have a salting out power in the first case and five in the second.

Dehydration by salting out, when applicable, is generally the most economical process, particularly when the organic compound forms, during distillation, a binary azeotrope with water with a percentage of water higher than the percentage of water in the organic liquid-rich layer obtained in the salting out process.

An elegant example of application of absorption of water by a concentrated salt solution would be in an esterification operation where the water of esterification would be removed continuously by distillation in the form of a binary or ternary azeotrope and the water would be absorbed in a concentrated solution of an appropriate salt; meanwhile the alcohol and eventual entraining agent would be recycled in the esterification apparatus.

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Vapor-Liquid Equilibrium Data for the Binary Mixtures Carbon Tetrachloride–1,1,2-Trichloroethane and 1,2-Dichloroethane–1,1,2-Trichloroethane

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INDUSTRIAL CHLORINATION of hydrocarbons produces a mixture of many products which are often separated by fractionation. Design of these distillation columns is severely limited by lack of experimental data; accordingly vapor-liquid equilibrium data for two such binary systems, carbon tetrachloride-1,1,2-trichloroethane and 1,2-dichloroethane-1,1,2-trichloroethane have been obtained by using an Othmer still. The system 1,2-dichloro-1,1,2-trichloroethane obeys Raoult's law, in contrast to the previous data of Portnov and Seferovich (3). However, the activity coefficient from the latter data do not satisfy the Gibbs-Duhem equation. Activity coefficients for the carbon tetrachloride-1,1,2-trichloroethane system can be represented by $\log \gamma = A(1-x)^2$, where A is calculated by the method of least squares to be 0.153 ± 0.015 with 95% confidence limits. This tolerance corresponds to a standard deviation of 0.0073 and a correlation coefficient of 0.958.

EXPERIMENTAL COMPOUNDS

Carbon tetrachloride (Fischer Scientific, reagent grade) and 1,2-dichloroethane (Fischer Scientific, reagent grade) were used. The 1,1,2-trichloroethane was obtained by distilling the technical grade (Fischer Scientific Laboratory Chemical) in a Podbielniak column (10 feet long, 1 inch in diameter, glass spiral packing having an equivalent of 500 theoretical plates at a reflux ratio of 40 to 1), and collecting the fraction boiling between 113.7° and 114.1° C.

PROCEDURE

A conventional Othmer still was used, and constant pressure of 740 mm. of Hg was maintained by a Cartesian

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manostat. Boilup rate in the still was adjusted to minimize both entrainment of liquid in the vapor and partial condensation of the vapor (*1*). Temperatures were measured by a copper-constantan thermocouple, obtainable accuracy being ±0.3° C. Compositions of liquid and vapor samples were measured using a refractomer (Bausch & Lomb, to five figures), the estimated accuracy being ±0.005 mole fraction.

THEORY

If the vapor phase is an ideal gas mixture, then the equality of the partial molal fugacities in the vapor and liquid phases yields

$$\Pi y_i = \gamma_i P_i x_i \qquad (1)$$

Activity coefficients were calculated by using Equation 1. If the activity coefficients do not vary greatly with temperature, the Gibbs-Duhem equation may be written:

$$\left(\frac{\partial \log \gamma_1}{\partial (1 - x_1)^2}\right)_P = \left(\frac{\partial \log \gamma_2}{\partial (1 - x_2)^2}\right)_P \qquad (2)$$

The present data satisfy this condition. Further activity coefficients can be represented by the Margules two-suffix equation:

$$\log \gamma = A\,(1 - x)^2 \qquad (3)$$

RESULTS

Vapor pressure data for the pure components was obtained from the Handbook of Chemistry and Physics (*2*). Interpolation for the present range was performed by using the equations:

$$CCl_4 \qquad \log_{10} P = 7.3479 - \frac{1563}{T} \qquad (4)$$

$$C_2Cl_4Cl_2 \qquad \log_{10} P = 7.4218 - \frac{1617}{T} \qquad (5)$$

$$C_2Cl_3Cl_3 \qquad \log_{10} P = 7.8920 - \frac{1939}{T} \qquad (6)$$

Table I presents the experimental results for the $ClCl_4$-$C_2H_3Cl_3$ system, while the representive activity coefficients are plotted *vs.* $(1 - x)^2$ (Figure 1). In the $C_2H_3Cl_3$-$C_2H_4Cl_2$ system, individual activity coefficients did not differ significantly from unity over the entire concentration range, thus indicating the validity of Raoult's law.

Table I. Experimental Data for CCl_4-$C_2H_3Cl_3$ System

	CCl_4, Mole Fraction	
Temperature, ° C.[a]	Liquid phase	Vapor phase
77.6	0.927	0.970
79.4	0.837	0.927
80.2	0.792	0.906
86.9	0.490	0.750
89.8	0.403	0.687
93.6	0.270	0.587
96.4	0.210	0.494
104.0	0.090	0.262

[a] Total pressure 740 mm. Hg.

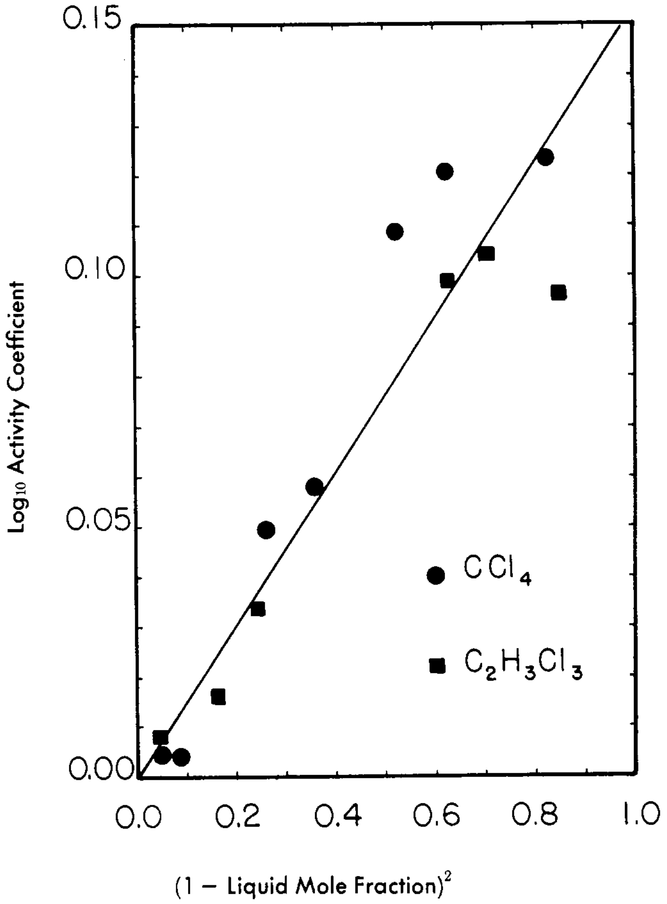

Figure 1. Activity coefficients *vs.* composition

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NOMENCLATURE

A = Margules two-suffix equation constant
P = vapor pressure of pure component, mm. Hg
T = absolute temperature, ° K.
x = mole fraction, component in liquid phase
y = mole fraction, component in vapor phase
γ = liquid phase activity coefficient
Π = total pressure on system, mm. Hg

Subscripts

1, 2 = components 1 and 2, respectively

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