

# Vapour-Liquid Equilibrium for the Binary System Dimethylformamide—Ethylene Glycol\*

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Vapour-liquid equilibrium data are given for the binary system dimethylformamide—ethylene glycol at 30 °C, 40 °C, and 50 °C. The data have been measured by a differential semimicromethod. The dependence of the excess Gibbs energy on composition was expressed by the 4th-order Redlich—Kister, two-constant Margules, and NRTL equations. The system has negative deviations from ideal behaviour.

The binary system dimethylformamide—ethylene glycol is a polar mixed solvent used in aromatic extraction. Solvent such as dimethylformamide (DMF), which has high solvent capacity is considered as basic solvent and solvent such as ethylene glycol (EG), which has high selectivity is considered as a blending solvent. Studies on the selectivity improvement of DMF using ethylene glycol were presented by *Ethirajulu et al.* [1] in 1981. The thermodynamic description of the equilibrium system containing this mixed solvent DMF—EG with the binary modelling system (cyclohexane—benzene) was reported as late as 1998 (*Aspi et al.* [2]). The authors applied a quasi-ternary data processing of four-component system – the binary mixed solvent considered as one component. This thermodynamic description had to be simplified because no information is available about the behaviour of the mixed solvent DMF—EG at temperatures of extraction (from 30 °C to 50 °C).

*Surový* and *Dojčanský* [3] presented isothermal vapour-liquid equilibrium data for the system DMF—EG measured by a static method at 100 °C. No equilibrium data for DMF—EG at lower temperatures are available in the literature. This paper presents new sets of experimental vapour-liquid equilibrium data of the above-mentioned system at 30 °C, 40 °C, and 50 °C, measured by a differential method [4, 5]. The experimental data have been correlated using the 4th-order Redlich—Kister, two-constant Margules, and NRTL equations that include the dependence of the excess Gibbs energy on the composition ( $G^E$  equations). The parameters of the  $G^E$  equations were evaluated using

an objective function based on the maximum likelihood method.

## THEORETICAL

The objective function  $F$  for the set of isothermal  $y-x$  equilibrium data was used in the following form [4]

$$F = \sum_n (x_1 - x_{\text{calc},1})_n^2 + \sum_n (y_1 - y_{\text{calc},1})_n^2$$
$$n = 1, 2, \dots, N \quad (1)$$

where  $y_1$  and  $y_{\text{calc},1}$  ( $x_1$  and  $x_{\text{calc},1}$ ) are measured and calculated mole fractions of the component 1 in the vapour (liquid) phase, respectively. The objective function (1) is minimized in two independent iteration cycles, utilizing the procedure suggested by *Rod* and *Hančil* [6]. By this procedure, the estimates of the parameters of  $G^E$  equations,  $A_r$ , and independent variables  $x_{1n}$  (incidental parameters) are obtained.

In the first cycle, the set of  $R$  equations, formed from the conditions

$$\left( \frac{\partial F}{\partial A_r} \right)_{A_q \neq r, x_1} = 0 \quad r = 1, 2, \dots, R \quad (2)$$

is solved. The solution is obtained simultaneously for all experimental data (at constant values of incidental parameters  $x_{1n}$ ) and offers the first approximation of  $A_r$ .

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In the second cycle, the estimates of  $x_{1n}$  are calculated by solving the conditions

$$\left(\frac{\partial F}{\partial x_1}\right)_{A_r} = 0 \quad n = 1, 2, \dots, N \quad (3)$$

separately for each measurement (at constant values of the parameters  $A_r$ ). The alteration of both the iteration cycles is repeated until the difference of values of the objective function for both the adjacent iterations is smaller than the tolerance required (similar to that of the procedure [7]).

