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Reevaluation of Vapor−Liquid Equilibria for Butadiene + Styrene

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In order to correct the system pressures predicted for butadiene + styrene by the model proposed by Wilhelm and Collier (1948), a different approach has been adopted to evaluate the liquid activity coefficients for butadiene and styrene using their reported pressure measurement for butadiene + styrene at 0 °C, and a simple temperature function has been used for extrapolating these liquid activity coefficients to higher temperatures. The validity of the proposed approach is verified by some of the hitherto proprietary experimental results.

Introduction

Vapor−liquid equilibria of butadiene + styrene have been presented by Wilhelm and Collier (1948). In the production of butadiene + styrene copolymer latexes, the copolymerization reaction is usually allowed to go to 77% completion. The vapor−liquid equilibrium values are of fundamental use in the recovery, separation, and purification of the unreacted monomers.

Whitwell et al. (1944) indicated three reasons for not making direct experimental measurements of vapor and liquid equilibrium compositions: the large volatility difference results in vapors extremely dilute with respect to styrene, the close similarity of the two compounds makes the analysis extremely difficult, and the ease with which polymerization can occur would make data taken at temperatures much above 25 °C subject to a considerable amount of uncertainty.

In their experimental work, Wilhelm and Collier made total pressure measurements using a differential vapor pressure apparatus at several concentrations of butadiene-rich and styrene-rich solutions at 0 °C. It should be mentioned that 0 °C was the only temperature at which they have made the measurements, and the reported total pressures are the only set of experimentally determined data reported in the open literature. The isobaric vapor−liquid equilibria presented by Wilhelm and Collier (1948) at three pressures were obtained by extrapolation based on this set of data. Although the assumptions adopted in their thermodynamic model appeared to be reasonable, there is evidence in practice that the predicted total pressures based on their model are much too high, up to 40% higher, in a certain range of concentrations.

It is for this reason that an attempt has been made to rectify the situation by adopting a different approach to evaluate the liquid activity coefficients based on the data of Wilhelm and Collier at 0 °C, and to select a simple temperature function for extrapolating the liquid activity coefficients from 0 °C to higher temperatures. Subsequently, some of the hitherto proprietary experimental results obtained at higher temperatures are used to verify the validity of the proposed new model for the correlation of the liquid activity coefficients of butadiene and styrene, which can be used further for calculating equilibrium vapor−liquid compositions either at isothermal or at isobaric conditions.

Examination of Calculated Equilibrium Values Reported in the Literature

In their paper, Wilhelm and Collier (1948) reported their calculated partial pressures and partial molar excess enthalpies of butadiene and styrene over the complete concentration range at five isothermal conditions, (−15, 0, 25, 50, and 80) °C. In their work, the regular solution model was followed with the assumption that the butadiene + styrene system is nonpolar and nonassociating and that any deviations from Raoult's law are due to enthalpy effects resulting from differences in molar volumes of the two pure components. With some additional assumptions, they derived an expression for calculating the partial molar excess enthalpies.

In this work, liquid activity coefficients γ of butadiene and styrene in butadiene (1) + styrene (2) mixtures were recalculated by means of the following two relations:

$$\ln \gamma_1 = \ln \frac{y_1 P}{x_1 p_1} + \frac{(B_{11} - V_1)(P - p_1)}{RT} + \frac{P\delta_{12} {y_2}^2}{RT} \quad (1a)$$

$$\ln \gamma_2 = \ln \frac{y_2 P}{x_2 p_2} + \frac{(B_{22} - V_2)(P - p_2)}{RT} + \frac{P\delta_{12} {y_1}^2}{RT} \quad (1b)$$

where P, p, T, V, x, and y are the total pressure, pure-component vapor pressure, temperature, pure-component liquid molar volume, and mole fractions in the liquid and vapor phases, respectively. The quantity δ_{12} is related to the second virial coefficients by

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (2)$$

B_{11} and B_{22} are the second virial coefficients for the pure gases at the temperature of the solution, and B_{12} is the cross second virial coefficient. The expressions of eq 1 are valid at low and moderate pressures when the volume-explicit virial equation terminated after the second virial coefficient is adequate to describe the vapor phase of the individual pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The second virial coefficients were estimated by means of the Pitzer−Curl correlation modified by Tsonopoulos (1974). The values of B_{12} were estimated by means of the combining rules suggested by Prausnitz (1969). The acentric factors and

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the critical properties of butadiene and styrene were taken from Reid et al. (1987).

