Activity Coefficients at Infinite Dilution using the Dilutor Method

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Introduction

Activity Coefficient (γ)

- Definition : the ratio of activity to some convenient measure of the concentration in the liquid mixture

$$\gamma_i \equiv \frac{a_i}{x_i} = \frac{f_i}{x_i f_i^0} = \frac{y_i P}{x_i P_i^s}$$

- Important relation with excess Gibbs energy

$$g^E = RT\sum_i x_i \ln\gamma_i \xrightarrow[\text{mixture}]{\text{Binary}} \frac{g^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$$

Introduction

Activity Coefficient at Infinite dilution (γ^{∞})

- Characterizing the behavior of a single solute molecule completely surrounded by solvent
- A maximum non-ideality(excess property) : solute-solvent interactions in the absence of solute-solute interactions
- Prediction of the phase behavior of a mixture over the entire concentration range
- Separation factor in extractive distillation column : used for the selection of selective solvents

Introduction

Determination methods for γ^∞

- Indirect measurement
  - Extrapolation of VLE data in whole or highly dilute composition region
  - Dilutor method
- Direct measurement
  - Differential ebulliometry method
  - Differential static technique
- In this work : Dilutor Method
  - Based on the inert gas flow in the highly dilute solution
  - Possible to measure γ^∞ in solvent mixtures

Scope

- Activity coefficients at infinite dilution for the solutes of *n*–heptane and benzene in the solvent of DMF and DMF/water mixtures(10 wt% of water) were measured with the help of the dilutor technique at the temperature of 30, 40 and 50 °C.
- Activity coefficients at infinite dilution for methanol+dimethyl cabonate(DMC), and the solutes of 1–propanol and toluene in the solvent of DMC were measured with the help of the dilutor technique at the temperature of 20, 30, 40 and 50 °C.
- The measured values for benzene in DMF were compared with the reference data, and all experimental data were compared with the estimated values using modified UNIFAC(Dortmund) at the same conditions.

Theory

- Basic relation for the highly dilute component

Solute i : $x_i \gamma_i \varphi_i^s P_i^s Poy_i = y_i \varphi_i^v P$

Pure solvent : $x_{\text{solv}} \gamma_{\text{solv}} \varphi_{\text{solv}}^s P_{\text{solv}}^s Poy_{\text{solv}} = y_{\text{solv}} \varphi_{\text{solv}}^v P$

At the condition of infinite dilution

$$\gamma_i = \gamma_i^\infty$$
$$\gamma_{\text{solv}} = 1 \left(x_{\text{solv}} \approx 1 \right)$$
$$Poy_i \approx 1$$
$$\frac{\varphi_{\text{solv}}^s Poy_{\text{solv}}}{\varphi_{\text{solv}}^v} \approx 1$$

⇒

$$x_i \gamma_i^\infty \varphi_i^s P_i^s = y_i P$$
$$P_{\text{solv}}^s = y_{\text{solv}} P$$

