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Vapor−Liquid Equilibria of Binary Systems of Ethene Oxide + Dodecane, Ethene Oxide + 1-Decanol, and Ethene Oxide + 1-Dodecanol and Prediction with the Predictive Soave−Redlich−Kwong (PSRK) Equation of State

Matthias Süssmuth,* Heike Fitzner, Sven Degenkolbe, and Werner Witt

Lehrstuhl Anlagentechnik und Sicherheitstechnik, Brandenburgische Technische Universität Cottbus, Burger Chaussee 2, 03044 Cottbus, Germany

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Vapor−liquid equilibrium (VLE) measurements have been made for the binary systems ethene oxide + dodecane at four temperatures from (303.15 to 393.15) K, ethene oxide + 1-decanol at three temperatures from (303.15 to 363.15) K, and ethene oxide + 1-dodecanol at four temperatures from (313.15 to 433.15) K for varying mole fractions. An adiabatic calorimeter was used as a static apparatus for the VLE measurement. The obtained temperature, pressure, and liquid mole fraction data ($T-p-x$ data) were used for fitting binary interaction parameters for the predictive Soave−Redlich−Kwong equation of state (PSRK EoS). The applicability of fitted parameters to other systems containing identical structural groups is shown by means of the binary system ethene oxide + 2-methylpropane and ethene oxide + 1-dodecanol.

Introduction

Despite the broad use of ethene oxide (EO) in industry (the world consumption of EO in 2006 was 18 million tonnes[1]), there are very little VLE data reported containing alkanes and alkanols.[2] The main focus of this work is the improvement of the prediction of VLE data for the ethoxylation processes. The ethoxylates are formed during a poly addition reaction of EO to fatty substances, for example, alkanols or phenols.[2] They are primarily used as surfactants. About 13 % of worldwide EO consumption accounts for the production of ethoxylates.[3]

Reliable VLE data are frequently required for the process design and evaluation of incidents, for example, runaway reactions. According to Lohmann et al.,[4] the prediction of vapor−liquid phase equilibria containing EO with epoxy-group parameters (i.e., PSRK, mod. UNIFAC) fitted to propene oxide systems give commonly poor results. Furthermore, the authors found by the use of dynamic simulation of an industrial ethoxylation process using the above-mentioned parameters that the predicted pressure was always lower than the measured process pressure, especially at elevated temperatures.

Therefore, VLE measurements of binary systems containing EO and alkanes were performed over an extended temperature and concentration range. New binary interaction parameters for EO-containing mixtures were fitted to improve the prediction of these VLE data using the predictive Soave−Redlich−Kwong equation of state (PSRK EoS).

Experimental Setup

Since the high hazard potential of EO[3], especially at elevated temperatures, a pressure proof standard apparatus was used for experiments. Temperature, pressure, and liquid composition data ($T-p-x$) were collected in a static system using HEL's Phitec II computer controlled adiabatic calorimeter[5] (Figures 1 and 2) with a cylindrical thin-walled (0.2 mm) stainless steel cell (volume = 112 cm^3; mass = 60 g). Agitation is performed with a magnetic stirrer. The cell has a 1/16” connection of a dosing line and a 1/8” connection for the pressure transducer. Fröhlich[6] used the same experimental setup for phase equilibrium measurements. Figure 3 shows a comparison of experimental data of the binary system EO + 4-nonylphenol from Fröhlich[6] and Patel.[7]

Temperature was measured using a K-type thermocouple. It was calibrated with a Pt100 resistance thermometer, which has an accuracy of ± 0.03 K. The achieved accuracy of the thermocouple was ± 0.1 K. Pressure was measured using an electronic absolute pressure transducer and a difference pressure transducer. It was calibrated with a Druck Limited DPI 705 pressure indicator ($p_{\max} = 3500$ kPa; $\sigma = 0.035$ % of $p_{\max}$). The quality of the pressure measurement system used was found to be $\sigma = \pm\ 0.5p + 1.2$ kPa.

