*2, 4*) through the condenser (d). The accuracy of pressure measurements was higher than 0.2 mm Hg, and those of temperatures were higher than 0.1°C. Ethylene chlorohydrin of 99.98% purity was used in all runs. The composition of the phases in equilibrium was analyzed by the refractometric method by use of the calibrating curve established by weighed samples, whose refractive indices are reported in Table III. The analytical errors by use of the refractometric method were less than 0.1 wt %. The obtained equilibrium data at 100-mm Hg pressure and the activity coefficients computed by Equation 2, neglecting the vapor-phase correction therms, are shown in Table IV. The deviation of the data from the consistency test (Equation 1) was 2% as computed by use of the values $\log \gamma_1/\gamma_2$ in Table IV.

The dependence of the azeotropic composition on the total pressure was studied with the same still and analytical method. Because of the inaccuracy in determining the azeotropic points by means of boiling-point measurements, the dependence of the relative volatility on composition was used for this purpose, as computed from the equilibrium compositions of the phases. The relative volatilities obtained,

$$\alpha = \frac{y_1 \cdot x_2}{x_2 \cdot y_1} \qquad (4)$$

are given in Table V and are plotted against liquid-phase compositions at various pressures in Figure 2. The azeotropic compositions at various pressures were obtained as the intersects of the lines fitted to the data points at constant pressure, and the abscissa $\alpha = 1$. The obtained dependence of the azeotropic composition on total pressure is shown with all available literature data in Figure 3.

According to the obtained experimental data, the water content of the azeotrope ranges from 57 wt % at normal pressure to 59 wt % at 50 mm Hg.

The experimental data were correlated by use of the Wilson equations (*12*):

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**Table I. Vapor Pressures of Ethylene Chlorohydrin**

| Vapor press, mm Hg | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 120 | 140 |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp, °C | 42.3 | 49.9 | 55.2 | 59.9 | 63.4 | 66.3 | 69.1 | 71.7 | 77.6 | 81.2 |

**Table II. Values of Constants Used in Antoine's Equation**

| Components | Temp range, °C | A | B | C |
|---|---|---|---|---|
| Water | 50–90 | 8.001121 | 1689.13889 | 229.8895 |
|  | 90–130 | 7.916818 | 1635.41202 | 224.74278 |
| Ethylene chlorohydrin | 50–90 | 10.15911 | 3254.74961 | 324.98751 |
|  | 90–130 | 6.360209 | 1003.73346 | 160.1130 |

