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Isobaric Vapor–Liquid Equilibria in Mixtures of Acetaldehyde and Methyl Iodide

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Vapor–liquid equilibria at 750 Torr were measured for acetaldehyde with methyl iodide. The NRTL equation was used to correlate the experimental results. There was no evidence of a binary azeotrope at high mole fractions of acetaldehyde.

Introduction

The vapor–liquid equilibrium of the acetaldehyde–methyl iodide system is of interest in the production of vinyl acetate. Since a search of the literature failed to find useful information about this equilibrium, the present study was undertaken.

Experimental Section

Chemicals. The acetaldehyde was a BDH laboratory reagent with 99.5 mol % minimum purity. In the course of the work, samples of methyl iodide from two different sources were used: analyzed reagent with 99.8 mol % minimum purity from the J. T. Baker Chemical Co. and material with specified boiling point 41–43 °C from Anachemia Chemicals Ltd.

Pure methyl iodide is a colorless liquid but becomes pale yellow or violet on standing due to the liberation of free iodine. The coloration can be removed by immersing a thin strip of copper or a drop of mercury. Apart from this treatment, the component liquids were used as received without further purification.

Measurements. Vapor–liquid equilibria were established at 750 Torr in a modified Dvořák and Boublík circulating still (*1*). The auxiliary equipment for measuring the temperature and pressure was the same as used by Hull and Lu (*2*). Preliminary experimental runs showed that the previous operational procedure (*1*, *3*) needed modification in view of the low boiling point of acetaldehyde, the extremely large difference in the densities of the two components, and the possible reaction between acetaldehyde and free iodine released during operation of the still. Consequently, the insulation of the still was increased around the equilibrium chamber, the liquid and condensate reservoirs, and the mixing vessel. The entire still was covered with aluminum foil to reduce exposure of the contents to light; small windows were provided for occasional observation of the operation. The still was filled with nitrogen prior to introducing the liquid. Vigorous stirring of the liquids in the reservoirs was initiated before starting to heat the mixing vessel. It was crucial to keep the liquid level in the mixing vessel somewhat lower than that maintained in our previous work, in order to avoid any "air lock" occurring in the tube connecting the liquid reservoir with the mixing vessel.

Table I. Isobaric Vapor–Liquid Equilibria for Acetaldehyde (1)–Methyl Iodide (2): Boiling Temperature, t, and Liquid- and Vapor-Phase Mole Fractions, x_1 and y_1, at 750 Torr

x_1	y_1	t/°C	y_1(calcd) − y_1(exptl)	[t(calcd) − t(exptl)]/°C
		Set 1		
1.0000	1.0000	19.94		
0.9642	0.9686	19.95	−0.0024	0.01
0.9578	0.9618	19.95	−0.0011	0.02
0.9320	0.9390	19.99	0.0006	0.04
0.8990	0.9120	20.07	0.0029	0.06
0.8464	0.8740	20.29	0.0054	0.06
0.8134	0.8526	20.49	0.0062	0.02
0.6662	0.7678	21.55	0.0072	−0.05
		Set 2		
0.0000	0.0000	41.72		
0.0128	0.0559	40.32	0.0001	0.05
0.0443	0.1692	37.42	−0.0013	0.08
0.1092	0.3112	33.33	0.0094	−0.08
0.1283	0.3412	32.33	0.0120	−0.04
0.1895	0.4188	29.81	0.0180	0.00
0.2518	0.5070	27.80	−0.0050	0.08
0.3220	0.5658	26.18	−0.0037	−0.01
0.4128	0.6282	24.52	−0.0009	−0.07
		Set 3		
0.3730	0.6060	25.06	−0.0059	0.08
0.4081	0.6258	24.49	−0.0016	0.04
0.5170	0.6880	23.02	0.0037	−0.04
0.6026	0.7346	22.06	0.0055	0.00
0.6710	0.7694	21.48	0.0083	−0.02
0.7250	0.8000	21.08	0.0075	−0.02

The temperature of the cooling medium used in the operation of the still was reduced to −4 °C or lower. Vapor formation in the sampling tube was avoided as much as possible by keeping the time of the sampling procedure as short as possible and by maintaining the temperature of the sampling tube and the covered sample container below 4 °C. Immediately after the sampling, the containers were placed in a refrigerator near the still.

