VAPOUR–LIQUID EQUILIBRIUM
IN STRONGLY ASSOCIATED SYSTEMS.
THE PROPIONIC ACID-*n*-HEPTANE SYSTEM*

Ivona MALIJEVSKÁ and Dagmar VLČKOVÁ

Department of Physical Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6

Vapour–liquid equilibrium in the propionic acid–n-heptane system was measured at normal pressure. When treating the data, emphasis was laid on the correct expression of volumetric behaviour in the vapour phase and the analysis of the data obtained.

The present experimental and prediction techniques make it possible, for prevailing systems around normal pressure, to obtain very precise data on vapour–liquid equilibrium and their very good prediction.

Rather lower accuracy is reached for strongly associated systems, *e.g.* for those where one component is a lower fatty acid. In the experimental region it is especially caused by aggressiveness, higher heat of vaporization and hydroscopicity of these substances, in the region of the data treatment by the fact that neglecting the real behaviour in the vapour phase brings about approximately ten times higher percent error in activity coefficient than with common systems, in the region of the experimental data storage by inability of the generally used correlation equations to describe the measured data within their experimental inaccuracy.

In this work we have focused on the correct expression of volumetric behaviour in the vapour phase and analysis of the data obtained.

The reasonable description of deviations from the ideal behaviour in the vapour phase is a prerequisite of obtaining the acitivity coefficients consistent with the Gibbs––Duhem equation. It is well-known that the assumption of ideally dimerizing mixture, usually used to model the volumetric behaviour of fatty acids, does not suffice to a thorough description. Attempts were therefore made to approach reality by considering the existence of a small amount of another associate in the mixture[1-3] which would have remained thenceforth an ideal mixture of ideal gases. In this work we have attempted to give an adequate description[3] in terms of the model

---

of real mixture of real gases consisting only of three components: of monomers and dimers of acids and of a nonassociated component.

To express the activity coefficient for the standard state of pure component at the system temperature and pressure, it holds for the associating component

$$\gamma_A = \frac{v_{A1} y_{A1} P}{v_{A1}^* y_{A1}^* P_A^0 x_A} \exp \left[\frac{1}{RT} \int_P^{P_A^0} V_{m,A}^{01} \, dP \right] \tag{1}$$

and for the nonassociating one

$$\gamma_B = \frac{v_{B1} y_{B1} P}{v_{B1}^0 P_B^0 x_B} \exp \left[\frac{1}{RT} \int_P^{P_B^0} V_{m,B}^{01} \, dP \right]. \tag{2}$$

Meaning of single symbols is summarized at the end of this work.

To calculate activity coefficients, it is necessary to solve the set of equations for y_{A1} and y_{B1}:

$$y_{A1} + y_{A2} + y_{B1} = 1, \tag{3}$$

$$y_A = (y_{A1} + 2y_{A2})/(1 + y_{A2}), \tag{4}$$

$$K = (v_{A2} y_{A2} P_{st})/(v_{A1}^2 y_{A1}^2 P), \tag{5}$$

(standard state pure component in the state of ideal gas at the temperature T and pressure P_{st}) and the set of equations which arises from the foregoing equations in the limit for $y_A = 1$, for y_{A1}^*:

$$y_{A1}^* + y_{A2}^* = 1, \tag{6}$$

$$K = (v_{A2}^* y_{A2}^* P_{st})/(v_{A1}^{*2} y_{A1}^{*2} P_A^0). \tag{7}$$

The fugacity coefficients in Eqs (1), (2), (5), and (7) can be calculated, knowing the values of the second virial coefficients, from the equation

$$\ln v_k = 2 \sum_i x_i B_{ik}/V_m - \ln \left| 1 + \frac{B}{V_m} \right|, \tag{8}$$

where

$$B = \sum_i \sum_j B_{ij} x_i x_j.$$

The virial coefficients can be estimated, for the system defined by us, from generalized relations[4].

EXPERIMENTAL

Preparation of Pure Substances

Propionic acid (supplied by Soyuzkhimexport) was dried with Na_2SO_4 and, after adding several $KMnO_4$ crystals, rectified on a twenty plate glass column. Heat losses were partly compensated by additional heating of the column jacket.

n-Heptane (supplied by Lachema, Brno) was distilled with sodium on a packed rectification column.

The physico-chemical constants of substances used are given in Table I.

Apparatus

The equilibrium was measured using a recirculation still of the Dvořák–Boublík type whose capacity was about 250 ml liquid. The difference between the normal and actual barometric pressure was adjusted by bubbling nitrogen through corresponding column of glycerine.