Taking into account the following approximations

$$y_1 = y_{\text{calc},1}^{\circ} + \left(\frac{\partial y_{\text{calc},1}}{\partial x_1}\right)^{\circ} \Delta x_1$$

for

$$y_{\text{calc},1}^{\circ} = y_1 \quad (x_1 = x_{\text{calc},1}^{\circ}) \quad (4)$$

$$x_{\text{calc},1}^{\circ} = x_{\text{calc},1}^{\circ} + \Delta x_1 \quad (5)$$

we suggested then for the increment  $\Delta x_1$  the following expression

$$\Delta x_1 = \frac{(x_1 - x_{\text{calc},1}^{\circ}) + (y_1 - y_{\text{calc},1}^{\circ}) \left(\frac{\partial y_{\text{calc},1}}{\partial x_1}\right)^{\circ}}{1 + \left(\left(\frac{\partial y_{\text{calc},1}}{\partial x_1}\right)^{\circ}\right)^2} \quad (6)$$

The superscript "°" denotes the value from the last iteration.

## EXPERIMENTAL

Ethylene glycol was prepared from EG of anal. grade (Loba Chemie, Wien) and dimethylformamide from DMF of anal. grade (Lachema, Neratovice), both by double vacuum rectification in a column with an efficiency of about 10 theoretical plates. The products were dried with molecular sieves. The purity of chemicals was checked by gas chromatography and was found to be higher than 99.8 %.

The isothermal vapour-liquid equilibrium data for the binary mixed solvent DMF—EG were measured at 30°C, 40°C, and 50°C in the semimicrostill by a differential method [4, 5]. The temperature was measured with an accuracy of 0.1°C. The value of pressure in the vacuum part was about 5 Pa, in the equilibrium flask this value varied from 15 Pa to 2300 Pa according to composition of the binary system. The pressure measurements served only for checking. The analyses of the liquid and vapour phases were carried out chromatographically after completing the measurement with the accuracy higher than 0.5 mole %.

## RESULTS AND DISCUSSION

The measured isothermal  $y$ — $x$  equilibrium data for the system DMF—EG at 30°C, 40°C, and 50°C are given in Table 1 and graphically plotted in the form of  $y$ — $x$  equilibrium diagrams (Fig. 1). The system DMF—EG is characterized by negative deviations from an ideal behaviour. The sets of measured equilibrium data of the DMF—EG system at 30°C, 40°C, and 50°C were compared (Fig. 1) with the set of equilibrium data at 100°C calculated from  $P$ — $x$  experimental data [3].

The sets of experimental data were correlated by the  $G^E$  equations:

1. the 4th-order Redlich—Kister equation

$$G^E/RT = x_1 x_2 [B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2] \quad (7)$$

2. the Margules two-constant equation

$$G^E/RT = x_1 x_2 [x_1 A_{21} + x_2 A_{12}] \quad (8)$$

3. and NRTL equation

$$G^E/RT = x_1 x_2 \left[ \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right] \quad (9)$$

where

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \text{ and } G_{21} = \exp(-\alpha_{12}\tau_{21}) \quad (10)$$

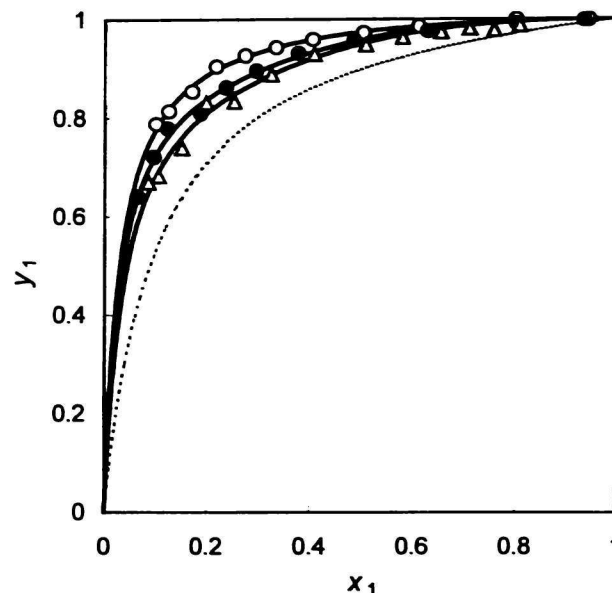


Fig. 1. The  $y$ — $x$  diagram of the binary system DMF(1)—EG(2) at various temperatures. ○ 30°C, ● 40°C, △ 50°C; the curves calculated by means of the Margules two-constant equation: — from experimental data, --- from published data [3] at 100°C.

