

Thermodynamic study of the vapor–liquid equilibrium (VLE) data of the mixture formed by diethylenimide oxide with benzene

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Abstract The thermodynamic evaluation of the experimental vapor–liquid equilibrium (VLE) data obtained at 760 mmHg in a recirculatory still, is presented for the binary system formed by diethylenimide oxide with benzene. The experimental VLE data were checked for thermodynamic consistency and reduced to the binary parameters calculated from three activity coefficients models.

Keywords VLE · Correlation · Thermodynamic consistency · Morpholine · Benzene

Introduction

Diethylenimide oxide (DEO) having the molecular formula C_4H_9NO and IUPAC name morpholine is a versatile chemical with different industrial applications. It is widely used as a neutralizing amine, and as a corrosion inhibitor in steam boiler systems. In small quantities, DEO is used in the emulsion polymerization of monomers, such as isoprene and butadiene, and as temperature sensitive polymerization inhibitor. Exhibiting very good selectivity, DEO has many applications in various separation processes. As result, reliable vapor–liquid equilibrium (VLE) data are essential in the design, simulation, and operation of distillation equipment. In the last years, several studies of experimental VLE data in systems formed by DEO with different compounds have been published [1–4]. Palczewska-Tulinska et al. [5] published the experimental VLE data for the system DEO + benzene at 101.325 kPa. The data have been correlated using

local composition models, but the thermodynamic consistency of the experimental data was not verified. As recently pointed out [6], various ways of thermodynamic evaluation can yield different results. In this regard for a good prediction of VLE data in multicomponent systems, the thermodynamic evaluation requires the thermodynamic consistency analysis, as an efficient selection method of the reliable VLE data, among several published data sets.

The present paper presents the experimental VLE data obtained at 760 mmHg for the system benzene + DEO and the thermodynamic consistency evaluation and correlation of the data.

Experimental

Chemicals

All chemicals were high-purity grade (better than 99.5 mass% by GLC) purchased from Merck and were used without further purification. Physical properties of the pure components, such as densities, boiling points, refractive indexes were measured, and compared with literature [7] values, as listed in Table 1.

The refractive indices of the pure components were measured at 293.15 K using an Abbe refractometer with an accuracy of 0.0001.

The densities were measured at a temperature of 293.15 K using a pycnometer with the volume of 10 cm³, which was precalibrated with double-distilled water. All measured properties are in good agreement with the published data [7].

Apparatus and procedure

The VLE data were obtained at 760 mmHg using an all-glass recirculatory still, having about 50 cm³ capacity,

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Table 1 Comparison of the measured normal boiling temperatures, refractive indices, and densities of the pure compounds, used in this study, with literature [7] data

Compound	Boiling temperature/K		Refractive index/ n_{20}^D		Density/g cm ⁻³	
	Exp.	Lit.	Lit.	Exp.	Lit.	Exp.
Benzene	353.35	353.25	1.5012	1.5011	1.5011	1.5012
DEO	401.95	402.09	1.4553	1.4551	1.4551	1.4553

designed by Gothard et al. [8]. The equilibrium still has a magnetic stirrer, insuring a complete mixing of the liquids composing the binary system. The equipment design prevents the entrainment of liquid drops and avoids the partial condensation of the vapor phase. Thermal insulation, covering the entire apparatus, except the condenser, was performed to insure no loss of the heat. A precision manostate was used to maintain the total pressure at 760 mmHg, with a maximum deviation of 0.01 mmHg. During each experiment, the liquid mixture was heated in the recirculating still and the phase equilibrium was reached within an hour. The samples of the equilibrium phases were simultaneously collected and were analyzed by refractive index measurement, at 293.15 K, with an Abbe refractometer. The equilibrium compositions of both phases were obtained from the calibration curves n_D versus known liquid composition of mixture. The estimated precision of the composition measurements was ± 0.0001 mol fractions.

The equilibrium temperature was measured with a standard mercury thermometer, calibrated against the reference boiling points. The accuracy of the temperature measurements was ± 0.01 K. The experimental VLE data are reported in Table 2.

