

It is very difficult to represent the equilibria for these systems by the usual thermodynamically consistent polynomials. By truncating the data at a mole fraction amine of 0.6 (89.4 wt. %) and using a large number of constants, a good fit was obtained in some cases.

The data in Table IV were fitted with a 6-constant Chebyshev polynomial. The function fitted was  $\ln \gamma_a/x_a^2$ . The 13 pressure points in Table IV from 0.025 to 0.6 were represented with an average error of 0.3 mm. and a maximum error of 1.2 mm. at a mole fraction of 0.05. A Chebyshev fit tends to minimize the maximum error. Even so, a considerable error always occurs at low amine mole fractions.

The polynomial for ethyl-*sec*-butylamine at 20° C. in terms of mole fraction amine is

$$\frac{\ln \gamma_a}{x_a^2} = 3.9500 - 30.469x_a + 168.51x_a^2 - 478.89x_a^3 + 668.08x_a^4 - 358.15x_a^5$$

#### NOMENCLATURE

- $G^E$  = excess Gibbs free energy in cal. per gram-mole  
 $P$  = total pressure in mm. of Hg  
 $p$  = partial pressure in mm. of Hg  
 $x$  = mole fraction in the liquid  
 $y$  = mole fraction in the vapor

#### Greek

- $\gamma$  = activity coefficient,  $p/p^{\circ}x$

#### Subscripts

- 1 = component 1  
 2 = component 2  
 $w$  = water  
 $a$  = amine

#### Superscripts

- o = pure component

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## Vapor-Liquid Equilibria of Binary Systems of Water with Methanol and Ethanol at Extreme Dilution of the Alcohols

PER DALAGER

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**A new method for determining vapor-liquid equilibrium data for binary systems, including measurements at concentrations of one of the components in the parts per million range, is described. The method is based on the use of radioactive tracers, as the component in low concentration is added partly in an isotopic form. The method has been tried at 760 mm. of Hg pressure for two systems, methanol-water and ethanol-water, at low concentrations of the alcohols. Separation factors and activity coefficients for the alcohols at extreme dilution are given. The data have been tested for thermodynamic consistency and proved consistent.**

THE DEMAND for very pure chemicals has made extractive distillation, with a high grade of purification ability, an often-used separation operation. This means that experimentally verified values of separation factors, the  $K$ -values, at extreme dilution would be very useful.

Vapor-liquid equilibrium investigations reported in the literature have seldom been performed at concentrations of any of the components lower than 0.5 mole %, mostly because the available and reproducible methods of analysis such as density, index of refraction, etc., do not allow accurate determinations of concentrations lower than this limit.

This investigation presents a method for determining separation factors at very low concentrations of one of the components, using radioactive labeled compounds as tracers. The use of isotopic tracers makes it possible to measure very small amounts of the component in question.

This novel method has been used for the binary systems of water with methanol and ethanol at very low concentrations of the alcohols.

#### EXPERIMENTAL

**Apparatus.** A slightly modified equilibrium still modeled on the principle of Thornton (3) was used. The most important modification was the introduction of a cooling facility of the condensate trap to prevent the condensate, the boiling point of which is up to 10°C. lower than that of the liquid, from boiling and fractionizing.

Figure 1 shows the still, the working principle of which is well known. The temperature inside the cylinder surrounding the two traps, the Cottrell tube, and the disengagement chamber, is kept constantly about 1°C. above the boiling point that is measured in the disengagement chamber. The temperature in the vapor line is kept about 5°C. higher than the boiling point.

The temperatures are measured with thermistors and recorded on a strip chart recorder. The accuracy of the temperature measurements were  $\pm 0.02^\circ\text{C}$ .