A precision digital densimeter (Anton Paar, Model DMA 02C) was used for the analysis of the samples. It was kept at 4 °C by water circulating from a constant-temperature bath cooled by a Neslab bath cooler (Model PBC-4). At least two analyses were carried out for each sample. In the event of disagreement, a new sample was taken from the still.

Results and Discussion

The experimentally determined liquid and vapor compositions, x_1 and y_1, and Celsius temperatures, t, for the isobaric equi-

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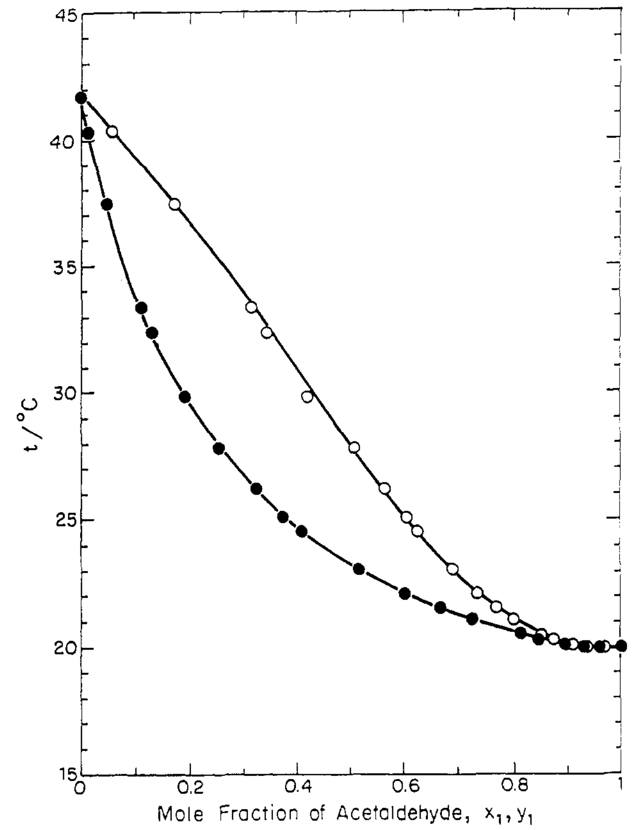

Figure 1. Comparison of calculated temperatures t and vapor mole fractions y_1 as functions of liquid mole fraction x_1 with experimental results for acetaldehyde (1)-methyl iodide (2) at 750 Torr.

libria of the acetaldehyde (1)-methyl iodide (2) system at pressure $P = 750$ Torr are listed in Table I and plotted in Figure 1. The estimated uncertainties in the measurements of the primary quantities are

$$\epsilon(x_1) = \epsilon(y_1) = \pm 0.005, \quad \epsilon(t) = \pm 0.02\ ^\circ\mathrm{C}, \quad \text{and} \quad \epsilon(P) = \pm 1\ \mathrm{Torr}$$

As shown in Table I, the entire composition range was covered by three overlapping sets of measurements. The first set began with pure acetaldehyde and the second with pure methyl iodide. An effort was made to keep the solutions in the equilibrium still as fresh as possible and thus to minimize the effect of any reaction between the acetaldehyde and iodine freed from the methyl iodide. For all the data points of sets 1 and 2, the solutions were in the still for less than 2 days. The third set of data points, in the central composition range, were determined for solutions purposely kept in the still longer than 2 days but less than 4 days. The agreement between the data points of set 3 and those of sets 1 and 2 attests to the reproducibility of the measurements. It also indicates that the reaction between acetaldehyde and freed iodine does not effect the vapor-liquid equilibrium significantly under the present experimental conditions. Furthermore, in all the data points measured, the concentration of acetaldehyde in the vapor phase is richer than that in the liquid phase, indicating that no azeotrope exists even in the high acetaldehyde region for $P = 750$ Torr.