Results and discussions

From the experimental VLE data, the activity coefficients, γ_i and the excess Gibbs free energy have been calculated according to the equations:

$$\gamma_i = \frac{Py_i}{P_i^s x_i} \exp \frac{(B_{ii} - v_i)(P - P_i^s) + Py_j^2 (2B_{ij} - B_{ii} - B_{jj})}{RT} \quad (1)$$

$$G_m^E/RT = \sum_{i=1}^2 x_i \ln \gamma_i \quad (2)$$

where P and T are the total pressure and the temperature in the equilibrium system, y_i and x_i are the mole fractions of the component i in the vapor, respectively, liquid phase. The saturation vapor pressure of the pure component, P_i^s was obtained from Antoine equation. The second virial coefficients required in Eq 1, B_{ii} , B_{ij} , B_{jj} , were estimated according to Hayden O'Connell method [9]. The molar volume of the component i in the liquid phase, v_i was calculated from the equation given by Rackett [10].

The experimental VLE data are listed in Table 2, together with the predicted data by UNIFAC contribution

Table 2 Experimental VLE data and predicted vapor compositions by UNIFAC for the system benzene (1) + DEO (2) at 760 mmHg

T_{exp}/K	Phase compositions/mole fraction			Activity coefficients		Excess Gibbs free energy G^E/RT
	$x_{1\text{exp}}$	$y_{1\text{exp}}$	$y_{1\text{UNIFAC}}$	γ_1	γ_2	
400.65	0.0314	0.1445	0.1141	2.1823	0.9048	0.0723
395.85	0.0683	0.2204	0.2164	1.7084	0.9837	0.0213
392.55	0.1061	0.3347	0.3126	1.8042	0.9645	0.0303
389.75	0.1442	0.4011	0.3945	1.7009	0.9867	0.0651
386.75	0.1961	0.4982	0.4924	1.6914	0.9801	0.0871
380.35	0.2901	0.6327	0.6201	1.6848	0.9798	0.1369
374.75	0.3953	0.7472	0.7322	1.6901	0.9525	0.1780
369.25	0.5185	0.8217	0.8194	1.6444	1.0185	0.2667
368.05	0.5702	0.8518	0.8438	1.6023	0.9892	0.2642
363.05	0.6785	0.9029	0.8973	1.6436	1.0362	0.3485
359.95	0.7728	0.9381	0.9283	1.6401	1.0477	0.3929
358.45	0.8211	0.9599	0.9508	1.6507	0.9118	0.3951
356.05	0.8667	0.9676	0.9653	1.6433	1.0423	0.4360
354.75	0.9126	0.9893	0.9817	1.6589	0.9551	0.4099
355.25	0.9563	0.9907	0.9901	1.6094	0.9776	0.4541

Table 3 Physical properties of the pure components

Compound	Critical parameters			Acentric factor, ω	Tsonopoulos parameters	
	P_c /Mpa	T_c /K	V_c /L mol ⁻¹		a_T	b_T
Benzene	4.898	562.16	0.259	0.211	0.0	0.0
DEO	5.472	619.20	0.253	0.356	-0.00123	-0.00227

method. Auxiliary data for the evaluation and correlation of the VLE data are indicated in Table 3.

According to the primary evaluation, the data show a moderately positive deviation from ideality, without the presence of an azeotrope. A relatively poor agreement between the experimental vapor compositions and the data generated by UNIFAC method is observed. This result is in accordance with earlier studies referring to VLE data in binary systems containing DEO and could be explained by a significant influence of the proximity effect [3].

The thermodynamic consistency of the experimental data was verified using two methods:

The first method (Kojima et al. [11] method) used in this paper is suitable for VLE data at low pressure, permits an overall check of the data by combining three tests: the point test for individual data check, the integral test, based on the generalized Gibbs–Duhem equation and infinite dilution test on the related thermodynamic equations.

According to the point test, the parameter δ and is calculated using the equation:

$$\delta = 100 \sum_{i=1}^n |\delta_i^*|/n \tag{3}$$

where n is the number of the experimental data.

