# Vapour Pressure and Activity Coefficients of Dilute 2,2,4 Trimethylpentane(Isooctane)-Acetone Mixtures

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Vapour pressure measurements are carried out to test Raoult's law at extreme concentrations, and the deviations are reported. — The azeotropic point is measured and qualitative discussions are presented.

The expressions for the activity coefficients of a binary mixture, considering a correction for the real gas behaviour are:

$$\ln f_1 = \ln \frac{x_1'' p}{x_1' p_{01}} + \frac{B_{11} - V_{01}'}{R\,T} (p - p_{01}) - \frac{B_{11} - 2\,B_{12} + B_{22}}{R\,T} x_2''^2 p\,, \tag{1}$$

$$\ln f_2 = \ln \frac{x_2'' p}{x_2' p_{02}} + \frac{B_{22} - V_{02}'}{R\,T} (p - p_{02}) - \frac{B_{22} - 2\,B_{12} + B_{11}}{R\,T} x_1''^2 p$$

with index 1 acetone and index 2 isooctane.

$p$ : total vapour pressure,
$p_{0i}$ : vapour pressure of the pure component $i$,
$x_i''$ : molar fraction of component $i$ in the gas phase,
$x_i'$ : molar fraction of component $i$ in the condensed phase,
$B_{ii}$ : virial coefficient of the pure component $i$,
$B_{12}$ : virial coefficient of the mixture $1-2$.
$V_{01}'$: partial molar volume of the component $i$; in the mixture we used the molar volume $V_{0i}$ of the pure component $i$ which is the same within 0,06%[1].

Raoult's law states: $x_i'' p/p_{0i} = x_i'$, and this law is expected to be valid when $x_i' \to 0$ if vapours are supposed to behave as ideal gases.

In the limit $x_2' \to 0$, $\left(\frac{\mathrm{d} \ln f_1}{\mathrm{d} x_1'}\right)_{x_2' \to 0} = 0$

and Eq. (1) becomes, with the substitution $x_1'' p = p_1$ (partial pressure of the component 1):

$$\frac{1}{p_{01}} \left(\frac{\mathrm{d} p_1}{\mathrm{d} x_1'}\right)_{x_2 \to 0} - 1 + \frac{B_{11} - V_{01}'}{R\,T} \left(\frac{\mathrm{d} p}{\mathrm{d} x_1'}\right)_{x_2 \to 0} = 0\,. \tag{2}$$

The aim of this work is to test Eq. (2) in the system isooctane acetone at 48 °C.

## Experimental Part

Measurements were made with the system recommended by SCHÄFER[2] which allows isothermal measurements above and below room temperature; some changes were made[3] at the measuring cell. Pressures were taken with a mercury manometer, and read with a cathetometer. The concentrations of both phases were known by taking densities.

The purification of the chemicals was begun by leaving them for two days with Sikkon Fluka. Then a distillation followed in a Schott adiabatic column and the central fraction was received on calcinated potassium carbonate.

## Error

Molar fractions were obtained by measurements of the density in its dependence on temperature and composition. With $\Delta t = 0{,}2$ °C and $\Delta m = 5 \cdot 10^{-5}$ gm a $\Delta x = 2{,}283 \cdot 10^{-4}$ is obtained as error of the molar fraction (results from this laboratory show that no appreciable error is introduced by taking the acetone temperature function equal to that of the mixture).

For the relative error of the activity coefficients one has

$$\varepsilon_{\ln f} = \varepsilon_f = \frac{\Delta x (x_i' - x_i'')}{x_i' \, x_i''} + \frac{\Delta p (p_{0i} - p)}{p_{0i} \, p} \leqq 0{,}411\%$$

$$[< \text{at the extreme value } x_i' = 0{,}0046]$$

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[1] J. EDWARDS, unpublished data.

[2] KL. SCHÄFER, W. RALL, and F. C. WIRTH-LINDEMANN, Z. Phys. Chem. Frankfurt **14**, 197 [1958].