Temperature was measured by a 100 Ω Pt thermometer calibrated by measuring boiling points of different pure substances. The values of boiling points of pure substances given in Table I were measured in the equilibrium still.

Analysis of the binary vapour and liquid samples was carried out by measuring density at 20°C. Twelve calibration points given in Table II were used for correlation of the dependence $x = x(d)$

TABLE I

Physico-chemical constants of substances used

Substance	n_D^{20}	d^{20}	t_{nbp}, °C
Propionic acid	1·3865	0·9935	141·35
	1·3865—1·3866 (ref.[5])	0·9934 (ref.[6])	140·83 (ref.[6])
			141·35 (ref.[5])
n-Heptane	1·3875	0·6838	98·39
	1·38756 (ref.[5])	0·6835—8 (ref.[5])	98·40 (ref.[5])

TABLE II

Dependence of density $(g\,cm^{-3})$ on composition in the propionic acid(A)–n-heptane(B) system

x_A	0	0·182	0·205	0·281	0·405	0·484	0·583
d^{20}	0·6838	0·7135	0·7177	0·7326	0·7598	0·7797	0·8083

x_A	0·658	0·701	0·841	0·925	1·000
d^{20}	0·8314	0·8475	0·9056	0·9488	0·9935

in the form

$$x_B = (73 \cdot 5955 - 74 \cdot 08d)/(71 \cdot 4872d - 25 \cdot 9492) +$$
$$+ Ad^{-4}(d - 0 \cdot 99346)(d - 0 \cdot 68384)$$

with $A = 0 \cdot 29424$ and a maximum deviation $\sigma_x^{max} = 4 \cdot 3 \cdot 10^{-4}$. The first term is calculated from the value of molar volume for ideal solution.

RESULTS AND DISCUSSION

The experimental equilibrium values of temperature and composition of the liquid and vapour phases are given in the first part of Table III. From the data measured, the values of activity coefficients of both components were calculated from Eqs (1) and (2).

The Antoine constants used for calculating the saturated vapour pressures of pure substances as a function of system temperature are given in Table IV. Values of the equilibrium dimerization constant were evaluated from its temperature dependence given for the standard state of pure component in an ideal gas state at the system temperature and the pressure of 1 Pa in the form

$$\ln K = 8\,858 \cdot 32/T - 33 \cdot 356 \, .$$

TABLE III

Equilibrium data for the propionic acid(A)–n-heptane(B) system, $P = 101 \cdot 325$ kPa

T, K	x_A	y_A	γ_A		γ_B		γ_A^{idas}	γ_B^{idas}	$w_{\ln \gamma A}$	$w_{\ln \gamma B}$
371·01	0·006	0·011	13·5	$\pm$ 2·2	1·011	$\pm$ 0·002	13·9	1·012	28·7	281 090
370·77	0·014	0·016	8·1	$\pm$ 0·9	1·021	$\pm$ 0·003	8·3	1·023	120·8	261 466
371·30	0·073	0·056	4·2	$\pm$ 0·2	1·037	$\pm$ 0·002	4·3	1·037	2 417	246 616
371·56	0·139	0·087	3·0	$\pm$ 0·2	1·081	$\pm$ 0·002	3·1	1·081	7 354	217 347
373·61	0·376	0·166	1·65	$\pm$ 0·08	1·324	$\pm$ 0·008	1·70	1·320	26 683	132 814
374·01	0·408	0·183	1·61	$\pm$ 0·08	1·36	$\pm$ 0·01	1·66	1·36	28 310	120 280
375·09	0·465	0·203	1·48	$\pm$ 0·07	1·44	$\pm$ 0·01	1·52	1·43	30 414	102 601
378·70	0·668	0·277	1·18	$\pm$ 0·05	1·96	$\pm$ 0·04	1·21	1·94	32 675	51 891
383·89	0·799	0·371	1·08	$\pm$ 0·04	2·55	$\pm$ 0·09	1·10	2·50	34 182	23 029
391·86	0·897	0·510	1·02	$\pm$ 0·03	3·3	$\pm$ 0·2	1·04	3·2	42 732	7 426
394·56	0·919	0·554	1·00	$\pm$ 0·03	3·6	$\pm$ 0·2	1·02	3·5	49 022	4 931
397·90	0·939	0·628	1·01	$\pm$ 0·02	3·8	$\pm$ 0·3	1·02	3·7	57 665	2 963
403·94	0·966	0·747	1·00	$\pm$ 0·01	4·2	$\pm$ 0·4	1·00	4·0	95 485	1 023
404·34	0·968	0·756	1·00	$\pm$ 0·01	4·3	$\pm$ 0·4	1·00	4·1	99 441	915
407·01	0·978	0·813	0·99	$\pm$ 0·01	4·5	$\pm$ 0·5	1·00	4·3	134 741	451
409·5	0·986	0·876	0·997	$\pm$ 0·007	4·6	$\pm$ 0·6	1·00	4·3	184 294	188
410·49	0·989	0·898	0·995	$\pm$ 0·006	4·7	$\pm$ 0·7	1·00	4·4	209 679	117