The parameter δ^* in the Eq. 3 is estimated from the relation:

$$\delta^* = \frac{\partial \Delta G_m^E / RT}{\partial x_1} - \ln \left(\frac{\gamma_1}{\gamma_2} \right) - \varepsilon \tag{4}$$

The excess Gibbs free energy change on mixing, ΔG_m^E is calculated using the activity coefficients of the components in the mixture.

An estimated value of 0.02 of the parameter ε was used in the calculation and takes into account the heat of mixing for isobaric data.

According to this test the data are considered thermodynamically consistent for values of δ less than 5.

The area test parameter, defined as:

$$A = \int_0^1 \ln \left(\frac{\gamma_2}{\gamma_1} \right) dx_1 + \int_0^1 \varepsilon dx_1 \tag{5}$$

should be <3 for thermodynamically consistent VLE data.

The infinite dilution test, consists of the estimation of parameters, I_1 and I_2 using the following relations:

$$I_1 = 100I_1^*; I_2 = 100I_2^*, \tag{6}$$

where

$$I_1^* = \left(\frac{G_m^E}{RTx_1x_2} \right)_{x_1=0} / \ln \left(\frac{\gamma_1}{\gamma_2} \right)_{x_1=0} - 1 \tag{7}$$

$$I_2^* = \left(\frac{G_m^E}{RTx_1x_2} \right)_{x_2=0} / \ln \left(\frac{\gamma_2}{\gamma_1} \right)_{x_2=0} - 1. \tag{8}$$

For thermodynamically consistent VLE data, the parameters I_1 and I_2 should be <30 . The results of the calculations of parameters from Kojima et al. method [11] are summarized in Table 4 and indicate the VLE data are thermodynamically consistent.

The second method used in this paper for verifying the thermodynamic consistency of the VLE data is a model-free test [12], taking into account the non-ideality of the vapor phase according to the coexistence equation:

$$\frac{dy_1}{dT} = 2.303X \left[\frac{B_1x_1}{(C_1+t)^2} + \frac{B_2x_2}{(C_2+t)^2} \right] - Y \left[\frac{d \ln \Delta_{12}}{dT} - \frac{\Delta_{12}}{T} \right]. \tag{9}$$

The parameters X and Y are calculated using the relations:

$$X = \frac{RTy_1y_2}{(RT - 2y_1y_2\Delta_{12}P)(y_1 - x_1)} \tag{10}$$

$$Y = \frac{RTy_1y_2P(1 - 2y_1)}{(RT - 2y_1y_2\Delta_{12}P)} \tag{11}$$

where y, x represent molar fractions in the vapor and liquid phases, P is the pressure in atm, T is the absolute temperature; B_1, C_1 are the Antoine coefficients. The parameter Δ_{12} is calculated using the second virial coefficients from the equation:

$$\Delta_{12} = 2B_{12} - B_{11} - B_{22}. \tag{12}$$

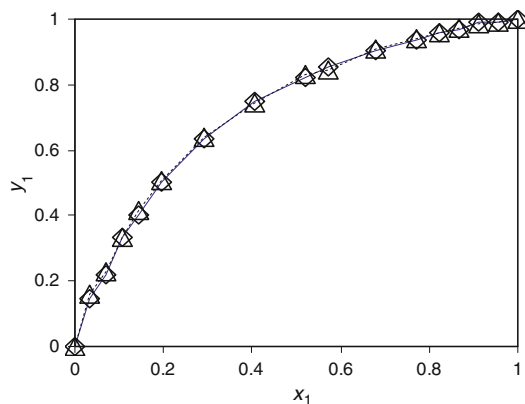
The Eq. 9 is solved by numerical integration using the predictor–corrector formulae of Adams [13, 14] to obtain the values of the vapor phase composition. The residuals of the vapor phase, calculated as differences between the experimental and estimated values from the Eq. 9, are statistically analysed to detect any systematic (SHIFT) and random (TREND) errors using the Student, t and Abbe, R parameters [15].

