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Vapor Pressure, Vapor−Liquid Equilibrium, and Excess Enthalpy Data for Compounds and Binary Subsystems of the Chlorohydrin Process for Propylene Oxide Production

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Vapor−liquid equilibrium (VLE), excess enthalpy (H^E), and vapor pressure (P_i^s) data for eight binary systems containing *cis*-1-chloropropene, *trans*-1-chloropropene, 1,2-dichloropropane, 1,2-propanediol, 1,2-propylene glycol diacetate, propylene oxide, and water are presented in a temperature range from 276 to 368 K. The VLE and vapor pressure data were obtained by means of a computer-controlled static apparatus, and the heat of mixing data were measured using an isothermal flow calorimeter. Temperature-dependent NRTL interaction parameters were regressed by a simultaneous correlation of the experimental VLE and H^E data. These parameters are required for a proper simulation of the different separation steps in the chlorohydrin process for the production of propylene oxide.

Introduction

For the synthesis, design, and optimization of separation processes and for the extension of thermodynamic models (G^E models, equations of state, and group contribution methods), a reliable knowledge of the phase equilibrium behavior is required. In the chlorohydrin process, propene is first hypochlorinated. After dehydrochlorination to propylene oxide, the mixture containing various byproducts must be separated in different stripping and distillation units. While for some of the binary subsystems appearing during the separation experimental data are available in the literature,[1−19] only a limited number of experimental vapor−liquid equilibrium (VLE) and excess enthalpy (H^E) data are published for systems containing 1-chloropropene and 1,2-propylene glycol diacetate.[20]

In this study, isothermal $P-x$ data for eight binary systems as well as pure-component vapor pressures for the components *cis*-1-chloropropene, *trans*-1-chloropropene, and 1,2-propylene glycol diacetate were measured in a computer-operated static apparatus. In addition, H^E data were measured by means of an isothermal flow calorimeter for all systems at two different temperatures.

Excess enthalpy data are important to describe the temperature dependence of the activity coefficients following the Gibbs−Helmholtz equation

$$\left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_{P,x} = \frac{H_i^{E}}{R} \qquad (1)$$

The experimental VLE and H^E data of this work are compared with correlated data using temperature-dependent NRTL interaction parameters.

Table 1. Experimental Vapor Pressure Data for *cis*-1-Chloro-1-propene

T/K	P_i^s/kPa	T/K	P_i^s/kPa
276.33	32.16	294.87	69.93
276.62	32.92	298.56	80.60
279.09	36.63	301.30	88.11
279.36	37.02	310.75	123.67
283.48	44.03	317.74	156.27
286.27	49.97	319.00	162.19
289.99	58.00	332.73	246.51
290.27	58.68	332.99	248.37
292.45	63.78		

Table 2. Experimental Vapor Pressure Data for *trans*-1-Chloro-1-propene

T/K	P_i^s/kPa	T/K	P_i^s/kPa
277.18	26.68	314.68	115.59
283.82	35.65	314.76	115.83
288.11	42.65	319.79	136.89
293.48	53.03	319.80	136.93
298.30	64.12	328.34	179.15
305.18	82.88	334.25	213.99
309.83	97.59	340.63	257.21

Table 3. Experimental Vapor Pressure Data for 1,2-Propylene Glycol Diacetate

T/K	P_i^s/kPa	T/K	P_i^s/kPa
318.21	0.196	356.90	1.887
322.83	0.266	363.87	2.690
338.18	0.667	367.61	3.244
347.73	1.153		

Experimental Section

Materials. All chemicals except water, which was distilled twice, were supplied by DOW and dried over a molecular sieve. For the VLE measurements, the chemicals were distilled and degassed as described by Fischer and Gmehling.[21] For the H^E measurements, the compounds were used without degassing. The final purities and water concentrations were checked by gas chromatography and

