DETERMINATION OF BINARY VAPOR LIQUID EQUILIBRIA (VLE) OF REACTIVE SYSTEMS

M. Tischmeyer, W. Arlt

Technische Universitaet Berlin, Institut fuer Verfahrenstechnik, Fachgebiet
Thermodynamik und Thermische Verfahrenstechnik,
Building TK7, Strasse des 17. Juni 135, D-10623 Berlin, Germany,
w.arlt@vt.tu-berlin.de

ABSTRACT

The simulation of reactive distillation processes requires binary phase equilibrium data and information about the reaction kinetics and equilibrium. The phase equilibrium data for the binary reacting sub-systems are difficult to measure experimentally since the products of reaction affect the binary equilibrium as soon as they are formed. A novel apparatus has been constructed to measure these data for reaction rates with half-life time of 30 minutes and below. Experimental data are presented for compounds of ethanol and isopropanol with formic acid at 40 – 60°C as a model reaction for reactive distillation. The synthesis of ethyl formate is realized at these temperatures in technical columns. The proposed method can be applied to obtain binary interaction parameters of reactive compounds for commonly used g^E-models, if the half-life time of the non-catalyzed reaction at the desired temperature is above 10 minutes.

INTRODUCTION

Conventional chemical production processes are usually performed in a sequence manner i.e. first reaction and then the distillation. In certain cases this sequence may be replaced by a reactive distillation in order to lower the production costs or to improve the purity of the products. Therefore, the (catalyzed) reaction must have sufficient reaction rates at the conditions where distillation is practicable. Several advantages can be achieved by this combined process, the most important are:

- reduced downstream processing for separation of the product from residual components,
- utilization of the heat of reaction directly for evaporation of liquid phase,
- increasing of the selectivity by removal of product(s), in case of parallel or consecutive reactions

- overcoming of azeotropic limitations,
- lowering of resident time since the concentrations of reactants and thus the product yield is higher.

On the other hand the process implies new limitations, such as reactive azeotropes and multiple steady states (and hence an increased effort of process control). A reliable phase equilibrium model is crucial for the process synthesis or to carry out a feasibility study. The emphasis of that study would be to determine whether the reactive distillation is preferable.

The simulation of a reactive column needs both as input: reaction kinetics or equilibrium constants *and* binary vapor-liquid equilibrium data for well-known g^E-models. These data are usually not available because the reaction prevents the experimental determination of binary phase equilibrium data, using standard measurement technique. For example, by a literature search for compounds of organic acids with alcohols, only 64 isothermal or isobar vapor-liquid equilibrium (VLE) data sets were found in the DECHEMA data base [1] which were measured either in chemical equilibrium or at very low temperatures. Only four of them were found to be thermodynamically consistent with the Redlich-Kister area test [1].

In this work, our method of determining the binary phase equilibria of reactive systems is described. As example systems, the esterification of formic acid with ethanol and formic acid with isopropanol is examined. These reactions have half-life times of some minutes up to several hours, depending on the temperature and the amount of formic acid present in the system.

The measuring method applied in this work follows a proposal by Patel and Young [2] for calorimetry. It is shown that this method is appropriate for the certain class of reaction systems used in the reactive distillation.

THEORETICAL BACKGROUND

Phase equilibrium calculations

For description of the VLE, a γ-φ model was chosen:

$$x_i \gamma_i f_{0i}^L = y_i \varphi_i^V P \tag{1}$$

The activity coefficient γ_i is calculated from a model for the Gibbs excess enthalpy g^E. The Wilson model [3] was chosen according to the strongly non-ideal nature of the system:

$$\ln \gamma_i = -\ln\left(\sum_j x_j \Delta_{ij}\right) + 1 - \sum_k \frac{x_k \Delta_{ki}}{\sum_j x_j \Delta_{kj}} \tag{2}$$

$$\text{with} \quad \Delta_{ij} = \frac{v_{0j}^L}{v_{0i}^L} \exp\left(\frac{-\lambda_{ij}}{T}\right) \tag{3}$$

where v_{0i}^{L} and v_{0j}^{L} are the molar volumes of liquid i and j as given in [1] and λ_{ij} are the binary interaction parameters of the model.

To calculate the liquid fugacity it is also necessary to include the standard state fugacity f_{0i}^{L}, which is the fugacity of the pure liquid component *i* at system pressure and temperature. It can be expressed by

$$f_{0i}^{L} = \varphi_{0i}^{LV} P_{0i}^{LV} \exp\left(\frac{v_{0i}^{L}(P - P_{0i}^{LV})}{RT} \right) \tag{4}$$

where φ_{0i}^{LV} is the fugacity coefficient of the component *i* at saturated vapor pressure P_{0i}^{LV}, and $\exp\left(\frac{v_{0i}^{L}(P - P_{0i}^{LV})}{RT} \right)$ is the Poynting correction, which accounts for the expansion or compression of the liquid from saturated vapor pressure to system pressure.

The fugacity coefficient φ_{i}^{V} is calculated with the virial equation of state by the method of Hayden and O'Connell [4] to get the second virial coefficient. They assume that the vapor is ideal except for association between molecules, usually due to hydrogen bonding. The method incorporates the "chemical theory of dimerization". Therefore, it accounts for strong association and solvation effects, including such as found in systems containing organic acids like in the present system.

Reaction Space

The possible phase equilibrium conditions of a quaternary mixture can best be depicted in a tetrahedron. All points within the tetrahedron are possible phase equilibrium compositions for a system without reaction. When one or more reactions occur, the degree of freedom F_G is reduced by the number of independent chemical equilibrium reactions, see Gibbs phase rule (5):

$$F_G = 2 + C - Ph - R \tag{5}$$

where C is the number of components, Ph is the number of phases and R is the number of independent chemical equilibrium reactions.

In a quaternary system with two phases and one reversible reaction (the back-reaction is independent), the degree of freedom is two. This number is identical to the dimension of the concentration space in which the equilibrium conditions are fulfilled. This part of the concentration space is called reaction space [5]. The geometrical shape of the reaction space varies with the type of reaction, the position of the chemical equilibrium (i.e. the quantity of the equilibrium constant K_a) and the presence of inert components.