**Table 1.** Experimental Isothermal Equilibrium Data  $x_1$ — $y_1$  for the System DMF(1)—EG(2) at 30 °C, 40 °C, and 50 °C

30 °C		40 °C		50 °C	
$x_1$	$y_1$	$x_1$	$y_1$	$x_1$	$y_1$
0.1001	0.7871	0.0662	0.6402	0.0860	0.6697
0.1257	0.8133	0.0973	0.7213	0.1056	0.6825
0.1705	0.8538	0.1240	0.7789	0.1513	0.7390
0.2191	0.9037	0.1886	0.8104	0.1987	0.8310
0.2746	0.9267	0.2378	0.8621	0.2533	0.8333
0.3356	0.9424	0.2974	0.8963	0.3264	0.8881
0.4057	0.9581	0.3786	0.9307	0.4088	0.9293
0.5054	0.9725	0.4872	0.9564	0.5092	0.9477
0.6131	0.9849	0.6300	0.9754	0.5814	0.9633
0.8024	0.9990	0.8033	0.9902	0.6564	0.9738
0.9464	0.9999	0.9363	0.9975	0.7118	0.9807
				0.7596	0.9779
				0.8093	0.9872

**Table 2.** Values of Parameters of the NRTL, Margules, and Redlich—Kister Equations, Mean and Standard Deviations of Mole Fractions of the Liquid and Vapour Phase for the System DMF(1)—EG(2) at 30 °C, 40 °C, and 50 °C

Parameters	30 °C	40 °C	50 °C
NRTL equation			
$\alpha_{12}$	0.44	0.44	0.44
$\tau_{12}$	-1.3191	-1.4229	-1.3981
$\tau_{21}$	2.3506	3.1458	3.2895
$d(x) \cdot 10^2$	0.12	0.27	0.31
$d(y) \cdot 10^2$	0.25	0.43	0.70
$\sigma(x) \cdot 10^2$	0.18	0.44	0.50
$\sigma(y) \cdot 10^2$	0.30	0.55	0.84
Margules equation			
$A_{12}$	-0.2823	-0.1181	-0.1278
$A_{21}$	-0.7927	-1.5500	-1.4471
$d(x) \cdot 10^2$	0.12	0.17	0.32
$d(y) \cdot 10^2$	0.20	0.31	0.49
$\sigma(x) \cdot 10^2$	0.22	0.44	0.58
$\sigma(y) \cdot 10^2$	0.28	0.46	0.72
Redlich—Kister equation			
$B_{12}$	-0.5451	-0.7984	-0.8230
$C_{12}$	-0.2786	-0.5749	-0.7787
$D_{12}$	-0.0360	0.1843	-0.1971
$d(x) \cdot 10^2$	0.13	0.18	0.31
$d(y) \cdot 10^2$	0.20	0.32	0.55
$\sigma(x) \cdot 10^2$	0.22	0.33	0.50
$\sigma(y) \cdot 10^2$	0.27	0.45	0.70

The parameters of the  $G^E$  equations were evaluated by minimization of objective function (1). The mole fraction in the vapour phase  $y_{\text{calc},1}$  was calculated from the relation

$$y_{\text{calc},1} = \frac{x_{\text{calc},1} \gamma_1 P_1^0}{(x_{\text{calc},1} \gamma_1 P_1^0 + x_{\text{calc},2} \gamma_2 P_2^0)} \quad (11)$$

With respect to the low pressure in the system (from 15 to 2300 Pa) the ideal behaviour of the vapour phase was considered. The saturated vapour pressure  $P^0$  of DMF and EG at the above-mentioned temperatures was calculated from data listed in Ref. [8]. The values of  $P_{\text{EG}}^0$  at 30 °C and 40 °C were extrapolated from the range of presented data.