Theory

- Calculation of γ^{∞} in Dilutor method

Slope of decrease of solute : $$a = \frac{\ln(A_i / A_0)}{t}$$

From the material balance in the cells and thermodynamic relations

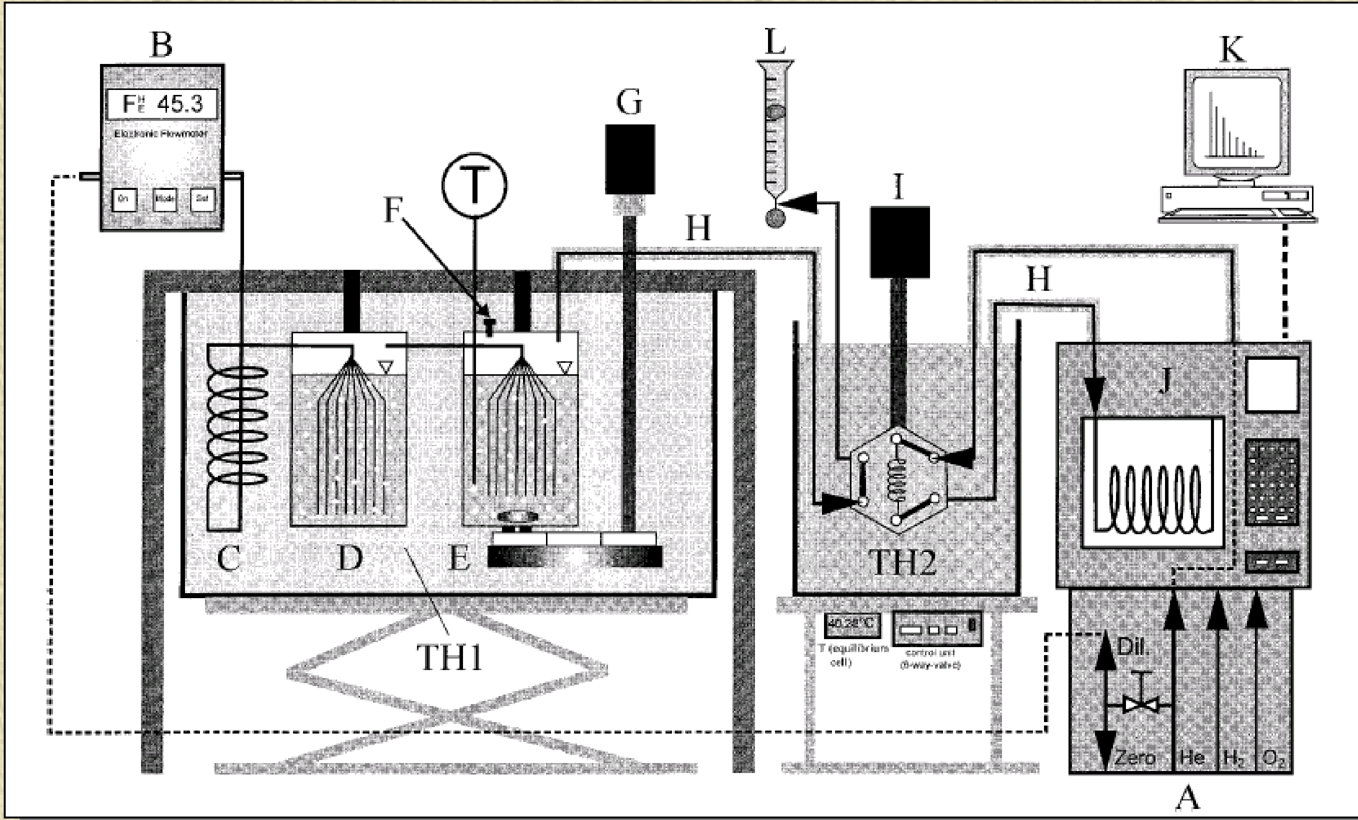
$$\frac{\ln(A_i / A_0)}{t} = -\frac{\gamma_i^{\infty} \varphi_i^s P_i^s}{n_{\mathrm{solv}}\left(1 + \frac{\gamma_i^{\infty} \varphi_i^s P_i^s V_{\mathrm{g}}}{n_{\mathrm{solv}} RT}\right)} \frac{\dot{F}_{\mathrm{in}}}{RT}$$

$$\Rightarrow \quad \gamma_i^{\infty} = -\frac{n_{\mathrm{solv}} RT}{\varphi_i^s P_i^s \left(\frac{\dot{F}_{\mathrm{He}}\left(1 + P_{\mathrm{solv}}^s / P\right)}{a} + V_{\mathrm{g}}\right)}$$

Experiment

Figure. Picture of the dilutor system for measuring γ^{∞}.

Experiment

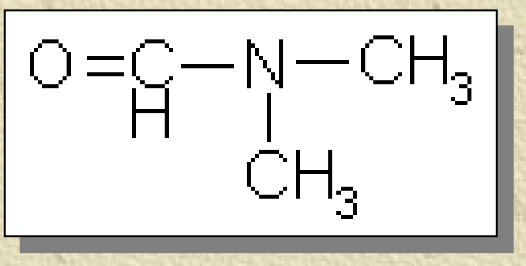


A : carrier gas
B : elec. flowmeter
C : heating coil
D : saturation cell
E : equilibrium cell
F : septum
G : stirring motor
H : transfer line
I : sampling valve
J : GC
K : PC
L : bubble flowmeter
TH1, TH2 : thermostats

Figure. Schematic diagram of the dilutor system.

Experiment

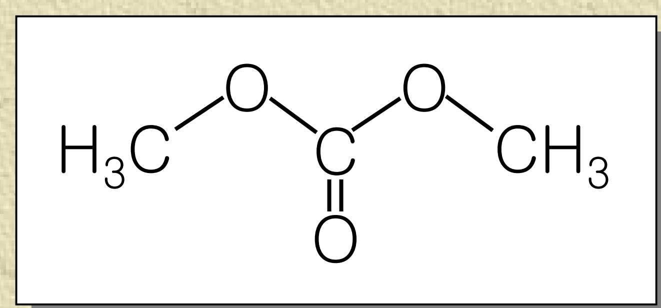
- **DMF (C_3H_7NO)**



Molecular Weight	73.10 g/mol
Normal Boiling Point	153 ^oC
Density (25 ^oC)	0.9440 g/cm^3
Antoine Constants	A : 7.10850 B : 1537.78 C : 210.390

Experiment

- **DMC ($C_3H_6O_3$)**



Molecular Weight	98.08 g/mol
Normal Boiling Point	90.3 °C
Density (20 °C)	1.0694 g/cm³
Antoine Constants	A : 7.09722 B : 1285.21 C : 214.536