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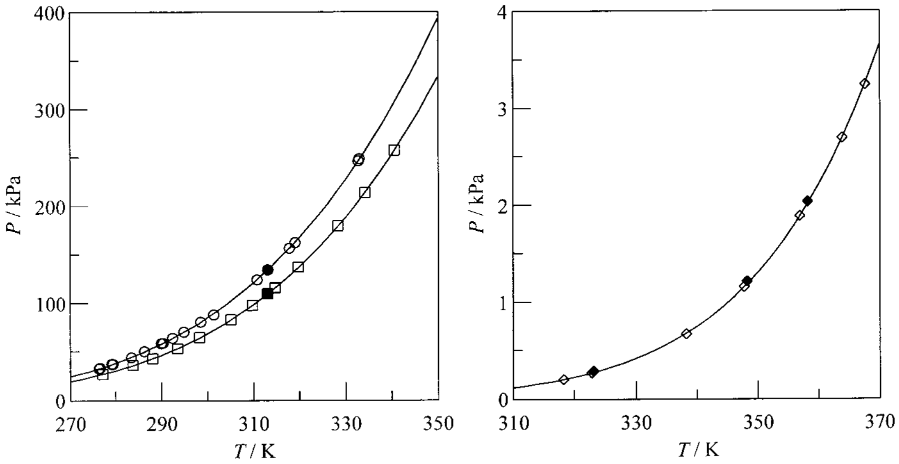

Figure 1. Experimental and calculated vapor pressure data. *cis*-1-Chloropropene: (○) vapor pressure measurement; (●) VLE measurement. *trans*-1-Chloropropene: (□) vapor pressure measurement; (■) VLE measurement. 1,2-Propylene glycol diacetate: (◇) vapor pressure measurement; (◆) VLE measurement. (—) Antoine.

Table 4. Pure-Component Parameters: Antoine Coefficients A_i, B_i, and C_i, Range of Validity, and Liquid Densities at 298.15 K

component	A_i	B_i/K	C_i/K	range of validity/K	ρ(298.15 K)/ kg·dm^{-3}
cis/*trans*-1-chloropropene	6.049 68	1074.90	−40.150	280−338	0.9200[a]
cis-1-chloropropene	5.870 99	971.54	−53.543	276−332	0.9221[a]
trans-1-chloropropene	6.113 76	1118.16	−38.688	277−340	0.9140[a]
1,2-dichloropropane	6.105 64	1308.14	−50.305	318−369	1.1490
1,2-propanediol	8.079 36	2692.19	−17.940	318−461	1.0328
1,2-propylene glycol diacetate	8.796 53	3193.84	17.879	318−367	1.0515[a]
propylene oxide	6.139 33	1086.37	−44.556	254−388	0.8209
water	7.196 21	1730.63	−39.724	273−373	0.9970

[a] Measured by means of a vibrating tube densimeter (model DMA 02 D, Anton Paar).

Table 5. Experimental $P-x$ Data for the System Water (1) + 1,2-Propylene Glycol Diacetate (2) at 358.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	2.036	0.690 75	59.407	0.982 75	59.420
0.016 91	6.137	0.723 77	59.420	0.986 18	59.434
0.034 89	10.236	0.753 52	59.421	0.989 25	59.442
0.052 26	14.011	0.781 13	59.435	0.991 97	59.400
0.069 26	17.490	0.803 17	59.430	0.993 93	59.260
0.085 11	20.630	0.822 75	59.445	0.995 51	59.096
0.100 59	23.513	0.840 69	59.447	0.996 53	58.961
0.115 63	26.243	0.855 32	59.461	0.997 36	58.837
0.130 00	28.706	0.869 64	59.459	0.998 00	58.732
0.143 54	30.947	0.881 37	59.480	0.998 60	58.618
0.161 46	33.726	0.913 92	59.430	0.998 92	58.566
0.177 47	36.107	0.922 08	59.423	0.999 17	58.516
0.205 93	40.024	0.930 39	59.419	0.999 33	58.491
0.243 80	44.813	0.937 16	59.415	0.999 48	58.460
0.284 98	48.877	0.944 03	59.414	0.999 56	58.452
0.333 06	52.715	0.951 02	59.420	0.999 63	58.432
0.384 02	55.949	0.957 40	59.423	0.999 70	58.418
0.441 77	58.496	0.963 50	59.423	0.999 77	58.391
0.501 32	59.375	0.968 97	59.414	0.999 85	58.368
0.559 40	59.391	0.974 50	59.409	0.999 92	58.348
0.612 79	59.392	0.978 98	59.400	1.000 00	58.320
0.654 67	59.395				

