

# Correlation of Vapour—Liquid Equilibrium Data of Ternary Systems\*

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Received 1 April 2004

*Dedicated to the 80th birthday of Professor Elemír Kossaczký*

A method for correlation of vapour—liquid equilibrium (VLE) data of ternary systems is tested. For thermodynamic description of ternary VLE the excess molar Gibbs energy equation – NRTL equation, extended by the universal ternary contribution was used. Binary parameters of NRTL equation were obtained from the binary equilibrium data of corresponding systems; parameters of the universal ternary contribution were evaluated from the ternary VLE data. Execution of the proposed procedure for ternary VLE correlation is simple and the binary and ternary NRTL model parameters retain their physical meaning. Moreover, these parameters could be used also for VLE prediction of multicomponent systems containing the corresponding binary and ternary subsystems.

Procedure was applied for correlation of VLE of twelve ternary systems. Introduction of the ternary contribution into the original NRTL expression improved significantly correlation of ternary VLE data compared to the prediction based on binary equilibrium data only. Due to the use of ternary contribution, the mean deviation of the pressure values decreased 1.2 to 4.5 times and also the deviation of the component mole fraction in the vapour phase was partially improved. The results of correlation are comparable and sometimes even better than the direct fit of ternary VLE data.

Thermodynamic description of vapour—liquid and liquid—liquid equilibria (VLE, LLE) requires knowledge of excess Gibbs energy variation with the liquid-phase mixture composition, *i.e.* one has to know the values of parameters of corresponding  $G^E$  equations used for calculation of activity coefficients of the mixture components. Already the early attempts to predict multicomponent two-phase equilibria showed that the calculation based on binary equilibria only is not able to fit quantitatively the experimental multicomponent equilibrium data. In order to improve the consistency of experimental and computed VLE data, also ternary equilibria should be regarded [1, 2]. In practice, two approaches are used to improve the ternary VLE correlation by considering the experimental ternary equilibrium data.

The first one is based on evaluation of binary  $G^E$  model parameters from experimental ternary VLE (*e.g.* DECHEMA). Such parameters correlate the cor-

responding three-component region well, however, the description of other two-phase regions is poor. Moreover, these parameters are not able to reproduce the vapour—liquid or liquid—liquid equilibrium data of the corresponding binary subsystems. Binary  $G^E$  model parameters obtained by direct correlation of experimental ternary data are purely mathematical values, thus could not be used for the prediction of four- or multicomponent equilibria.

The second approach consists in extension of the excess molar Gibbs energy expressions with ternary contribution parameters. These parameters are evaluated from experimental ternary equilibria using the binary  $G^E$  model parameters obtained from equilibrium data of corresponding binary subsystems.

In the present study, the second approach based on extension of NRTL equation by the universal ternary contribution of *Surový et al.* [3] was adopted and applied to correlation of VLE of twelve ternary systems presented in Table 1.

\*Presented at the 31st International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, 24—28 May 2004.

## THEORETICAL

Aspiring to improve the ternary LLE description, Surový *et al.* [3, 4] proposed the universal ternary contribution to the excess molar Gibbs energy of a ternary mixture in the following form

$$\Delta_t G^E/RT = (G^E/RT) - (G_b^E/RT) = x_1 x_2 x_3 (E_1 x_1 + E_2 x_2 + E_3 x_3) \quad (1)$$

$G^E$  being excess molar Gibbs energy of the mixture,  $G_b^E$  excess molar Gibbs energy of the mixture calculated from binary equilibrium data only, and  $\Delta_t G^E$  ternary contribution to the excess molar Gibbs energy.  $E_i$  are parameters of the universal ternary contribution,  $x_i$  represents the  $i$ -th component mole fraction in the liquid phase,  $R$  is the universal gas constant, and  $T$  the thermodynamic temperature.

Ternary contribution (1) could be used in the same form for all  $G^E$  model equations. Moreover, ternary contribution was successfully applied also for prediction of quaternary liquid—liquid equilibria [5–7].

