

Equilibrium Data for Acetone–vinyl Acetate Binary Mixtures

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Liquid – vapor equilibrium data for mixtures containing monomers can be used for the separation of the compounds by rectification from the effluents coming from the polymerization reactors. Due to the high tendency of polymerization of monomers these data are more difficult to obtain by experiment.

The paper presents some experimental data for the binary system acetone–vinyl acetate obtained in an original device and the correlation of these data against results obtained using a simple algebraic equation.

Keywords: vapor pressures, vinyl acetate, monomers, correlation of data

Equilibrium data in systems containing monomers are not quite spread in literature while is rather difficult to operate such systems with various concentrations around the boiling point without polymerization in the absence of any inhibitor. On the other hand, large sets of consistent and confident data are expected to be reported even rarely because keeping the same conditions during data acquisition seems to be a major obstacle in these cases.

Calculating boiling and equilibrium curves from isobar equilibrium diagrams by activity coefficients method implies knowing the vapor pressure of the pure components and successive approximations for each point on the curve. Even in that case, the curves obtained are not always very accurate. The aim of this work was the experimental determination of the equilibrium data for acetone–vinyl acetate binary mixtures and further correlation of these data. It should be reminded that correlation with many terms equations against relatively poor experimental sets is not very reliable, while experimental errors are big enough in such systems containing monomers (even if they are reproducible!).

Experimental part

All the experimental data were obtained in the Chemical Engineering Department of University Politehnica of Bucharest using an original device, already presented in some previous papers [1, 3, 8]. The device is made up of two interconnected equilibrium units. Each unit has a *Cottrell* pump that allows the recirculation of phases, the liquid and the condensed vapor. The fact that two units are interconnected allows the realization of two complete equilibrium determinations or, for incipiently polymerizable mixtures (by thermal initiation) the continuous renewal of the mixture of the left unit in which the polymer does not reach determines the polymer to accumulate in the right unit. Obviously in such cases only the second unit provides accurate equilibrium data.

The concentrations were determined by the refractometric method. The experimental liquid – vapor equilibrium data obtained are presented in table 1.

Results and discussions

Algebraic correlation of boiling curve and equilibrium curve

The experimental data were fitted against the ones obtained with the algebraic equation proposed by Danciu [1,2]. The method used to obtain boiling curves from experimental data is reviewed below. It starts by defining

Table 1
EXPERIMENTAL LIQUID – VAPOR EQUILIBRIUM DATA FOR
ACETONE-VINYL ACETATE BINARY MIXTURES

T [°C]	x ₁	y ₁	T [°C]	x ₁	y ₁
56.7	0.996179	1	60.7	0.690577	0.826977
57	0.960032	0.99123	62.9	0.622201	0.765337
57.3	0.957098	0.988703	63.4	0.593305	0.728951
57.5	0.937166	0.97824	63.9	0.560498	0.716381
57.8	0.908849	0.964366	64.3	0.554418	0.690577
58	0.894639	0.961485	64.8	0.49278	0.671989
58.2	0.885471	0.957098	65.3	0.468881	0.639115
58.5	0.881741	0.945009	65.8	0.435565	0.593305
58.8	0.862565	0.925815	66.5	0.41268	0.554418
59.2	0.836315	0.917442	67.1	0.348411	0.501312
59.4	0.821562	0.903586	67.3	0.304615	0.418576
59.7	0.799735	0.894639	68.2	0.274711	0.362727
60	0.772376	0.881741	72	0.01	0.02

some variables, using the equilibrium temperature, in order to avoid the influence of small pressure variations ($\Delta p < 2 \pm 3$ Torr).

$$X_1 = \frac{x_1}{1-x_1} = \frac{1}{X_2} \quad (1)$$

$$X_1 \cdot X_2 = 1$$

For a binary system, without azeotropic point, the following dimensionless normalized temperatures are defined by analogy with molar fractions and ratios:

$$\vartheta_1 = \frac{t-t_1}{t_2-t_1}; \quad \vartheta_2 = \frac{t_2-t}{t_2-t_1}; \quad \vartheta_1 + \vartheta_2 = 1 \quad (2)$$

$$\theta_1 = \frac{\vartheta_1}{\vartheta_2} = \frac{t-t_1}{t_2-t} = \frac{1}{\theta_2} \quad \theta_1 \cdot \theta_2 = 1 \quad (3)$$