Results

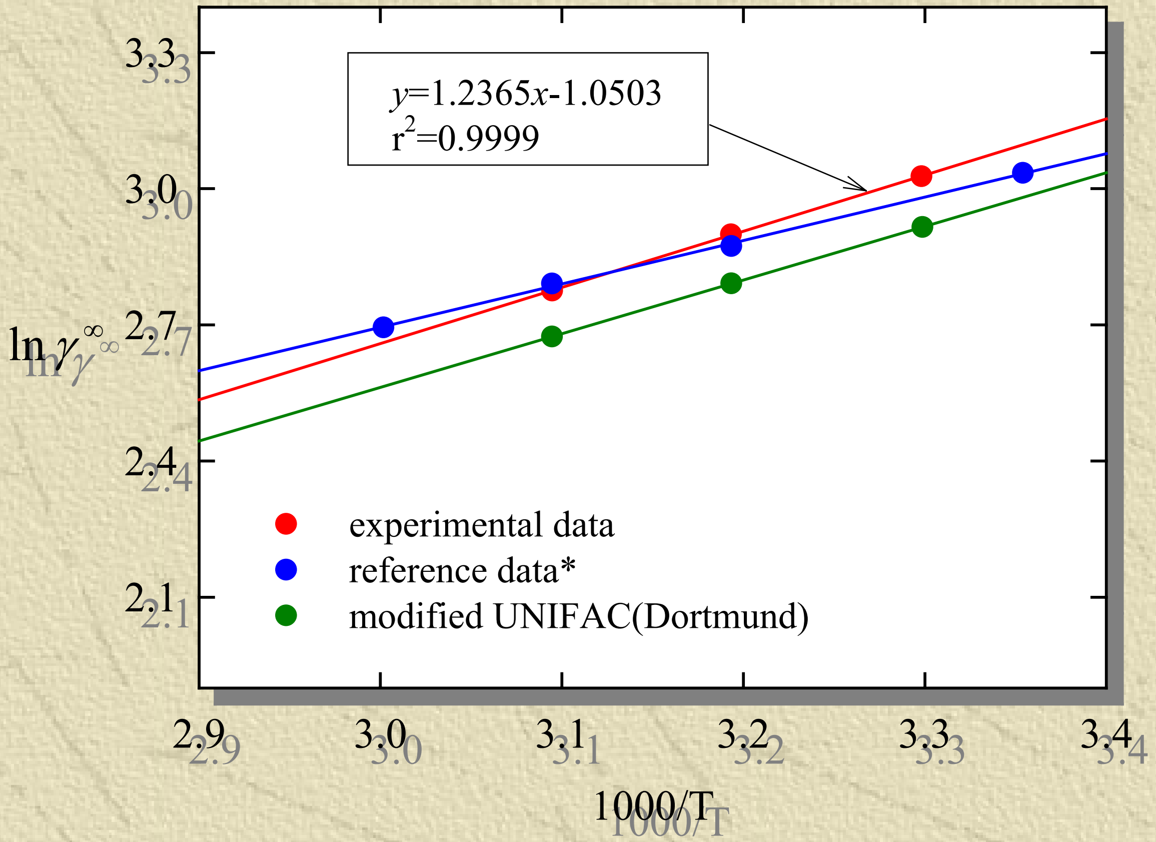


Figure. Comparison of the experimental γ^{∞} values with the reference data* for *n*-heptane in DMF at various temperatures.

[* Popescu, R. et al., *Rev.Roum.Chim.*, 18, 746 (1967)]