The stoichiometric reaction mechanism is

$$\nu_A A + \nu_B B \leftrightarrow \nu_C C + \nu_D D, \tag{6}$$

where A and B are the reactants (alcohol and organic acid), C and D are the products (ester and water) and ν_i are the stoichiometric coefficients. The latter are unity for the esterification reactions considered here. If the equilibrium constant K_a (see eq. (7)) has a quantity about unity and an ideal mixture behavior (i.e. also K_x=1), the reaction space forms a saddle area as depicted in Figure 1.

$$K_a = \frac{a_C \cdot a_D}{a_A \cdot a_B} \tag{7}$$

where a_i are the activities

$$a_i = x_i \gamma_i . \tag{8}$$

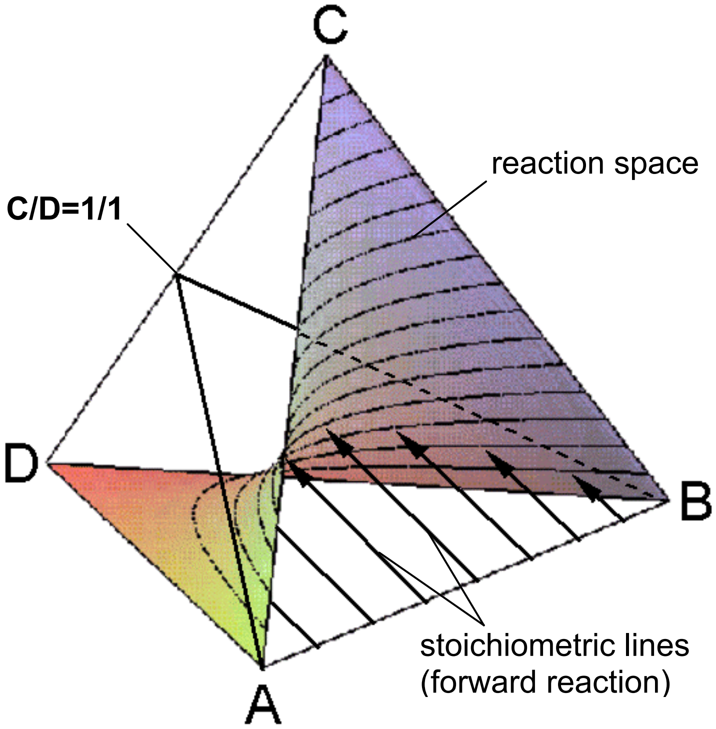

Figure 1: Reaction space of an equimolar reaction A + B $\leftrightarrow$ C + D

The saddle area is stretched between the non-reacting binary systems A-C, A-D, B-C and B-D. The arrows represent the stoichiometric lines which show the change in concentration caused by the forward reaction. Since the reaction does not change the number of moles, all stoichiometric lines are parallel. Their endpoints represent the chemical equilibrium concentrations corresponding to the initial composition of the components A and B. All reactions which are started by mixing of pure A and B yield stoichiometric lines within the triangle outlined by A, B, (C/D=1/1).

The backward reaction (not depicted here for clarity reasons) would, if started by mixing of pure C and D, produce stoichiometric lines directing from the C-D-border to the chemical equilibrium surface.

EXPERIMENTAL

Chemicals

Isopropanol and ethanol used for experimental procedure were of analytical grade (purity 99,9%, Merck). Formic acid was given with 98% purity (Merck). For calibration of the gas chromatograph, ethyl formate, isopropyl formate (both with purity > 98%, Merck) and distilled water were used. The chemicals were processed without further purification except for degassing.

Equipment and experimental procedure

The experiments were carried out in a 550 cm^3 static equilibrium cell which is located in a thermostatic oil bath at a given temperature with an accuracy of ±0.1 K. The set up is given in Figure 2 and explained below.