This temperature dependence was calculated from the Taylor data[8] by fixing to the Mac Dougall data[9] for Taylor assumed when treating his data that at 0°C there exists only dimer of propionic acid in the vapour phase. The temperature dependence given leads to rather lower values of equilibrium constants in the temperature range considered. Critical constants for the monomer and dimer of propionic acid were estimated in foregoing work[3] to

$$P_{c,A1} = 5\cdot5 \text{ MPa}, \quad T_{c,A1} = 600 \text{ K},$$
$$P_{c,A2} = 3\cdot3 \text{ MPa}, \quad T_{c,A2} = 630 \text{ K}.$$

The temperature dependences of molar volumes[5] $(\text{cm}^3\text{mol}^{-1})$ were expressed by the following relations:

for propionic acid

$$V_m^{01} = 51\cdot3183 + 7\cdot918 \cdot 10^{-2}T$$

and for n-heptane

$$V_m^{01} = 97\cdot07 + 0\cdot17T.$$

For calculating the fugacity coefficients of monomer and dimer of propionic acid and n-heptane from Eq. (8), the estimates of the second virial coefficients from the generalized Martin relation[4,10] were used:

$$B_i = \left\{0\cdot188 - \frac{0\cdot468}{T_{r,i}} \left[1 + 18\cdot952 \exp\left(-5T_{r,i}\right)\right]\right\} R \frac{T_{c,i}}{P_{c,i}}.$$

The cross virial coefficient was calculated from the same relation but the critical constants were taken as a geometrical mean of critical constants of corresponding pure substances.

TABLE IV
Constants of the Antoine equation[a]

Substance	A	B	C
Propionic acid[7]	23·29189	4 442·377	−36·807
n-Heptane[7]	22·12922	3 988·814	4·604

[a] $\ln P^0 = A - B/(T + C)$, the values of constants correspond to P^0 in Pa.

For computing, the following errors in input quantities were considered

$$s_y = s_x = 0 \cdot 001 , \quad s_T = 0 \cdot 05 \text{ K}, \quad s_P = 50 \text{ Pa} ,$$

$$s_K/K = 0 \cdot 1 , \quad s_B/B = 0 \cdot 1 .$$

The weights of single values of logarithms of activity coefficients, given also in Table III, are calculated on their basis.
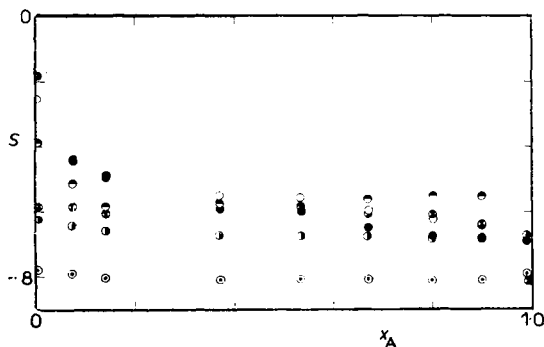

FIG. 1

Effect of errors in input data in the propionic acid(A)–n-heptane(B) system on the value of activity coefficient of propionic acid for different compositions. S denotes the values of natural logarithm of standard deviation in natural logarithm of activity coefficient, $\bigcirc$ y $s_y =$ $= 0 \cdot 001$, $\bullet$ x $s_x = 0 \cdot 001$, $\circ$ T $s_T = 0 \cdot 05$ K , $\odot$ P $s_P = 50$ Pa, $\ominus$ K $s_K/K = 0 \cdot 1$, $\otimes$ B $s_B/B = 0 \cdot 1$
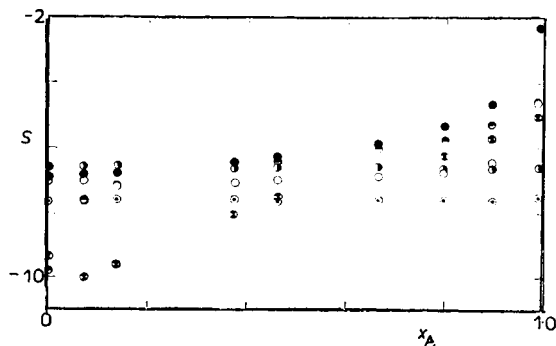

FIG. 2

Effect of errors in input data in the propionic acid(A)–n-heptane(B) system on the value of activity coefficient of n-heptane for different compositions.