The values of parameters of the NRTL, Margules, and Redlich—Kister equations and the corresponding values of mean and standard deviations in the mole fractions are given in Table 2. It is evident from the table that the Margules equation is comparable with the 4th-order Redlich—Kister equation namely for all sets of experimental data. The values  $d(x)$  of the mean deviations and  $\sigma(x)$  of the standard deviations in mole fractions of the liquid phase are ranging within 0.0012—0.0032 and 0.0022—0.0058, respectively. The values  $d(y)$  of the mean deviations and  $\sigma(y)$  of the standard deviations in mole fractions of the vapour phase are within 0.0020—0.0055 and 0.0027—0.0072, respectively. The deviations  $d(x)$  and  $\sigma(x)$  of the mea-

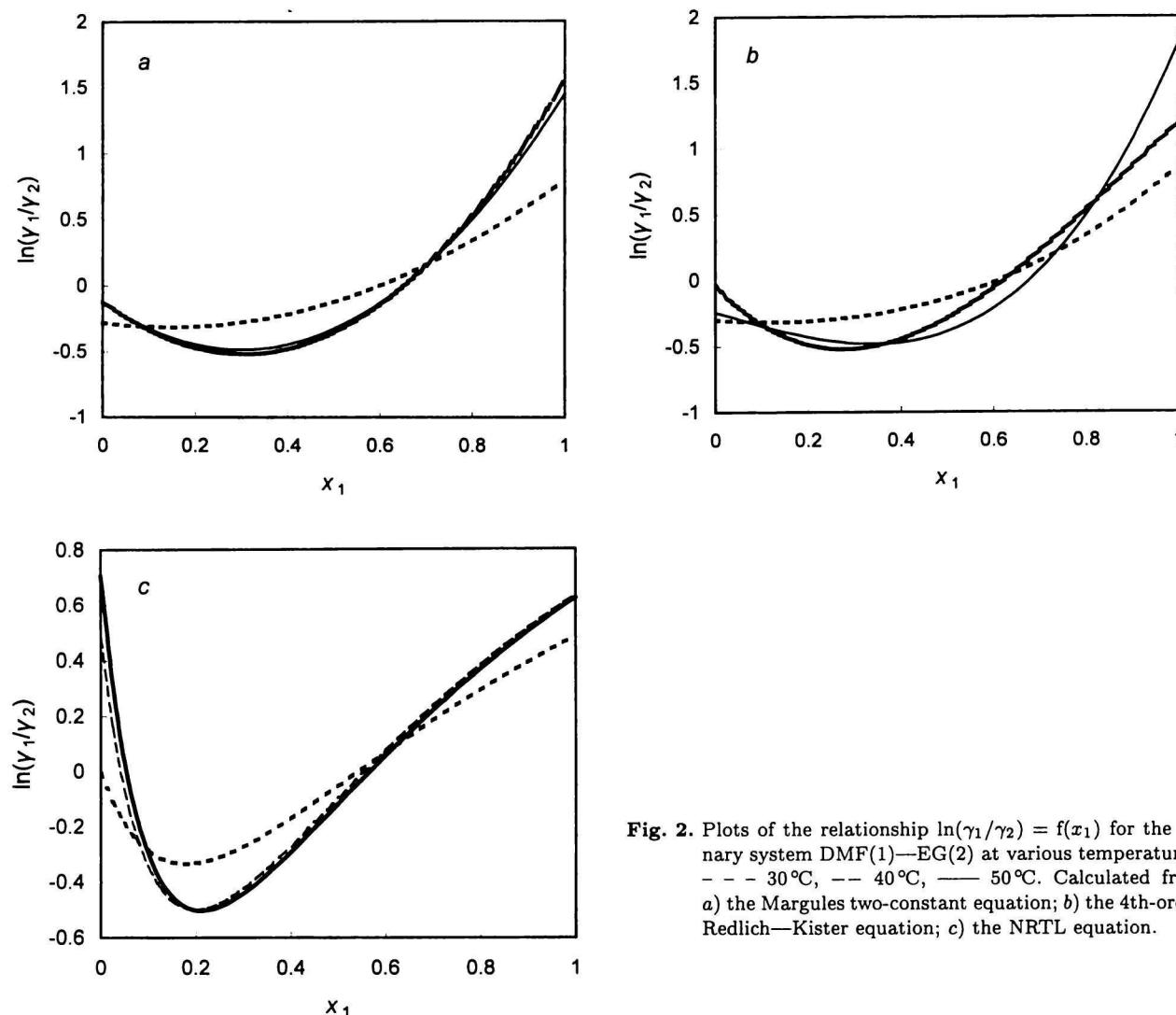


Fig. 2. Plots of the relationship  $\ln(\gamma_1/\gamma_2) = f(x_1)$  for the binary system DMF(1)—EG(2) at various temperatures: --- 30°C, -- 40°C, — 50°C. Calculated from a) the Margules two-constant equation; b) the 4th-order Redlich—Kister equation; c) the NRTL equation.

sured mole fractions in the liquid phase from those calculated on the basis of the NRTL equation are comparable with the above-mentioned equations. The agreement of experimental and calculated mole fractions of the vapour phase is with NRTL lower, the deviations  $d(y)$  and  $\sigma(y)$  are ranging within 0.0025—0.0070 and 0.0030—0.0084, respectively.

Figs. 2a—c represent the calculated relationships  $\ln(\gamma_1/\gamma_2) = f(x_1)$  for measured system at 30°C, 40°C, and 50°C using all three  $G^E$  equations. From the plots is obvious the agreement of the curves calculated from the Margules two-constant equation and 4th-order Redlich—Kister equation. The curves  $\ln(\gamma_1/\gamma_2)$  vs.  $x_1$  corresponding to the NRTL equation (Fig. 2c) exhibit a more pronounced minimum.