All the experiments are run at 760 mm. of Hg pressure, kept constant within  $\pm 1$  mm. of Hg with a mercury-

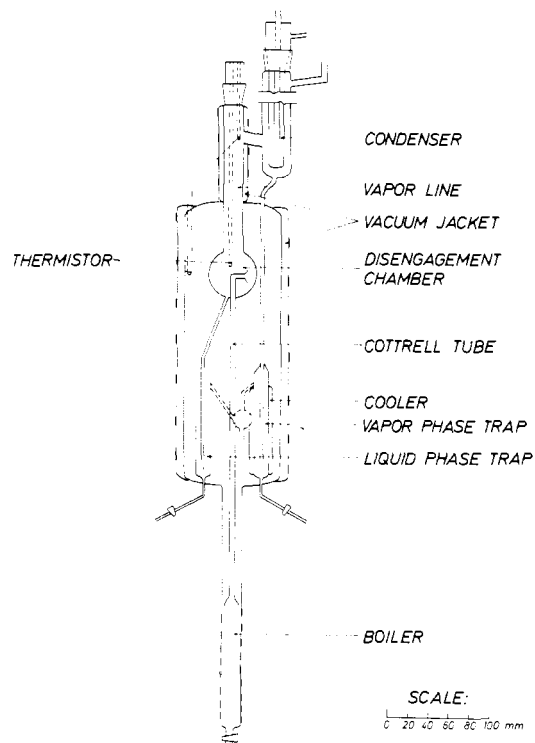


Figure 1. The equilibrium still

manostat, and measured with an ordinary mercury-manometer.

**Chemicals.** The alcohols used are methanol, Baker Analyzed, water content 0.03%, and ethanol, "99.9%" (De Danske Spritfabrikker). The two alcohols are used as they are delivered, but corrections for the water content are incorporated in the calculations.

The carbon-14-labeled alcohols, specific activity about 10 mc. per mmole, are purchased from The Radiochemical Centre, Amersham, and are diluted about 5000 times with the alcohols.

These labeled alcohols were purified by preparative gas chromatography to remove all radioactive impurities.

**Procedure.** Known amounts of alcohol and water are mixed, and 10  $\mu$ l. of labeled alcohol is added to the mixture. Five milliliters is withdrawn from this mixture for analysis. The rest of the mixture, about 200 ml., is charged to the still, and the heating is started. After about 30 minutes, about 2 ml. of the liquid- and condensate-phase is withdrawn and rejected. The pressure is adjusted to 760 mm. of Hg. After the pressure adjustment, it will be 10 to 20 minutes until the temperature in the disengagement chamber is constant, i.e., within  $\pm 0.05^\circ\text{C}$ ., and after that, the experiment is kept running for 2 hours to ensure real equilibrium. The suitability of a 2-hour run has been checked by runs of shorter and longer duration and has proved satisfactory.

After the 2-hour distillation, heating is stopped and samples are withdrawn from the liquid and the condensate. From each sampling trap the first 2 ml. is withdrawn and discarded; then 1.5-ml. samples are withdrawn three times and used for the following measurements.

From each of these six samples, as well as from two samples of the charge, a portion of 1.000 ml. is pipeted into a scintillation vial, and 20 ml. of a scintillator solution is added.

The solutions are counted in a two-channel Packard liquid scintillation spectrometer for 100.00 minutes or 900,000 counts, whichever is reached first.

Being of very different compositions, the samples are counted with different efficiency. The efficiency can be calculated with sufficient accuracy by counting at different

settings of the two counting channels. The correlation used is based upon exact measurements of efficiency by the internal standardization method.

The method of analysis used has been checked by gas chromatographic analyses, in cases where this was suitable.

## CALCULATIONS

The measured and efficiency-corrected activities of the charge, the liquid, and the condensate are  $a_{ch}$ ,  $a_{liq}$ , and  $a_{cond}$  counts per minute per ml., respectively.