Table 4 Benzene vapor phase composition/ y_1 by ICE method and the second virial coefficients

T/K	y_{1ICE}	Second virial coefficients/cm ³ mol ⁻¹			$\Delta_{12}/\text{cm}^3 \text{ mol}^{-1}$
		$-B_{11}$	$-B_{22}$	$-B_{12}$	
400.65	0.0000	574.48	721.73	660.56	-34.91
392.55	0.1583	587.31	731.55	670.33	-21.20
385.85	0.2276	597.14	747.22	683.81	-23.26
389.75	0.3324	604.10	758.44	693.42	-24.30
386.25	0.4136	610.15	768.27	701.81	-25.21
380.35	0.5058	617.88	780.98	712.62	-26.37
374.75	0.6398	631.42	803.55	731.69	-28.40
369.25	0.7749	644.89	826.42	750.87	-30.42
368.05	0.8302	658.78	850.43	770.84	-32.47
363.05	0.8467	661.90	855.89	775.36	-32.93
359.95	0.9086	675.28	879.54	794.95	-34.87
358.45	0.9424	683.92	895.01	807.51	-36.11
357.05	0.9578	688.18	902.70	813.80	-38.03
355.25	0.9717	697.50	919.68	827.61	-38.03
354.25	0.9995	700.46	925.15	832.03	-37.43

The parameters t and R are calculated according to the relations:

$$t = \frac{\Delta\bar{y}}{\sqrt{\frac{\sum_i (y_i - \Delta\bar{y})^2}{n(n-1)}}} \quad (13)$$

**Fig. 1** Phase diagram x_1, y_1 for the system benzene (1) + DEO (2) at 760 mmHg; experimental (diamond) and estimated (ICE) values

$$R = \frac{\frac{1}{2(n-1)} \sum_i (\Delta y_{i+1} - \Delta y_i)^2}{\frac{1}{n-1} \sum_i (y_i - \Delta\bar{y})^2} \quad (14)$$

where $\Delta\bar{y}$ represents the mean value of the residuals, Δy_i of the vapor phase compositions.

The thermodynamic consistency of the data is confirmed by simultaneously satisfying the “No Trend” and “No Shift” criteria, resulting from the conditions $t < t_{\text{critic}}$ and respectively, $R > R_{\text{critic}}$. The results of the integration of the coexistence equation (ICE) are presented in Table 4, together with the second virial coefficients, estimated by Hayden-O’Connell correlation [9]. Figure 1 illustrates the phase diagram, drawn from experimental and calculated data (by ICE) and shows a good agreement between the data.

The parameters t and R , calculated according to the relations (12) and (13) are presented in Table 5 together with their critical values and indicate the data which satisfy the conditions for the thermodynamic consistency.

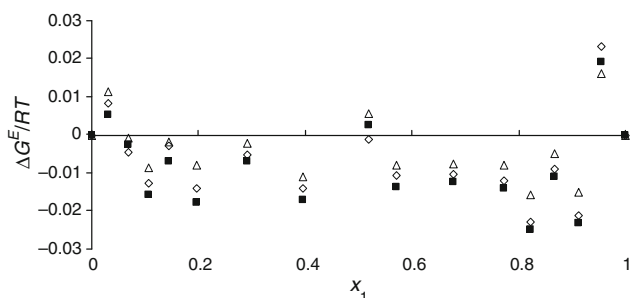
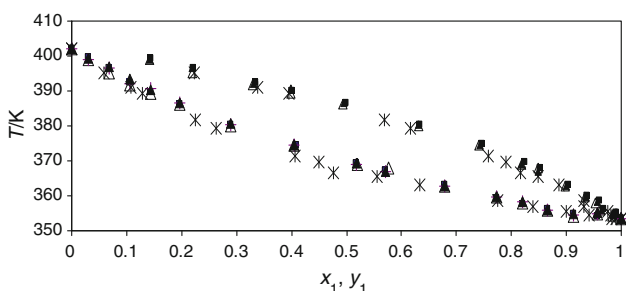
The consistent data were reduced to the binary parameters in the equations given by Wilson [16], NRTL [17], and Gothard [18], using a procedure proposed by