The semimicrostill used in this work was suggested and tested for the systems the pressure of which was ranging within 10 Pa—250 Pa (*N*-methylpyrrolidone—ethylene glycol). The value of the saturated vapour pressure  $P^\circ$  for DMF at 50°C is 2309 Pa. Hence, this can make the inaccuracy of measure-

ments. On the other hand, with regard to the accuracy of the analytical method used (gas chromatography), it is possible to consider the agreement between the measured and calculated data at experimental temperatures 30°C, 40°C, and 50°C as good.

With regard to the absence of equilibrium data for the binary systems DMF—EG at a temperature lower than 100°C, the new equilibrium data reported in this paper are an important contribution, particularly to the thermodynamic description of multi-component liquid—liquid systems.

## SYMBOLS

$A_{ij}$	parameter of the Margules equation
$A_r$	parameters of $G^E$ equations
$B_{ij}, C_{ij}, D_{ij}$	parameters of the Redlich—Kister equation
$d$	mean deviation
$F$	objective function

$G^E$	molar excess Gibbs energy	$\text{J mol}^{-1}$
$n$	number of measurements	
$N$	total number of measurements	
$P_i^o$	saturated vapour pressure of component $i$	Pa
$R$	gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
$R$	total number of parameters	
$T$	absolute temperature	K
$x_i$	mole fraction of component $i$ in the liquid	
$y_i$	mole fraction of component $i$ in the vapour	
$\alpha_{ij}, \tau_{ij}$	parameters of the NRTL equation	
$\gamma_i$	activity coefficient of component $i$	
$\sigma$	standard deviation	

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