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Vapor−Liquid Equilibria of Selected Components in Propylene Oxide Production

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Vapor−liquid equilibrium (VLE) of binary systems formed by 1,2-dichloropropane and propylene chlorohydrine or bis(2-chloroisopropyl) ether at a pressure of 10 kPa as well as the variation of the saturated vapor pressure of propylene chlorohydrine and bis(2-chloroisopropyl) ether with temperature were measured by a static method. Binary VLE data were fitted to the Redlich−Kister, Wilson, NRTL, and UNIQUAC models employing the maximum likelihood procedure. Binary parameters of individual excess molar Gibbs energy models were obtained assuming the ideal behavior of the vapor phase. A good agreement between the experimental and correlated data was found. A comparison of the fit goodness of the selected G^E models is presented. The experimental data of the single component equilibrium measurements were correlated by the Antoine equation applying the least-squares method.

Introduction

Propylene chlorohydrine is an intermediate in propylene oxide production from propylene via the wet synthesis.[1] During this process, several byproducts are formed, e.g., 1,2-dichloropropane and bis(2-chloroisopropyl) ether, due to unwanted consecutive and side reactions. As a consequence, the desired product, propylene oxide, is always accompanied with these impurities and should be separated downstream. After propylene oxide separation, the effluent stream still contains both valuable as well as harmful components. As thermal incineration of chlorinated compounds can produce other toxic pollutants, this traditional procedure is being replaced by further separation steps.[2] During the recovery of waterfree 1,2-dichloropropane, which serves as a chemical intermediate and solvent, remaining chlorinated volatile organic compounds could be separated by means of distillation at a reduced pressure. To simulate this process, reliable vapor−liquid equilibrium data of the mixture components are needed.

In this study, isobaric binary VLE of 1,2-dichloropropane with these components at 10.00 kPa are presented as well as the phase equilibria of pure propylene chlorohydrine and bis(2-chloroisopropyl) ether.

Experimental

1,2-Dichloropropane and bis(2-chloroisopropyl) ether were supplied by NCHZ (Nováky, Slovak Republic). 1,2-Dichloropropane was purified by contacting the raw material with $CaCl_2$ for several days and decanted. Pure DCP was obtained by fractional distillation in a column with 20 theoretical plates. Pure bis(2-chloroisopropyl) ether was prepared by fractional distillation of the material supplied in a packed bed column with 20 theoretical plates. Propylene chlorohydrine was purchased from Fluka (Buchs, Switzerland) as a mixture of α (1-chloro-2-propanol) and β (2-chloro-1-propanol) isomers in mole ratio of 3:1 with a declared purity better than 97 %.

All chemicals were stored with the added molecular sieves to avoid a possible contamination with atmospheric moisture. The results of the measurement of refractive index for all compounds used are given in Table 1. Moreover, purity of all components was assessed chromatographically, showing the values better than 99.1 %.

Table 1. Comparison of Experimental and Tabulated Refractive Indices of Chemicals Used

component	refractive index, n_D^{20} experimental	refractive index, n_D^{20} tabulated	ref
1,2-dichloropropane	1.4383	1.4384	3
propylene chlorohydrine	1.4377	1.4385	4
bis(2-chloroisopropyl) ether	1.4473	1.4505	5

Measurement of both isobaric binary VLE of the systems 1,2-dichloropropane + propylene chlorohydrine and 1,2-dichloropro-

Table 2. Vapor−Liquid Equilibrium Data of the Systems Including 1,2-Dichloropropane at $P = 10.00$ kPa

1,2-dichloropropane (1) + propylene chlorohydrine (2)		1,2-dichloropropane (1) + bis(2-chloroisopropyl) ether (2)	
x_1	t/°C	x_1	t/°C
0.0199	57.30	0.0658	90.60
0.0751	51.95	0.1104	80.50
0.1376	47.50	0.2203	67.30
0.2179	43.20	0.3285	58.35
0.3787	37.20	0.4509	50.80
0.4817	35.70	0.5610	45.55
0.6224	33.80	0.6503	41.65
0.7594	32.00	0.7716	38.20
0.8192	30.70[a]	0.8812	35.00
0.9461	30.70		
0.9774	30.75		

[a] Visually detected limited miscibility.