[3] J. EDWARDS and F. IBAÑEZ, Z. Phys. Chem. Frankfurt **58**, 45 [1968].

with

$$\Delta x = 2{,}283 \cdot 10^{-4}, \qquad \Delta p = 0{,}5 \text{ mm}.$$

## Results

Table 1 shows the logarithm of the activity coefficient of isooctane and acetone, calculated by Eq. (1); $p_1$ and $p_2$ are here partial pressures according to Dalton's law.

| $x_1'$ acetone | $x_1''$ | $p_1 = x_1'' p$ | $p_2 = x_2'' p$ | $\log f_1$ (aceton | $\log f_2$ i-octane |
|---|---|---|---|---|---|
| 1,00 | 1,00 | 530,00 | — | — | — |
| 0,99882 | 0,9970 | 529,43 | 1,57 | 0,00 | 1,0122 |
| 0,99744 | 0,9938 | 528,73 | 3,27 | 0,00 | 0,9769 |
| 0,9960 | 0,9906 | 528,02 | 4,98 | 0,00 | 0,9659 |
| 0,9905 | 0,9828 | 525,30 | 9,19 | 0,0001 | 0,8560 |
| 0,9868 | 0,9785 | 523,50 | 11,50 | 0,0002 | 0,8105 |
| 0,9796 | 0,9702 | 520,03 | 15,97 | 0,0004 | 0,7640 |
| 0,9730 | 0,9629 | 517,08 | 19,92 | 0,0009 | 0,7382 |
| 0,9651 | 0,9539 | 513,68 | 24,82 | 0,0015 | 0,7222 |
| 0,9592 | 0,9489 | 511,46 | 27,54 | 0,0023 | 0,7000 |
| 0,9547 | 0,9438 | 509,46 | 30,34 | 0,0026 | 0,6959 |
| 0,9444 | 0,9348 | 504,89 | 35,21 | 0,0034 | 0,6716 |
| 0,9379 | 0,9295 | 502,39 | 38,11 | 0,0042 | 0,6679 |
| 0,9255 | 0,9231 | 499,40 | 41,60 | 0,0073 | 0,6170 |
| 0,9195 | 0,9184 | 496,95 | 44,15 | 0,0080 | 0,6092 |
| 0,9135 | 0,9135 | 494,48 | 46,82 | 0,0087 | 0,6034 |
| 0,9005 | 0,9121 | 493,45 | 47,55 | 0,0140 | 0,5494 |
| 0,8811 | 0,9018 | 486,97 | 53,03 | 0,0178 | 0,5195 |
| 0,0596 | 0,4395 | 89,88 | 114,62 | 0,456 | — 0,0298 |
| 0,052 | 0,388 | 74,10 | 115,90 | 0,4416 | — 0,0224 |
| 0,0288 | 0,2557 | 41,30 | 120,20 | 0,4341 | — 0,0194 |
| 0,1450 | 0,123 | 17,13 | 122,17 | 0,3624 | — 0,0193 |
| 0,0046 | 0,0410 | 5,39 | 126,11 | 0,3590 | — 0,0095 |
| 0,00 | 0,00 | — | 129,5 | — | — |

Table 1. (48 °C).

For testing Eq. (2) it is necessary to know

$$(\mathrm{d}p_1/\mathrm{d}x_1')_{x_2' \to 0} \quad \text{and} \quad (\mathrm{d}p/\mathrm{d}x_1')_{x_2 \to 0}.$$

Since for $x_2' \to 0$, $p_1 \to p_{01}$

$$\lim_{x_2' \to 0} \frac{p_{01} - p_1}{x_2' \, p} = \frac{1}{p_1} \left( \frac{\mathrm{d}p_1}{\mathrm{d}x_1'} \right)_{x_2' \to 0} = \frac{1}{p_{01}} \left( \frac{\mathrm{d}p_1}{\mathrm{d}x_1'} \right)_{x_2' \to 0}$$

and also

$$\lim_{x_2' \to 0} \frac{p - p_{01}}{x_2' \, p} = \lim_{x_2 \to 0} \frac{p - p_{01}}{x_2' \, p \, (x_1' - x_2')^2} = - \frac{1}{p_{01}} \left( \frac{\mathrm{d}p}{\mathrm{d}x_1'} \right)_{x_2 \to 0}.$$