Results

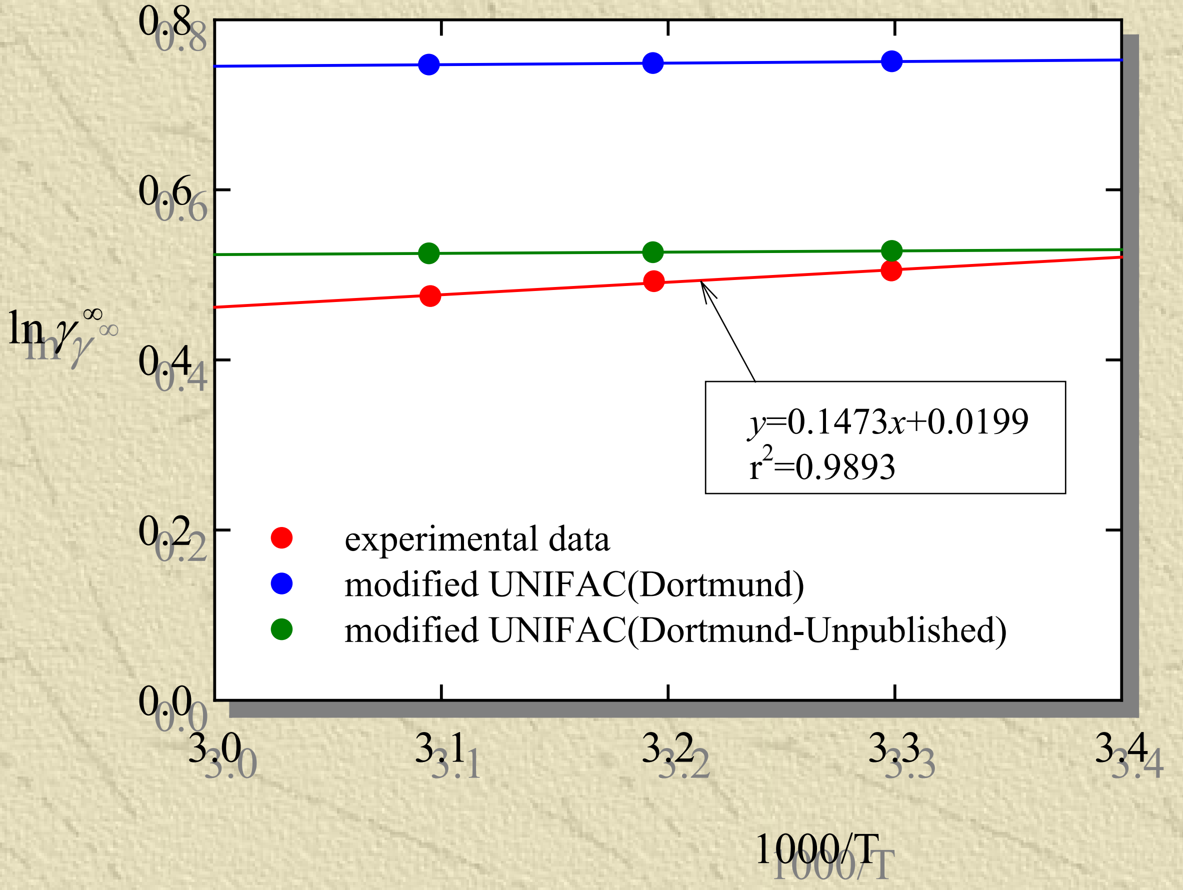


Figure. Activity coefficients at infinite dilution for benzene as a function of temperature in DMF.

