

VAPOR-LIQUID EQUILIBRIA FOR THREE BINARY MIXTURES OF PROPIONALDEHYDE*

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Vapor-liquid equilibria were determined for propionaldehyde-cyclohexane, propionaldehyde-methanol, and propionaldehyde-methyl ethyl ketone systems at 45.0°C use by of a modified Gillespie still.

A minimum boiling azeotrope was found to occur at 691.4 mmHg and 0.915 mole fraction of aldehyde for the propionaldehyde-cyclohexane system, and a maximum boiling azeotrope at 326.4 mmHg and 0.126 mole fraction of aldehyde for the propionaldehyde-methanol system. Propionaldehyde-methanol system has a maximum or a minimum in the plot of each activity coefficient versus mole fraction. Propionaldehyde-methyl ethyl ketone system is almost an ideal one.

Introduction

Vapor-liquid equilibria for mixtures of aldehyde have been reported by several authors with a view to industrial applications^{3,16}. It is difficult, however, to obtain accurate vapor-liquid equilibria for these mixtures because of the extreme reactivity of aldehyde¹⁰. Moreover, few data for the systems are fit for theoretical treatment.

Vapor-liquid equilibria for three new binary systems have been determined at 45.0°C. In each system propionaldehyde is one component, the other being cyclohexane, methanol, or methyl ethyl ketone (MEK).

Propionaldehyde-cyclohexane system is a mixture consisting of a polar substance and an inert solvent, and is interesting in its equilibrium behavior from the theoretical point of view. Propionaldehyde-methanol system is an aldehyde-alcohol system of industrial importance, and self-association of alcohol molecules and association (or solvation) between aldehyde and alcohol molecules are expected.

Propionaldehyde-MEK system was selected as an example of aldehyde-ketone systems encountered frequently in chemical processes. For example, the elimination of a trace of propionaldehyde from crude acetone is commercially done by extractive distillation with water¹⁴.

In this investigation the experimental results are analyzed thermodynamically and the differences between aldehydes and ketones in liquid phase activity

coefficients are discussed.

Experimental

Materials

Propionaldehyde has an aqueous azeotrope containing 1.9 wt% water, and the water present as impurity partially combines with the aldehyde to form a hydrate whose concentration is a function of temperature¹⁵. Therefore, propionaldehyde of extra-pure reagent grade was first dried with molecular sieve 3A and then distilled in a nitrogen atmosphere. The product contained 0.1 wt% water, and other impurities in it were negligible judging from the gas chromatogram. Cyclohexane, methanol, and MEK used were extra-pure reagents prepared specially for spectroscopy from Wako Chem. Co., Ltd. Impurities in these materials were negligible according to their gas chromatograms and these materials were used without further purification. The physical properties of the materials used are listed in **Table 1**.

Apparatus and procedure

The experimental apparatus for the measurement of vapor-liquid equilibria is schematically shown in **Fig. 1**⁵. The Cottrell tube is 10 mm in inside diameter. The boiling flask (200 ml) is wound with a heating spiral; small temperature deviations during boiling are compensated by the internal heater made of a nichrome wire. Asbestos tapes were used for preventing partial condensation of vapor. The procedure consists of making up a mixture by weighing each component to obtain the desired composition, feeding the prepared mixture to the still, and boiling the liquid at the correct recirculation rate. Adjustments in pressure by Cartesian manostat were made so as to maintain the temperature at 45.0°C. After steady-

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Table 1 Physical properties of materials used

Material	Boiling point [°C]		Vapor pressure at 45°C [mmHg]		Second virial coefficient ⁴⁾ [cc/mol]
	Obtained	Reported ¹⁾	Obtained	Reported ^{a 1)}	
Propionaldehyde	48.04	47.93	682.1	685.8	-1202 ^b
Cyclohexane	80.67	80.74	224.7	224.9	-1390
Methanol	64.56	64.51	334.1	334.2	-1259
MEK	79.59	79.59	216.8	222.1	-1910

