EVALUATION OF HETERODIMERIZATION CONSTANT FROM SOLID–LIQUID AND VAPOR–LIQUID EQUILIBRIUM DATA

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Dedicated to Professor Ľudovít Treindl on the occasion of his 70th birthday.

Activity coefficients obtained from the solid–liquid equilibrium data were used to fit the isobaric vapor–liquid equilibrium data to evaluate the vapor-phase equilibrium constant of heterodimerization of the system propanoic acid–trifluoroethanoic acid. The found hetero-dimerization constant is several times higher than that estimated on the basis of the "double-geometric-mean" rule and its temperature dependence has the form $\ln K_{AB} = 7\,196.7/T - 26.80$.

Key words: Vapor–liquid equilibrium; Solid–liquid equilibrium; Equilibrium constants; Dimerization; Carboxylic acids; Activity coefficients; Thermodynamics.

We have been studying behavior of strongly interacting carboxylic acids for a long time. There are strong forces of attraction between molecules of carboxylic acids causing vapors of these substances to deviate largely from ideal gas behavior even at low pressures. The "chemical" model of an ideally associating mixture describes this behavior quite satisfactorily. This model postulates existence of chemically distinct species that are assumed to be in chemical equilibrium and to behave ideally. According to this model, the observed nonideality is merely an apparent one because it is based on an apparent, rather then a true, account of the vapor composition.

The nonideality of vapor phase behavior of a pure monocarboxylic acid can be described by using a single homodimerization constant that is known for many acids[1–6]. However, at least two kinds of homodimer and one kind of heterodimer species occur in a binary mixture of two monocarboxylic acids such that knowledge of one heterodimerization and two homodimerization constants is needed to describe behavior of this system in the vapor phase.

Low pressure vapor–liquid equilibrium data are usually used to obtain values of activity coefficients of the solution. A good description of the equilibrium vapor phase is essential especially for a highly nonideal systems to get activity coefficient that are consistent with the Gibbs–Duhem equation. In the case of a binary mixture of carboxylic acids it means that we must know three constants of dimerization from other sources.

A reverse approach is suggested in the present paper: to determine a value of the vapor-phase heterodimerization constant from values of activity coefficient obtained from solid–liquid equilibrium measurements. This approach is examined on the system propanoic acid–trifluoroethanoic acid which forms a 1 : 1 compound in the solid state and, for which both vapor–liquid and solid–liquid equilibrium data were obtained in our laboratory[7,8].

METHOD OF CALCULATION

Assuming that the 1 : 1 compound is unstable in the liquid phase, the Wilson equation was originally used to fit the activity coefficients of the system propanoic acid–trifluoroethanoic acid. However, the temperature dependence of this equation was not found to be reliable. Using the Wilson equation for calculation of the activity coefficients at temperatures where vapor–liquid equilibrium data were available, positive deviations from the ideal solution were obtained for this highly associated system.

Unfortunately, no data on excess enthalpy (H^E) are available in the literature for the system and even the UNIFAC method cannot be used for H^E evaluation as not all the group interaction parameters needed are known. A new fit of solid–liquid equilibrium data to the Redlich–Kister equation in the form

$$\frac{G^E}{RT} = x_1 x_2 \sum_{k=0}^{3} b_k (x_1 - x_2)^k , \qquad (1)$$

where subscript 1 denotes propanoic acid and 2 trifluoroethanoic acid, has been done. The Redlich–Kister equation with the following four parameters fits our data satisfactorily: $b_0 = -2.928$, $b_1 = -0.358$, $b_2 = 0.6907$ and $b_3 = 0.2101$. In the following calculation, an uncertainty in the activity coefficient (s_γ/γ) caused by its temperature dependence was presumed to be 10%.