Table 5 Results of the thermodynamic consistency (TC) evaluation of the VLE data

TC method	Criteria for TC	Critical values of the TC parameters	Calculated values of the TC parameters
Kojima et al. [11]	$\delta < \delta_{\text{cr}}$	$\delta_{\text{cr}} = 5$	$\delta = 1.56$
	$A < A_{\text{cr}}$	$A_{\text{cr}} = 3$	$A = 2.32$
	$I_1, I_2 < I_{\text{cr}}$	$I_{\text{cr}} = 30$	$I_1 = 3.43, I_2 = 1.94$
ICE	$t < t_{\text{critic}}$	$t_{\text{critic}} = 2.120$	$t = 1.369$
	$R > R_{\text{critic}}$	$R_{\text{critic}} = 0.475$	$R = 2.276$

Table 6 Binary parameters from Wilson, Renon-Prausnitz, and Gothard models; statistical criterion, ρ

Wilson			Renon-Prausnitz (NRTL)			Gothard		
$\lambda_{12}-\lambda_{11}$ /J mol ⁻¹	$\lambda_{21}-\lambda_{22}$ /J mol ⁻¹	ρ	$g_{12}-g_{22}$ /J mol ⁻¹	$g_{21}-g_{11}$ /J mol ⁻¹	ρ	n_1	n_2	ρ
-2354.56	-3547.54	2.89	-3143.31	-2855.58	2.70	1.16	0.57	0.766

**Fig. 2** Excess Gibbs free energy residuals for the system benzene (1) + DEO (2); data correlated with the model: (*diamond*) NRTL, (*filled square*) Wilson, (*triangle*) Gothard**Fig. 3** $T-x-y$ diagram for benzene (1) + DEO (2) system at 121.3 kPa: (*filled square*) experimental data in this study, (*plus*) data by NRTL, (*empty triangle*) data by Wilson, (*filled triangle*) data by Gothard, (*asterisk*) literature data [4]

Panaitescu [19] based on the maximum likelihood principle. The reliability parameter, ρ from the confidence ellipses, related to the statistical significance level, α was also calculated:

$$\alpha = \exp(-\rho^2). \quad (15)$$

The values were compared with the critical value 2.45 for a significance level, $\alpha = 0.05$.

All binary parameters were obtained by minimizing the objective function:

$$Q_p = \sum_i \left[(G^E/RT)_{\text{exp}} - (G^E/RT)_{\text{calc}} \right]^2 \quad (16)$$

The results of the correlation of the experimental data are summarized in Table 6, presenting the parameters and the reliability criteria ρ , calculated for each model. The residuals of the excess Gibbs free energy, $\Delta G^E/RT$,

obtained as differences between the data calculated from experimental VLE data and the corresponding values, estimated using the three models are displayed in Fig. 2.

The results indicate that the three models considered in this paper (Wilson, NRTL, Gothard) are adequate for the description of the experimental VLE data without any significant difference between them. However, it has to be mentioned that, in this case, Gothard model gives the best fit of the data.

The same result can be observed in Fig. 3 where, the experimental $T-x-y$ data are represented, together with the data estimated using the three models and literature [5] values.

For the correlation of the data by NRTL method the non-randomness parameter, α_{12} was taken as 0.30. The average absolute deviations of calculated G^E/RT from experimental data are: 0.0087, 0.0077, and 0.0066 for Wilson, NRTL, and Gothard model, respectively and the values are in good agreement with the reliability criteria, ρ calculated for each model.

Conclusions

The isobaric experimental VLE data for the system benzene-DEO have been obtained at atmospheric pressure using a recirculatory still. The system has a positive deviation from ideality and has no azeotrope. Two methods were used to verify the quality of the data and they were found to be thermodynamically consistent. The correlation of the data, using activity coefficients models, indicated the best fit of the data was obtained using Gothard model.

A good agreement between the experimental VLE data and previously published [5] values is observed.

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