Table 3. Results of Saturated Vapor Pressure Measurement for Propylene Chlorohydrine and Bis(2-chloroisopropyl) Ether

propylene chlorohydrine			bis(2-chloroisopropyl) ether		
t/°C	P^0/kPa	ref	t/°C	P^0/kPa	ref
20.00	1.199	this study	30.00	0.240	this study
30.00	2.225		40.00	0.564	
40.00	3.981		49.95	0.867	
50.00	6.662		59.90	1.280	
60.00	10.879		69.85	1.919	
70.00	17.197		79.75	2.822	
80.00	26.480		85.00	3.673	
90.00	39.801		85.30	3.348	
96.00	50.097		88.00	4.237	
−	−		91.00	4.806	
−	−		94.00	5.477	
128[a]	101.325	7	20.0	0.013	9
131[b]	101.325	7	187.4	101.325	9
126.106[a]	101.314	8	187 to 188	101.458	5

[a] α and [b] β isomers.

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Table 4. G^E Model Parameters Evaluated from VLE Data of the System 1,2-Dichloropropane (1) + Propylene Chlorohydrine (2) at $P = 10.00$ kPa

model equation	model parameter	value	mean deviation d_x	mean deviation d_t/°C	remark
Redlich−Kister	B_{12}	1.14995	0.0134	0.37	heteroazotrope:
	C_{12}	0.71765			$t = 32.19$ °C, $y_1 = 0.8902$, $x_{11} = 0.9061$, $x_{12} = 0.7104$
	D_{12}	0.75294			
Wilson	$(\lambda_{12} - \lambda_{11})/(\text{J}\cdot\text{mol}^{-1})$	−1000.02	0.0055	0.27	azeotrope:
	$(\lambda_{21} - \lambda_{22})/(\text{J}\cdot\text{mol}^{-1})$	31567.7			$t = 32.05$ °C, $x_1 = 0.9231$
NRTL	$(g_{12} - g_{22})/(\text{J}\cdot\text{mol}^{-1})$	21840.9	0.0087	0.14	heteroazotrope:
	$(g_{21} - g_{11})/(\text{J}\cdot\text{mol}^{-1})$	1528.56			$t = 31.71$ °C, $y_1 = 0.9131$, $x_{11} = 1.0000$, $x_{12} = 0.7629$
	α	0.387			
UNIQUAC	$(u_{12} - u_{22})/(\text{J}\cdot\text{mol}^{-1})$	5140.73	0.0065	0.17	heteroazotrope:
	$(u_{21} - u_{11})/(\text{J}\cdot\text{mol}^{-1})$	−1782.24			$t = 31.83$ °C, $y_1 = 0.9056$, $x_{11} = 0.9782$, $x_{12} = 0.7329$

Table 5. Model Parameters Evaluated from VLE Data of the System 1,2-Dichloropropane (1) + Bis(2-chloroisopropyl) Ether (2) at $P = 10.00$ kPa

model equation	model parameter	value	mean deviation d_x	mean deviation d_t/°C
Redlich−Kister	B_{12}	0.05141	0.0054	0.09
	C_{12}	0.10757		
	D_{12}	0.31597		
Wilson	$(\lambda_{12} - \lambda_{11})/(\text{J}\cdot\text{mol}^{-1})$	−1653.94	0.0051	0.06
	$(\lambda_{21} - \lambda_{22})/(\text{J}\cdot\text{mol}^{-1})$	7533.95		
NRTL	$(g_{12} - g_{22})/(\text{J}\cdot\text{mol}^{-1})$	6231.00	0.0068	0.09
	$(g_{21} - g_{11})/(\text{J}\cdot\text{mol}^{-1})$	−3248.21		
	α	0.35		
UNIQUAC	$(u_{12} - u_{22})/(\text{J}\cdot\text{mol}^{-1})$	3700.82	0.0045	0.06
	$(u_{21} - u_{11})/(\text{J}\cdot\text{mol}^{-1})$	−2046.84		

pane + bis(2-chloroisopropyl) ether and the saturated vapor pressure variation with temperature for propylene chlorohydrine and bis(2-chloroisopropyl) ether were carried out in a modified static apparatus described by Surový et al.[6] The temperature of the still measuring compartment was kept constant within ± 0.05 K. Using a precise U-manometer, the uncertainty of the pressure was ± 13 Pa. The components of the binary mixture were weighted using an analytical balance with an accuracy of $\pm\ 5\cdot 10^{-4}$ g corresponding to a mass fraction uncertainty of ± 0.02 %.