In the recalculation of the liquid activity coefficients using the predicted data of Wilhelm and Collier (1948), the Cox equations presented originally in their paper were used to calculate the vapor pressures of the two pure components, and the molar volumes of pure liquids were taken from Table II of their paper. The calculated values indicate that the activity coefficients at constant compositions increase from 0 °C to higher temperatures.

Neglecting the effect of pressure on ln γ, the variation of ln γ with temperature at constant composition is given by

$$\frac{\partial \ln \gamma_i}{\partial T} = \frac{H_i^{\mathrm{o}} - H_i}{RT^2} = \frac{H_i^{\mathrm{E}}}{RT^2} \qquad (3)$$

where H_i^{o} is the molar enthalpy of pure i, H_i is the partial molar enthalpy of component i, and H_i^{E} is the partial molar excess enthalpy of component i. Predicted values of H_i^{E} have been reported by Wilhelm and Collier (1948) at five temperatures for butadiene and styrene in mixtures of butadiene + styrene. These values are positive over the complete concentration range. Consequently, the liquid activity coefficients of butadiene and styrene should decrease with increasing temperature as dictated by eq 3. In other words, there is an obvious thermodynamic inconsistency between the above calculated γ values and the reported H_i^{E} values. This observation leads to the conclusion that the thermodynamic consistency of the reported phase equilibria is doubtful. The larger values of γ appear to be the cause for the higher than expected total pressures obtained from their reported partial pressures at plant operating conditions.

Their predicted partial pressures at 0 °C (Tables III and IV of their paper) were used to calculate the total pressures; the recalculated differences between the vapor pressure of pure butadiene and the total pressure are quite different from those observed experimentally. In other words, the deviations are much greater than those depicted in Figure 2 of their original paper, indicating that different vapor pressures were used by Whilhem and Collier in their Figures 2 and 3 and in their Tables III and IV. The Cox equation presented by these authors yields a vapor pressure of butadiene higher than the more recent and more reliable data (Scott et al., 1945) by more than 3% at 0 °C and is not good enough for representing the vapor pressure of pure butadiene at 0 °C. For these reasons, it was decided to recalculate the γ values at 0 °C using the experimental data determined by Wilhelm and Collier.

Recalculation of Liquid Activity Coefficients at 0 °C

In the work of Wilhelm and Collier, experimental values were reported in terms of the vapor pressure of butadiene minus the total pressure of the mixture as a function of styrene concentration up to 10 mol % styrene for a total of 14 points, and the total pressure of the mixture minus the vapor pressure of styrene as a function of butadiene concentration up to 24 mol % butadiene for a total of 4 points. Both sets of data were presented graphically. Numerical values were not listed in the original report (Whitwell et al., 1944) either. Since these data were the only experimental values available at a low temperature where the total pressure over the concentration range is low, it was decided to further process them but with an approach different from that adopted by Wilhelm and Collier.

An attempt was made to obtain the numerical values from the graphs of Wilhelm and Collier. As the original data points were rather scattered, they were judiciously smoothed. The only restriction is that the final calculated pressures must be in agreement with the original data reported by Wilhelm and Collier. In this work, the smoothed pressures obtained from the graphs were used to obtain the liquid activity coefficients for butadiene and styrene in the following manner.