According to the definition relations the boundary conditions are:

$$x = x_1 = 0 \Rightarrow X_1 = 0 \quad t = t_2 \Rightarrow \vartheta_1 = 1; \quad \theta_1 = \infty,$$

$$x = x_1 = 1 \Rightarrow X_1 = \infty \quad t = t_1 \Rightarrow \vartheta_1 = 0; \quad \theta_1 = 0.$$

The equation proposed for the boiling curve is:

$$X_1 = A_1 \cdot \theta_2^{B_1} \quad \text{or} \quad X_2 = A_2 \cdot \theta_1^{B_2} \quad (4)$$

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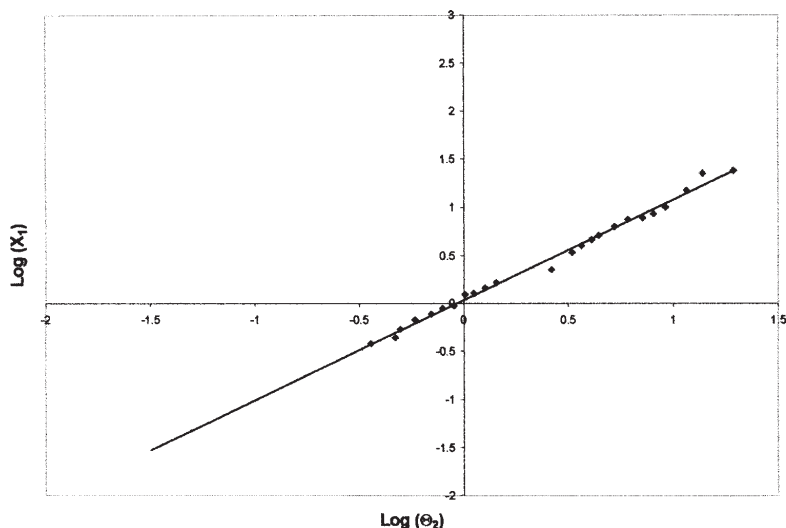


Fig. 1. Boiling curve linearization for acetone-vinyl acetate system

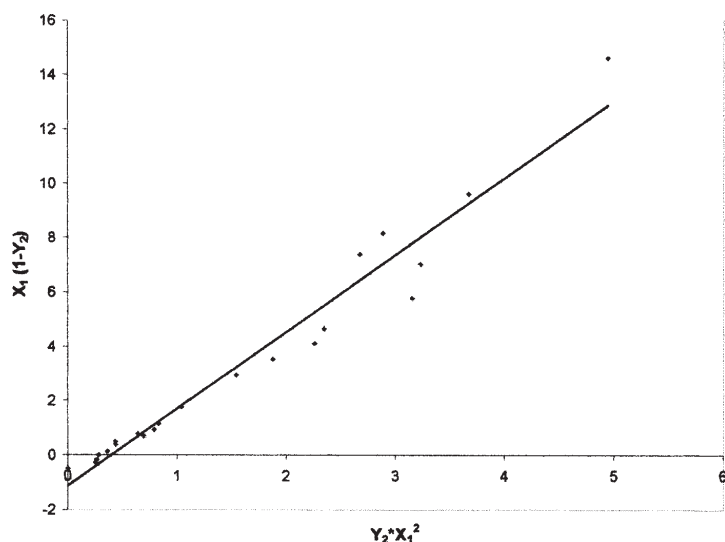


Fig. 2. Equilibrium curve linearization for acetone-vinyl acetate system

where: $A_1 \cdot A_2 = 1$ and $B_1 = B_2 = B$. The equation constants result from the model design based on the properties of fractions and ratios, and relation (4) has, in fact, only two unknown coefficients.

Using the experimental data obtained, the molar ratios of the two components and the dimensionless temperatures were calculated in order to determine the coefficients used in the boiling curve equation. Although, always the first diagram is verified with a second one, only one of them is shown in figure 1.

According to the experimental data the constants obtained for the binary system acetone- vinyl acetate were:

$$A_1 = 1.133705 \quad A_2 = 0.882064 \quad B_1 = B_2 = 1.021$$

The equilibrium equation proposed for the correlation of experimental data is based on a kinetic model assuming bimolecular interactions between the molecules at interface and the activated molecules in the mass of the two phases [1-4]. The constants of the equilibrium equation can be determined by regression or graphical methods. Therefore the two equations were linearized:

$$\left. \begin{aligned} X_1 \cdot (1 - Y_2) &= \alpha_1 \cdot Y_2 \cdot X_1^2 - \alpha_2 \\ X_2 \cdot (Y_1 - 1) &= \alpha_1 - \alpha_2 \cdot Y_1 \cdot X_2^2 \end{aligned} \right\} \quad (5)$$

the first equation being usually used for the representation of the experimental data in the concentrations domain $0 < X_1 < 1$, and the second one for the domain $0 < X_2 < 1$. This