The total amount of added EO and alkanes or alkanols was measured with a lab scale Mettler Toledo PB 3002 (calibrated to $\sigma = 0.03$ g). The maximum uncertainty of the mole fraction, caused by the scale ($\sigma = 0.002\ \text{mol}\cdot\text{mol}^{-1}$), affects the pressure less than ± 1.5 %. The vacuum was created with a slide vane rotary vacuum pump Vacuubrand RE 2.5 ($p_{\min} < 0.03$ kPa).

The maximum overall uncertainty of the experimental data obtained was estimated to be ± 5 % of the experimental pressure.

The cell was suspended in the center of a set of metal plates, which were controlled to match the sample's temperature. To prevent the test cell from deforming when pressure rose, the outside pressure of the cell was controlled close to the cell pressure.

A sample of Fluka research grade EO, purity mass fraction > 0.998, was used without further purification. Merck research grade 1-decanol (mass fraction > 0.998), Merck research grade 1-dodecanol (mass fraction > 0.98), and VWR research grade dodecane (mass fraction > 0.99) were used without further purification other than degassing after drying over molecular sieves. Purities of all pure compounds were verified by gas chromatography. All stated purities of the compounds were in good agreement with the results from the gas chromatography.

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* Corresponding author. E-mail: matthias_suessmuth@web.de.

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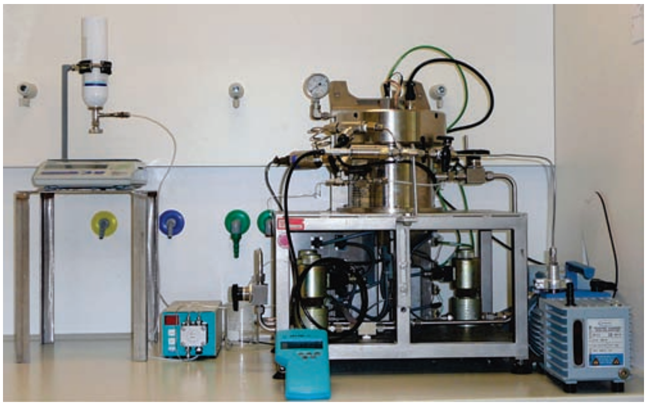

Figure 1. Static VLE apparatus based on the adiabatic calorimeter Phitec II.

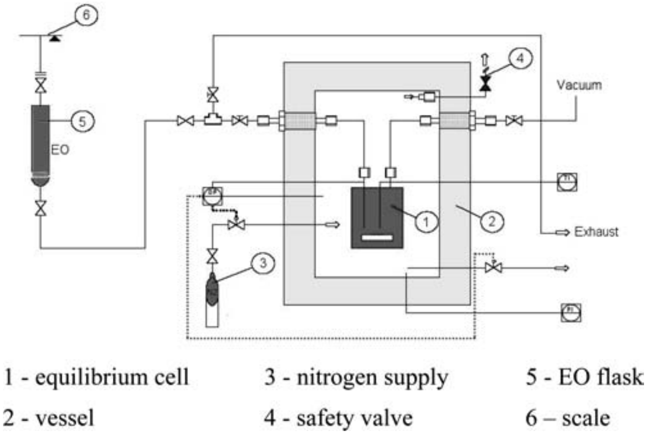

Figure 2. Scheme of static VLE apparatus based on the adiabatic calorimeter Phitec II.