a. estimated from Antoine equation

b. estimated from the value of acetoaldehyde

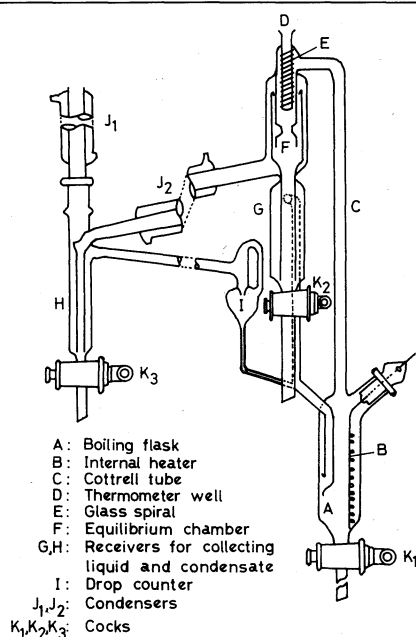


Fig. 1 Apparatus for vapor-liquid equilibrium measurements

state conditions were reached (based on constancy of temperature, pressure, and boiling rate) the still was operated further for approximately half an hour before liquid and liquefied vapor samples were withdrawn. The samples were cooled in an ice box before analysis. A new mixture was supplied for every experimental run, and each experiment was carried out in a nitrogen atmosphere.

The samples in this investigation were analyzed by gas chromatography under the consideration of the sensitivity in peak-area for each component. The temperature was measured with a calibrated thermistor while equilibrium pressure was measured by means of a mercury-in-glass manometer. The established limits of error in the determination of the equilibrium data and measurement of the conditions were as follows;

Temperature $\pm 0.03^\circ\text{C}$

Pressure ± 0.5 mmHg

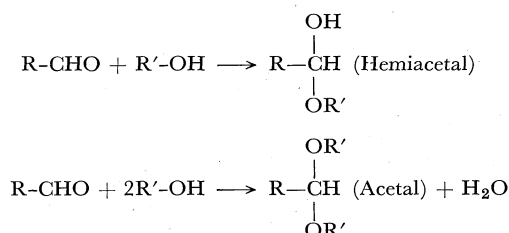
Composition ± 0.0040 mole fraction ($x=0.5$)

± 0.0014 mole fraction ($x=0.1, 0.9$)

± 0.0003 mole fraction ($x=0.02, 0.98$)

Acetal formation

Formations of hemiacetal and/or acetal have been reported for mixtures of aldehyde and alcohol^{8,9)}.



In this investigation, considerable heat was generated on mixing of propionaldehyde and methanol. The hot solution was analyzed by gas chromatography (at 90°C), but no new peaks were recognized. However, a new peak appeared when the solution was placed for a few days at room temperature or kept for several hours under boiling condition. The third component was isolated with gas chromatography, analyzed with *n.m.r.*, and verified to be acetal. In the propionaldehyde-methanol system the experiments were carried under such conditions that acetal formation was negligible.

Results

The vapor-liquid equilibrium data for the three binary systems are shown in **Tables 2, 3** and **4**. Included also are the logarithms of the experimental liquid-phase activity coefficients. The P - x - y data are shown in **Figs. 2, 3** and **4** and the $\log \gamma_i$ - x data in **Figs. 5, 6** and **7**.

The activity coefficients were calculated by

$$\log \gamma_i = \log \gamma'_i + \frac{1}{2.303RT} \{ (P - P_i^\circ)(B_{ii} - v_i^\circ) + 2P(\delta B)_{ij} y_j^2 \} \quad (1)$$

in which

$$\gamma'_i = \frac{Py_i}{P_i^\circ x_i} \quad (2)$$

and

$$(\delta B)_{ij} = B_{ij} - \frac{(B_{ii} + B_{jj})}{2} \quad (3)$$

The second virial coefficients of the four substances are listed in Table 1. The value of propionaldehyde (-1202 cc/mol) was estimated from that of acetoaldehyde. The difference between methyl and ethyl radicals is counted in the estimation by comparing the