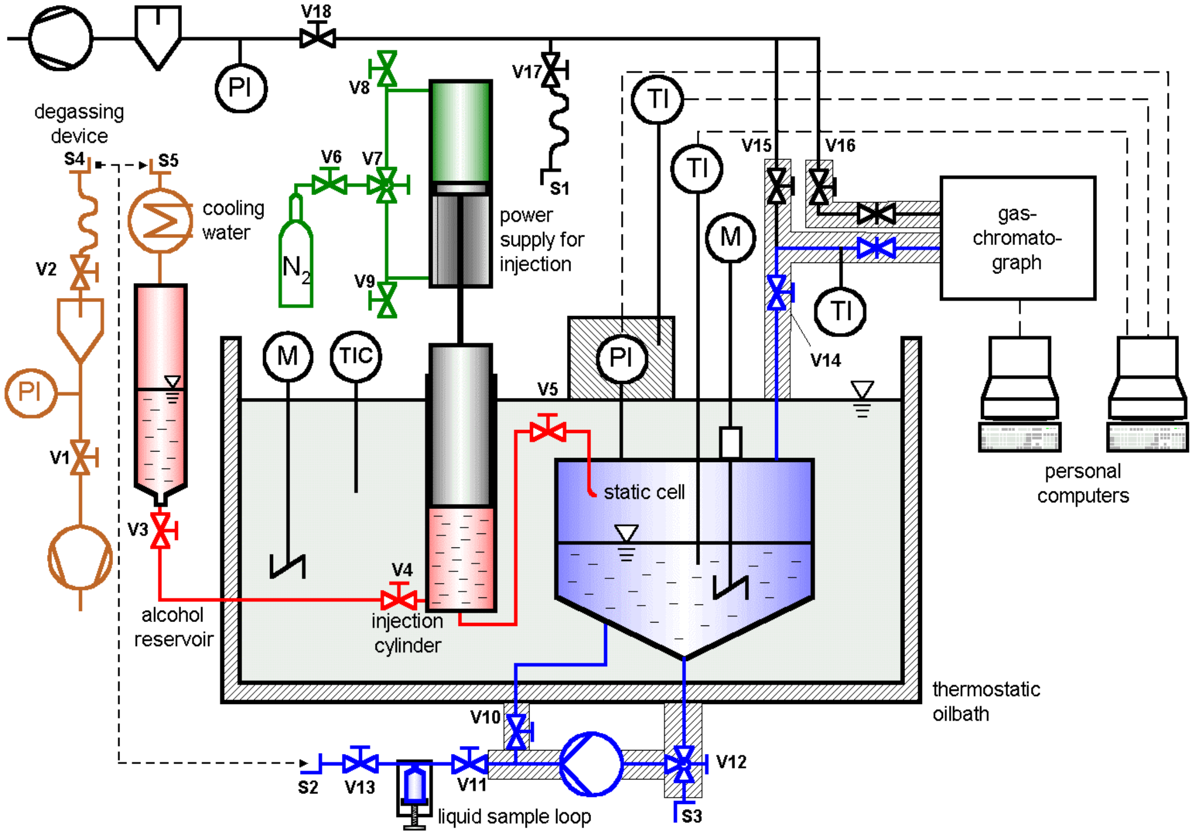

Figure 2: Experimental set-up for measuring VLE data of fast reacting systems

Stainless steel 1.4435, Teflon and glass have been used for construction. The temperature inside the cell was measured by a platinum resistance thermometer PT-100 (Conatex) with an accuracy of ±0.01 K. The pressure was measured using a calibrated high accuracy sensor head (MKS Baratron Type 121A connected to the signal conditioner Type PDR-D-1) attached to the top of the cell. The sensor head and the connecting line from the cell to the sensor were thermostated at 398.15 K ± 0.1 K. The sensor was calibrated by the ambient pressure (measured with a mercury manometer), high vacuum (10^{-4} Pa) and the vapor pressure of pure water, methanol, ethanol and formic acid at a temperature range of 313.15 to 353.15 K.

According to these measurements, the experimental pressure is assessed to be reliable within ±0.5% of the measured value.

Phase equilibrium is reached quickly by mixing the two phases intensively using a stirrer head with magnetic coupling (bmd 075, Büchi GmbH). The measurement starts by injection of the necessary amount of alcohol in order to obtain a desired mole fraction of the mixture. The alcohol is degassed and filled into the injection cylinder (manufactured by the Laboratory for Thermophysical Properties of the University of Oldenburg). When the equilibrium temperature of the oil bath is established, the vapor pressure of pure organic acid is measured. At the time t_0 the predefined amount of alcohol is injected into the cell within less than 2 seconds by means of the pressure pump, powered with 1 MPa from a nitrogen vessel. The precision of the injection is controlled by a linear transducer (Haidenhain, type ND221) with an accuracy of ±10 μm which is calibrated to determine the injected mass of alcohol at a given temperature. With the addition of a second component, the equilibrium is disturbed due to the heat of mixing and heat of reaction. We checked with non-reacting mixtures like acetic acid + water and methanol + water that the cell reaches phase equilibrium after 60 s of mixing. During the ongoing reaction, pressure and temperature are monitored continuously, liquid and vapor samples are taken in short intervals and the gas phase is analyzed immediately. An example for the recorded temperature and pressure curves during a typical reaction experiment (formic acid with ethanol at x_{i0}=0.5, T=60°C) is given in Figure 3.

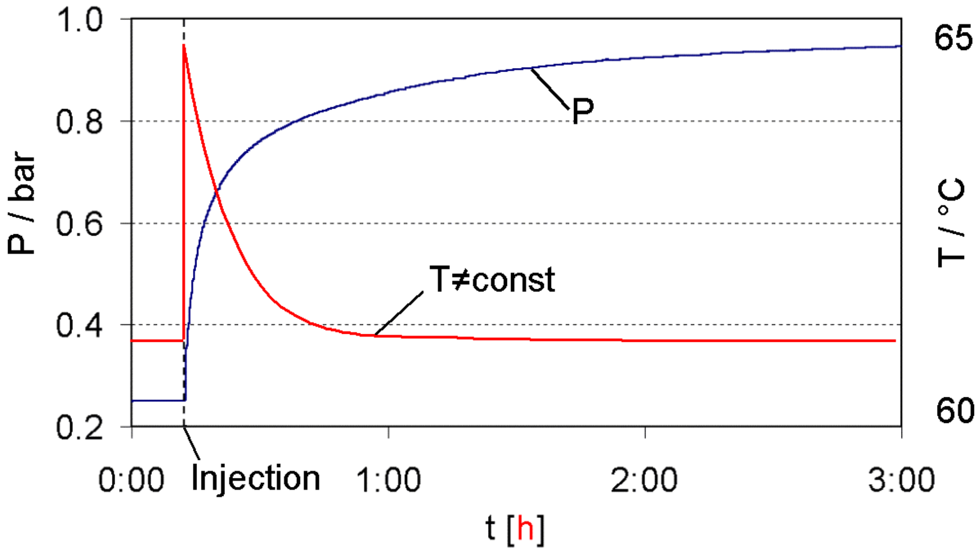

Figure 3: Curve shape of an experiment with a low boiling organic acid in the cell and alcohol injected.

The liquid samples are withdrawn every minute at the pump circuit by connecting an evacuated sample vial. The reaction is stopped immediately in the sample vial by addition of 5g 1,4-dioxane per 1g sample liquid and cooling down to 263 K. The stop of the reaction was verified by comparing the analysis of a sample right after withdrawing with the analysis of the same sample after 10 hours. Since the results were identical, liquid samples are analyzed after the experiment by use of a gas chromatograph HP-GC 5890A Series II with split/splitless-injector, TCD and FID detector and a six port valve (for gas phase sampling). A HP-FFAP capillary column, length = 25 m, i.d. = 0.53 mm, film thickness 0.1 μm is used with helium 5.0 as carrier gas (Messer-Griesheim). An auto injector type G1895A, Agilent Technologies is installed in order to inject samples.

Online gas phase samples were taken additionally every 12 minutes during the experiments although they are not essential to obtain the binary VLE curves. When x_i, P and T are known, y_i can be calculated by fitting a g^E-model and a convenient vapor phase model to the experimental pressure data at given x_i and T. The deviation of the calculated pressure to the measured value is minimized by adjusting the binary interaction parameters of the g^E-model. However, experimental y_i data can be used to verify the model quality.

Obtaining binary VLE Parameters

Since it is not possible to measure the reacting binary phase equilibrium directly, another method has to be used for regressing binary interaction parameters. In our method the phase equilibrium is measured during the reaction right from the beginning. Liquid samples are taken as frequent as possible especially during the first minutes of the reaction. This yields quaternary VLE data which are measured as close as possible to the reacting binary.

To apply a phase equilibrium model at these conditions the interaction parameters of all occurring binaries in the system have to be taken into account. Most of the required binary data are available in literature (see Figure 4 for formic acid – ethanol system) so that Wilson parameters could be regressed. Missing parameters were estimated using modified UNIFAC [6]. In case of the formic acid – isopropanol system, VLE data for all binary systems (except acid – alcohol) were available.