As the density of alcohol-water mixtures varies non-stoichiometrically with the mole fraction of the alcohol, all samples are withdrawn with equal volumes. The measured activity must be evaluated as specific activities per weight unit in order to be able to compare them. Thus, the following calculations are necessary for determining  $K_A$  and  $K_W$ . A 1.000 ml. charge contains  $[M_A \cdot d_{ch} \cdot x_{ch}] / [M_A \cdot x_{ch} + M_W(1 - x_{ch})]$  grams of alcohol. 1.000 ml. of liquid must then contain

$$\frac{a_{liq} \cdot M_A \cdot d_{ch} \cdot x_{ch}}{a_{ch} \cdot M_A \cdot x_{ch} + M_W(1 - x_{ch})} \text{ grams of alcohol}$$

and

$$d_{liq} - \frac{a_{liq} \cdot M_A \cdot d_{ch} \cdot x_{ch}}{a_{ch} \cdot M_A \cdot x_{ch} + M_W(1 - x_{ch})} \text{ grams of water}$$

These amounts of alcohol and water, and similar ones for the condensate, give

$$x_{liq} = \frac{\frac{a_{liq} \cdot x_{ch}}{a_{ch}}}{\frac{a_{liq} \cdot x_{ch}}{a_{ch}} + (1 - x_{ch}) \cdot \frac{d_{liq}}{d_{ch}} + \frac{M_A}{M_W} \cdot x_{ch} \left( \frac{d_{liq}}{d_{ch}} - \frac{a_{liq}}{a_{ch}} \right)} \quad (1)$$

and

$$x_{cond} = \frac{\frac{a_{cond} \cdot x_{ch}}{a_{ch}}}{\frac{a_{cond} \cdot x_{ch}}{a_{ch}} + (1 - x_{ch}) \cdot \frac{d_{cond}}{d_{ch}} + \frac{M_A}{M_W} \cdot x_{ch} \left( \frac{d_{cond}}{d_{ch}} - \frac{a_{cond}}{a_{ch}} \right)} \quad (2)$$

From Equations 1 and 2,  $K_A$  and  $K_W$  are

$$K_A = \frac{x_{cond}}{x_{liq}}$$

and

$$K_W = \frac{1 - x_{cond}}{1 - x_{liq}}$$

The density of liquid and condensate is found by a trial-and-error method, using a formula relating density to mole fraction of the alcohol. As a first approximation to  $x_{liq}$  (or  $x_{cond}$ )

$$x_{liq} \text{ (or } x_{cond}) = \frac{a_{liq} \text{ (or } a_{cond})}{a_{ch}} \cdot x_{ch}$$

The density is calculated and used in these formulas to calculate the mole fraction. This procedure is continued until the numerical error in density is less than 0.001.

## CALCULATION OF ACTIVITY COEFFICIENTS

The activity coefficients at each experimental point were calculated according to Van Ness (4) by Equation 3, which is valid only at low pressures for binary mixtures.

$$\ln \gamma_i = \ln K_i \cdot \frac{P}{P_i^s} + \frac{(B_{ii} - V_i^s)(P - P_i^s)}{RT} + \frac{P \cdot \gamma_i^s \cdot \delta_{ij}}{RT} \quad (3)$$

where  $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ .

The third term on the right side of Equation 3, which corrects for nonideal solution of the nonideal gases in the vapor phase, can be calculated only with great uncertainty, due to few and divergent experimental determinations of the interaction virial-coefficient  $B_{ij}$  and some approximate correlating equations for determining  $B_{ij}$ .

As the maximum contribution to the activity coefficient from this third term is less than 1%, and as the uncertainty in determining it is so great, this term has been neglected in the present calculations.

In this work with polar components, some correlations of Prausnitz *et al.* (2) for determining  $P_i^s$ ,  $V_i^L$ ,  $B_{ii}$ , and the necessary constants for these calculations were used.

## RESULTS AND DISCUSSION

The present experimental work has covered the concentration range from nearly 0 to 100 mole % alcohol, but as good investigations have been reported in the range from 1 to 100 mole %, special attention has been focused on the very low concentrations. All experiments were performed in the same type of equilibrium still.

Tables I and II contain experimental and calculated results of the investigation for the methanol-water and ethanol-water systems, respectively.

To show the trend of the  $K$ -values—the same trends are found for the activity coefficients—at very low concentrations of the alcohol, a logarithmic scale has been used for the mole fraction in Figure 2.