These values will be taken by extrapolation of the graph of $x_2'$ as function of $(p_{01} - p_1)/x_2' p$ and $(p - p_{01})/[x_2' p (x_1' - x_2')^2]$. (This last term was chosen because it has the same limit as $(p - p_{01})/x_2' p$ and gives better values by extrapolation.) The plots are shown in Fig. 1 and the extrapolated values are:

$$0{,}935 = \frac{1}{p_{01}} \left( \frac{\mathrm{d}p_1}{\mathrm{d}x_1} \right)_{x_2' \to 0} \text{and} \quad 1{,}60 = - \frac{1}{p_{01}} \left( \frac{\mathrm{d}p}{\mathrm{d}x_1'} \right)_{x_2 \to 0}$$

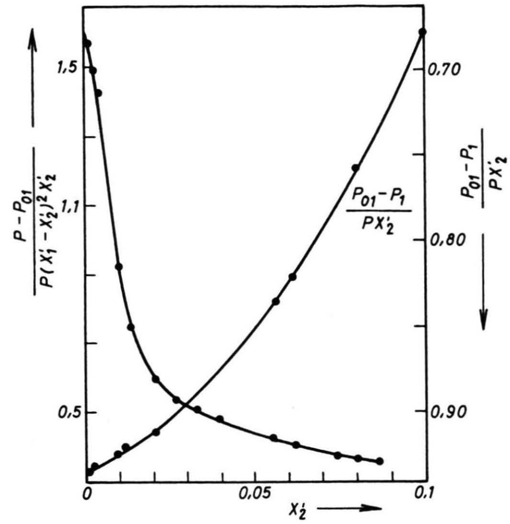

Fig. 1. Limit of $(p - p_{01})/x_2' \, p$ and $(p - p_{01})/[p\,(x_1' - x_2')^2 \, x_2']$ at low isooctan concentration.

Substitution in Eq. (2) gives:

$$0{,}935 = 1 - \frac{(-1590 - 78{,}0284) \cdot 530}{321 \cdot 82{,}057 \cdot 760} \cdot (-1{,}60) = 0{,}93$$

using

$B_{11} = -1590$ cm$^3$/mol and $V_{01}' = 78{,}0284$ cm$^3$/mol. Raoult's law and the limit Eq. (2) show a difference of about 6,5% at high concentrations of acetone.

### *Activity Coefficients*

Determinations of the azeotropic point allow to know the analytic function of the curve activity coefficient vs. molar fraction [4] since

$$p = p_{01} \, x_1' \, f_1 + p_{02} \, x_2' \, f_2; \tag{3}$$

at the azeotropic point $\mathrm{d}p/\mathrm{d}x_2' = 0$ and with Duhem-Margules equation we obtain

$$(p_{01}/p_{02})_{\mathrm{az}} = (f_2/f_1)_{\mathrm{az}}, \tag{4}$$

Dividing Eq. (3) by $p_{02}$ and transforming we get

$$(p/p_{02})_{\mathrm{az}} = (f_2)_{\mathrm{az}}. \tag{5}$$

A carefull determination of the azeotropic points gave:

| $x_1'$ | $t_{\mathrm{az}}$ °C | $p_{\mathrm{az}}$ (torr) |
|---|---|---|
| 0,931 | 30 | 326,5 |
| 0,9135 | 48 | 541,3 |
| 0,890 | 52,5 | 718,0 |

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[4] Kl. Schäfer and H. Plüdemann, Z. Elektrochem. **63**, 1024 [1959].

These data are related by

$$\log p_{\mathrm{az}} = 7{,}275 - 1450/T\,,$$
$$x_{\mathrm{az}}{}' = 0{,}338 + 179{,}714/T\,.$$

Expressing the logarithm of the activity coefficients according to Redlich and Kister with two constants:

$$\log f_1 = x_2{}'^2 (B - 3\,C + 4\,C\,x_2{}')\,,$$
$$\log f_2 = x_1{}'^2 (B + 3\,C - 4\,C\,x_1{}')\,. \qquad (6)$$

From Eq. (1) and (5) we get

$$(f_1)_{\mathrm{az}} = 1{,}0213 \quad \text{and} \quad (f_2)_{\mathrm{az}} = 4{,}1799$$

and substitution in (6) gives

$$B = 0{,}59 \quad \text{and} \quad C = -0{,}239.$$

Then

$$\log f_1 = (0{,}351 + 0{,}956\,x_1{}')\,x_2{}'^2,$$
$$\log f_2 = (0{,}829 - 0{,}956\,x_2{}')\,x_1{}'^2.$$

The points in Fig. 2 show these functions.