Parameters of the universal ternary contribution,  $E_i$ , were evaluated through minimization of the objective function,  $F$ , by the simplex method. For the sets of ternary isothermal  $P$ - $x$ ,  $y$  data the following form of objective function was used

$$F = \sum_i \sum_n (y_i - y_{\text{calc},i})_n^2 + \sum_n \left( \frac{P - P_{\text{calc}}}{P} \right)_n^2$$

$$n = 1, 2, \dots, N; \quad i = 1, 2, 3 \quad (2)$$

where  $P$  and  $P_{\text{calc}}$  are measured and calculated total pressures,  $y_i$  and  $y_{\text{calc},i}$  are experimental and calculated mole fractions of the  $i$ -th component in the vapour phase.

Assuming ideal behaviour of vapour and real behaviour of liquid phase the total pressure  $P_{\text{calc}}$  and

mole fraction  $y_{\text{calc},i}$  were calculated using the relations

$$P_{\text{calc}} = x_1 \gamma_1 P_1^o + x_2 \gamma_2 P_2^o + x_3 \gamma_3 P_3^o \quad (3)$$

$$y_{\text{calc},i} = \frac{x_i \gamma_i P_i^o}{P_{\text{calc}}} \quad i = 1, 2, 3 \quad (4)$$

$\gamma_i$  being the activity coefficient and  $P_i^o$  saturated vapour pressure of component  $i$ . For calculation of activity coefficients of ternary systems the NRTL equation extended by the ternary contribution was used in the following form

$$\ln \gamma_i = \frac{\sum_{j=1}^3 \tau_{ji} G_{ji} x_j}{\sum_{k=1}^3 G_{ki} x_k} + \sum_{j=1}^3 \frac{x_j G_{ij}}{\sum_{k=1}^3 G_{kj} x_k} \left( \tau_{ij} - \frac{\sum_{k=1}^3 x_k \tau_{kj} G_{kj}}{\sum_{k=1}^3 G_{kj} x_k} \right) + \Delta_t \ln \gamma_i \quad (5)$$

where  $G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$  and  $\tau_{ij} \neq \tau_{ji}$ ,  $\tau_{ii} = \tau_{jj} = \tau_{kk} = 0$ ,  $\alpha_{ij} = \alpha_{ji}$  are the model parameters.

Ternary contribution to the activity coefficient of component  $i$ ,  $\Delta_t \ln \gamma_i$ , is expressed by the relation (1) as follows

$$\Delta_t \ln \gamma_i = x_j x_k [E_i x_i (2 - 3x_i) + E_j x_j (1 - 3x_i) + E_k x_k (1 - 3x_i)] \quad (6)$$

where  $i, j, k = 1, 2, 3$ , and  $i \neq j \neq k$  correspond to individual components.

**Table 1.** Parameters of Ternary Contribution to the NRTL Equation for Ternary VLE Correlation

Ternary system (1—2—3)	$t/^\circ\text{C}$	$N$	Ref.	Page	Ternary parameters		
					$E_1$	$E_2$	$E_3$
1 Acetone—ethanol—hexane	55	20	[9]	663	0.20119	-1.15036	1.92724
2 Acetone—methanol—cyclohexane	35	20	[9]	627	1.28613	0.57589	0.50830
3 Acetone—methanol—propan-2-ol	55	27	[9]	625	0.30993	0.44205	0.04072
4 Benzene—cyclohexane— <i>tert</i> -pentanol	70	24	[15]	734	-2.39093	0.61901	-1.02609
5 Benzene—thiophene—heptane	55	8	[13]	475	0.69940	-0.27129	-0.97275
6 Butan-2-one—benzene—propan-2-ol	50	19	[14]	493	1.85051	0.53618	0.01547
7 Cyclohexane—heptane—toluene	25	16	[12]	591	0.08065	-0.11786	-0.11693
8 Dichloromethane—chloroform—tetrachloromethane	45	40	[18]	586	-0.53940	0.09466	0.37395
9 Ethanol—water—furfural	50	25	[17]	636	-2.04599	-0.33697	0.74335
10 Methylcyclohexane—toluene—aniline	80	7	[13]	464	-0.61874	0.26051	-0.03637
11 Toluene—1,4-dioxane—2-methylpropan-1-ol	80	21	[14]	512	-0.06214	0.00220	0.57357
12 Water—methanol—ethanol	25	37	[16]	494	0.81317	-0.43614	-0.24421