Figures 3 and 4 show ordinary graphs of activity coefficients vs. mole fraction.

As can be seen from Figure 2, some scattering of the results for very low concentrations is observed, but nevertheless, it must be possible to use these graphs—and the analogous graphs for activity coefficients—to estimate  $K$ -values and activity coefficients at extreme dilution of the alcohols in water.

These values with their standard deviation are  $K(\text{MeOH}/\text{H}_2\text{O}) = 8.51 \pm 0.42$ ;  $K(\text{EtOH}/\text{H}_2\text{O}) = 13.4 \pm 0.5$ ;

Table II. Vapor-Liquid Equilibrium Data for Ethanol-Water

Temp., °C.	Mole Fraction EtOH in Liquid	Mole Fraction EtOH in Vapor	$K_{\text{EtOH}}$	$K_{\text{H}_2\text{O}}$	$\gamma_{\text{EtOH}}$	$\gamma_{\text{H}_2\text{O}}$
100.00	0.000002	0.000034	13.8	1.00	6.41	0.998
100.00	0.000002	0.000024	14.0	1.00	6.51	0.998
100.00	0.000022	0.000308	14.1	1.00	6.56	0.998
100.00	0.000014	0.000280	19.5	1.00	9.07	0.998
100.00	0.000014	0.000183	13.1	1.00	6.09	0.998
100.00	0.000208	0.002454	11.8	0.998	5.50	0.997
100.00	0.000148	0.001591	10.7	0.999	5.00	0.998
100.00	0.000187	0.002475	13.2	0.998	6.18	0.997
100.00	0.000150	0.001957	13.1	0.998	6.09	0.997
98.50	0.004815	0.072680	15.1	0.932	7.39	0.980
98.60	0.004014	0.059219	14.8	0.945	7.21	0.992
98.55	0.004307	0.059815	13.9	0.944	6.79	0.992
93.00	0.0315	0.2582	8.19	0.766	4.83	0.983
92.95	0.0370	0.3625	9.79	0.662	5.77	0.851
87.95	0.0740	0.3881	5.25	0.661	3.68	1.02
85.10	0.1218	0.4658	3.83	0.608	2.97	1.05
84.85	0.1283	0.4878	3.80	0.588	2.98	1.03
81.85	0.2548	0.5626	2.21	0.587	1.93	1.15
81.90	0.2597	0.5539	2.13	0.603	1.86	1.18
80.50	0.3937	0.6201	1.58	0.627	1.45	1.30
80.35	0.3971	0.6128	1.54	0.642	1.43	1.34
79.30	0.5472	0.6789	1.24	0.709	1.19	1.54
78.50	0.6980	0.7568	1.08	0.805	1.07	1.81
78.20	0.8400	0.8416	1.00	0.990	1.00	2.25
78.20	0.8393	0.8391	1.00	1.00	1.00	2.28
78.20	0.9140	0.9223	1.01	0.904	1.01	2.06
78.20	0.9099	0.9189	1.01	0.901	1.01	2.05