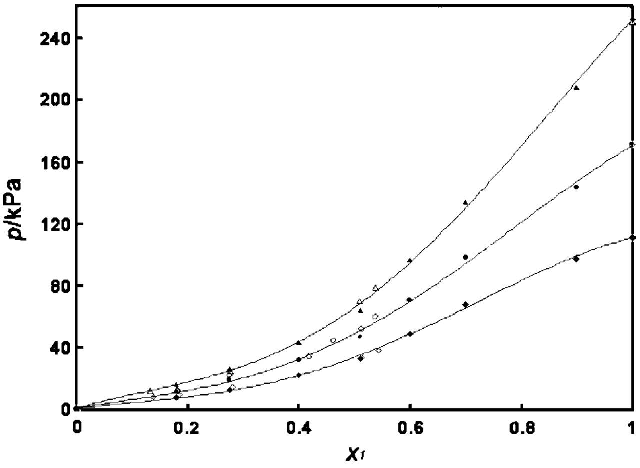

Figure 3. Experimental pressure, p, and liquid mole fraction of EO, x_1, behavior of the system EO (1) + 4-nonylphenol (2) at T = 363.15 K, ◇; 383.15 K, ○; and 403.15 K, △. Experimental data Patel[7] (boxes) and Fröhlich[6] (dots); predicted data (straight lines). Figure taken from Fröhlich.[6]

Table 1. Vapor−Liquid Equilibria (Temperature *T*, Pressure *p*, Pressure Deviation Δ*p*, and Liquid Mole Fraction of EO x_1) for EO (1) + Dodecane (2)

experimental data			predicted pressure	
			parameters, this work	parameters, Horstmann[11]
T/K	p/kPa	x_1	Δp/kPa[a]	Δp/kPa[a]
302.52	116.5	0.2982	2.2	−11.0
302.56	140.8	0.3994	1.6	0.5
302.63	155.6	0.4994	−2.1	7.8
302.56	170.2	0.5993	0.0	17.6
302.63	182.2	0.6993	3.0	23.4
302.78	190.0	0.7994	3.8	21.3
333.72	170.2	0.1961	0.7	−65.5
332.30	234.1	0.2966	−0.7	−54.9
332.80	294.8	0.3978	−3.6	−36.7
332.66	343.2	0.4979	−4.3	−11.8
332.78	386.6	0.5980	−2.5	12.0
332.67	421.6	0.6986	0.9	29.3
332.59	452.5	0.7989	5.4	35.3
361.17	143.8	0.0964	1.9	−91.7
364.73	293.2	0.1938	0.6	−144.1
362.62	414.9	0.2948	−1.1	−138.8
363.18	539.3	0.3960	−3.8	−113.2
362.98	648.0	0.4961	−2.5	−66.1
363.09	752.5	0.5964	3.1	−13.6
363.59	841.1	0.6978	−4.8	15.8
395.18	447.5	0.1916	1.2	−254.3
369.77	657.2	0.2934	4.9	−264.1
393.46	871.6	0.3946	0.2	−241.6
393.04	1069.0	0.4947	2.6	−171.4
391.17	1402.2	0.6975	−0.3	13.6

[a] $\Delta p = p_{exp} - p_{calc}$.

The experimental procedure was as follows: The alkane or alkanol was filled in the test cell and degassed by applying vacuum at elevated temperature for approximately 1 h. Keeping the pressure just above the pure components' vapor pressure ensured no significant material loss by vaporisation. The procedure was finished after stably matching the vapor pressure. After cooling down, the cell was reweighed and reassembled. As Patel[7] has mentioned, condensation may occur in a cavity in the pressure transducer. Since the pressure transducer was located outside the heated space, the cavity was filled with alkane or alkanol to avoid condensation of the high volatile EO. Afterward a predefined mass of liquid EO was added in the liquid phase of the test cell. Then the equilibrium cell was heated up to the predefined temperature. Equilibrium is ensured by a constant temperature inside the cell and its surroundings and the liquid agitated by use of a magnetic stirrer. Usually a time of (1 to 2) h was required to obtain a stable pressure, indicating the phase equilibrium.

Experimental Results

Measurements were performed for EO mole fractions of 0.1 to 0.8 with an increment of 0.1. The temperature range covered (303.15 to 393.15) K with an increment of 30 K for the binary system EO + dodecane and (303.15 to 363.15) K for EO + 1-decanol. For this system a pressure drop was observed at temperatures above 373 K. It was most probably caused by a slow reaction.[7] Thus the temperature range was limited to 363.15 K. Binary VLE data ($T-p-x$ data) obtained are shown in Tables 1 and 2. Experiments of the binary system EO + 1-dodecanol were performed in a temperature range from (313.15 to 433.15) K. The resulting VLE data are presented in Table 3.