Table 6. Experimental H^E Data for the System Water (1) + 1,2-Propylene Glycol Diacetate (2)

323.15 K and 1.55 MPa		363.15 K and 1.27 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0505	408.57	0.0506	453.00
0.0968	766.87	0.0968	821.86
0.1783	1170.2	0.1783	1328.7
0.2480	1427.4	0.2480	1668.3
0.3082	1564.9	0.3082	1883.8
0.4070	1451.7	0.4070	2063.3
0.4847	1272.2	0.4847	2066.4
0.5990	976.92	0.5990	1613.7
0.6791	783.64	0.6791	1308.2
0.7839	518.09	0.7839	887.87
0.8495	352.58	0.8495	624.24
0.8943	241.66	0.8944	449.59
0.9270	159.97	0.9270	317.99
0.9518	97.982	0.9518	222.58
0.9713	49.613	0.9713	144.96
0.9796	30.366	0.9796	111.76

Karl Fischer titration, respectively. The cis/trans isomeric mixture of 1-chloroprepene was composed of a cis/trans ratio of about 75:25 mass %. To obtain the pure isomers, a distillation column with a diameter of 30 mm equipped with 2 m labor packings (model DX ID 30, Sulzer) was used.

Apparatus and Procedures. The vapor pressure and the isothermal $P-x$ data were measured with a computer-driven static apparatus. The experimental procedure for the determination of the VLE data is based on that proposed by Gibbs and Van Ness,[22] where the total pressure P for different overall compositions is measured at constant temperature. The apparatus was described previously[23,24] and can be used at temperatures between 278 and 368 K and pressures up to 0.3 MPa.

The thermostated, purified, and degassed compounds are charged into the VLE cell, which is evacuated and kept in a thermostatic oil bath. The pressure inside the cell is monitored with a Digiquartz pressure sensor (model 245A, Paroscientific), and the temperature is measured with a Pt100 resistance thermometer (model 1506, Hart Scientific). The overall compositions are determined from the known quantities of liquids injected into the equilibrium cell by stepping motor-driven injection pumps and auto-

Table 7. Experimental $P-x$ Data for the System 1,2-Dichloropropane (1) + 1,2-Propylene Glycol Diacetate (2) at 348.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	1.208	0.318 00	15.927	0.867 48	44.819
0.003 85	1.371	0.360 40	18.010	0.892 13	46.152
0.007 72	1.543	0.401 02	20.031	0.912 96	47.274
0.011 91	1.729	0.441 04	22.046	0.931 13	48.247
0.015 54	1.896	0.476 11	23.839	0.950 05	49.250
0.019 71	2.096	0.509 16	25.544	0.965 82	50.079
0.023 50	2.266	0.541 17	27.219	0.976 06	50.607
0.027 34	2.432	0.571 75	28.828	0.983 46	50.985
0.030 90	2.590	0.577 24	29.115	0.987 88	51.203
0.034 89	2.768	0.598 51	30.249	0.991 29	51.377
0.040 65	3.023	0.599 02	30.268	0.993 84	51.498
0.045 86	3.258	0.622 54	31.519	0.995 17	51.557
0.059 60	3.882	0.647 99	32.882	0.996 07	51.609
0.077 22	4.664	0.670 86	34.114	0.997 00	51.650
0.099 18	5.658	0.695 41	35.443	0.997 43	51.672
0.125 56	6.856	0.721 85	36.878	0.997 86	51.694
0.156 83	8.307	0.750 42	38.434	0.998 27	51.715
0.195 23	10.080	0.781 37	40.124	0.998 69	51.740
0.235 63	11.971	0.808 09	41.586	0.999 12	51.765
0.276 70	13.930	0.836 72	43.149	1.000 00	51.812