Table I. Vapor-Liquid Equilibrium Data for Methanol-Water

Temp., °C.	Mole Fraction MeOH in Liquid	Mole Fraction MeOH in Vapor	$K_{\text{MeOH}}$	$K_{\text{H}_2\text{O}}$	$\gamma_{\text{MeOH}}$	$\gamma_{\text{H}_2\text{O}}$
100.00	0.000006	0.000045	7.54	1.00	2.31	0.998
100.00	0.000004	0.000044	9.79	1.00	3.00	0.998
100.00	0.000004	0.000037	8.74	1.00	2.68	0.998
100.00	0.000054	0.000516	9.52	1.00	2.92	0.998
100.00	0.000053	0.000458	8.72	1.00	2.67	0.998
100.00	0.000047	0.000428	9.08	1.00	2.78	0.998
100.00	0.000048	0.000423	8.88	1.00	2.72	0.998
99.95	0.000450	0.003849	8.55	0.997	2.62	0.997
99.95	0.000394	0.003296	8.36	0.997	2.56	0.996
99.25	0.005719	0.045222	7.91	0.960	2.48	0.983
99.25	0.005840	0.045705	7.83	0.960	2.45	0.983
95.10	0.0342	0.2222	6.50	0.805	2.31	0.957
95.00	0.0335	0.2195	6.56	0.807	2.33	0.963
94.95	0.0329	0.2179	6.62	0.809	2.36	0.967
90.35	0.0761	0.3674	4.83	0.685	1.98	0.969
90.15	0.0738	0.3665	4.97	0.684	2.05	0.975
86.50	0.1176	0.4855	4.13	0.583	1.92	0.955
86.45	0.1207	0.4694	3.89	0.603	1.81	0.990
79.15	0.2646	0.6184	2.34	0.519	1.38	1.13
75.20	0.4092	0.7305	1.79	0.456	1.21	1.17
71.80	0.5810	0.8079	1.39	0.458	1.07	1.36
71.80	0.5816	0.8313	1.43	0.403	1.09	1.19
69.10	0.7218	0.8542	1.18	0.524	0.997	1.74
66.50	0.8808	0.9417	1.07	0.489	0.993	1.82
64.95	0.9657	0.9569	0.991	1.26	0.975	5.01
64.70	0.9871	0.9778	0.991	1.72	0.984	6.92

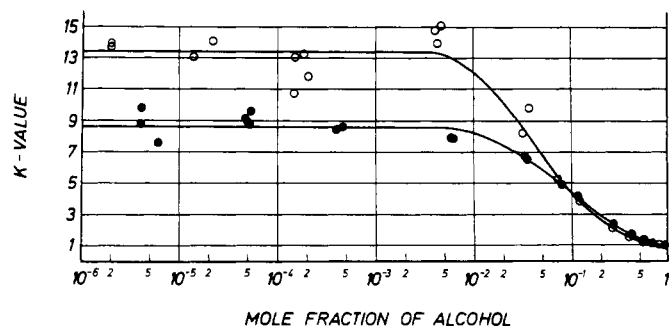


Figure 2.  $K$ -values vs. mole fraction of alcohol

● Methanol  
○ Ethanol

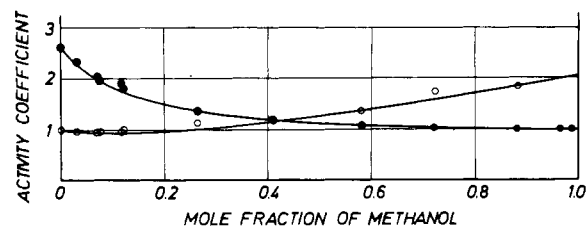


Figure 3. Activity coefficients vs. mole fraction of methanol

● Methanol  
○ Water

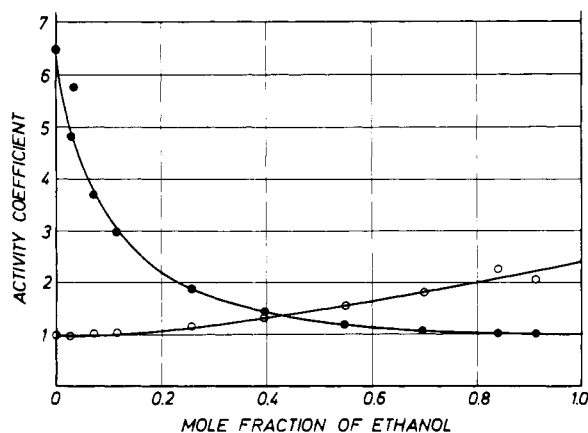


Figure 4. Activity coefficients vs. mole fraction of ethanol  
 ● Ethanol  
 ○ Water

$\gamma(\text{MeOH}/\text{H}_2\text{O}) = 2.62 \pm 0.11$  and  $\gamma(\text{EtOH}/\text{H}_2\text{O}) = 6.48 \pm 0.36$ .