Results

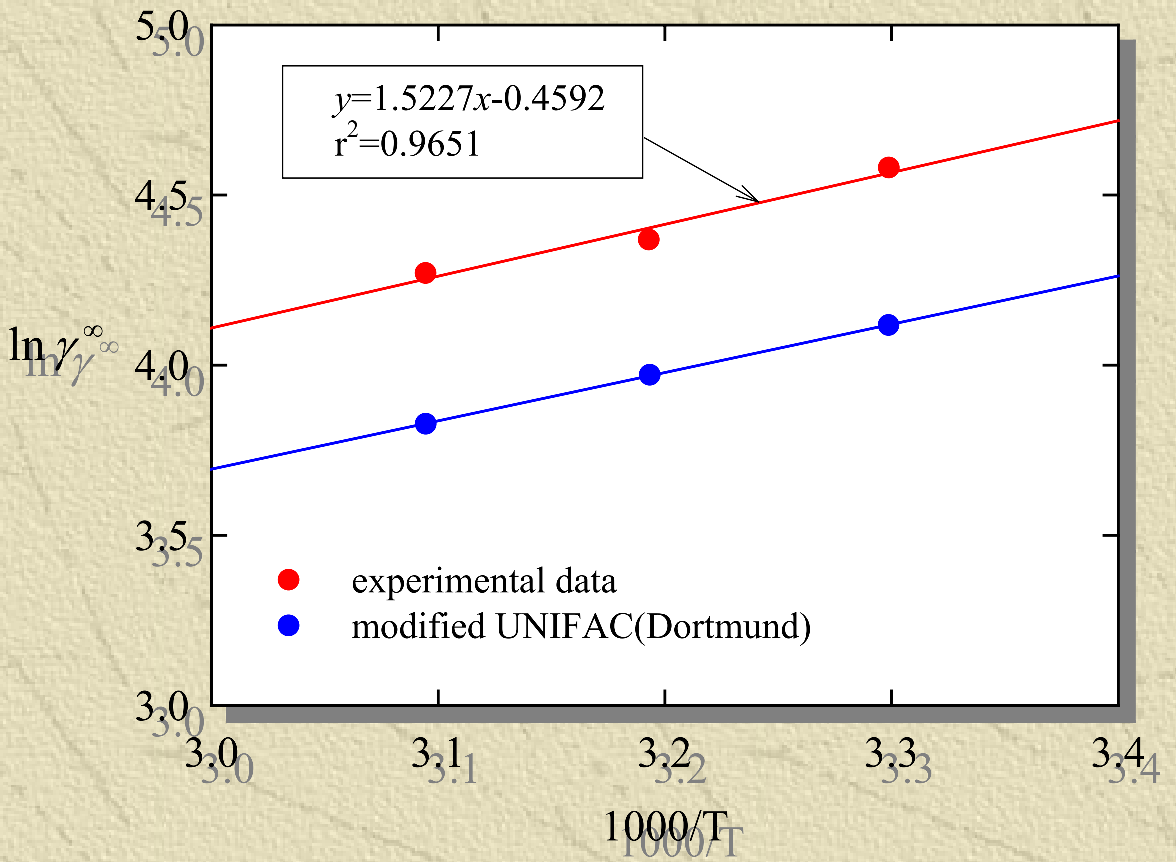


Figure. Activity coefficients at infinite dilution for *n*-heptane as a function of temperature in the solvent mixture DMF/water(10wt%).

Results

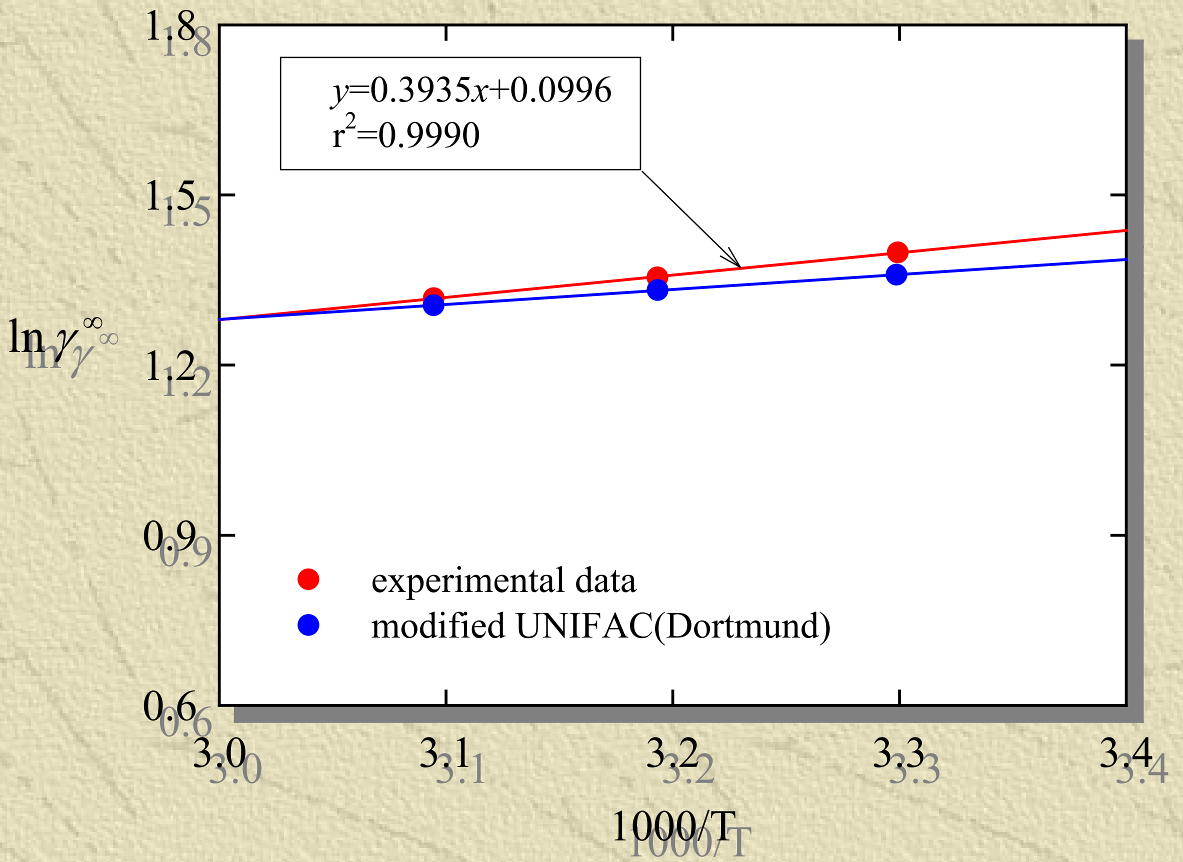


Figure. Activity coefficients at infinite dilution for benzene as a function of temperature in the solvent mixture DMF/water(10wt%).