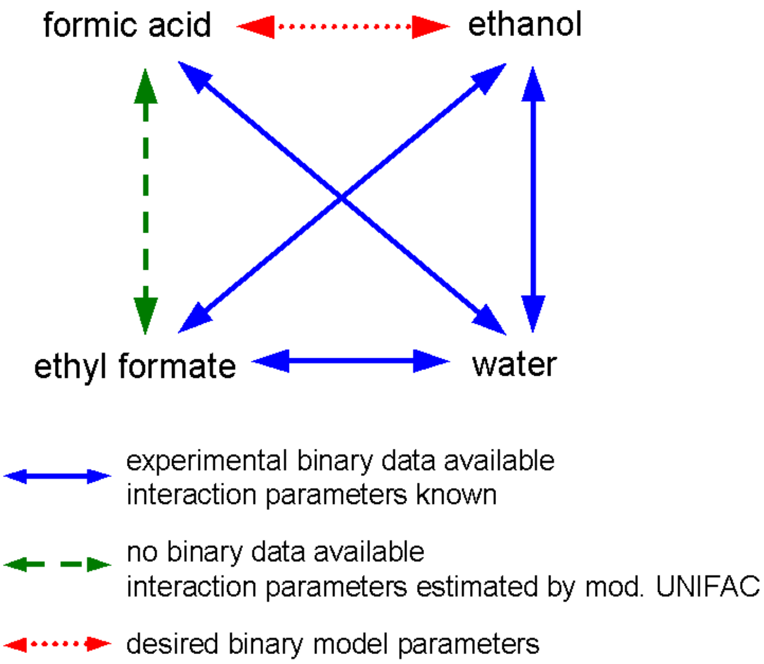

Figure 4: Six Pairs of Interaction Parameters in Quaternary Esterification System

The Wilson model was applied to calculate the activity coefficients although it is not capable of LLE calculation. Since no phase split occurred in the liquid samples taken during experiments (which are the basis for VLE calculations), the model was used mainly at homogeneous phase equilibrium conditions. However, the ester - water binary shows a liquid-liquid immiscibility which has to be calculated by the g^E-model as well. The constant pressure within the mixing gap can be fitted by a very slight slope so that a sufficient approximation is achieved (see Figure 5).

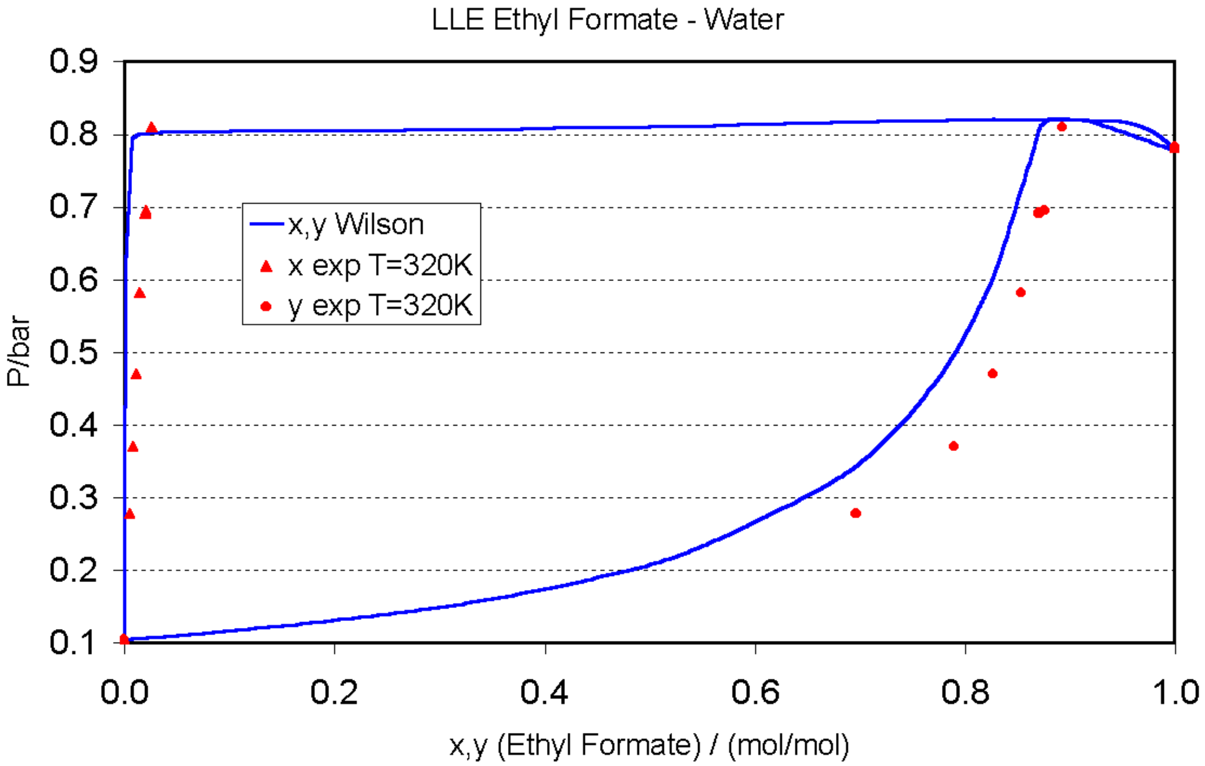

Figure 5: Comparison of Wilson regression to experimental LLE data (experimental data by Marsh [8])

This estimation is necessary since it is possible that during the optimization procedure the phase split area is modified in a way that some data points lie within the mixing gap (of the model). In this case, the NRTL or UNIQUAC equations would produce unreasonable results if used without checking the number of phases by a flash algorithm. A flash calculation will be implemented in our model in future work. For a compilation of all used Wilson interaction parameters see Table 1 and Table 2.