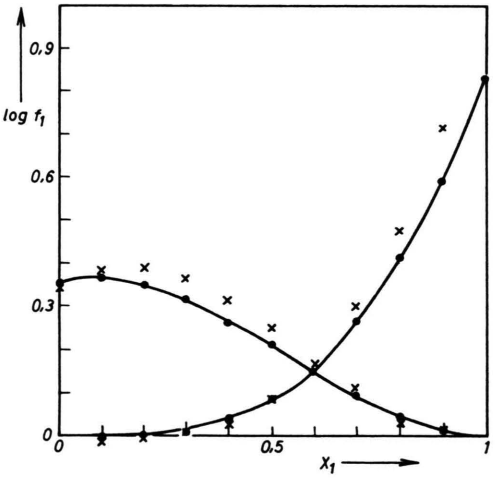

Fig. 2. Dalton's partial pressure vs. acetone concentration.

A second checking of Redlich's constants was made by studying the limit attained by Eq. (6) when either $x_2{}'$ or $x_1{}' \to 0$.

$$\text{When} \quad x_1{}' \to 0 \quad \log f_1 = B + C = 0{,}342\,,$$
$$x_1{}' \to 1 \quad \log f_2 = B - C = 1{,}018\,.$$

This leads to the slightly different values of

$$B = 0{,}68 \quad \text{and} \quad C = -0{,}338$$

being then

$$\log f_1 = (0{,}342 + 1{,}352\,x_1{}')\,x_2{}'^2,$$
$$\log f_2 = (1{,}018 - 1{,}352\,x_2{}')\,x_1{}'^2.$$

Fig. 2 shows these functions with crosses.

It is surprising that at low acetone concentration the activity coefficient of isooctane is smaller than the ideal value 1; this made us think on partial miscibility of the system at low temperature, which was carefully checked[1].

The negative log of activity coefficients at low acetone concentration should be understood by the formation of "complexes" acetone-isooctane because of the high dipolar moment of acetone which electrically induces neighbouring isooctane molecules. Taking the mixture as formed by complexes of molar fraction

$$x_2{}^* = (x_2{}' - m\,x_1{}')/(1 - m\,x_1{}')$$

and

$$x_1{}^* = x_1{}'/(1 - m\,x_1{}')$$

and assuming that Raoult's law $p_2 = x_2{}^*\,p_{02}$ would represent our points with this molar fraction, we see that for $m = 10$ (Fig. 3) we get a fairly good agreement for the region $x_1{}' = 0 - 0{,}009$.

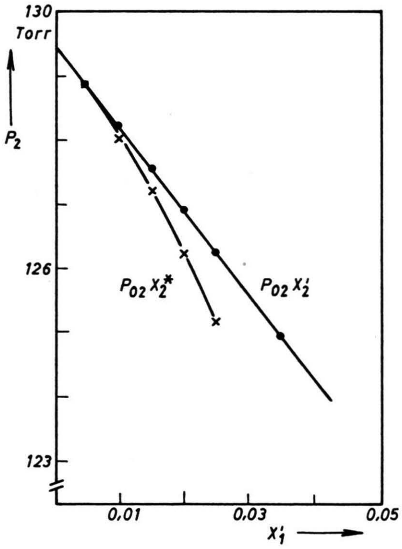

Fig. 3. Logarithm of activity coefficients of the system acetone-isooctane: × according to azeotropic data. ●——● According to extrapolation at limit concentration.

At high acetone concentration the deviation is completely explained by the second virial coefficient and the molar volume of acetone; otherwise the mixture behaves there nearly as an ideal one.

We feel grateful to Industria Copec S.A. for kindly giving us isooctane.