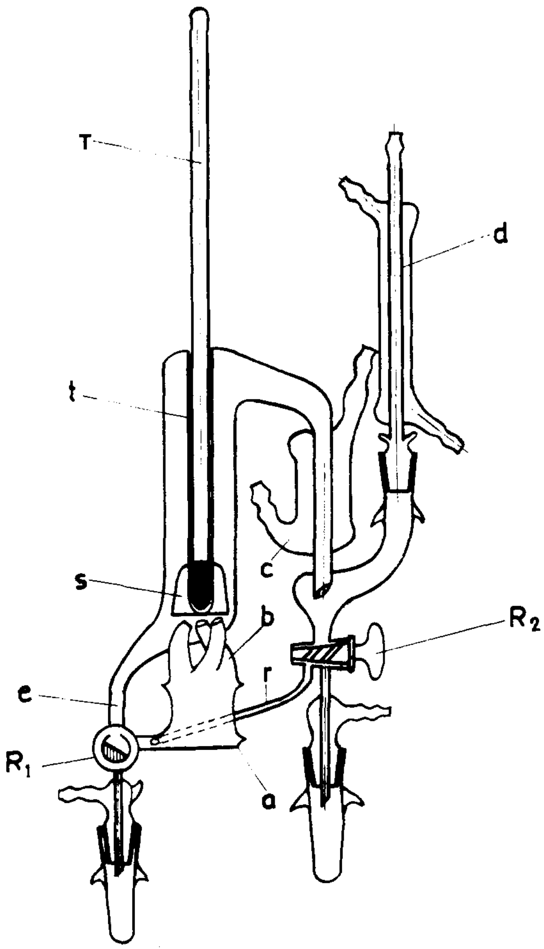

**Figure 1.** Liquid-vapor equilibrium still

**Table III. Refractive Indices of Water-Ethylene Chlorohydrin Mixtures at 20°C**

| Water content of mixture, wt % | $n^{20}D$ | Water content of mixture, wt % | $n^{20}D$ |
|---|---|---|---|
| 0 | 1.44227 | 56.37 | 1.3804 |
| 18.66 | 1.4218 | 59.05 | 1.3775 |
| 28.77 | 1.4107 | 68.43 | 1.3672 |
| 37.55 | 1.4010 | 75.70 | 1.3592 |
| 41.57 | 1.3968 | 76.73 | 1.3579 |
| 42.07 | 1.3960 | 100 | 1.3330 |
| 50.14 | 1.3872 |  |  |

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12} \cdot x_2) + x_2 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12} \cdot x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} \cdot x_1} \right]$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21} \cdot x_1) - x_1 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12} \cdot x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} \cdot x_1} \right] \quad (5)$$

where

$$\Lambda_{12} = \frac{V_2}{V_1} \cdot \exp \left( - \frac{\lambda_{12} - \lambda_{11}}{RT} \right),$$

$$\Lambda_{21} = \frac{V_1}{V_2} \cdot \exp \left( - \frac{\lambda_{21} - \lambda_{22}}{RT} \right) \quad (6)$$

The same data were correlated also by the third-order Margules equations,

$$\log \gamma_1 = x_2^2 [A_{12} + 2 x_1 (A_{21} - A_{12})],$$

$$\log \gamma_2 = x_1^2 [A_{21} + 2 x_2 (A_{12} - A_{21})] \quad (7)$$

by use of either constant or temperature-dependent parameters of the form:

$$A_{ij} = \frac{a_i}{2,3\, RT} - \frac{b_i}{R} \cdot \log T + c_i \quad (8)$$

The temperature dependence of the parameters (Equation 8) may be obtained by integrating the Gibbs-Helmholtz equation $-\Delta H/T^2 = \partial(\Delta G/T)/\partial T$ at constant pressure and infinite dilution (5) and substituting $\Delta G_i^\circ/RT = 2,3 \cdot \log \gamma_i^\circ = 2,3\, A_{ij}$, hence

$$\frac{dA_{ij}}{dt} = - \frac{\Delta H_i^\circ}{2,3\, RT^2} \quad (9)$$

and expressing the temperature dependence of heats of mixing at infinite dilution by

$$\Delta H_i^\circ = a_i + b_i \cdot T \quad (10)$$

The temperature dependence of molar volumes, necessary in computing the Wilson parameters (Equation 6) by use of the data shown in Table VI, was correlated by the second-degree equation

$$V_i = V_i^{(0)} + V_i^{(1)} \cdot T + V_i^{(2)} \cdot T^2 \quad (11)$$

The heats of mixing, necessary in computing the parameters $a_i$ and $b_i$ in Equations 8 and 10 were obtained at 50 and 80°C by use of the microcalorimeter described previously (6) and were correlated by the least-squares method by means of the equation

$$\Delta H = x_1 \cdot x_2 \cdot [x_1 \cdot (\Delta H_2^\circ) + x_2 \cdot (\Delta H_1^\circ)] \quad (12)$$

Both the Wilson as well as the Margules parameters and the integrating constants $c_i$ in the temperature-dependent parameters (Equation 8) were computed by minimizing the objective function (7)

$$\phi = \frac{\sum_{1}^{n} (\gamma_{1,\text{exp}} - \gamma_{1,\text{calc}})^2}{\sum_{1}^{n} (\gamma_{1,\text{exp}} - 1)} + \frac{\sum_{1}^{n} (\gamma_{2,\text{exp}} - \gamma_{2,\text{calc}})^2}{\sum_{1}^{n} (\gamma_{2,\text{exp}} - 1)} \quad (13)$$

The molar heats of mixing at infinite dilution and the parameters in Equation 8 are summarized in Table VII.

The parameters obtained by use of the Wilson equations are $\lambda_{12} - \lambda_{11} = 956.18$ and $\lambda_{21} - \lambda_{22} = 628.64$ cal/mol, the value of the objective function $\phi = 0.03$, and the fit of the experimental data, expressed as the average root mean square deviation of vapor-phase compositions, is 0.047.