**Table 2.** Binary NRTL Parameters of Selected Binary Systems

Binary system (1—2)	$t/^\circ\text{C}$	Binary parameters			Ref.	Page
		$\tau_{12}$	$\tau_{21}$	$\alpha_{12}$		
Acetone—cyclohexane	35	0.80442	1.16384	0.2911	[11]	210
Acetone—ethanol	55	-0.14322	0.74721	0.3056	[9]	240
Acetone—hexane	55	1.14437	0.65085	0.2918	[11]	224
Acetone—methanol	35	0.35079	0.31079	0.3008	[10]	74
Acetone—methanol	55	0.43558	0.23445	0.3008	[10]	240
Acetone—propan-2-ol	55	0.07153	0.59568	0.3011	[14]	240
Benzene—cyclohexane	70	0.16312	0.22105	0.3017	[12]	219
Benzene—heptane	55	0.07870	0.51603	0.29960	[13]	138
Benzene—propan-2-ol	50	1.53420	0.84660	0.5966	[14]	68
Benzene— <i>tert</i> -pentanol	70	1.92145	-0.46549	0.2907	[15]	451
Benzene—thiophene	55	-0.53254	0.77227	0.30450	[19]	188
Butan-2-one—benzene	50	-0.56516	0.87600	0.252	[11]	286
Butan-2-one—propan-2-ol	50	-0.11181	0.80112	0.2999	[14]	53
Chloroform—tetrachloromethane	45	0.44391	-0.27787	0.30880	[18]	61
Cyclohexane—heptane	25	0.61832	-0.42332	0.2867	[12]	269
Cyclohexane— <i>tert</i> -pentanol	70	1.89406	0.79652	1.0133	[15]	453
Cyclohexane—toluene	25	0.42735	0.07890	0.3023	[12]	251
Dichloromethane—chloroform	45	-0.28570	0.36393	0.29470	[18]	203
Dichloromethane—tetrachloromethane	45	0.22497	0.19136	0.30160	[18]	67
1,4-Dioxane—2-methylpropan-1-ol	80	-0.09216	0.51959	0.2983	[14]	278
Ethanol—hexane	55	2.24647	1.34229	0.4389	[9]	452
Ethanol—furfural	50	1.57957	1.01598	0.77710	[9]	382
Ethanol—water	50	-0.23815	2.09058	0.29510	[17]	161
Heptane—toluene	25	-0.22034	0.080108	0.3021	[13]	182
Methanol—cyclohexane	35	1.94125	2.34874	0.4161	[9]	240
Methanol—ethanol	25	-0.06129	0.02615	0.3041	[10]	59
Methanol—propan-2-ol	55	-0.97283	1.40587	0.2816	[10]	240
Methylcyclohexane—toluene	80	0.13728	0.14349	0.30190	[13]	39
Methylcyclohexane—aniline	80	1.42437	1.36786	0.44270	[13]	15
Thiophene—heptane	55	1.68954	-0.49662	0.30340	[13]	102
Toluene—aniline	80	0.62191	0.25985	0.29940	[19]	428
Toluene—1,4-dioxane	80	0.09238	0.09855	0.3023	[11]	476
Toluene—2-methylpropan-1-ol	80	0.98605	0.40482	0.2930	[14]	290
Water—ethanol	25	1.35157	0.13401	0.2957	[16]	125
Water—furfural	50	3.57670	0.71174	0.40810	[16]	358
Water—methanol	25	0.90813	-0.24880	0.2982	[16]	49

## RESULTS AND DISCUSSION

In this study, for thermodynamic description of ternary vapour—liquid equilibria the NRTL model equation extended by the universal ternary contribution, eqn (5), was chosen. This procedure was applied to twelve ternary systems (Table 1). Experimental VLE data of corresponding ternary systems and binary subsystems were taken from VLE Data Collection DECHEMA. From the same source the independent binary parameters of the NRTL equation were taken (Table 2) and used to predict the vapour—liquid equilibrium data of selected ternary systems. Prediction quality was evaluated on the basis of mean deviations of the calculated and measured values, *i.e.* total pressure and the component mole fractions in the vapour phase. Prediction quality is summarized in Table 3 ( $E_i = 0$ ).