Table 1: Wilson Parameters used in Formic Acid - Ethanol System [1]

WILSON	1)	2)	3)	4)	5)
Comp. 1	**Ethanol**	**Ethanol**	**Formic Acid**	**Formic Acid**	**Ethyl Formate**
Comp. 2	**Ethyl Formate**	**Water**	**Ethyl Formate**	**Water**	**Water**
R/cal/(molK) 1.98721	DECHEMA	DECHEMA	UNIFAC	DECHEMA	FITTED EXP
WILSON12	712.7894	173.3876	115.7602	-1073.6764	3262.02
WILSON21	186.8666	890.3253	297.3702	1074.6210	2374.16
Temp/°C	45.00	40.00	-	45.00	46.85
WILSON12		339.1783		-1157.1753	
WILSON21		881.1112		1159.0655	
Temp/°C		55.00		60.00	

1) Nagata I.; Ohta T.; Ogura M.; Yasuda S.; J. Chem. Eng. Data 21 (1976) 310
2) Mertl I.; Collect. Czech. Commun. 37 (1972) 366
4) 45°C Udovenko V.V., Aleksandrova L.P., Zh. Fiz. Khim. 34, 1366 (1960)
4) 60°C Vrevsky M.S., Glagoleva A.A., Zh. Russ. Fiz. Khim. Obshch. 59, 608 (1927)
5) Marsh K.N.; J.Chem.Eng.Data 41 (1996) 1219

Table 2: Wilson Parameters used in Formic Acid - Isopropanol System [1]

WILSON	1)	2)	3)	4)	5)
	Isopropanol	**Isopropanol**	**Formic Acid**	**Formic Acid**	**Isopropyl Formate**
	Isopropyl Formate	**Water**	**Isopropyl Formate**	**Water**	**Water**
R/cal/(molK) 1.98721	DECHEMA	DECHEMA	DECHEMA	DECHEMA	FITTED EXP
WILSON12	625.7902	385.2801	227.5687	-1073.6764	3890.37
WILSON21	127.8289	1178.1219	202.2207	1074.6210	2093.03
Temp/°C	55.00	35.01	55.00	45.00	0.00
WILSON12		642.8480		-1157.1753	
WILSON21		1218.7931		1159.0655	
Temp/°C		55.03		60.00	

1) Tunik E.K., Zharov V.T., Viniti 1242 (1980)
2) Sada E., Morisue T., J. Chem. Eng. Jap. 8, 191 (1975)
3) Tunik E.K., Zharov V.T., Viniti 1242 (1980)
4) 45°C Udovenko V.V., Aleksandrova L.P., Zh. Fiz. Khim. 34, 1366 (1960)
4) 60°C Vrevsky M.S., Glagoleva A.A., Zh. Russ. Fiz. Khim. Obshch. 59, 608 (1927)
5) Stephenson, R.; Stuart, J., J. Chem. Eng. Data, 31, 56-70 (1986)

To obtain the desired binary interaction parameters for the organic acid – alcohol pair, only these two are fitted to the P,T,x_i data of the quaternary mixture while all other parameters remain unchanged. Since the VLE data were taken close to the binary conditions, the resulting parameters are most suitable for calculating the binary VLE.

The vapor phase association was taken into account by the chemical theory. The degree of association is represented by the η_{ij} parameter which is taken from Prausnitz [7] for binary i and j (see Table 3). If no association coefficients were available they were estimated basing on data available for similar components.

Table 3: Binary Interaction Parameters for Chemical Theory [4]

η_{ij}	Isopropanol	Formic Acid	Isopropyl Formate	Water
Water[1]	1.55	2.5	1.3	1.7
Isopropyl Formate[2]	*1.3*	*2*	*0.53*	
Formic Acid[1]	2.5	4.5		
Isopropanol[1]	1.32			
η_{Ij}	Ethanol	Formic Acid	Ethyl Formate	Water
Water[1]	1.55	2.5	1.3	1.7
Ethyl Formate[1]	1.3	2	0.53	
Formic Acid[1]	2.5	4.5		
Ethanol[1]	1.4			

[1] Prausnitz [7]

[2] estimated by analogy to other esters (ethyl formate and several acetates)

Further pure component parameters used for calculation of γ_i and φ_i^V with the Wilson model and the chemical theory are given in Table 4.

Table 4: Pure Component Parameters for Wilson Model and Chemical Theory

	Isopropanol	Formic acid	Isopropyl Formate	Water
v_{0i}^L /(cm^3/mol)[1]	76.92	37.91	100.95	18.07
Mw / (g/mol)[1]	60.096	46.03	88.1	18.02
T_c /K[2]	508.32	574	*513.03*[4]	647.37
P_c / bar[2]	47.64	61	*41.1*[4]	221.2
rg[3]	2.726	1.48	*3.39*[5]	0.615
dm[3]	1.66	1.52	*1.89*[5]	1.83

	Ethanol	Ethyl Formate
v_{0i}^L /(cm^3/mol)[1]	58.68	80.88
Mw / (g/mol)[1]	46.07	74.08
T_c /K[2]	516.26	508.5
P_c / bar[2]	63.8	47.4
rg[3]	2.25	2.8
dm[3]	1.69	1.7

[1] DECHEMA data base [1]

[2] VDI-Wärmeatlas [9]

[3] Prausnitz et al [7]

[4] calculated by method of Lydersen [10]

[5] estimated by comparison with n-propyl formate

The three coefficients A_i, B_i and C_i of the Antoine equation used for calculation of the pure component vapor pressure are listed in Table 5.

Table 5: Antoine Coefficients A_i, B_i and C_i for pure components

$$P_{0i}^{LV} / \mathrm{bar} = \exp\left(A_i - \frac{B_i}{C_i + T/K}\right) \cdot \frac{1013.25}{760}$$

	A_i	B_i	C_i
Isopropanol[1]	18.6929	3640.20	-53.54
Formic Acid[1]	16.9882	3599.58	-26.09
Isopropyl Formate[2]	17.6710	3585.41	-16.68
Water[1]	18.3036	3816.44	-46.13
Ethanol[1]	18.9119	3803.98	-41.68
Ethyl Formate[1]	16.1611	2603.30	-54.15

[1] Reid et al. [11]

[2] DECHEMA data base (Gmehling et al. 1977)

RESULTS

P,T,x data were measured during the reactions of

isopropanol + formic acid → isopropyl formate + water
and
ethanol + formic → ethyl formate + water

at 40°C and 60°C. Figure 6 and Figure 7 exemplary show experimental liquid compositions of the isopropanol – formic acid system at both temperatures. A complete set of all measured data is given by Tischmeyer [12].