The liquid-phase molar compositions of EO (x_1) were derived from injected quantities by solving mass and volume balance and VLE. The uncertainty of the liquid mole fraction was σ_x = 0.002. This is caused mainly by the uncertainty of the scale used. Since measurement was performed at the 80 % liquid level, the liquid concentration matched the total amount concentration with a deviation of 0.005 in terms of mole fraction.

Parameter Fitting

PSRK EoS was used for flash calculations.[8] The model combines the Soave−Redlich−Kwong equation of state with the universal functional activity coefficient (UNIFAC) method.

Table 2. Vapor−Liquid Equilibria (Temperature T, Pressure p, Pressure Deviation Δp, and Liquid Mole Fraction of EO x_1) for EO (1) + 1-Decanol (2)

experimental data			predicted pressure	
			parameters, this work	parameters, Horstmann[11]
T/K	p/kPa	x_1	Δp/kPa[a]	Δp/kPa[a]
302.72	35.9	0.1091	0.7	6.1
302.79	64.1	0.2005	1.8	12.9
302.56	88.0	0.2981	−0.1	17.3
302.54	112.1	0.3991	0.1	23.4
302.71	132.3	0.4963	−0.3	27.1
303.24	151.7	0.5991	−1.2	28.1
302.56	164.2	0.6995	0.0	26.5
302.53	178.7	0.7996	2.6	22.3
332.09	66.1	0.1086	−1.3	16.6
332.01	122.5	0.1991	1.2	31.1
332.25	177.6	0.2965	−0.4	40.0
332.67	233.2	0.3979	−2.2	46.3
332.44	281.9	0.4952	−2.3	50.0
332.64	380.8	0.6988	0.8	47.9
332.12	419.6	0.7992	2.8	37.5
361.50	107.4	0.1080	−2.6	36.8
361.48	205.1	0.1977	3.0	64.2
362.21	310.0	0.2947	3.8	79.7
362.85	415.6	0.3966	−3.1	79.1
361.87	516.6	0.4939	1.9	81.9
362.62	630.0	0.5968	−3.2	71.1

[a] $\Delta p = p_{\mathrm{exp}} - p_{\mathrm{calc}}$.

Table 3. Vapor−Liquid Equilibria (Temperature T, Pressure p, Pressure Deviation Δp, and Liquid Mole Fraction of EO x_1) for EO (1) + 1-Dodecanol (2)

experimental data			predicted pressure	
			parameters, this work	parameters, Horstmann[11]
T/K	p/kPa	x_1	Δp/kPa[a]	Δp/kPa[a]
313.06	41.5	0.1050	−1.2	6.3
313.28	75.5	0.1991	−3.8	10.9
313.56	142.3	0.4037	−8.6	20.6
313.39	195.9	0.6055	−10.3	25.8
312.94	242.8	0.8110	−3.3	22.0
353.53	86.9	0.1043	−4.9	23.9
353.62	162.0	0.1982	−12.9	33.6
353.41	328.2	0.4018	−25.5	38.1
353.59	506.0	0.6044	−25.4	37.5
353.05	688.5	0.8102	−11.3	32.6
393.32	151.8	0.1038	−2.5	61.7
394.14	291.2	0.1975	−13.6	85.2
393.84	624.4	0.3999	−35.2	67.9
393.54	1051.9	0.6035	−20.0	43.3
391.75	1504.4	0.8092	−14.5	25.9
432.38	224.9	0.1036	1.6	109.4
433.98	448.6	0.1974	−4.0	158.9
433.86	1047.3	0.3988	6.7	137.6
431.17	1859.3	0.6035	77.3	82.4
432.60	2898.6	0.8088	15.6	−11.9

[a] $\Delta p = p_{\mathrm{exp}} - p_{\mathrm{calc}}$.

The predictive character of the model is based on fitted binary interaction parameters for structural groups (a_{ij}, and if necessary b_{ij} and c_{ij}) instead of fitted binary parameters for the substances. The advantage is that there are millions of mixtures, but it requires only pure substance properties and hundreds of structural groups to predict VLE data instead of millions of binary parameters.