First, the equilibrium vapor compositions were approximated by means of the following relationship between the total pressure and compositions of the liquid and the vapor phases:

$$\left(\frac{\partial \ln P}{\partial y}\right)_T = \frac{y - x}{y(1 - y)} \qquad (4)$$

There are two assumptions involved in the development of this expression: the vapor phase is considered to be a perfect mixture, and the ratio of the saturated liquid molar volume and the saturated vapor molar volume is very small compared to unity. Equation 4 may be rearranged to give

$$\frac{\Delta P}{P} = \frac{y - x}{y(1 - y)}\Delta y \qquad (5)$$

making it feasible to estimate y by a stepwise calculation (Ho et al., 1961). It was performed with extremely small increments of liquid composition. Approximate values of γ_i can be obtained by means of $\gamma_i = Py_i/x_ip_i$. Then, the vapor phase deviations from the ideal behavior were considered. Again, the generalized reduced second virial coefficient expressions of Tsonopoulos (1974), the combining rules of Prausnitz (1969), and the acentric factors and the critical properties of butadiene and styrene compiled by Reid et al. (1987) were used for the estimation. At 0 °C, the vapor pressure of butadiene was taken to be 117.97 kPa (Scott et al., 1945) and the vapor pressure of styrene was taken to be 0.1805 kPa (Whitwell et al., 1944). The molar volumes of pure liquids were taken from Table II of Wilhelm and Collier (1948).

Rearranging eq 1 gives

$$\ln y_1 = \ln \frac{\gamma_1 x_1 p_1}{P} - \frac{(B_{11} - V_1)(P - p_1)}{RT} - \frac{P\delta_{12}{y_2}^2}{RT} \qquad (6a)$$

$$\ln y_2 = \ln \frac{\gamma_2 x_2 p_2}{P} - \frac{(B_{22} - V_2)(P - p_2)}{RT} - \frac{P\delta_{12}{y_1}^2}{RT} \qquad (6b)$$

Using the approximated values of γ, y_i and P were adjusted on the basis of eq 6 together with the condition that $y_1 + y_2 = 1$ in a trial-and-error manner. The adjusted P values were used to calculate $p_1 - P$ and $P - p_2$ and compared with the experimental values. The subscripts 1 and 2 refer to butadiene and styrene, respectively. Further adjustment of γ_i was required to make the adjusted P acceptable. The approximated y_i and γ_i and the smoothed P values served as a guide in the adjustment. During the examination of the partial pressures reported by Wilhelm and Collier, it was observed that the controlling quantity for obtaining the total pressure of the mixture is the γ of butadiene due to the low vapor pressure of styrene; more weight therefore was given to the γ values of butadiene during the adjustment.

Correlation of the Liquid Activity Coefficients

In order to smooth the γ values obtained at 0 °C and to facilitate calculations of γ at other temperatures, the van

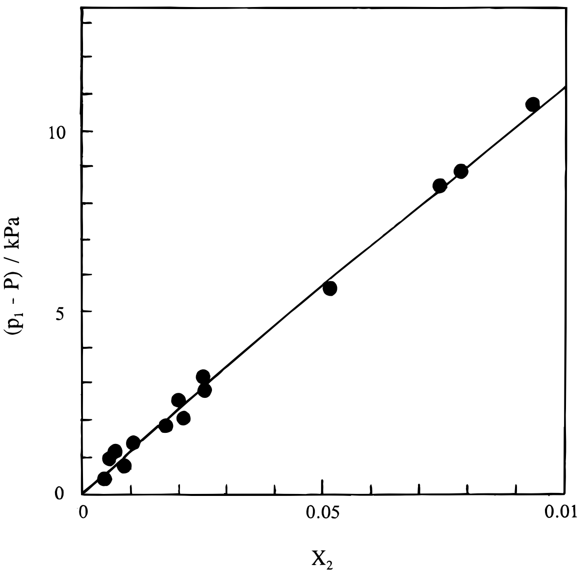

Figure 1. Calculated and experimental differential vapor pressures in the styrene-lean region of the butadiene (1) + styrene (2) system at 0 °C: ●, experimental points (Wilhelm and Collier, 1948); —, calculated, this work.