Ternary VLE data of these systems were used for evaluation of the ternary contribution parameters by

an original computing program (flow sheet of this program was described in detail elsewhere [8]). Calculated parameters of ternary contribution are listed in Table 1. Results of ternary VLE correlation using original binary parameters and parameters of ternary contribution are summarized in Table 3 ( $E_i \neq 0$ ).

The results presented in Table 3 show that the use of universal ternary contribution improves significantly the thermodynamic description of the ternary vapour—liquid equilibria even using the original binary parameters of the NRTL model. Mean deviation of the total pressure decreased 1.2 to 4.5 times. Less important effect was observed when comparing the mean deviation of component mole fractions.

Correlation of the experimental ternary VLE data calculated using the model parameters obtained from binary equilibria and ternary VLE data improved by the ternary contribution parameters is equally good (Table 3; see systems No. 1, 4, 5, 7, 9) or even better (remaining seven ternary systems in Table 3) than

**Table 3.** Quality of the Ternary VLE Calculation; Mean Deviation of the Total Pressure,  $d_P$ , and Component Mole Fraction in the Vapour Phase,  $d_y$ 

Ternary system	Prediction		Correlation			
	$E_i = 0$		$E_i \neq 0$		[9, 12—18]*	
	$d_P$ /kPa	$d_y$	$d_P$ /kPa	$d_y$	$d_P$ /kPa	$d_y$
1 Acetone—ethanol—hexane, $t = 55^\circ\text{C}$	3.193	0.0149	1.352	0.0158	1.356	0.0095
2 Acetone—methanol—cyclohexane, $t = 35^\circ\text{C}$	1.629	0.0091	0.3594	0.0080	0.653	0.0078
3 Acetone—methanol—propan-2-ol, $t = 55^\circ\text{C}$	0.593	0.0048	0.397	0.0047	0.852	0.0048
4 Benzene—cyclohexane— <i>tert</i> -pentanol, $t = 70^\circ\text{C}$	1.703	0.0165	0.840	0.0130	0.841	0.0138
5 Benzene—thiophene—heptane, $t = 55^\circ\text{C}$	0.322	0.0045	0.207	0.0031	0.223	0.0026
6 Butan-2-one—benzene—propan-2-ol, $t = 50^\circ\text{C}$	1.170	0.0110	0.372	0.0102	0.499	0.0090
7 Cyclohexane—heptane—toluene, $t = 25^\circ\text{C}$	0.114	0.0027	0.113	0.0025	0.105	0.0029
8 Dichloromethane—chloroform—tetrachloromethane, $t = 45^\circ\text{C}$	0.429	0.0054	0.315	0.0053	1.425	0.0057
9 Ethanol—water—furfural, $t = 50^\circ\text{C}$	0.853	0.0108	0.833	0.0099	0.797	0.0084
10 Methylcyclohexane—toluene—aniline, $t = 80^\circ\text{C}$	0.327	0.0033	0.241	0.0020	0.337	0.0019
11 Toluene—1,4-dioxane—2-methylpropan-1-ol, $t = 80^\circ\text{C}$	0.600	0.0089	0.420	0.0087	0.576	0.0066
12 Water—methanol—ethanol, $t = 25^\circ\text{C}$	0.073	0.0035	0.046	0.0026	0.060	0.0020

\*NRTL binary model parameters evaluated from the ternary VLE data only.

the direct fitting of ternary VLE data presented by DECHEMA [9, 12—18] (last two columns in Table 3).