Table 8. Experimental H^E Data for the System 1,2-Dichloropropane (1) + 1,2-Propylene Glycol Diacetate (2)

323.15 K and 1.41 MPa		363.15 K and 1.55 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0750	−38.417	0.0750	−29.125
0.1462	−72.627	0.1462	−61.698
0.2138	−102.42	0.2138	−87.680
0.2781	−127.38	0.2781	−108.12
0.3394	−147.04	0.3394	−127.54
0.3978	−162.41	0.3978	−146.21
0.4535	−174.16	0.4535	−155.25
0.5068	−181.42	0.5068	−161.74
0.5577	−184.84	0.5577	−166.55
0.6532	−178.44	0.6532	−161.70
0.6980	−171.17	0.6981	−154.41
0.7411	−160.17	0.7411	−147.48
0.7824	−146.12	0.7824	−135.02
0.8222	−129.39	0.8222	−113.77
0.8604	−109.10	0.8604	−97.602
0.8973	−85.999	0.8973	−77.615
0.9327	−61.110	0.9328	−54.703
0.9670	−33.878	0.9670	−27.232

Table 9. Experimental $P-x$ Data for the System *cis/trans*-1-Chloro-1-propene (1) + 1,2-Propylene Glycol Diacetate (2) at 323.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	0.286	0.472 63	82.515	0.871 19	147.69
0.006 62	1.456	0.510 90	88.891	0.895 40	151.68
0.013 60	2.716	0.543 98	94.370	0.915 84	155.08
0.020 89	4.018	0.574 76	99.455	0.933 64	158.08
0.028 03	5.292	0.584 49	101.10	0.952 15	161.23
0.034 97	6.536	0.604 22	104.28	0.967 56	163.88
0.041 09	7.669	0.606 13	104.65	0.977 52	165.62
0.047 72	8.887	0.629 46	108.46	0.984 69	166.87
0.054 40	10.089	0.632 02	108.83	0.988 94	167.62
0.060 70	11.223	0.654 68	112.57	0.992 21	168.17
0.070 38	12.913	0.656 13	112.75	0.994 33	168.54
0.079 52	14.509	0.677 33	116.25	0.995 57	168.75
0.101 87	18.547	0.678 35	116.37	0.996 20	168.86
0.126 95	22.944	0.697 70	119.51	0.996 85	168.95
0.155 21	27.987	0.701 64	120.18	0.997 52	169.06
0.187 07	33.552	0.714 82	122.29	0.998 13	169.17
0.222 86	39.800	0.727 77	124.41	0.998 74	169.28
0.264 18	47.003	0.755 97	128.97	0.999 07	169.30
0.306 92	54.396	0.786 49	133.91	0.999 39	169.36
0.349 66	61.705	0.812 80	138.16	0.999 68	169.40
0.391 33	68.820	0.840 96	142.74	1.000 00	169.45
0.433 18	75.892				

Table 10. Experimental H^E Data for the System *cis/trans*-1-Chloro-1-propene (1) + 1,2-Propylene Glycol Diacetate (2)

323.15 K and 1.45 MPa		363.15 K and 1.48 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0883	39.748	0.0883	40.244
0.1698	73.958	0.1698	65.825
0.2452	99.558	0.2452	85.490
0.3151	118.48	0.3151	101.65
0.3802	132.16	0.3802	111.27
0.4410	140.07	0.4410	117.10
0.4977	145.29	0.4977	117.82
0.5510	146.48	0.5510	116.41
0.6009	143.89	0.6009	112.58
0.6479	140.97	0.6479	108.86
0.6923	133.38	0.6923	101.68
0.7341	124.43	0.7341	94.458
0.7737	112.61	0.7737	84.695
0.8111	99.555	0.8111	75.134
0.8467	86.467	0.8467	63.550
0.8804	71.055	0.8804	51.830
0.9125	54.961	0.9125	38.474
0.9431	38.128	0.9431	25.292
0.9722	18.723	0.9722	11.285