Laar equation in the form given by Li and Coull (1948) and White (1945) was adopted:

$$T \ln \gamma_1 = \frac{A}{(1 + Ax_1/Bx_2)^2} \tag{7a}$$

$$T \ln \gamma_2 = \frac{B}{(1 + Bx_2/Ax_1)^2} \tag{7b}$$

It has been pointed out by Yu and Coull (1952) that if these equations are valid, a plot of ln γ_i against $1/T$ at constant composition should yield a straight line passing through the origin, and found that for the systems they studied over a short temperature range, straight lines were obtained but not passing through the origin. In view of the fact that the experimental data for the butadiene + styrene system are available at only one temperature, eq 7 was adopted with the anticipation that this simple temperature function can fairly represent the change of ln γ with T in the temperature range of interest in this work. Equation 7 indictes that at constant composition

$$T \ln \gamma_i = \text{constant} \tag{8}$$

and the values of activity coefficients decrease with an increase of temperature. At a given temperature, the calculated γ values would inherently satisfy the Gibbs–Duhem equation. The values of liquid activity coefficients at infinite dilutions are related to A and B:

$$A = (RT \ln \gamma_1)_{x_1=0}, \quad B = (RT \ln \gamma_2)_{x_2=0} \tag{9}$$

The values finally arrived at for the liquid activity coefficients of butadiene and styrene at infinite dilutions based on the experimental data reported by Wilhelm and Collier at 0 °C are

$$(\gamma_1)_{x_1=0} = 1.5745, \quad (\gamma_2)_{x_2=0} = 2.1757 \tag{10}$$

These values were used to calculate γ and then y and P. Comparisons of the calculated and the experimental pressures at 0 °C were plotted in the same manner and in the concentration ranges as those reported by Wilhelm and Collier and shown in Figures 1 and 2. The agreement obtained is obviously acceptable. Furthermore, the differential vapor pressures obtained seem to be more reasonable than those presented by Wilhelm and Collier in their Figures 2 and 3. Typical calculated values at (0 and 50) °C are reported in Table 1. Further justification of using eq 7 is made subsequently using the hitherto proprietary experimental results.

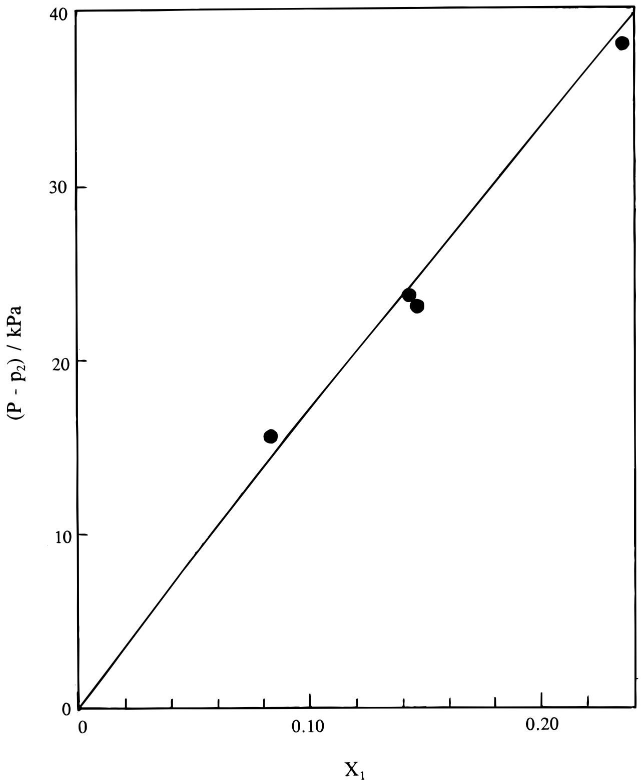

Figure 2. Calculated and experimental differential vapor pressures in the butadiene-lean region of the butadiene (1) + styrene (2) system at 0 °C: ●, experimental points (Wilhelm and Collier, 1948); —, calculated, this work.