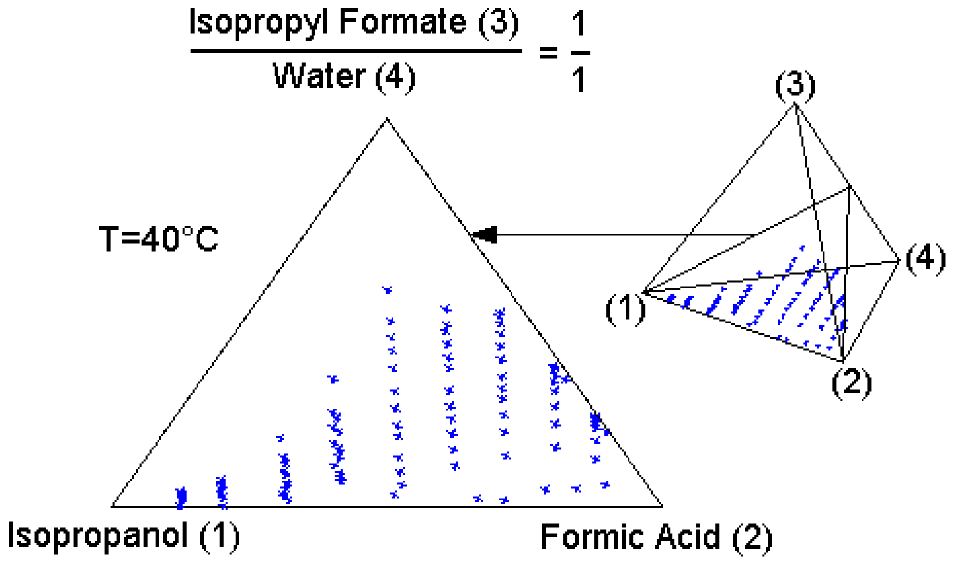

Figure 6: Liquid compositions of the Isopropanol – Formic Acid Reaction at 40°C

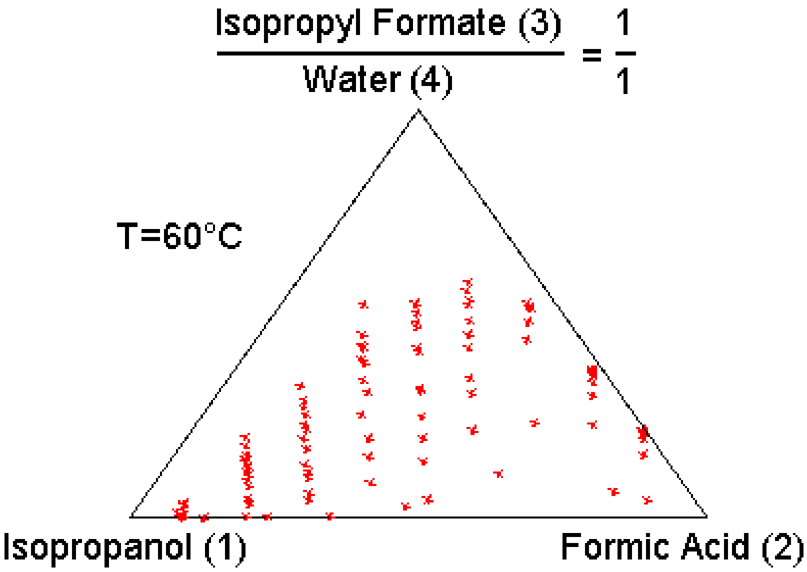

Figure 7: Liquid compositions of the Isopropanol – Formic Acid Reaction at 60°C

Since the esterification reactions are auto-catalyzed by formic acid, the reaction rate rises with the amount of acid present in the system. On the right side of the diagrams at high acid concentrations the reaction has a half-life time of some 10 minutes. Therefore it is difficult to get a sufficient amount of liquid samples close to the reacting binary, especially at a elevated temperatures.

At high isopropanol concentrations the half-life time rises to several hours, chemical equilibrium is reached after more than 15 hours. Since this information is not essential to the determination of the desired VLE parameters the experiments were stopped after about 8 hours which yields the short reaction paths at the left side of both diagrams.

Figure 8 exemplary shows the measured pressure over time curves for the isopropanol – formic acid system at 40°C. Initial isopropanol concentrations change between x_{i0} = 0.1 up to 0.8. The discrete pressure points correspond to the time points where liquid samples were taken.