Results

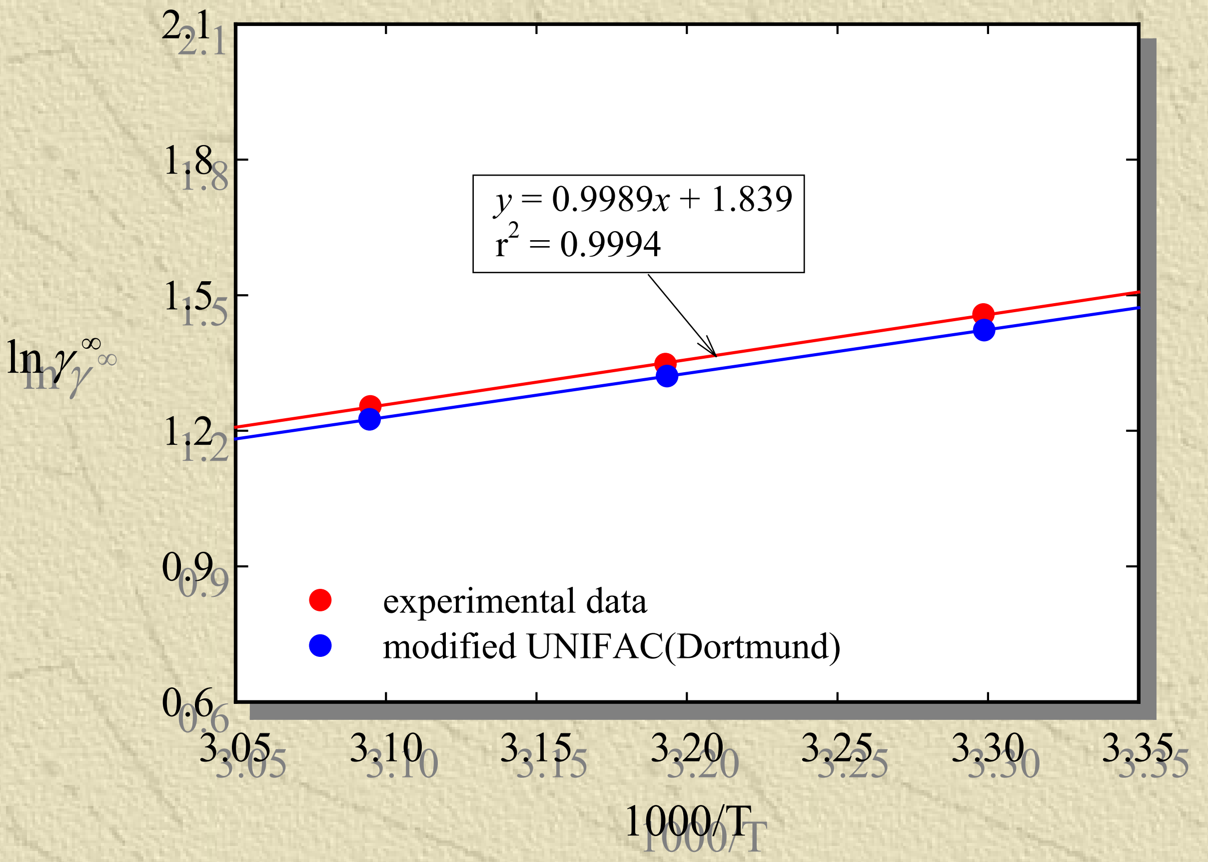


Figure. Activity coefficients at infinite dilution for methanol as a function of temperature in DMC.