Table 2 Vapor-liquid equilibrium data for propionaldehyde(1) - cyclohexane(2) system at 45.0°C [$B_{12} = -1097$ cc/mol*]

x_1 [-]	y_1 [-]	P [mmHg]	$\log \gamma_1$	$\log \gamma_2$
0.0000	0.0000	224.7	—	0.0000
0.0090	0.1057	250.3	0.6470	0.0013
0.0161	0.1709	270.6	0.6362	0.0048
0.0268	0.2518	295.7	0.6227	0.0029
0.0471	0.3548	338.8	0.5841	0.0054
0.0926	0.4832	408.0	0.5028	0.0092
0.1617	0.5824	482.2	0.4120	0.0218
0.2798	0.6626	560.0	0.2929	0.0586
0.4026	0.7118	603.0	0.1963	0.1020
0.5151	0.7422	632.4	0.1276	0.1646
0.6160	0.7736	652.6	0.0807	0.2227
0.7099	0.8054	670.8	0.0481	0.2906
0.8137	0.8514	684.1	0.0211	0.3748
0.9105	0.9113	691.3	0.0060	0.4735
0.9555	0.9504	690.1	0.0025	0.5246
0.9813	0.9779	686.1	0.0009	0.5487
0.9907	0.9888	684.9	0.0010	0.5592
1.0000	1.0000	682.1	0.0000	—

* estimated by the method of O'Connell and Prausnitz¹¹⁾

Table 3 Vapor-liquid equilibrium data for propionaldehyde(1) - methanol(2) system at 45.0°C [$B_{12} = -1699$ cc/mol*]

x_1 [-]	y_1 [-]	P [mmHg]	$\log \gamma_1$	$\log \gamma_2$
0.0000	0.0000	334.1	—	0.0000
0.0105	0.0081	333.3	-0.4194	-0.0005
0.0224	0.0174	331.5	-0.4199	-0.0011
0.0518	0.0437	329.0	-0.3873	-0.0029
0.0997	0.0932	328.1	-0.3425	-0.0046
0.2119	0.2410	331.3	-0.2520	-0.0204
0.3376	0.4616	362.0	-0.1327	-0.0577
0.4038	0.5667	388.9	-0.0900	-0.0765
0.5020	0.7073	439.0	-0.0366	-0.1198
0.5991	0.7997	493.7	-0.0104	-0.1432
0.6938	0.8690	542.5	0.0022	-0.1723
0.8271	0.9330	608.8	0.0051	-0.1698
0.9049	0.9641	643.7	0.0034	-0.1593
0.9520	0.9814	661.0	-0.0003	-0.1379
0.9799	0.9919	676.9	0.0019	-0.1134
0.9893	0.9955	680.6	0.0018	-0.0937
1.0000	1.0000	682.1	0.0000	—

* estimated by the method of O'Connell and Prausnitz¹¹⁾

Table 4 Vapor-liquid equilibrium data for propionaldehyde(1) - methyl ethyl ketone (MEK)(2) system at 45.0°C [$B_{12} = -1480$ cc/mol*]

x_1 [-]	y_1 [-]	P [mmHg]	$\log \gamma_1$	$\log \gamma_2$
0.0000	0.0000	222.1	—	0.0000
0.0167	0.0472	229.9	-0.0080	0.0007
0.0435	0.1170	241.4	-0.0087	0.0004
0.1420	0.3337	284.9	0.0032	-0.0046
0.2048	0.4305	313.1	-0.0051	0.0002
0.3021	0.5653	355.3	-0.0017	-0.0069
0.3619	0.6287	385.3	0.0000	-0.0028
0.4441	0.7052	423.8	0.0013	-0.0032
0.5272	0.7683	468.3	0.0061	0.0042
0.6438	0.8445	517.4	0.0025	-0.0044
0.7285	0.8888	557.7	0.0023	-0.0012
0.7833	0.9168	584.7	0.0043	-0.0095
0.9176	0.9701	641.2	-0.0012	0.0042
0.9690	0.9894	662.9	-0.0030	-0.0085
1.0000	1.0000	682.1	0.0000	—