In an application of the area test for the thermodynamic consistency of the present isobaric data, the algebraic sum of the areas of the positive and negative parts of a plot of $RT \ln (\gamma_1/\gamma_2)$ as a function of x_1 amounted to ~3.5% of the sum of their absolute values. However, since independent excess enthalpies of the system are not available, the significance of this test is questionable.

Table II. Values of A, B, and C for Equations 8 and 9, Describing Vapor Pressures $P_i°$, Molar Volumes, $V_i°$, and Molar Virial Coefficients B_{ij} of Acetaldehyde (1) and Methyl Iodide (2) as Functions of the Temperature t

	eq	A	B	C	ref
$P_1°$/Torr	8	7.05807	1070.60	236.00	5[a]
$P_2°$/Torr	8	6.99281	1146.368	236.677	6[a]
$V_1°/(\mathrm{cm^3\ mol^{-1}})$	9	54.743	0.089731	0.0002536	7, 8
$V_2°/(\mathrm{cm^3\ mol^{-1}})$	9	60.790	0.071187	0.0001542	5
$B_{11}/(\mathrm{cm^3\ mol^{-1}})$	9	−1784.3	27.247	−0.18477	5
$B_{22}/(\mathrm{cm^3\ mol^{-1}})$	9	−1070.6	11.432	−0.05070	9
$B_{12}/(\mathrm{cm^3\ mol^{-1}})$	9	−909.6	8.419	−0.03890	10

[a] A adjusted to give observed boiling point at 750 Torr.

The nonrandom two-liquid (NRTL) theory (*4*) was used to correlate the experimental data. According to this treatment, the activity coefficients in the liquid phase are

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \tag{1}$$

and

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \tag{2}$$

where

$$\tau_{21} = \Delta g_{21}/RT \qquad \tau_{12} = \Delta g_{12}/RT \tag{3}$$

$$G_{21} = \exp(-\alpha_{12}\tau_{21}) \qquad G_{12} = \exp(-\alpha_{12}\tau_{12}) \tag{4}$$

These formulas contain three adjustable parameters: Δg_{21}, Δg_{12}, and α_{12}.

The pressure and vapor compositions are given by

$$P = \gamma_1 p_1' + \gamma_2 p_2' \tag{5}$$

and

$$y_i = \gamma_i p_i'/P \tag{6}$$

where

$$p_i' = x_i P_i° \exp\{[(V_i° - B_{ii})(P - P_i°) + (B_{11} + B_{22} - 2B_{12})(1 - y_i)^2 P]/RT\} \tag{7}$$

The quantities $P_i°$, B_{ii}, and $V_i°$ are the vapor pressure, molar second virial coefficient, and liquid molar volume of pure component i at temperature T, and B_{12} is the cross molar second virial coefficient in the mixture. If these properties are known functions of the temperature, eqs 1-7 can be solved iteratively for the values of y_1 and T, corresponding to given x_1, P, and a set of values of the three NRTL parameters.

The Antoine equation in the form

$$\log (P°/\mathrm{Torr}) = A - B/[C + (t/°\mathrm{C})] \tag{8}$$

was used to provide estimates of $P_i°$. Values of B and C were taken from the literature for acetaldehyde (*5*) and for methyl iodide (*6*). The values of A were determined from the present measurements of the boiling points at 750 Torr. In this regard, it may be noted that large differences exist in the boiling point values reported in the literature for both pure components. For the present samples of acetaldehyde and methyl iodide, the boiling points at 750 Torr are 0.10 and 0.32 °C lower than those calculated from ref 5 and 6, respectively. The values of A, B, and C for eq 8 are listed in Table II.

The temperature variations of the other pure-component properties $V_i°$ and B_{ii}, and also of the cross virial coefficient B_{12}, were expressed as quadratic functions of t:

$$Q/(\mathrm{cm^3\ mol^{-1}}) = A + B(t/°\mathrm{C}) + C(t/°\mathrm{C})^2 \tag{9}$$

Values of the coefficients were obtained by fitting data from the literature (*5*, *7–9*) or, in the case of B_{12}, from estimates by the method of Hayden and O'Connell (*10*). The coefficients for eq 9 are also listed in Table II.