An OCTAVE computer routine with the implemented PSRK model was developed to fit binary interaction parameters for related structural groups. The method is based on minimizing a least-squares function[8] (eq 1), where n_p and n_c are the number of data points and components. The subscript "exp" refers to experimental and "calc" to calculated data. The denominator refers to the accuracy of experimental pressure measurement.

$$F = \sum_{n_p} \sum_{n_c} \left(\frac{p_{\mathrm{calc}} - p_{\mathrm{exp}}}{0.5 p_{\mathrm{exp}} + 1.2\ \mathrm{kPa}} \right)^2 \qquad (1)$$

The fitting algorithm is based on the PSRK flash calculation, matching the experimental pressure. It includes the vapor−liquid mass balance and was derived from a procedure proposed by Fischer.[9] Pure substance properties and group data (PSRK group area and volume parameter R_k and Q_k, critical properties of pure compounds) used were taken from Horstmann.[8]

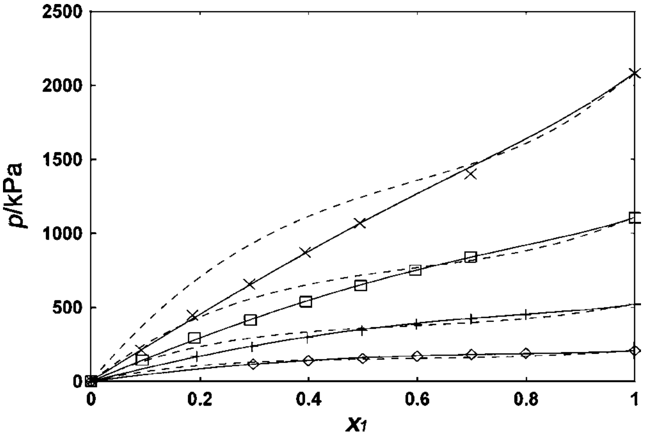

Figure 4. Experimental and predicted pressure, p, and liquid mole fraction of EO, x_1, behavior of the system EO (1) + dodecane (2) at T = 303.15 K, ◇; 333.15 K, +; 363.15 K, □; and 393.15 K, ×. Experimental data from this work (dots); prediction PSRK with parameters fitted to this system from this work (straight lines); prediction PSRK with epoxy-parameters[11] (dashed lines).

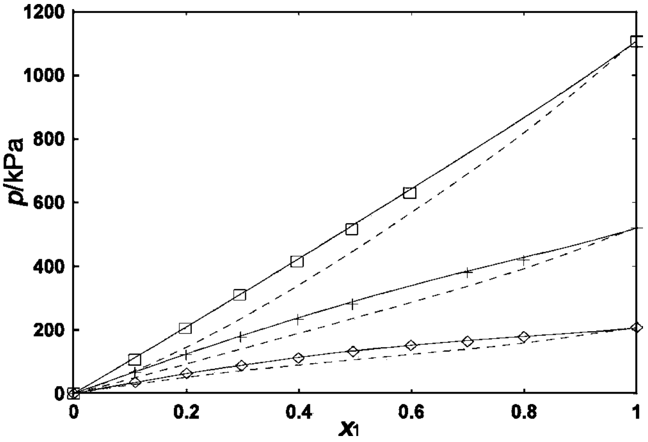

Figure 5. Experimental and predicted pressure, p, and liquid mole fraction of EO, x_1, behavior of the system EO (1) + 1-decanol (2) at T = 303.15 K, ◇; 333.15 K, +; and 363.15 K, □. Experimental data from this work (dots); prediction PSRK with parameters fitted to this system from this work (straight lines); prediction PSRK with epoxy-parameters[11] (dashed lines).