* estimated by the method of O'Connell and Prausnitz¹¹⁾

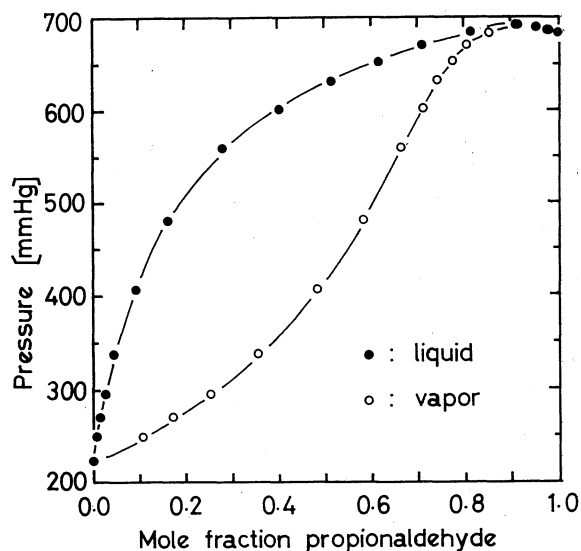


Fig. 2 Pressure-composition diagram for propionaldehyde-cyclohexane system at 45.0°C

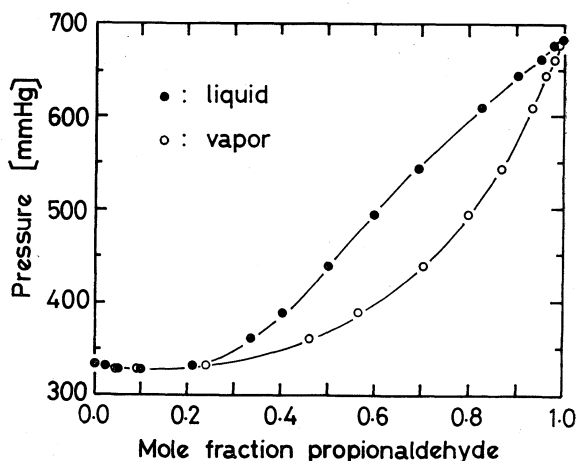


Fig. 3 Pressure-composition diagram for propionaldehyde-methanol system at 45.0°C

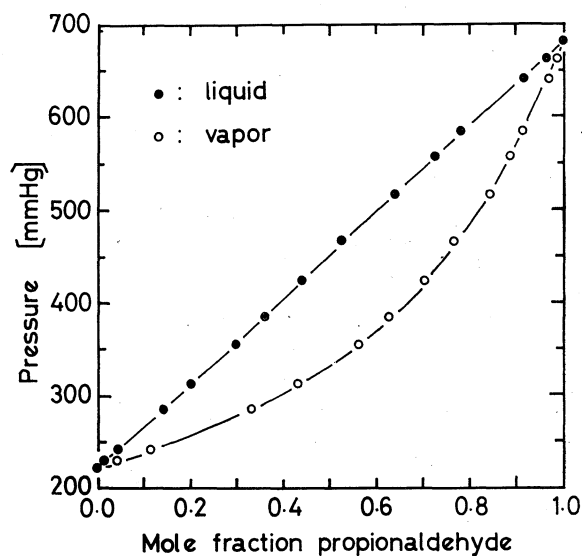


Fig. 4 Pressure-composition diagram for propionaldehyde-methyl ethyl ketone (MEK) system at 45.0°C