By use of the Margules equations (Equation 7), even with temperature-dependent parameters, the fit of the experimental data was unsatisfactory, the value of the objective function was 0.07, and the mean root square deviation of the vapor-phase compositions was 0.091.

For accuracy of the fit of the data near the azeotropic point, the isobaric vapor-liquid equilibria were computed by solving at various liquid-phase compositions the system formed by the activity coefficient equations (Equation 5 or 7, respectively), the vapor-pressure equations (Equation 3), and the conditions:

$$x_1 + x_2 = 1, P_1 \cdot \gamma_1 \cdot x_1 + P_2 \cdot \gamma_2 \cdot x_2 = P \quad (14)$$

By use of the Wilson equations (Equation 5) with constant interaction energy difference parameters given above at $P$ = 100 mm Hg, the computed azeotropic data are: boiling point, 50.4°C, and concentration of water in the azeotrope, 60.4 wt %, about 1.4% higher than obtained by relative volatility measurements. At $P$ = 760 mm Hg, the boiling point of 97.9°C and the water concentration of 56.6 wt % in the azeotrope were obtained, in satisfactory agreement with the concentration obtained by the relative volatility measurements.

By use of the Margules equations with temperature-dependent parameters (Equation 8), the water concentration computed in the azeotrope at $P$ = 100 mm Hg was 55.6 wt %, about 3% lower than determined by the relative volatility method.

**Table IV. Experimental Vapor-Liquid Equilibrium Data for Water(1)-Ethylene Chlorohydrin(2) System at 100 mm Hg**

| Temp, °C | Concn of water, molar fraction | | Activity coefficients | | log $\gamma_1/\gamma_2$ |
|---|---|---|---|---|---|
| | Liquid phase | Vapor phase | $\gamma_1$ | $\gamma_2$ | |
| 64.8 | 0.0875 | 0.4193 | 2.58 | 0.99 | 0.416 |
| 64.8 | 0.0953 | 0.4111 | 2.32 | 1.01 | 0.476 |
| 64.3 | 0.1029 | 0.4253 | 2.28 | 1.02 | 0.349 |
| 59.5 | 0.1570 | 0.5854 | 2.56 | 1.00 | 0.410 |
| 56.6 | 0.3320 | 0.7111 | 1.68 | 1.01 | 0.219 |
| 57.2 | 0.3441 | 0.7020 | 1.56 | 1.03 | 0.178 |
| 56.2 | 0.3441 | 0.7173 | 1.67 | 1.03 | 0.208 |
| 51.2 | 0.5152 | 0.8013 | 1.584 | 1.275 | 0.0942 |
| 51.2 | 0.5580 | 0.8186 | 1.494 | 1.277 | 0.0682 |
| 50.4 | 0.7030 | 0.8384 | 1.263 | 1.766 | −0.1455 |
| 50.4 | 0.7182 | 0.8427 | 1.243 | 1.812 | −0.1636 |
| 50.4 | 0.8279 | 0.8564 | 1.096 | 2.709 | −0.3931 |
| 50.4 | 0.8876 | 0.8709 | 1.039 | 3.728 | −0.5546 |
| 50.4 | 0.8918 | 0.8710 | 1.035 | 3.859 | −0.5717 |
| 50.4 | 0.9164 | 0.8808 | 1.018 | 4.622 | −0.6569 |
| 50.4 | 0.9375 | 0.8968 | 1.013 | 5.363 | −0.7237 |
| 50.6 | 0.9557 | 0.9142 | 1.004 | 6.225 | −0.7924 |
| 50.8 | 0.9642 | 0.9223 | 0.993 | 6.891 | −0.8412 |