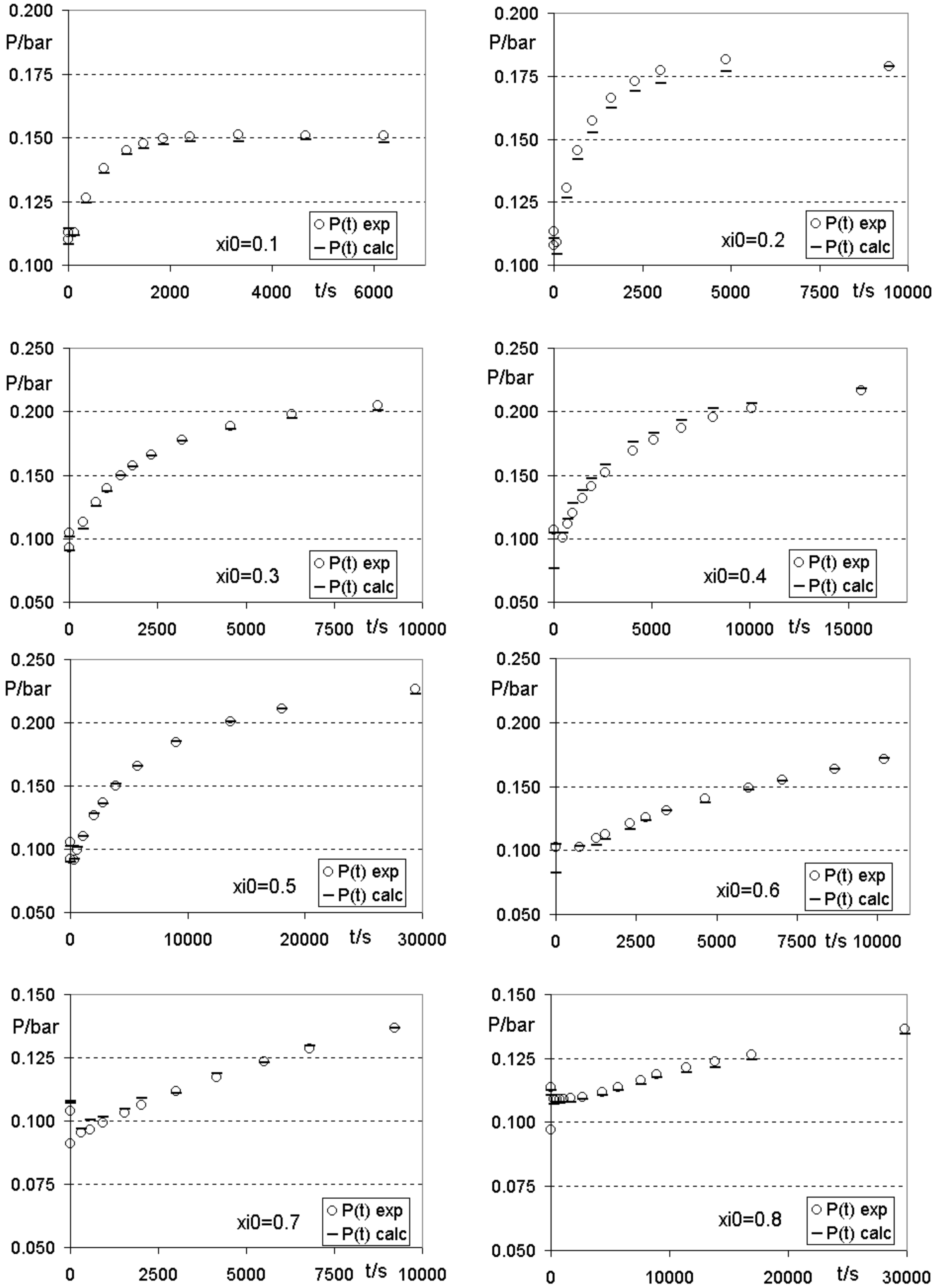

Figure 8: P(t) diagrams for the Isopropanol – Formic Acid System at 40°C

The respective liquid concentrations x_1 to x_4 at these time points and the measured temperatures are used to calculate the system pressure and vapor concentrations by use of equation (1) with the Wilson g^E model for liquid phase and the chemical theory for vapor phase. The relative deviation of all experimental to calculated pressure data is then minimized during the model fitting procedure by variation of the binary interaction parameters of the reacting pair. Binary parameters for the Wilson model were obtained at 40°C and 60°C for all reacting systems. In case of the ethanol – formic acid binary, experimental h^E-data measured by Zhao et al. [13] were also included in the regression. The resulting binary parameters are given in Table 6. Vapor phase data are not reproduced here due to problems in the determination of the compositions.

Table 6: Regressed binary Interaction Parameters for the Wilson Model

Component *i* Component *j*	Isopropanol Formic Acid		Ethanol Formic Acid	
Temperature / °C	40	60	40	60
Wilson λ_{ij}	-978.3222	-1200.0105	-489.8492	-156.5872
Wilson λ_{ji}	681.7373	1346.5472	-57.8520	-325.6978
ΔP_{mean} over all data	1.8%	3.1%	12.3%	4.4%
ΔP_{max} over all data	6.7%	8.8%	31.0%	12.0%

ΔP_{mean} and ΔP_{max} are the relative mean and maximum deviations of the calculated pressure and measured data. The ethanol - formic acid reaction at 40°C was the first one examined. The apparatus (especially the accuracy and speed of liquid sampling) was advanced and improved after completing the measurement of this phase equilibrium. Since each experiment consists of approximately 9 reaction runs with about 12 liquid samples each, the amount of data points to be fitted by the model is immense. Deviations larger as compared to standard VLE measurements were inevitable.

In Figure 9 and Figure 10 the resulting binary phase equilibria of the reacting acid – alcohol pairs can be seen. Both show a minimum pressure azeotrope at low to medium alcohol concentrations which shifts to lower alcohol concentrations at higher temperatures.