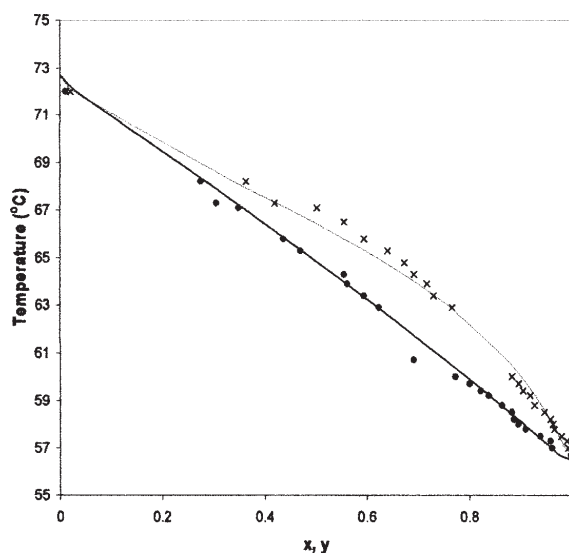


Fig. 3. Boiling diagram for acetone-vinyl acetate mixture

way can be drawn two diagrams that give the same values α_1 and α_2 .

After several transformations the molar ratio of component 1 in the vapor phase can be calculated as a function of its ratio in the liquid phase:

$$Y_1 = \frac{\alpha_1 \cdot X_1 + 1}{\alpha_2 X_2 + 1} \quad (6)$$

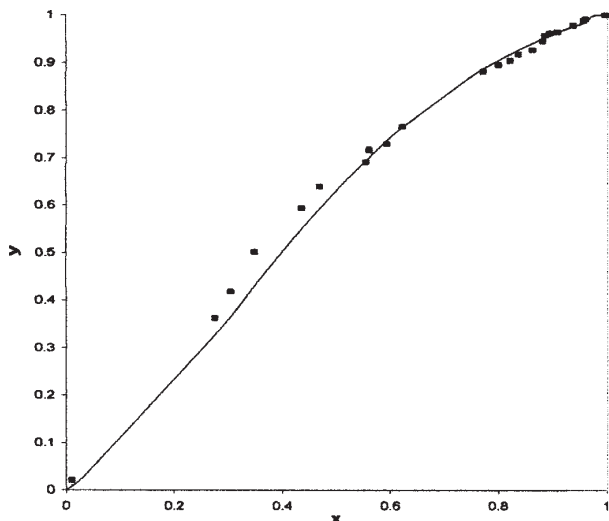


Fig. 4. Equilibrium diagram for acetone–vinyl acetate system

As previously stated, the constants can be obtained against the experimental data.

For drawing the equilibrium curve the first step is the graphical determination of the equation coefficients.

For the studied system the following values for the equation coefficients were obtained: $\alpha_1 = 2.8586$ and $\alpha_2 = 1.254$. These were used to calculate and draw the equilibrium diagram.

The calculated curves were close to the experimental obtained data, as can be observed in figures 3 and 4.

Conclusions

Generally, mixtures containing monomers are difficult to handle, from the point of view of equilibrium data, due to the sensitivity to temperature, the equilibrium being changed by the presence of inhibitors or by the monomers' tendency to polymerize. The main advantage of the above correlation stands in the low number of constants to be

found against experimental data. Anyone could verify that, using for example the so-called "extended Antoine equation" from HYSYS database, almost the same profiles for vapor pressures are to be obtained. Once again, this agreement shows, first of all, satisfactory experiments. On the other hand, the strength of the presented correlation is verified for these substances. The correlation method was previously verified for the mixtures vinyl acetate – benzene [2, 8] and benzene – styrene. In a previous paper [5], one of the authors has shown a brief history of vapor pressure correlations, up to the equation (denoted there with the names of Prausnitz and Xu Zhong):

$$\ln P = A + \frac{B}{T} + C \cdot \ln T + D \cdot T + E \cdot T^2 + \dots + N \cdot T^m \quad (7)$$

It is obvious that, for relatively large sets of experimental data (such as the one presented in Table 1), even an equation with 6, 7 or more constants could be used, but in other cases, with only a reduced number of available experimental points, perhaps an equation with 2 constants is more suitable and reliable for correlation. This is often the case in systems involving monomers.

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