(For designation see Fig. 1)

The effect of errors in single input quantities on the logarithms of both activity coefficients can be seen in Figs 1 and 2. In case of propionic acid, the predominant effect in the region of its low concentration has the error in the composition of the liquid (and vapour) phase. However, in the region of higher concentration the effect of inaccuracy in the equilibrium constant predominates. The greatest effect on the accuracy of the n-heptane activity coefficient in the region of low concentrations shows inaccuracy in the liquid phase composition, followed by inaccuracies in the equilibrium constant. In the region of more concentrated solutions, the effect of errors in measuring temperature comes forward. Small is in both cases the effect of error in measuring pressure.

It follows from Table III, where the sixth and seventh columns give the values of activity coefficients calculated from the model of ideally associating mixture $(v_{A1} = v_{A2} = v^*_{A1} = v^*_{A2} = 1)$, that only if more than double precision in input quantities is used, the correction for real behaviour of associating mixture becomes significant in this system.

The calculated activity coefficients were subjected to tests of consistence. They fully satisfied the Herington integral test of consistence[11], the differential Councell and Hicks test[12] proved the data to be consistent, and without the first two points subject to the highest absolute error — which is not considered by the test — really very consistent.

The correlation of activity coefficients on composition of the liquid phase was carried out by minimizing the weighted deviations in logarithms of the ratio of activity coefficients. The Wilson, Orye, and HMW equations were used for the correlation, none of them expressed the given dependence with experimental accuracy. The values of constants obtained by correlation along with their standard deviations and co-variances are given in Table V. Forms of the equations used are given below.

TABLE V

Constants of correlation equations

Equation	$k_1 \pm s_k$	$k_2 \pm s_k$	Covariance (k_1, k_2)	Standard deviation[a]
Wilson	749 ± 37	18 ± 22	$-39\ 600$	4·5
NRTL $(\alpha = 0·47)$	290 ± 22	462 ± 35	$-31\ 329$	5·2
HMW	475 ± 12	-105 ± 11	$-\ 7\ 225$	5·3
Orye	428 ± 16	-177 ± 14	$-14\ 400$	5·7

$^a\ [\sum_{i=1}^{n} w_i((\ln \gamma_{A,i}/\gamma_{B,i})_{exp} - (\ln \gamma_{A,i}/\gamma_{B,i})_{out})^2]^{1/2} (n-2)^{-1/2}$.

The course of activity coefficients is best described by the Wilson equation even though nor it expresses the high values of activity coefficients at concentration ends with sufficient accuracy.

Back calculation of the vapour phase compositions from the experimental P, T, x values on using the computed constants of the Wilson equation brings out the experimental values with an average error in the vapour phase composition about 0·005, the other equations still worse.

The estimations by the UNIFAC method lead to an average error in the vapour phase composition 0·009.

Forms of the correlation equations used:

Wilson

$$\ln \gamma_1 = 1 - \ln\left(x_1 + x_2\lambda_{12}\right) - \frac{x_1}{x_1 + x_2\lambda_{12}} - \frac{x_2\,\lambda_{21}}{x_2 + x_1\lambda_{21}}$$

$$\ln \gamma_2 = 1 - \ln\left(x_2 + x_1\lambda_{21}\right) - \frac{x_2}{x_2 + x_1\lambda_{21}} - \frac{x_1\,\lambda_{12}}{x_1 + x_2\lambda_{12}},$$

where

$$\lambda_{12} = \frac{V_{m,2}}{V_{m,1}}\exp\left(-k_1/T\right), \quad \lambda_{21} = \frac{V_{m,1}}{V_{m,2}}\exp\left(-k_2/T\right)$$

NRTL

$$\ln \gamma_1 = x_2^2\left[\frac{k_2}{T}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{k_1}{T}\frac{G_{12}}{\left(x_2 + x_1 G_{12}\right)^2}\right]$$

$$\ln \gamma_2 = x_1^2\left[\frac{k_1}{T}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{k_2}{T}\frac{G_{21}}{\left(x_1 + x_2 G_{21}\right)^2}\right],$$

where

$$G_{12} = \exp\left(-\alpha \cdot k_1/T\right), \quad G_{21} = \exp\left(-\alpha \cdot k_2/T\right)$$