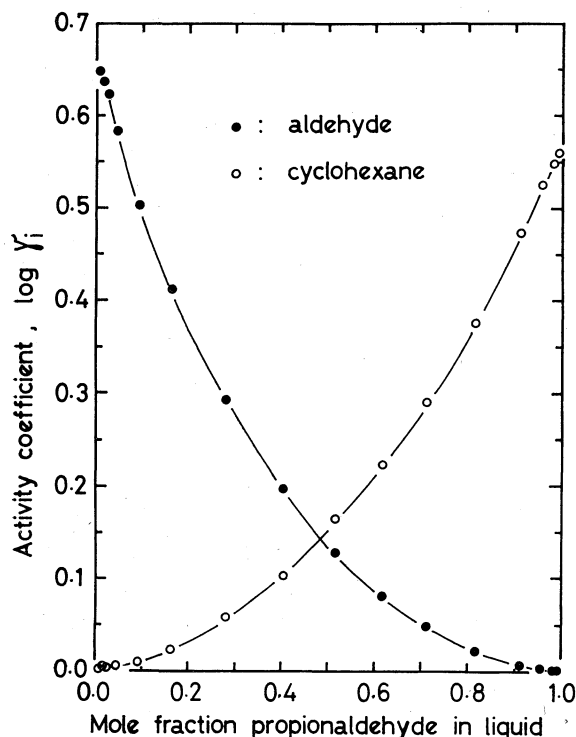


Fig. 5 Activity coefficients for propionaldehyde-cyclohexane system at 45.0°C

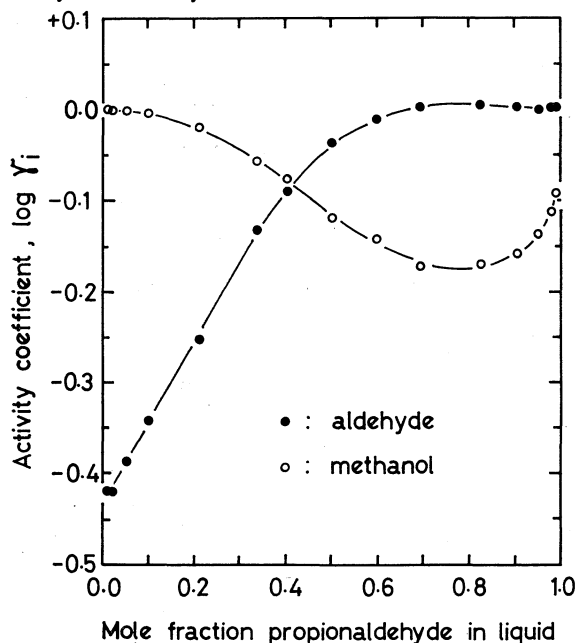


Fig. 6 Activity coefficients for propionaldehyde-methanol system at 45.0°C

values between methanol and ethanol, and between methyl formate and ethyl formate in the literature⁴⁾.

The cross virial coefficients of the three systems were calculated by using the estimation method proposed by O'Connell and Prausnitz¹¹⁾.

When the values of $\log \gamma_i$ are plotted against composition, those for propionaldehyde-cyclohexane system are relatively symmetrical, and the terminal value of propionaldehyde is slightly larger than that of cyclohexane (Fig. 5). Propionaldehyde-methanol system shows considerable asymmetry in the $\log \gamma_i$ - x

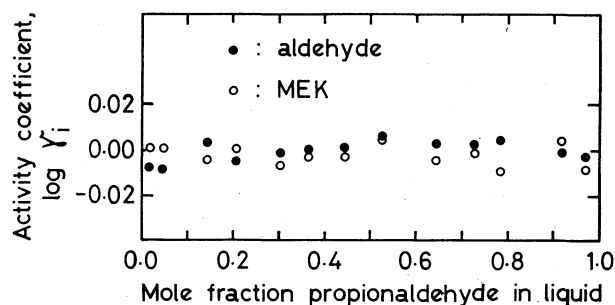


Fig. 7 Activity coefficients for propionaldehyde-methyl ethyl ketone (MEK) system at 45.0°C

plot, in which the activity coefficient of methanol has a minimum in the range between 70 and 90 mole % of propionaldehyde, while that of propionaldehyde passes through a maximum for the same region of composition (Fig. 6). Propionaldehyde-MEK system shows almost ideal behavior (Fig. 7).

The azeotropic compositions and pressures were estimated from the $\log(\gamma_i/\gamma_j)-x_i$ plots and the larger scale pressure-composition plots, respectively. These values were $x_{\text{aldehyde}}=0.915$ and $P=691.4$ mmHg for propionaldehyde-cyclohexane system, and $x_{\text{aldehyde}}=0.126$ and $P=326.4$ mmHg for propionaldehyde-methanol system. These two azeotropes were not reported by Horsley⁷⁾.

The data were checked for consistency by plotting the values of $\log(\gamma_i/\gamma_j)$ vs. the mole fraction of propionaldehyde, and comparing the positive and negative areas. The areas differed by 0.3% for propionaldehyde-cyclohexane system, and 17% for propionaldehyde-methanol system. The inconsistency of the latter system is considered in the following discussion.