Table 4. Fitted EO Group Interaction Parameters a_{ij} and b_{ij} for the PSRK Model (Optional Parameter c_{ij} Was Not Fitted)

i	j	a_{ij}/K	b_{ij}	c_{ij}/K^{-1}	a_{ji}/K	b_{ji}	c_{ji}/K^{-1}
H_2COCH_2	CH_2	11.52	0.00532	0	584.58	−0.83399	0
H_2COCH_2	OH	1210.00	−2.59061	0	−14.21	0.0024314	0

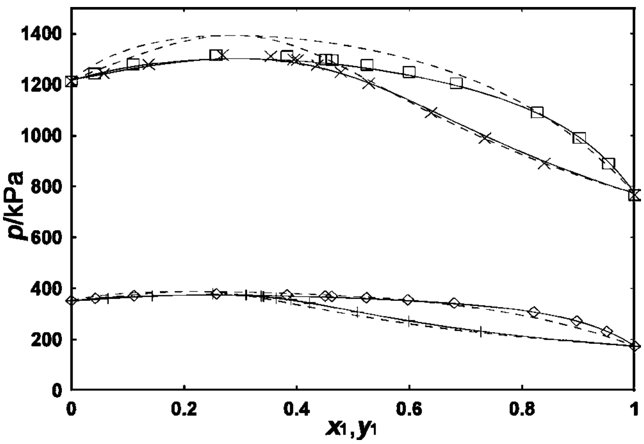

Figure 6. Experimental and predicted pressure, *p*, and liquid and vapor mole fractions of EO, x_1 and y_1, behavior of the system EO (1) + 2-methylpropane (2) at T = 298.15 K, ◇, +; and 348.15 K, □, ×. Experimental data from Giles and Grant[10] (dots); prediction PSRK with parameters fitted to the system EO + dodecane from this work (straight lines); prediction PSRK with epoxy-parameters[11] (dashed lines).

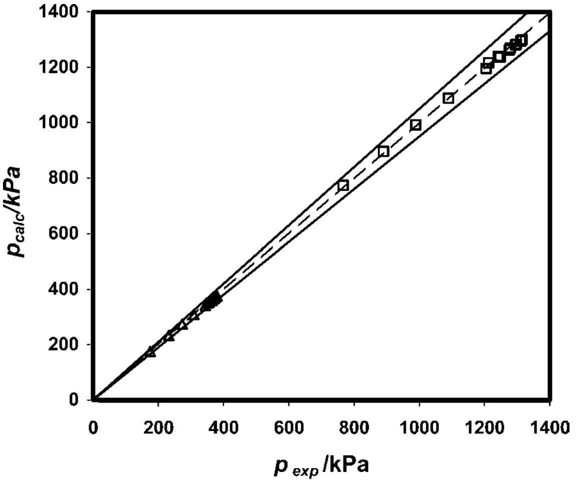

Figure 7. Experimental pressure, p_{exp}, vs predicted pressure, p_{calc}, of the system EO (1) + 2-methylpropane (2) at T = 298.15 K, △; and 348.15 K, □. 5 % deviation (straight lines): experimental data from Giles and Grant;[10] prediction PSRK with parameters fitted to the system EO + dodecane from this work.

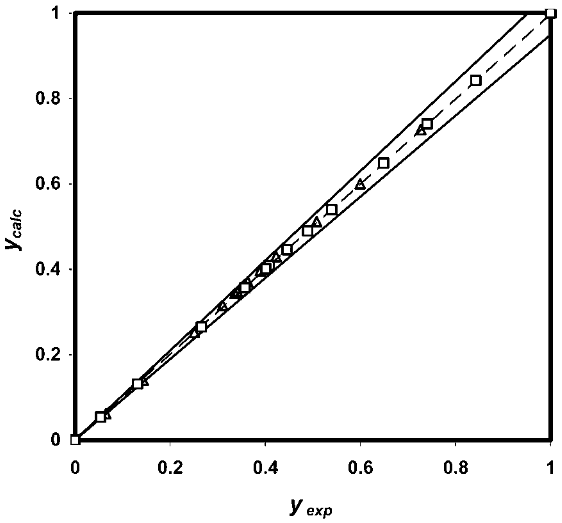

Figure 8. Experimental vapor mole fraction of EO, y_{exp}, vs predicted vapor mole fraction of EO, y_{calc}, of the system EO (1) + 2-methylpropane (2) at T = 298.15 K, △; and 348.15 K, □. 5 % deviation (straight lines): experimental data from Giles and Grant;[10] prediction PSRK with parameters fitted to the system EO + dodecane from this work.