Curiously, ternary contribution parameters are able to improve the correlation presented by DECHEMA [9, 12—18]. Ternary contribution parameters evaluated from the ternary VLE data using NRTL parameters obtained by direct fitting of these data improved significantly the goodness of fit. These results were observed for all studied ternary systems.

*Acknowledgements.* The authors acknowledge the Slovak Grant Agency VEGA for the financial support in a form of Grant No. 1/0063/03.

## SYMBOLS

$d$	mean deviation	
$E_i$	parameters of universal ternary contribution	
$G_{ij}$	parameters of eqn (5)	
$G^E$	excess molar Gibbs energy of the mixture	$\text{J mol}^{-1}$
$G_b^E$	excess molar Gibbs energy of the mixture calculated from binary equilibrium data only	$\text{J mol}^{-1}$
$\Delta_t G^E$	ternary contribution to the excess molar Gibbs energy	$\text{J mol}^{-1}$
$N$	total number of experimental points	
$n$	number of experimental points	
$P$	total pressure	kPa
$P_i^\circ$	saturated vapour pressure of pure component $i$	kPa
$R$	universal gas constant	$\text{J K}^{-1} \text{mol}^{-1}$
$T$	absolute temperature	K
$t$	temperature	$^\circ\text{C}$
$x_i$	mole fraction of the $i$ -th component in the liquid phase	

$y_i$	mole fraction of the $i$ -th component in the gas phase
$\alpha_{ij}, \tau_{ij}$	binary parameters of the NRTL equation
$\gamma_i$	activity coefficient of the $i$ -th component
$\Delta_t \ln \gamma_i$	ternary contribution to the activity coefficient of component $i$

## REFERENCES

- Guffey, Ch. G. and Wehe, A. H., *AIChE J.* 18, 913 (1972).
- Anderson, T. F. and Prausnitz, J. M., *IEC Process Des. Dev.* 17, 561 (1978).
- Surový, J., Dojčanský, J., and Bafrncová, S., *Collect. Czech. Chem. Commun.* 47, 2380 (1982).
- Dojčanský, J., Surový, J., and Bafrncová, S., *Chem. Pap.* 39, 577 (1985).
- Graczová, E., Surový, J., and Bafrncová, S., *Collect. Czech. Chem. Commun.* 57, 7 (1992).
- Graczová, E. and Surový, J., *Collect. Czech. Chem. Commun.* 57, 16 (1992).
- Graczová, E., *Habilitation*. Slovak University of Technology, Bratislava, 2001.
- Graczová, E., Steltenpohl, P., and Bafrncová, S., in *Proceedings of the 31st International Conference of the Slovak Society of Chemical Engineering* (Markoš, J. and Štefuca, V., Editors), p. 111. Full text cd. ISBN 80-227-2052-6. Tatranské Matliare, 2004.
- Gmehling, J. and Onken, U., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 2a. Frankfurt, 1977.
- Gmehling, J., Onken, U., and Arlt, W., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 2c. Frankfurt, 1982.
- Gmehling, J., Onken, U., and Arlt, W., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Parts 3 + 4. Frankfurt, 1979.
- Gmehling, J., Onken, U., and Kolbe, B., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 6c. Frankfurt, 1983.

13. Gmehling, J., Onken, U., and Arlt, W., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 6b. Frankfurt, 1980.
14. Gmehling, J., Onken, U., and Arlt, W., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 2b. Frankfurt, 1978.
15. Gmehling, J., Onken, U., and Weidlich, U., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 2d. Frankfurt, 1982.
16. Gmehling, J., Onken, U., and Arlt, W., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 1a. Frankfurt, 1981.
17. Gmehling, J. and Onken, U., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 1. Frankfurt, 1977.
18. Gmehling, J., Onken, U., and Arlt, W., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 8. Frankfurt, 1984.
19. Gmehling, J., Onken, U., and Arlt, W., *Vapor—Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. I, Part 7. Frankfurt, 1980.