The results of isobaric VLE measurement for the systems 1,2-dichloropropane + propylene chlorohydrine and 1,2-dichloropropane + bis(2-chloroisopropyl) ether are summarized in Table 2. The results of the measurements of saturated vapor pressure for propylene chlorohydrine and bis(2-chloroisopropyl) ether are given in Table 3.

Results and Discussion

VLE data of the binary systems were described using several excess molar Gibbs model equations, namely, Redlich−Kister, Wilson, NRTL, and UNIQUAC ones. In all cases, the model parameters were obtained using the maximum likelihood principle by minimizing the objective function according to the procedure described by Graczová and Surový[10]

$$F = \sum_n \left[(P - P_{\text{calcd}})^2 + \left(\frac{\partial P_{\text{calcd}}}{\partial x_1} \right)^2 (x_1 - x_{\text{calcd},1})^2 \right]_n \qquad (1)$$

where P represents the system total pressure and x_1 the component in 1 mole fraction in the liquid phase. Equilibrium temperature was optimized indirectly by optimizing total pressure, while the values of the component mole fractions in the liquid phase were obtained using a one-parameter optimization.[10] The values of total pressure were calculated from the relation

$$P_{\text{calcd}} = \gamma_1 x_1 P_1^{\text{o}} + \gamma_2 x_2 P_2^{\text{o}} \qquad (2)$$

where P_i^{o} and γ_i correspond to the i-th component saturated vapor pressure and activity coefficient, respectively.

The overview of G^E model parameters and the respective statistical indices is given in Tables 4 and 5 for the studied binary systems. Relatively large differences were found when comparing the correlation of the 1,2-dichloropropane + propylene chlorohydrine equilibrium at 10.00 kPa by the chosen G^E model equations. As expected, the Wilson equation is

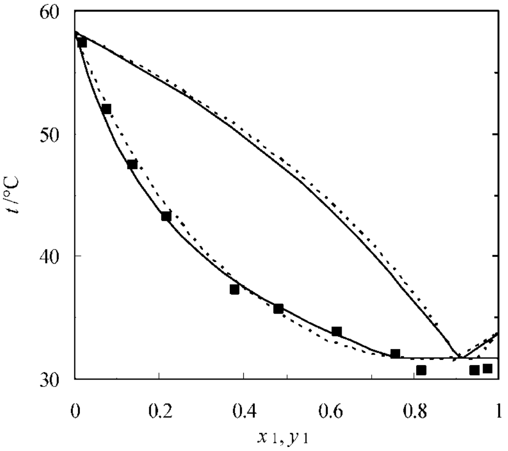

Figure 1. Experimental (squares) and calculated by the NRTL (solid line) and UNIQUAC (dotted line) vapor−liquid equilibrium data of the 1,2-dichloropropane (1) + propylene chlorohydrine (2) system at $P = 10.00$ kPa.

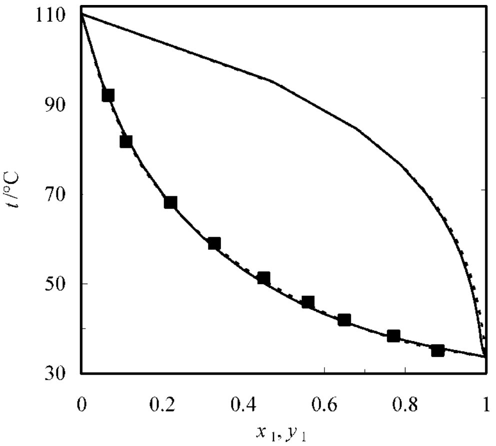

Figure 2. Experimental (squares) and calculated by the NRTL (solid line) and UNIQUAC (dotted line) vapor−liquid equilibrium data of the 1,2-dichloropropane (1) + bis(2-chloroisopropyl) ether (2) system at $P = 10.00$ kPa.

Table 6. Antoine Equation Parameters for Propylene Chlorohydrine and Bis(2-chloroisopropyl) Ether with the Mean Deviation of Pressure

	Antoine equation parameters[a]			temperature interval	d_p
component	*A*	*B*	*C*	°C	kPa
1,2-dichloropropane[b]	6.08324	1292.640	220.630	20 to 100	–
propylene chlorohydrine	7.30842	1908.380	244.271	20 to 96	0.023
bis(2-chloroisopropyl) ether	6.34631	1765.630	220.000	30 to 94	0.137

[a] $\log(P^0/\text{kPa}) = A - B/(C + t/°\text{C})$. [b] Ref 5.