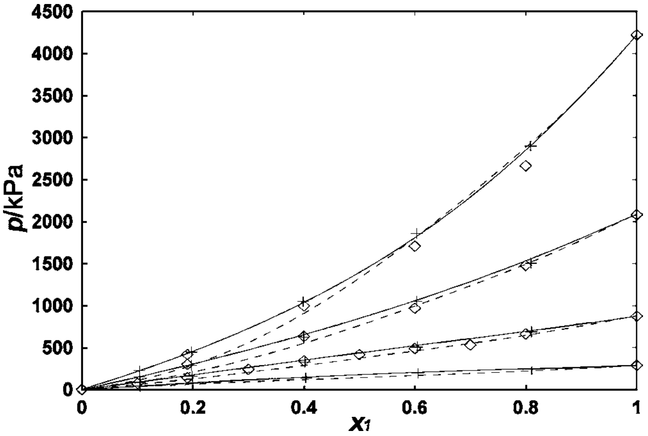

Figure 9. Experimental and predicted pressure, *p*, and liquid mole fraction of EO, x_1, behavior of the system EO (1) + 1-dodecanol (2) at T = (313.15, 353.15, 393.15, and 433.15) K: ◇, experimental data from Fröhlich;[6] +, experimental values from this work; prediction PSRK with parameters fitted to the system EO + decanol from this work (straight lines); PSRK with epoxy-parameters[11] (dashed lines).

Generally the vapor mole fraction *y* is an additional parameter equivalent to the partial pressures, frequently used for validation. Since the partial pressure of EO is at least hundred times higher than the partial pressures of the alkanes or alkanols, the vapor mole fraction of EO is in this case always nearly $y_{\mathrm{EO}} = 1$. Thus, the overall pressure is strongly dominated by the partial pressure of EO. The VLE data of EO + 2-methylpropane from literature[10] include the vapor mole measurement. The prediction of the VLE with the parameter from this work shows that the predicted vapor mole fraction is in good agreement with the experimental data (Figures 6 and 8).

To avoid fitting errors caused by interaction of different binary groups in a system, interaction parameters should be fitted, if possible, only to one pair of binary groups.

The system EO + dodecane (for experimental data see Table 1) contains only the EO and the CH_2 groups. In a first step that system was chosen to fit the binary parameters EO−CH_2 without further interaction to other groups.

In a second step, the parameters for the binary group EO−OH were fitted to the binary system EO + 1-decanol (for experimental data see Table 2) which contains the EO, CH_2, and OH groups. The binary parameters for EO−CH_2 group used in this analysis were obtained in the first step of the procedure. Binary interaction parameters for fitted PSRK groups EO−CH_2 and EO−OH are presented in Table 4.

The experimental VLE data of EO + 1-dodecanol presented in Table 3 were used for validation. In addition to the experimental data, predicted pressure data were included for comparison in Tables 1 to 3.

The results of the parameter fitting for the system EO + dodecane are shown in Figure 4. For the system EO + 1-decanol results are presented in Figure 5. Vapor pressures of the pure substances (mole fractions of EO = 0 and 1) used for reference were not measured.

Validation

Unfortunately, very few experimental data are known in the literature. All known literature data were used for validation.