Values of the parameters Δg_{21}, Δg_{12}, and α_{12} were selected to minimize the object function

$$\Phi = \sum_{j=1}^{21}\{W_y[y_1(\text{exptl}) - y_1(\text{calcd})]_j^2 + W_t[t(\text{exptl}) - t(\text{calcd})]_j^2\} \quad (10)$$

where the sum was taken over the 21 mixture compositions. The relative weights W_y and W_t were assigned proportional to the inverse squares of the error estimates $\epsilon(y_1)$ and $\epsilon(t)$. In order to obtain a reasonable fit of the results, it was necessary to consider Δg_{21} and Δg_{12} to be functions of t. A quadratic form in t was assumed for each of these. Minimization of Φ with respect to the seven parameters yielded

$$\Delta g_{21}/(\text{J·mol}^{-1}) = 2959.18 - 25.462(t/°\text{C}) + 0.00517(t/°\text{C})^2 \quad (11)$$

$$\Delta g_{12}/(\text{J·mol}^{-1}) = -1197.45 + 90.471(t/°\text{C}) + 1.9536(t/°\text{C})^2 \quad (12)$$

$$\alpha_{12} = 1.3213 \quad (13)$$

Deviations of the calculated values of y_1 and t from the experimental results are listed in Table I. The corresponding standard deviations are $\sigma_y = 0.0067$ and $\sigma_t = 0.05$ °C. Curves of t(calcd) against x_1 and against y_1(calcd) are plotted in Figure 1. These show that the NRTL theory with the parameters given by eqs 11–13 provides a good correlation of the experimental data.

Glossary

A, B, C	coefficients in Antoine and quadratic forms, eqs 8 and 9
B_{ii}	molar second virial coefficient of pure component i, cm^3/mol
B_{12}	cross molar second virial coefficient, cm^3/mol
$P_i°$	vapor pressure of pure component i, Torr
Q	quadratic function, eq 9
R	molar gas constant, 8.314 51 J K^{-1} mol^{-1}
T	thermodynamic temperature, K
t	Celsius temperature, °C
$V_i°$	molar volume of pure liquid i, cm^3/mol
x_i	mole fraction of component i in liquid
y_i	mole fraction of component i in vapor
α_{12}, Δg_{21}, Δg_{12}	NRTL parameters, eqs 3, 4, and 11–13
γ_i	activity coefficient of component i in liquid
ϵ	estimated experimental uncertainty
σ_q	standard deviation of q, defined by $\sigma_q = \{\sum[q(\text{calcd}) - q(\text{exptl})]^2/m\}^{1/2}$ where the sum is taken over the set of m experimental measurements

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Excess Volumes for Binary Mixtures of *n*-Butyl Methyl Ether with *n*-Alkanes at 298.15 K

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Excess volumes, obtained from density measurements at 298.15 K, are reported for binary mixtures of *n*-butyl methyl ether ($C_4H_9OCH_3$) with the *n*-alkanes (C_nH_{2n+2}, n = 6, 7, 8, 10, 12, and 16). The results are compared with values calculated from the Flory theory with use of interchange-energy parameters derived from a previous analysis of excess enthalpy data.

Introduction

A recent paper (*1*) from our laboratory reported measurements of excess enthalpies for mixtures of *n*-butyl methyl ether (BME) with each of the alkanes: *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, and *n*-hexadecane. As an extension of that investigation, we have determined excess volumes for the same set of binary mixtures.

Experimental Section

Sources of the component liquids and their densities measured at 298.15 K in an Anton Paar densimeter (Model DMA 02C) are listed in Table I, where densities from the literature (*2–4*) are given for comparison. In all cases, the manufacturers' specifications indicated purities of at least 99 mol %. Apart from storing the BME over Type 4A molecular-sieve beads, the component liquids were used without further purification.

Mixtures were prepared by weighing in onion cells (*5*), specially designed to minimize evaporation effects. The error in the mole fraction is estimated to be less than 1 × 10^{-4}. Excess molar volumes, V^E, were calculated from densities measured

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