When processing vapor–liquid equilibrium data, the following equation is used to calculate activity coefficients

$$\gamma_i = \frac{f_i}{f_i^{\varnothing} x_i} \exp\left(\frac{1}{RT}\int_p^{p^{\varnothing}} V_{\mathrm{m}i}^1 \, \mathrm{d}p\right). \tag{2}$$

In a mixture with associating species the chemical potential of a constituting (macroscopic) component is equal to that of the component monomeric form[9]. Therefore, the ratio of acid fugacity in mixed and neat vapors is equal to the ratio of corresponding partial pressures of the acid monomer for the ideally associating system.

$$\frac{f_i}{f_i^{\varnothing}} = \frac{p_{i1}}{p_{i1}^*}. \tag{3}$$

The following set of chemical reactions must be taken into account for a binary mixture of two acids A and B:

$$2\,\mathrm{A} = \mathrm{A}_2\,,$$

$$2\,\mathrm{B} = \mathrm{B}_2\,,$$

$$\mathrm{A} + \mathrm{B} = \mathrm{AB}\quad.$$
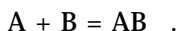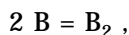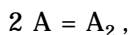
From material balances of the whole system:

$$p = p_{\mathrm{A1}} + p_{\mathrm{A2}} + p_{\mathrm{B1}} + p_{\mathrm{B2}} + p_{\mathrm{AB}} \tag{4}$$

$$y_i = \frac{p_{i1} + 2\,p_{i2} + p_{\mathrm{AB}}}{p + p_{\mathrm{A2}} + p_{\mathrm{B2}} + p_{\mathrm{AB}}}\,,\quad i = \mathrm{A, B} \tag{5}$$

and both neat acids:

$$p_i^{\varnothing} = p_{i1}^* + p_{i2}^*\,,\quad i = \mathrm{A, B} \tag{6}$$

and from three simultaneous chemical equilibrium conditions:

$$K_i = \frac{p_{i2}\,p_{\mathrm{st}}}{p_{i1}^2}\,,\quad i = \mathrm{A, B} \tag{7}$$

$$K_{AB} = \frac{p_{AB} \, p_{st}}{p_{A1} \, p_{B1}}, \tag{8}$$

the needed partial pressures can be calculated.

The activity coefficients thus obtained are very sensitive to the K_{AB} values as it is shown in Figs 1 and 2. In our case, the left-hand side of Eq. (2) is known from solid–liquid equilibrium measurements and, therefore, the monomer partial pressures (p_{A1} and p_{B1}) for every vapor–liquid equilibrium pair of T, and x_1 values can be calculated

$$p_{i1} = \gamma_i p_{i1}^* x_i \exp\left(\frac{-1}{RT} \int_p^{p^\varnothing} V_{mi}^l \, \mathrm{d}p \right), \tag{9}$$

as only pure component properties are needed to calculate p_{i1}^*

$$p_{i1}^* = \frac{1}{2K_i} \left(\sqrt{(1 + 2K_i p_i^\varnothing) - 1} \right). \tag{10}$$

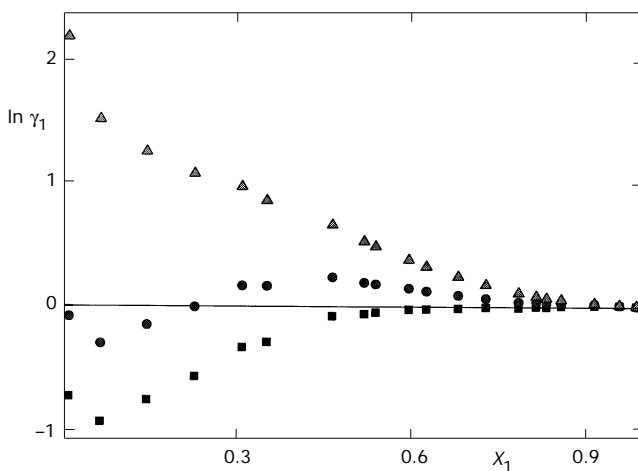No one from Eqs (4), (5) and (8) was so far used. They were applied to calculate K_{AB}.

FIG. 1
Influence of the heterodimerization constant on the activity coefficient of the first component for the propanoic acid (1)–trifluoroethanoic acid (2) system; ■ $K_{AB} = 0$, ○ $K_{AB} = 2(K_A K_B)^{1/2}$, △ $K_{AB} = 4(K_A K_B)^{1/2}$