Figure 2—and a similar graph for activity coefficients—shows the  $K$ -values and activity coefficients to be practically constant in the low concentration range, i.e., below 0.5 mole %.

This means that a few experimental determinations in this region are sufficient to determine the separation factor in the parts per million range.

In the past, extrapolation has been used to estimate these  $K$ -values, but often such extrapolations are made from concentrations of 1 mole % or even higher, and here it is shown that  $K$ -values increase until the mole fraction is less than 0.005.

Commonly used extrapolated  $K$ -values for the methanol-water and ethanol-water systems are  $K(\text{MeOH}/\text{H}_2\text{O}) = 7.5$  and  $K(\text{EtOH}/\text{H}_2\text{O}) = 11.5$ , but this investigation shows  $K$ -values for both systems which are about 15% higher.

The present method, with use of only one isotopic tracer, is not particularly suitable for the entire mole fraction range. When the mole fraction of the compound, part of which is labeled, is greater than about 0.75, the uncertainty in the results for the unlabeled component, here water, is rather great.

In case the whole concentration range has to be covered with equal uncertainty, isotopic labeled tracers of both components should be used alternately so that the component with the lower concentration is used in labeled form.

With this limitation in mind, tests for thermodynamic consistency of the results of this investigation may be of limited value. Nevertheless, such a test has been made.

If the data are consistent, they must satisfy the Gibbs-Duhem equation, which says for isobaric conditions

$$\int_0^1 \ln(\gamma_1/\gamma_2) dx_1 - \int_0^1 \frac{\Delta H^M}{RT^2} \left( \frac{\delta T}{\delta x_1} \right)_P dx_1 = 0$$

where  $\Delta H^M$  is the integral heat of mixing for one mole mixture.

From Figure 5 the value of the first integral is 0.0042 for the methanol-water system, and 0.0050 for the ethanol-water system.

Evaluation of the second integral, based on measurements of  $\Delta H^M$  at 25°C. by Lama and Lu (1) and the variation of the boiling point with the mole fraction, gives values of 0.018 and 0.009 for the methanol-water and ethanol-

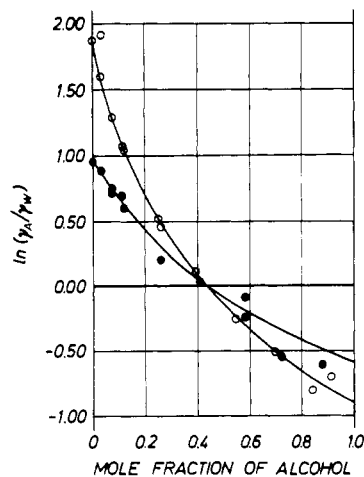


Figure 5.  $\ln(\gamma_A/\gamma_W)$  vs. mole fraction of alcohol  
 ● Methanol-water system  
 ○ Ethanol-water system

water systems, respectively. The fact that  $\Delta H^M$  decreases with increasing temperature indicates that the results are thermodynamically consistent.

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#### NOMENCLATURE

- $B_{ii}$  = second virial coefficient for pure component  $i$ , ml./mole
- $B_{ij}$  = interaction virial coefficient for components  $i$  and  $j$ , ml./mole
- $K$  = separation factor
- $M$  = molecular weight, g./mole
- $P$  = pressure of the system, atm.
- $P_i^0$  = vapor pressure of pure component  $i$ , atm.
- $R$  = gas constant, l·atm./mole/°K.
- $T$  = absolute temperature of the system, °K.
- $V_i^L$  = liquid molar volume of pure component  $i$ , ml./mole
- $d$  = density, g./cc.
- $x$  = mole fraction of the alcohol
- $y_i$  = mole fraction of component  $i$  in vapor phase
- $\gamma_i$  = activity coefficient for component  $i$

#### Subscripts

- A = alcohol
- W = water
- ch = charge
- liq = liquid phase
- cond = condensate phase

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