Discussion

Propionaldehyde-methanol system

It was reported by de Leeuw⁸⁾ that a reaction occurs in the gaseous phase of the acetoaldehyde-ethanol system, and also by Prausnitz¹²⁾ that the interaction between unlike molecules is very large in the gaseous phase of the acetonitrile-acetoaldehyde system and that the cross virial coefficient, B_{ij} , is almost equal to $(3/2)(B_{ii}+B_{jj})$ at 40°C. Strong interaction was, therefore, expected to occur in the gaseous phase of the propionaldehyde-methanol system in this investigation, as well as in the acetoaldehyde-ethanol or acetonitrile-acetoaldehyde system. Relatively large inconsistency of propionaldehyde-methanol system in the preceding results was, therefore, supposed to occur not only by experimental error, but also by the inadaptability of the estimation method for the cross virial coefficient.

Liquid-phase activity coefficients for the propionaldehyde-methanol system were calculated in the cases of several values of the B_{ij} being used. The logarithms of γ_i/γ_j were plotted against compositions, and it was found that the areas differed by 32%, 20%, 11%, and 0.1%, respectively, when $B_{ij}=B_{ii}=B_{jj}=0$ (ideal

gases), $B_{ij} = (1/2)(B_{ii} + B_{jj})$, $B_{ij} = (B_{ii} + B_{jj})$, and $B_{ij} = (3/2)(B_{ii} + B_{jj})$. This seems to show that the propionaldehyde-methanol system has a large value of B_{ij} just as does acetonitrile-acetaldehyde system, and this strong interaction in the gaseous phase of propionaldehyde-methanol system is consistent with the reactivity in the liquid phase of this system (Acetal formation). Moreover, it might be said that the non-ideal behavior of the gaseous phase in the vapor-liquid equilibrium must be considered even below atmospheric pressure in such a special system as this.

Aldehyde-alcohol system

As shown in Fig. 6, the values of $\log \gamma_i$ for propionaldehyde-methanol system at 45.0°C are negative as a whole. Reported are similar negative values of the $\log \gamma_i$ for acetaldehyde-ethanol system at 30°C³⁾ and positive values for propionaldehyde-ethanol system at 760 mmHg (48°C–78°C)¹⁶⁾. Therefore, it might be considered that liquid-phase activity coefficients in aldehyde-alcohol systems differ systematically owing to the carbon numbers.

The differences between aldehyde and ketone in the liquid-phase activity coefficients

Propionaldehyde-MEK system behaves as almost an ideal solution (Fig. 7). The plots of $\log \gamma_i$ vs. x in propionaldehyde-cyclohexane system at 45.0°C (Fig. 5) and MEK-*n*-hexane system at 60°C⁶⁾ show almost the same type. Accordingly, aldehyde and ketone seem to form almost an ideal solution with each other and to show similar behavior in binary systems having a non-polar substance as the second component.

Propionaldehyde-methanol system, however, shows negative deviation at 45.0°C (Fig. 6), while MEK-methanol system shows positive deviation at 760 mmHg (64°C–79°C)¹³⁾. Therefore, aldehyde and ketone are considered to show different behavior when each substance has alcohol as the second component. This is related to the fact that saturated aliphatic aldehydes with primary alcohols are converted to acetals with a good equilibrium conversion by use of a suitable catalyst while ketones, in general, are not²⁾.

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Nomenclature

B	= second virial coefficient	[cc/mole]
(δB)	= quantity defined by Eq.(3)	[cc/mole]
P	= total pressure	[mmHg]
R	= gas constant	[mmHg·cc/mole·°K]
T	= absolute temperature	[°K]
v	= molar volume	[cc/mole]
x	= mole fraction in liquid phase	[—]
	= mole fraction in vapor phase	[—]
γ	= activity coefficient in liquid phase	[—]
γ'	= apparent activity coefficient defined by Eq.(2)	[—]
<Subscripts>		
i, j	= component	
<Superscript>		
$^{\circ}$	= pure liquid	

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