RESULTS

The heterodimerization constant can be calculated from the pressure balance upon substituting Eqs (*7*) and (*8*) into Eq. (*4*),

$$K_{AB} = \frac{p - p_{A1} - K_A p_{A1}^2 - p_{B1} - K_B p_{B1}^2}{p_{A1} p_{B1}}, \qquad (11)$$

or from the composition balance upon substituting Eqs (*7*) and (*8*) into Eq. (*5*),

$$K_{AB} = \frac{y_1 (p + K_A p_{A1}^2 + K_B p_{B1}^2) - p_{A1} - 2K_A p_{A1}^2}{p_{A1} p_{B1} (1 - y_1)}, \qquad (12)$$

or from the pressure and composition balance

$$K_{AB} = \frac{y_1 (2p - K_A p_{A1}^2 - K_B p_{B1}^2) - p_{A1} - 2K_A p_{A1}^2}{p_{A1} p_{B1}}. \qquad (13)$$
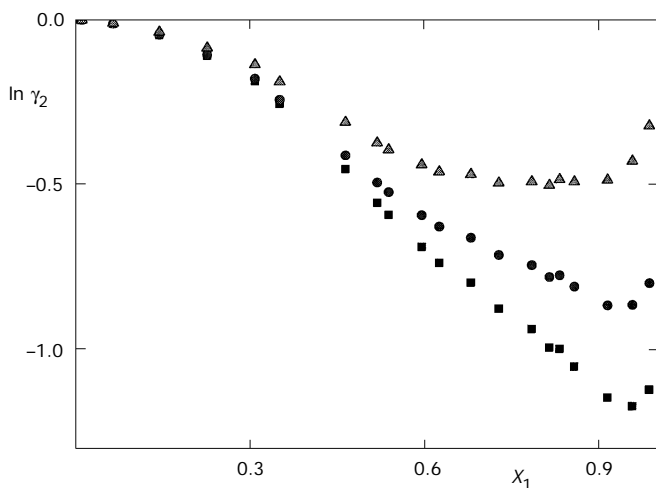

Fig. 2
Influence of heterodimerization constant on the activity coefficient of the second component for the propanoic acid (1)–trifluoroethanoic acid (2) system; ■ $K_{AB} = 0$, ○ $K_{AB} = 2(K_A K_B)^{1/2}$, △ $K_{AB} = 4(K_A K_B)^{1/2}$

Vapor–liquid equilibrium data for the propanoic acid (1)–trifluoro-ethanoic acid (2) system measured at normal pressure (Table I) were used for calculation of three sets of equilibrium constants K_{AB} according to Eqs (*11*), (*12*) and (*13*).

Saturated vapor pressure of propanoic acid was calculated from the Antoine equation[10]

$$\ln p^{\oslash} = 23.29198 - \frac{4\,442.277}{T - 36.807}, \tag{14}$$

while for trifluoroethanoic acid, Kreglewski's data[11] were fitted together with the critical point to the following equation

$$\ln p_r^{\oslash} = \frac{T_r - 1}{T_r}\left[\frac{T_r^{nbp}}{T_r^{nbp} - 1}\ln p_r^{nbp} + (T_r - T_r^{nbp})(A + BT_r)\right], \tag{15}$$

where P_c = 3.2574 MPa, T_c = 491.28 K, T^{nbp} = 344.95 K, A = –5.65835 and B = 7.16516.

Values of homodimerization constants were calculated from the following equations for propanoic acid:

$$\ln K_A = 7\,635.37/T - 29.839,$$

for trifluoroethanoic acid:

$$\ln K_B = 7\,071.30/T - 29.920,$$

both at the standard state of pure perfect gas at 1 Pa.

TABLE I
Vapor–liquid equilibrium data for the propanoic acid (1)–trifluoroethanoic acid (2) system

T	413.45	412.25	410.65	407.95	406.65	405.85	404.05	400.65	397.25	393.85
x_1	0.985	0.956	0.912	0.855	0.829	0.811	0.781	0.724	0.677	0.623
y_1	0.925	0.925	0.855	0.761	0.716	0.693	0.645	0.571	0.508	0.448
T	391.45	386.85	385.05	379.75	369.75	365.35	359.35	353.15	348.15	345.25
x_1	0.593	0.536	0.516	0.461	0.349	0.307	0.225	0.143	0.064	0.010
y_1	0.414	0.350	0.328	0.273	0.155	0.124	0.067	0.032	0.011	0.002

The results of the calculations are plotted in Fig. 3. The vertical lines are error bars (confidence level of 68%). They were calculated by the propagation error method in two steps. Uncertainties in p_{A1} and p_{B1} were estimated first, then in K_{AB}, both with the following uncertainties in the system pressure $s_p = 50$ Pa, mole fractions $s_x = s_y = 0.001$, temperature $s_T = 0.05$ K and activity coefficients $s_\gamma/\gamma = 0.1$.