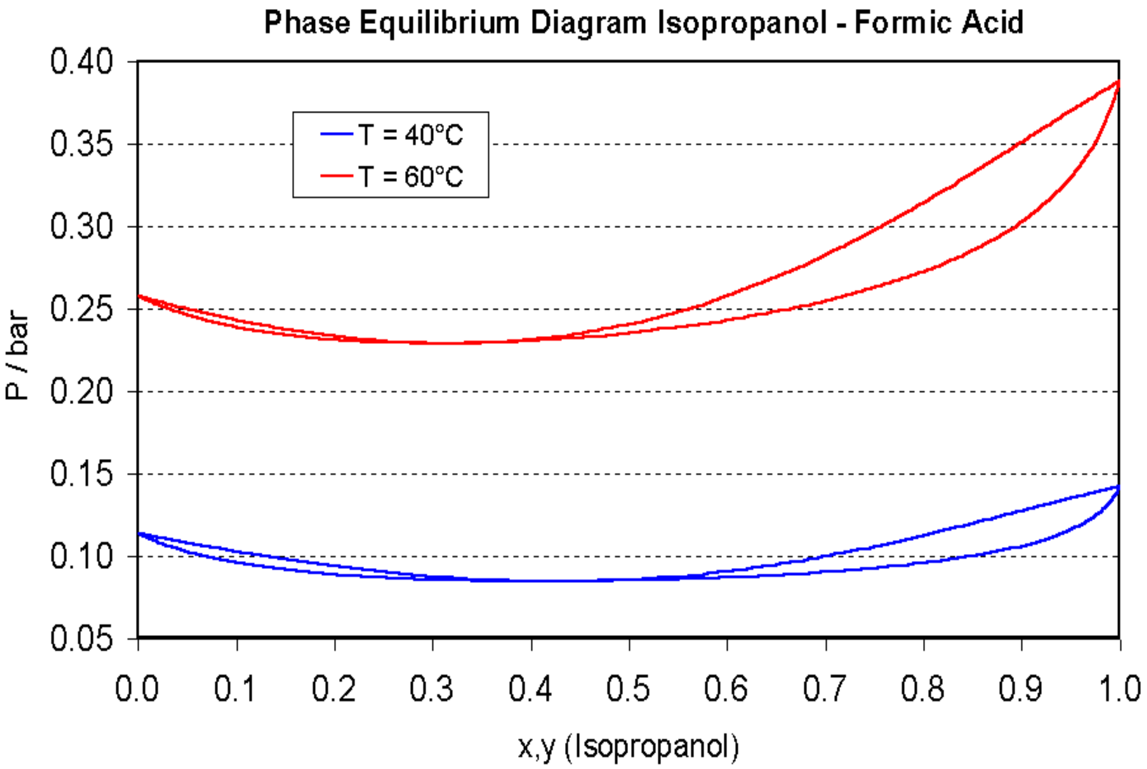

Figure 9: Calculated binary VLE diagram of the Isopropanol – Formic Acid System

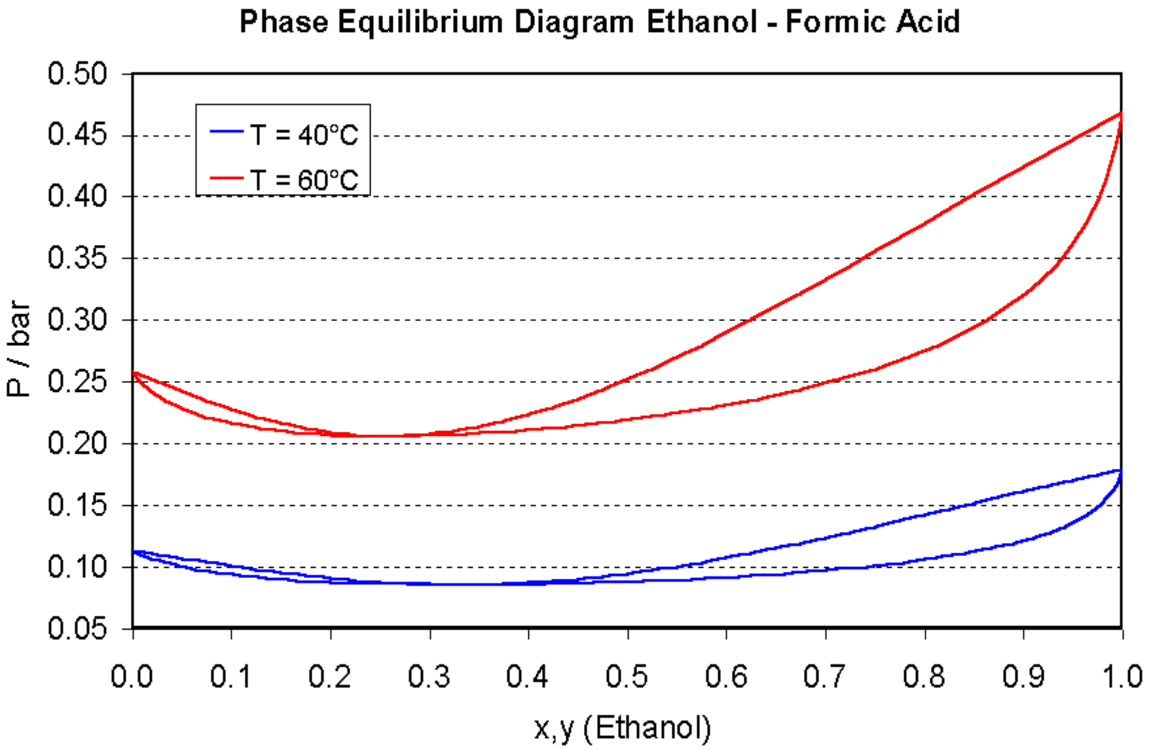

Figure 10: Calculated binary VLE Diagram of the Ethanol – Formic Acid System

CONCLUSIONS

Quaternary P,T,x data have been measured for the reacting systems isopropanol + formic acid and ethanol + formic acid (40°C to 60°C). A static cell with the possibility of adding thermostated, degassed components and immediate mixing as well as a quaternary regression method have been used. Wilson g^E-model parameters for the reacting binary systems were obtained. Calculated values and experimental data are in very good agreement in three out of four cases. The new regressed parameters for the chosen g^E-model can be recommended for accurate computation of the equilibrium conditions e.g. in simulation processes.

Further measurements will be carried out on the systems isopropanol + formic acid at 80°C and ethanol with propionic acid. Therefore the vapor phase sample system will be improved in order to obtain complete VLE data sets.

The results show that the applied method can be recommended to determine the binary interaction parameters of reacting systems with half-life times down to 10 minutes. Temperature deviations due to mixing effects (exothermic reactions) are covered by the regression method since each data point is evaluated at its own temperature.

NOMENCLATURE

latin letters:

a	activity	-
a_{12}, a_{21}	binary interaction parameters for g^E-models	
A_i, B_i, C_i	Antoine Coefficients, P(bar) and T(K)	-
dm	dipole moment	Debye
$E_{A,ij}$	energies of activation for reaction ij	-
f	fugacity	Pa
g	Gibbs energy per mole	J/mol
g_{ij}	energies of interaction between an i-j pair of molecules	J/mol
h_{mix}	enthalpy per mole	J/mol
k_{12}	reaction rate constants of the esterification	mol/s
k_{21}	reaction rate constants of the hydrolysis	mol/s
K_a	chemical equilibrium constant in terms of activities	-
K_f	chemical equilibrium constant in terms of fugacities	-
K_x	chemical equilibrium constant in terms of mole fractions	-
Mw	molecular weight	g/mol
n	number of components	-
n_i	number of moles of component *i*	-
P	pressure	Pa
P^{LV}	vapor pressure	Pa
r	reaction rate	mol/s
R	universal gas constant	J/mol K
rg	radius of gyration	nm
t	time	s

t_0	time of mixing, start of the reaction	s
T	temperature	K
v	molar volume	m^3/mol
x	liquid mole fraction	-
y	vapor mole fraction	-
X	transformed liquid coordinate	-
Y	transformed vapor coordinate	-

greek letters:

α_{ij}	non-randomness constant for binary ij interactions	-
Δ_{ij}	Wilson coefficient as defined in equation (2)	-
λ_{ij}	Wilson binary interaction parameters	cal/mol
ν_i	stoichiometric coefficient of component *i*	-
φ	fugacity coefficient	-
γ	activity coefficient	-
η	Hayden O'Connell association parameter	-

indices, superscript:

+	standard state conditions
E	excess
L	liquid
V	vapor
VLE	in phase equilibrium
VLE+CE	in phase and chemical equilibrium

indices, subscript:

0	pure component
A..D	Components A..D
c	critical
i0	initial composition of component *i*
i	component *i*
j	component *j*
max	maximum
mean	arithmetic mean
mix	mixture
∞	after time → ∞

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