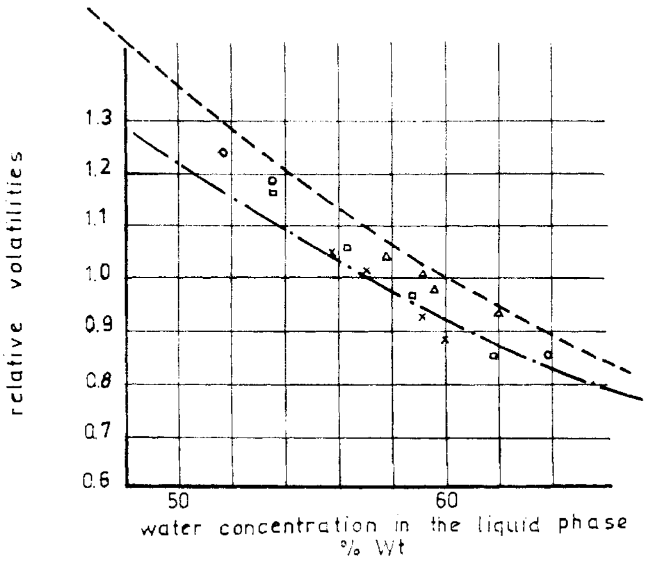

**Figure 2.** Relative volatilities in water-ethylene chlorohydrin system close to azeotropic point at various pressures

| Press, mm Hg | Exptl data | Predicted data |
|---|---|---|
| 50 | △ | |
| 100 | ○ | --- |
| 200 | □ | |
| 760 | × | —·— |

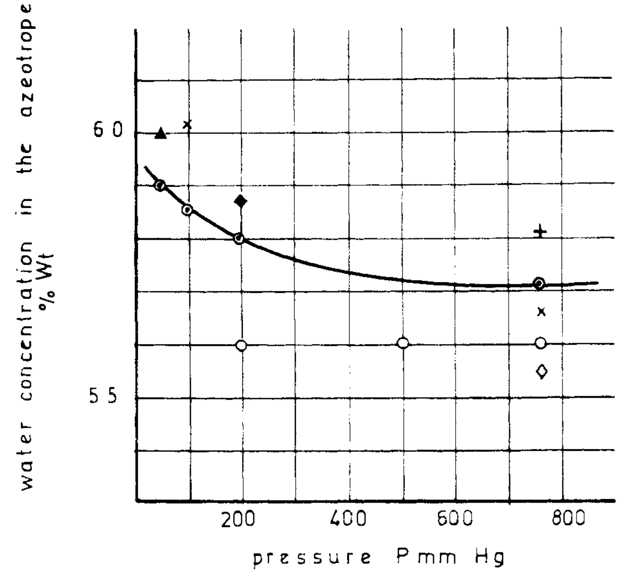

**Figure 3.** Dependence on pressure of water concentration in water-ethylene chlorohydrin azeotrope

| References | Sign |
|---|---|
| Komarov (10) | ♦ |
| Ababi and Mihaila (1) | ○ |
| Kogan and Ogorodnikov (9) | + |
| Kireev and Nikiforova (8) | ▲ |
| Experimental data | ⊙ |
| Predicted by Wilson equation | × |
| Predicted by Equations 7, 8 | ◊ |

Although the Margules equation was inadequate in predicting the equilibrium data in the whole range of compositions, the use of the temperature-dependent parameters (Equation 8) computed from the molar heats of mixing at infinite dilution enables prediction of the azeotropic data at various pressures if the integrating parameters $c_i$ are replaced by "local" values $c_i'$, computed by use of the

**Table V. Relative Volatilities in Vicinity of Azeotropic Point at Various Pressures**

| Pressure, mm Hg | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 50 | | | 100 | | | 200 | | | 760 | | |
| Concn of water, wt % | | Relative volatility, $\alpha$ | Concn of water, wt % | | Relative volatility, $\alpha$ | Concn of water, wt % | | Relative volatility, $\alpha$ | Concn of water, wt % | | Relative volatility, $\alpha$ |
| Liquid phase | Vapor phase | | Liquid phase | Vapor phase | | Liquid phase | Vapor phase | | Liquid phase | Vapor phase | |
| 57.2 | 59.3 | 1.09 | 51.8 | 57.2 | 1.239 | 53.5 | 57.1 | 1.17 | 55.8 | 57.1 | 1.05 |
| 57.8 | 58.8 | 1.04 | 53.6 | 57.8 | 1.186 | 56.3 | 57.7 | 1.06 | 57.0 | 57.5 | 1.02 |
| 59.2 | 59.5 | 1.01 | 63.8 | 60.1 | 0.854 | 58.8 | 58.1 | 0.97 | 59.1 | 57.3 | 0.93 |
| 59.6 | 59.1 | 0.98 | 64.8 | 55.3 | 0.819 | 62.0 | 58.1 | 0.85 | 60.0 | 57.0 | 0.885 |
| 61.0 | 59.5 | 0.94 | | | | | | | | | |