Weighed least-square fit gives

$$\ln K_{AB} = 7\,196.7/T - 26.80 \,,$$

which yields enthalpy of dissociation $\Delta H_{diss} = 59.83$ kJ/mol.

DISCUSSION

Values of the homodimerization and heterodimerization constants for two temperatures are summarized in Table II. The heterodimerization constant calculated for 20 °C in this work is close to that obtained for the ethanoic acid–trifluoroethanoic acid[12] by the vapor-density technique. Nearly 20% lower dissociation enthalpy of our system is the reason why at 100 °C our constant is more than double the other one. Heterodimerization constants of acids are often estimated as
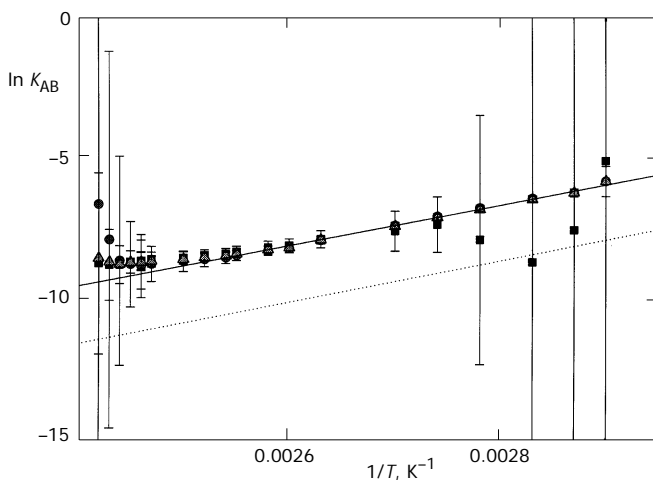

FIG. 3

Values of the heterodimerization constant K_{AB} calculated according to: ■ Eq. (*11*), ○ Eq. (*12*), △ Eq. (*13*). Dotted line: $K_{AB} = 2(K_A K_B)^{1/2}$, full line: linear fit of K_{AB}; vertical lines in every point are error bars

$$K_{AB} = 2\sqrt{K_A K_B} \, .$$

The rule of the double geometric mean is not valid for systems with trifluoroethanoic acid. This is caused by a very low value of the homo-dimerization constant of trifluoroethanoic acid on one hand and a high value of heterodimerization constant on the other.

TABLE II
Values of the dimerization constants of ethanoic acid (EA), propanoic acid (PA) and trifluoroethanoic acid (TFEA)

Constants	20 °C	100 °C
$K_{EA-TFEA}$	0.126	$2.1 \cdot 10^{-4}$
$K_{PA-TFEA}$	0.105	$5.4 \cdot 10^{-4}$
K_{PA-EA}	0.045	$1.67 \cdot 10^{-4}$
K_{EA}	0.2–0.23	$8.18–8.74 \cdot 10^{-5}$
K_{PA}	0.0225	$8.46 \cdot 10^{-5}$
K_{TFEA}	0.003	$1.73–1.82 \cdot 10^{-5}$
$2\sqrt{(K_{PA}K_{EA})}$	0.043	$1.72 \cdot 10^{-4}$
$2\sqrt{(K_{EA}K_{TFEA})}$	0.0159	$7.52–7.98 \cdot 10^{-5}$
$2\sqrt{(K_{PA}K_{TFEA})}$	0.0164	$7.65–7.85 \cdot 10^{-5}$

SYMBOLS

f	fugacity
G	Gibbs energy
H	enthalpy
K	equilibrium constant of dimerization
p	pressure, Pa
R	gas constant
T	temperature, K
V	volume
s	standard deviation
x	liquid-phase mole fraction
y	vapor-phase mole fraction
γ	activity coefficient

Subscripts

AB	mixed dimer
c	critical value
diss	dissociation
i	*i*-th component (macroscopic)
*i*1	*i*-th component monomer
*i*2	*i*-th component dimer
m	molar value
r	reduced value
st	standard value

Superscripts

E	excess value
nbp	normal boiling point
*	value for a pure *i*-th component at a given temperature
∅	saturated value at a given temperature

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