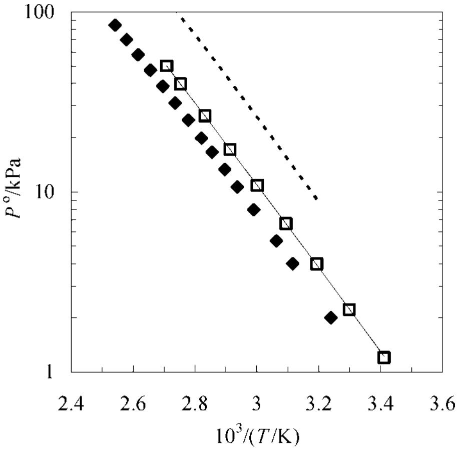

Figure 3. Variation of the saturated vapor pressure of propylene chlorohydrine with temperature. Comparison of the experimental data (squares) and their fit by the Antoine equation (solid line) with the data presented by Steele et al.[8] for pure α propylene chlorohydrine (diamonds) and the fit of experimental data by Kireev and Nikiforova[11] for β propylene chlorohydrine (dotted line).

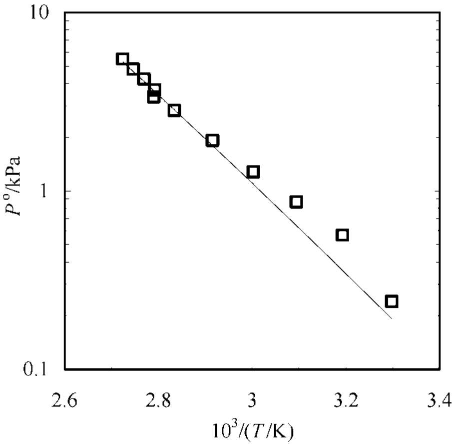

Figure 4. Variation of the saturated vapor pressure of bis(2-chloroisopropyl) ether with temperature. Experimental data (squares) fitted to the Antoine equation (line).

inappropriate to describe splitting of the liquid phase. Comparison of the fit obtained for the NRTL and UNIQUAC model equations is shown in Figures 1 and 2 representing the isobaric VLE data for 1,2-dichloropropane + propylene chlorohydrine and 1,2-dichloropropane + bis(2-chloroisopropyl) ether binaries, respectively.

It was found that the quality of the experimental data correlation is similar for both these models, especially considering the binary system containing bis(2-chloroisopropyl) ether. On the other hand, the prediction of the heteroazeotropic mixture formed by 1,2-dichloropropane and propylene chlorohydrine showed certain differences assuming the two G^E models. The difference between the experimental and NRTL predicted azeotrope temperature was slightly lower when compared with the difference obtained for the UNIQUAC equation.

The vapor pressure data of pure components (propylene chlorohydrine and bis(2-chloroisopropyl) ether) were fitted to the three-parameter Antoine model equation (Table 6) using the least-squares method. Comparison of experimental and calculated values of propylene chlorohydrine with the literature data is given in Figure 3. The discrepancy between the proprietary data and the data published by Steele et al.[8] could be attributed mainly to the fact that propylene chlorohydrine used in the present study is a mixture of two isomers, namely α propylene chlorohydrine (1-chloro-2-propanol) and β propylene chlorohydrine (2-chloro-1-propanol). On the other hand, even higher values of saturated vapor pressures were obtained for β propylene chlorohydrine on basis of the results of Kireev and Nikiforova[11] as shown in Figure 3.

Figure 4 presents the comparison of experimental and fitted data of the saturated vapor pressure for bis(2-chloroisopropyl) ether.

Conclusions

Vapor−liquid equilibrium data for the binary systems comprising 1,2-dichloropropane, propylene chlorohydrine, and bis(2-chloroisopropyl) ether were estimated. It was found that 1,2-dichloropropane forms a heteroazeotrope with propylene chlorohydrine at a pressure of 10 kPa. The composition of two liquids and vapor equilibrium phase and boiling temperature of this mixture were calculated using the Redlich−Kister, NRTL, and UNIQUAC model equations. Variations of the saturated vapor pressure of propylene chlorohydrine and bis(2-chloroisopropyl) ether with temperature were fitted using the Antoine equation.

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