Table 1. Typical Values of Calculated Liquid Activity Coefficients, Pressures, and Compositions of Butadiene and Styrene in Butadiene (1) + Styrene (2)

t/°C	x_1	γ_1	γ_2	y_1	P/kPa
0	0.05	1.471	1.011	0.9640	4.633
0	0.10	1.436	1.023	0.9910	17.39
0	0.20	1.367	1.051	0.9952	28.95
0	0.40	1.236	1.136	0.9980	59.47
0	0.60	1.121	1.297	0.9988	80.79
0	0.80	1.033	1.637	0.9994	99.25
0	0.90	1.007	1.956	0.9997	108.8
0	0.95	1.001	2.186	0.9998	114.1
50	0.05	1.279	1.026	0.9197	39.51
50	0.10	1.259	1.059	0.9585	74.69
50	0.20	1.220	1.122	0.9794	141.6
50	0.40	1.141	1.279	0.9905	261.9
50	0.60	1.067	1.514	0.9946	366.0
50	0.80	1.011	1.941	0.9973	461.1
50	0.90	0.997	2.322	0.9985	510.8
50	0.95	0.996	2.588	0.9992	538.3

Experimental Section

An experimental investigation of phase equilibria for the butadiene + styrene system was made at Polysar Corp. in Sarnia, Ontario. Both compounds used in the investigation were produced by Polysar Corp. with a purity of 99.9%.

Table 2. Experimental Vapor–Liquid Equilibrium Values for Butadiene (1) + Styrene (2)

t/°C	P/kPa	x_1	y_1
30	128.9	0.330	0.993
30	154.4	0.397	0.994
30	173.8	0.493	0.996
40	166.2	0.330	0.991
40	200.0	0.396	0.993
40	232.4	0.491	0.995
50	212.4	0.328	0.988
50	254.4	0.396	0.993
50	300.6	0.488	0.994
80	455.1	0.376	0.983

The temperatures investigated were higher than 0 °C and *N*,*N*-diethylhydroxylamine (85% purity, Elf Atochem North America, Philadelphia, PA) was used as the inhibitor. For experiments carried out at lower temperatures, 50 μg/g of solution were added, while 800 μg/g were added during 80 °C runs. All experiments were carried out in a 5400 cm^3 stainless steel reactor, which served as the equilibrium cell. It was first evacuated to a maximum attainable vacuum, and then styrene together with the inhibitor was admitted at room temperature, followed by the charging of butadiene. During the charging of butadiene, the mixture was agitated by a six-blade turbine at 220 rpm. At the end of the charging, the cell was heated to the desired temperature. A calibrated RTD temperature sensor supplied by JMS Southeast, Inc. (Statesville, NC), with a tolerance of ±0.03 °C at 0 °C and 0.10 °C at 80 °C and a calibrated pressure transmitter (model 841 GX, Foxboro Co., Foxboro, MA) with an accuracy of ±0.5% in the pressure range of (−101.34 to 2169.54) kPa were connected to a computer for recording the temperature and pressure of the system. Equilibrium pressure was taken 30 min after its variation was less than 3.45 kPa. From the amount of pure components charged into the cell, the vapor phase volume was estimated. It is known that the vapor phase is always very rich in butadiene. An approximated vapor composition was assumed, and the compressibility factors of the pure components in the vapor phase were estimated. The equilibrium liquid composition was then determined by a material balance with the assumption that the excess volumes in both the liquid and vapor phases are not significant. Due to the large amount of charge used in the experimental work, the error incurred in the approximated vapor composition would not significantly affect the liquid composition obtained from the material balance. The error of the estimated mole fractions is believed to be less than 0.005. Some selected experimental temperature–pressure–liquid composition values are presented in Table 2. The maximum errors in the reported temperature and pressure are estimated to be 0.2 °C and 10 kPa, respectively.

Comparison of Calculated Results with Experimental Values

The calculated total pressure at 50 °C are compared with that of the three experimental points reported in Table 2 in Figure 3, and the calculated values of Wilhelm and Collier are also included for comparison. The system pressures predicted by the new approach are in good agreement with the experimental values, and are much lower than the values provided by Wilhelm and Collier. Similar agreement is obtained between the calculated and experimental total pressures at (30 and 40) °C.

Additional comparison was made at 80 °C as shown in Figure 4. The total pressure of the single experimental point is somewhat lower than the predicted value (495 kPa). This difference may be caused by the inadequacy of eq 7 and/or the presence of the large amount of the inhibitor. In spite of the disagreement, the improvement over the predicted values of Wilhelm and Collier (1948) is substantial.