**Table VI. Molar Volumes of Pure Components**

| Components | $i$ | Temp, °C | $V_i$, cc/mol | Temp, °C | $V_i$, cc/mol | Temp, °C | $V_i$, cc/mol |
|---|---|---|---|---|---|---|---|
| Water | 1 | 4.0 | 18.06 | 50.0 | 18.278 | 100.0 | 18.844 |
| Ethylene chlorohydrin | 2 | 30.6 | 67.57 | 50.0 | 68.49 | 90.0 | 71.10 |

**Table VII. Parameters in Equations 7-10 and Molar Heats of Mixing at Infinite Dilution**

| Components | $i$ | $\Delta H_i°$, cal/mol | | $a_i$ | $b_i$ | $c_i$ | $c_i'$ |
|---|---|---|---|---|---|---|---|
| | | 50°C | 80°C | | | | |
| Water | 1 | 367.7 | 359.8 | 452.92 | −0.264 | −0.53281 | −0.79916 |
| Ethylene chlorohydrin | 2 | 621.1 | 609.2 | 748.73 | −0.395 | −0.07745 | −0.04480 |

activity coefficients corresponding to the azeotropic point at 100-mm Hg pressure. The "local" values of the Margules parameters, necessary in computing the integrating parameters $c_i'$ by Equation 8, were obtained by solving Equation 7 for

$$A_{12}^* = \frac{1 - 2x_1^*}{(1 - x_1^*)^2} \cdot \log \gamma_1^* + \frac{2}{x_1^*} \cdot \log \gamma_2^*$$

$$A_{21}^* = \frac{2x_1^* - 1}{x_1^{*2}} \cdot \log \gamma_2^* + \frac{2}{1 - x_1^*} \cdot \log \gamma_1^* \quad (15)$$

where $x_1^*$, $\gamma_1^*$, and $\gamma_2^*$ are the concentration of water and the activity coefficients at the azeotropic point, respectively. From the experimental data shown in Table IV, one obtains by interpolation $x_1^* = 0.87$, $\gamma_1^* = 1.07$, and $\gamma_2^* = 3.25$. The integrating constants $c_i'$ obtained are given in Table VII. The boiling point of the azeotrope at 760 mm Hg computed by solving the system of Equations 3, 7, 8, and 14 was 97.9°C, and the water content of the azeotrope was 55.6 wt %—in satisfactory agreement with the experimental data shown in Table V. The average root mean square deviations of the vapor-phase compositions given in Table V as computed by use of Equation 8 with "local" integrating constants $c_i'$ are 0.013 at 100-mm Hg pressure and 0.013 at 760-mm Hg pressure.

## Conclusions

The vapor-liquid equilibrium data determined for the water-ethylene chlorohydrin system at 100-mm Hg pressure by use of highly pure ethylene chlorohydrin and the vapor-pressure data fitted to Antoine's equation are thermodynamically consistent and may be correlated by use of the Wilson equation. The Wilson equation, with constant interaction energy difference parameters $\lambda_{12} - \lambda_{11} = 956.18$ and $\lambda_{21} - \lambda_{22} = 628.64$, may be used in predicting the azeotropic data at various pressures, in satisfactory agreement with the data obtained by vapor and liquid-phase composition measurements near the azeotropic point.

The fit of the experimental data to the Margules third-order equations, by use of temperature-dependent parameters computed from heats of mixing at 50° and 80°C, leads also to satisfactory prediction of the azeotropic data in the range of 100-760-mm Hg pressure, although the same equations were inadequate for the whole range of concentrations.

According to the correlated experimental data, the water-ethylene chlorohydrin azeotrope contains 59.7 ± 0.7 wt % water at 100-mm Hg and 57 ± 0.5 wt % water at 760-mm Hg pressure.

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