Orye

$$\ln \gamma_1 = -\ln\left(x_1 + x_2\lambda_{12}\right) + x_2\left[\frac{\lambda_{12}}{x_1 + x_2\lambda_{12}} - \frac{\lambda_{21}}{x_2 + x_1\lambda_{21}}\right] +$$

$$+ \frac{k_1 + k_2}{\left(x_1 + x_2\lambda_{12}\right)\left(x_2 + x_1\lambda_{21}\right)}\frac{x_2^2}{T}\left[\frac{\lambda_{12}}{x_1 + x_2\lambda_{12}} - x_1\frac{\lambda_{21} - 1}{x_2 + x_1\lambda_{21}}\right]$$

$$\ln \gamma_2 = -\ln\left(x_2 + x_1\lambda_{21}\right) - x_1\left[\frac{\lambda_{12}}{x_1 + x_2\lambda_{12}} - \frac{\lambda_{21}}{x_2 + x_1\lambda_{21}}\right] +$$

$$+ \frac{k_1 + k_2}{\left(x_1 + x_2\lambda_{12}\right)\left(x_2 + x_1\lambda_{21}\right)}\frac{x_1^2}{T}\left[x_2\frac{1 - \lambda_{12}}{x_1 + x_2\lambda_{12}} + \frac{\lambda_{21}}{x_2 + x_1\lambda_{21}}\right]$$

HMW

$$\ln \gamma_1 = \frac{x_2(k_1 + k_2)}{T(x_1 + x_2\lambda_{12})(x_2 + x_1\lambda_{21})}\left[1 + x_1\left(1 - \frac{1}{x_1 + \lambda_{12}x_2} - \frac{\lambda_{21}}{x_2 + \lambda_{21}x_1}\right)\right]$$

$$\ln \gamma_2 = \frac{x_1(k_1 + k_2)}{T(x_1 + \lambda_{12}x_2)(x_2 + \lambda_{21}x_1)}\left[1 + x_2\left(1 - \frac{1}{x_2 + \lambda_{21}x_1} - \frac{\lambda_{12}}{x_1 + \lambda_{12}x_2}\right)\right].$$

LIST OF SYMBOLS

P pressure
T absolute thermodynamic temperature
R gas constant
K equilibrium constant
B second virial coefficient
x mole fraction in the liquid phase
y mole fraction in the vapour phase
d density
w weight (reciprocal of variance at the given experimental point)
V_m molar volume
γ activity coefficient
v fugacity coefficient
s standard deviation

Superscripts

$\circ$ pure substance
$*$ value referring to pure acid at a given temperature
l liquid

Subscripts

A   value referring to fatty acid
B   value referring to nonassociating component
Z1   value for monomer of component Z (Z = A, B) in the mixture of monomers of nonassociating component, monomers of associating component, dimers of associating component
c   value of the given quantity at the critical point
A2   value for dimer of associating component
st   standard
r   reduced quantity

REFERENCES

1. Ritter H. L., Simons J. H.: J. Amer. Chem. Soc. *67*, 757 (1945).
2. Potter E. A., Bender P., Ritter H. L.: J. Phys. Chem. *59*, 250 (1955).
3. Malijevská I.: This Journal *48*, 2147 (1983).
4. Novák J. P., Malijevský A., Šobr J., Matouš J.: *Plyny a plynné směsi.* Academia, Prague 1972.
5. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds.* Elsevier, Amsterdam 1950.

6. Riddick J. A., Bunger W. B.: *Organic Solvents*. Wiley-Interscience, New York 1970.
7. Wichterle I., Linek J.: *Antoine Vapour Pressure Constants of Pure Compounds*. Academia, Prague 1971.
8. Taylor M. D., Bruton J.: J. Amer. Chem. Soc. *74*, 4151 (1952).
9. Mac Dougall F. H.: J. Amer. Chem. Soc. *63*, 3420 (1941).
10. Martin J. J.: Chem. Eng. Progr., Symp. Ser. *59* (*44*), 120 (1963).
11. Herington E. F. G.: Inst. Chem. Eng. Proc. Int. Symp. *3*, 17 (1969).
12. Counsell J. F., Hicks C. D.: NPL Report CHEM, 104 (1980).

Translated by J. Linek.