Results

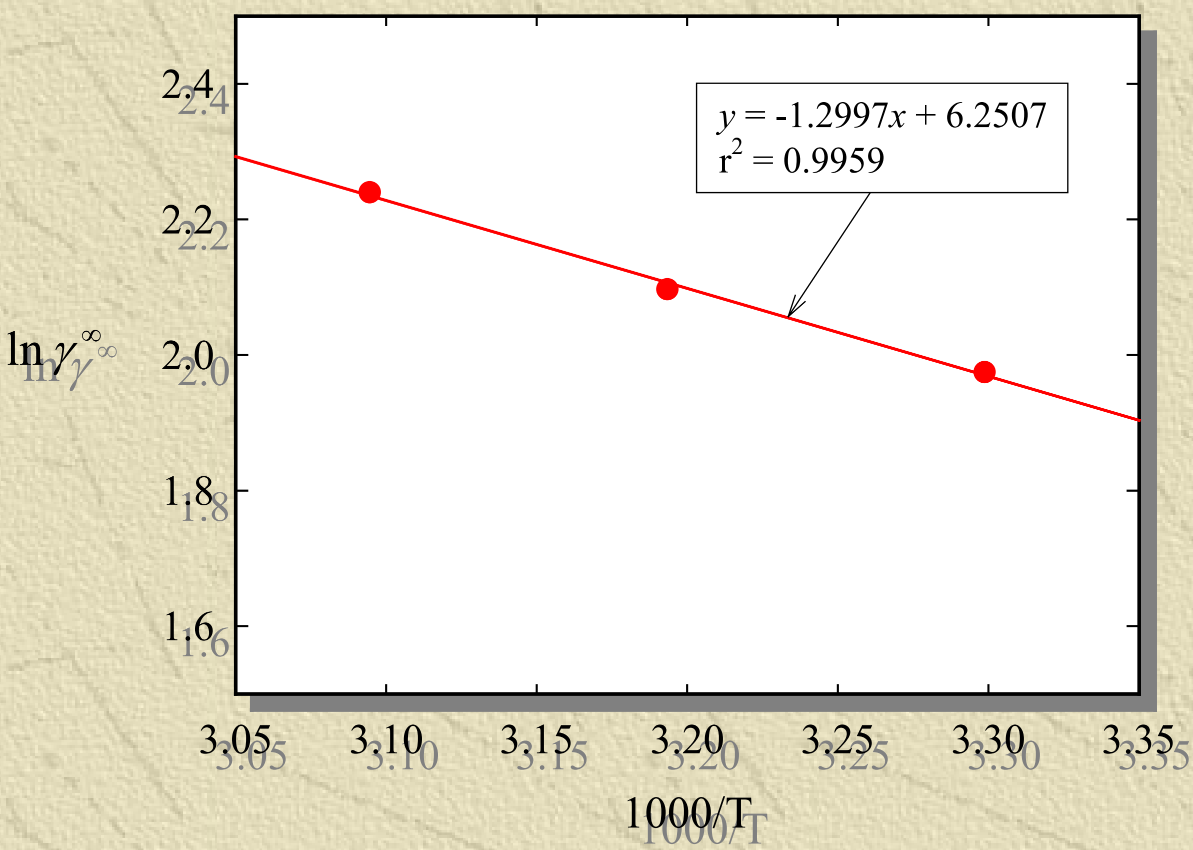


Figure. Activity coefficients at infinite dilution for DMC as a function of temperature in methanol.

Results

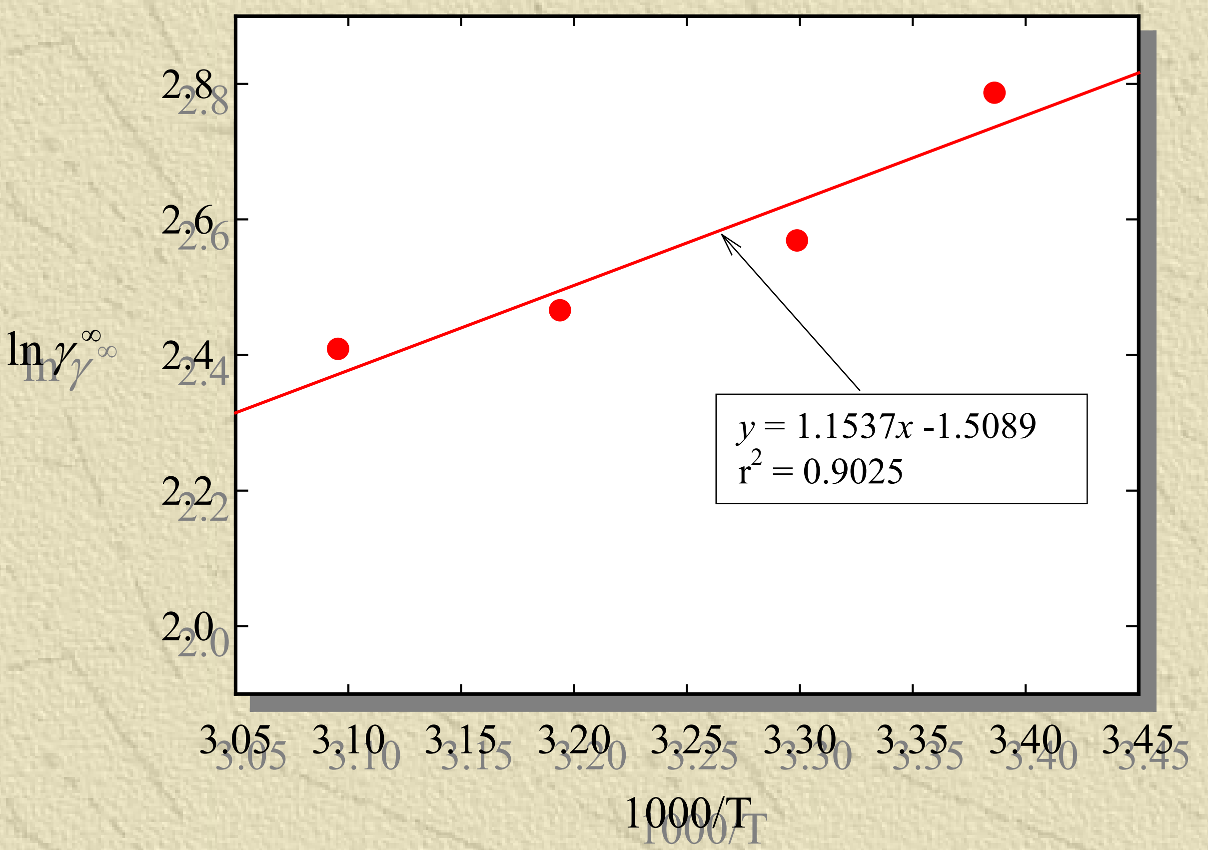


Figure. Activity coefficients at infinite dilution for 1-propanol as a function of temperature in DMC.