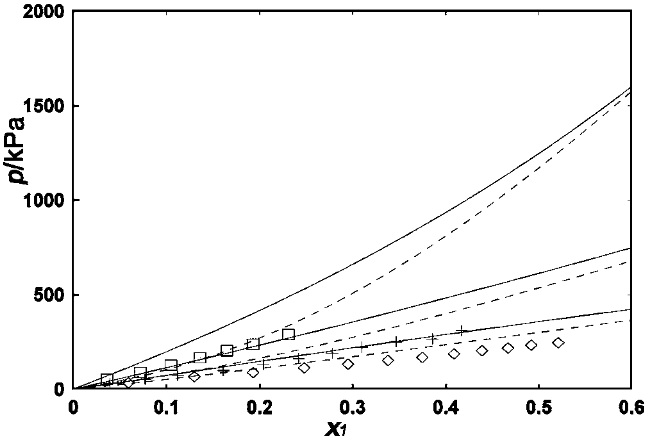

Figure 10. Experimental and predicted pressure, p, and liquid mole fraction of EO, x_1, behavior of the system EO (1) + 1-dodecanol (2) at $T = 343.15$ K, ◇; 372.15 K, +; and 423.15 K, □. Experimental data Di Serio et al.[2] (dots); prediction PSRK with parameters fitted to the system EO + decanol from this work (straight lines); prediction PSRK with epoxy-parameters by Horstmann et al.[11] (dashed lines).

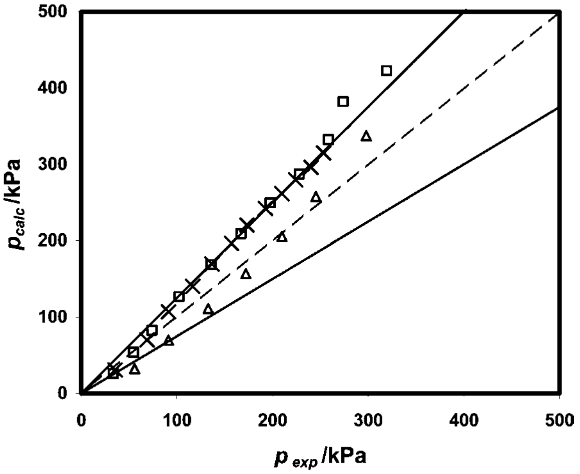

Figure 11. Experimental pressure, p_{exp}, vs predicted pressure, p_{calc}, of the system EO (1) + 1-dodecanol (2) at $T = 343.15$ K, △; 372.15 K, □; and 423.15 K, ×. 5 % deviation (straight lines): experimental data Di Serio et al.;[2] prediction PSRK with epoxy-parameters by Horstmann et al.[11]

Applicability of the predictive SRK model with the new binary interaction parameters EO−CH_2 (Table 4) to other systems is demonstrated using experimental VLE data of the system EO + 2-methylpropane from Giles and Grant.[10] The result is shown in Figure 6 (x_1: liquid mole fraction of EO; y_1: vapor mole fraction). The maximum error of the predicted pressure is ± 1.23 % (Figure 7) and related to the vapor mole fraction of EO 6.38 % (Figure 8).

Application of the new binary interaction parameters EO−CH_2 and EO−OH (Table 4) to the system EO + 1-dodecanol (exp. data: Table 3 and Fröhlich[6]) is shown in Figure 9. Improvements of the experimental apparatus Phitec II, especially enhanced vacuum, pressure measurement, and measures avoiding condensation are the reasons for differences between VLE data from Fröhlich[6] and this work (Table 4).

It should be mentioned, that a comparison of experimental data from Di Serio et al.[2] with predicted data (PSRK model) gives higher deviations (Figures 10 and 11). All predicted pressures are higher than the experimental pressures. The prediction with parameters of Horstmann et al.[11] gives better results, but also with a remarkable deviation. It might be that the experimental pressure may be affected by the condensation of the highly volatile EO.[7] Unfortunately, no detailed information about the experimental procedure was reported.

The flash calculations with the PSRK model using the parameters from this paper match experimental data with good accuracy, except for the experimental data of Di Serio et al.[2] A deviation of less than 5 % in terms of pressure was achieved for these systems.

Conclusion

Vapor−liquid equilibria ($T-p-x$ data) were measured for the binary systems EO + dodecane, EO + 1-decanol, and EO + 1-dodecanol using a static apparatus. At higher temperatures reactions may occur. A pressure drop indicates this effect. Binary interaction parameters for a new EO epoxy group were fitted for the PSRK EoS. Except for one data set, the prediction of VLE data for other binary systems containing the same structural groups achieved a good agreement with experimental data with a deviation of <5 %.

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