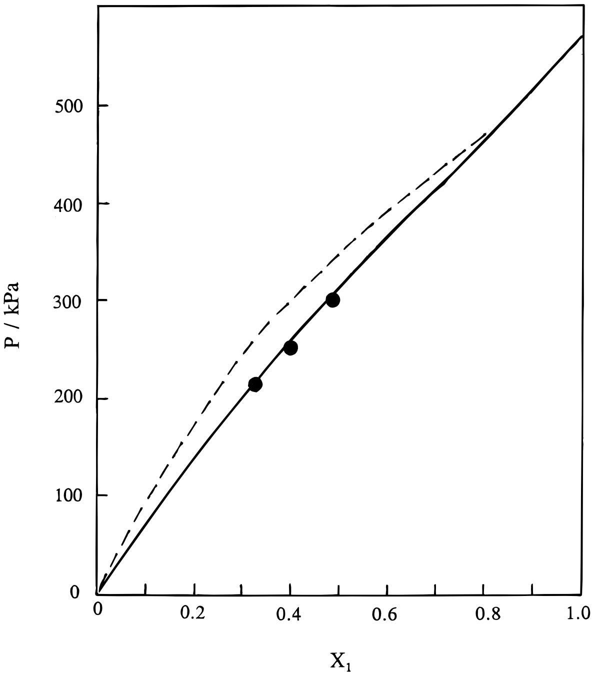

Figure 3. Calculated and experimental total pressures for the butadiene (1) + styrene (2) system at 50 °C: ●, experimental points; —, calculated, this work; - - -, calculated (Wilhelm and Collier, 1948).

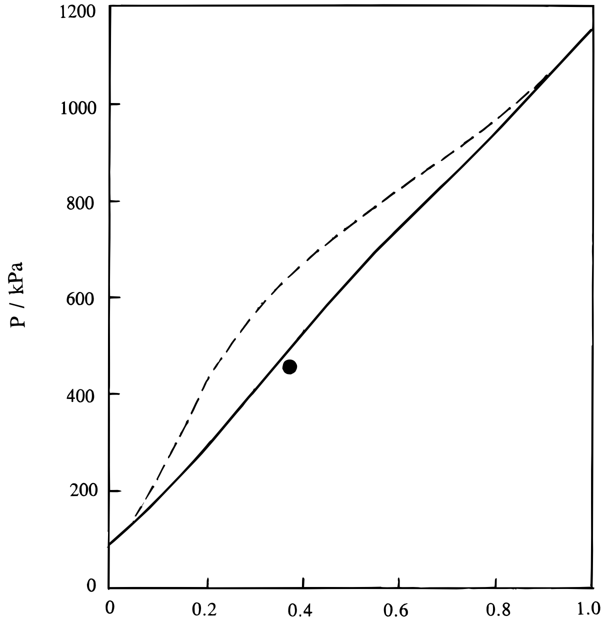

Figure 4. Calculated and experimental total pressures for butadiene (1) + styrene (2) at 80 °C: ●, experimental point; —, calculated, this work; - - -, calculated (Wilhelm and Collier, 1948).

Isobaric Vapor–Liquid Equilibria

Following the graphical procedure of Wilhelm and Collier (1948), the calculated total and partial pressures at (0, 30,

Table 3. Vapor−Liquid Equilibria for Butadiene (1) + Styrene (2) at 101.325 and 202.65 kPa

P/kPa	t/°C	x_1	y_1
101.325	80	0.061	0.882
101.325	50	0.137	0.961
101.325	40	0.182	0.982
101.325	30	0.245	0.989
101.325	0	0.820	0.999
202.65	80	0.133	0.943
202.65	50	0.301	0.987
202.65	40	0.399	0.992
202.65	30	0.561	0.997

40, 50, and 80) °C were used to obtain isobaric vapor−liquid equilibria at (101.325 and 202.65) kPa. The values obtained are presented in Table 3.

Conclusions

A thermodynamically consistent set of γ values at 0 °C is reported and used to extrapolate γ values to higher temperatures. The calculated system pressures are much lower than those reported by Wilhelm and Collier. The validity of the calculated results is confirmed with the hitherto proprietary experimental results.

Acknowledgment

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