Results

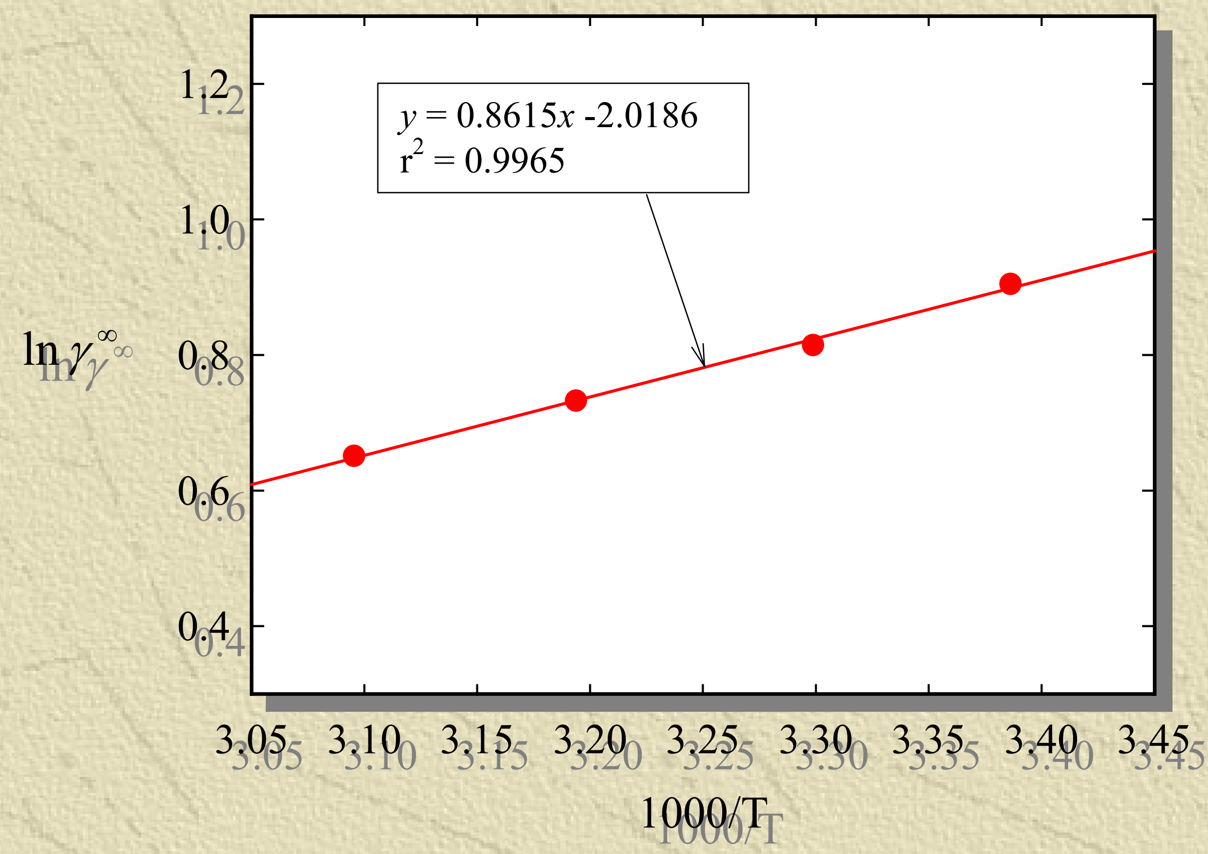


Figure. Activity coefficients at infinite dilution for toluene as a function of temperature in DMC.

Conclusions

- Activity coefficients at infinite dilution for the solutes of *n*-heptane and benzene in the solvent of DMF and DMF/water mixtures(10 wt% of water) were determined experimentally using the dilutor method at various temperatures. And the γ^{∞} data were measured for the system of methanol+DMC and the solutes of 1-propanol and toluene in the solvent of DMC at the same conditions

- The experimental results show good agreements with the reference data and the calculated values using modified UNIFAC(Dortmund).

- The dilutor method is excellently suitable for the measurement of activity coefficients at infinite dilution not only in pure solvent but also in solvent mixture.