Table 11. Experimental $P-x$ Data for the System 1,2-Dichloropropane (1) + 1,2-Propanediol (2) at 348.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	0.833	0.186 78	41.298	0.733 37	49.582
0.001 76	1.656	0.215 38	43.237	0.772 96	49.697
0.003 46	2.433	0.242 02	44.611	0.811 38	49.812
0.005 15	3.189	0.272 69	45.808	0.847 53	49.954
0.006 85	3.946	0.300 91	46.634	0.876 96	50.095
0.008 57	4.675	0.326 99	47.222	0.901 50	50.257
0.010 33	5.411	0.351 20	47.658	0.921 90	50.445
0.012 08	6.129	0.373 72	47.985	0.937 53	50.665
0.013 89	6.859	0.398 68	48.281	0.949 82	50.901
0.015 65	7.558	0.415 23	48.377	0.957 92	51.040
0.017 36	8.245	0.421 70	48.506	0.962 31	51.116
0.020 08	9.270	0.442 19	48.577	0.966 01	51.194
0.025 38	11.238	0.443 02	48.686	0.969 92	51.281
0.031 57	13.441	0.472 95	48.760	0.973 89	51.373
0.040 89	16.456	0.504 98	48.922	0.978 07	51.474
0.052 70	19.971	0.537 93	49.054	0.982 16	51.597
0.069 80	24.407	0.572 67	49.164	0.986 59	51.744
0.089 86	28.794	0.612 25	49.290	0.991 05	51.871
0.109 13	32.288	0.652 15	49.380	0.995 45	52.021
0.130 89	35.527	0.693 49	49.484	1.000 00	52.164
0.155 98	38.511				

Table 12. Experimental H^E Data for the System 1,2-Dichloropropane (1) + 1,2-Propanediol (2)

323.15 K and 1.27 MPa		363.15 K and 1.34 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0190	62.246	0.0190	110.04
0.0382	152.07	0.0382	234.01
0.0773	324.72	0.0773	485.86
0.1174	485.67	0.1174	712.96
0.1585	632.60	0.1586	917.82
0.2008	760.68	0.2008	1099.7
0.2441	870.38	0.2442	1260.0
0.2887	961.89	0.2887	1412.0
0.3344	1028.0	0.3344	1536.0
0.3814	1074.6	0.3815	1636.1
0.4298	1111.9	0.4298	1713.3
0.4795	1120.0	0.4795	1776.3
0.5306	1121.0	0.5307	1812.3
0.5833	1113.8	0.5833	1824.4
0.6375	1088.2	0.6375	1813.1
0.6933	1057.9	0.6934	1766.9
0.7509	1013.8	0.7509	1695.0
0.8103	945.06	0.8103	1563.1
0.8715	837.97	0.8715	1344.3
0.9347	654.13	0.9347	952.86
0.9671	471.91	0.9671	569.16

Table 13. Experimental $P-x$ Data for the System *cis/trans*-1-Chloro-1-propene (1) + 1,2-Propanediol (2) at 338.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	0.621	0.155 34	198.54	0.942 76	258.89
0.006 67	14.753	0.187 36	217.30	0.960 02	259.17
0.011 35	23.848	0.221 87	232.18	0.972 57	259.66
0.016 09	32.585	0.257 88	243.05	0.980 08	260.46
0.020 69	40.878	0.294 27	250.38	0.985 89	261.92
0.025 22	48.781	0.332 61	255.16	0.989 81	262.60
0.029 79	56.562	0.370 08	257.17	0.992 04	263.06
0.034 26	64.049	0.407 63	257.52	0.992 95	263.25
0.038 49	71.098	0.440 90	257.82	0.993 82	263.41
0.042 89	78.136	0.472 84	258.30	0.994 66	263.55
0.048 45	86.624	0.504 15	258.80	0.995 49	263.70
0.054 19	95.023	0.789 05	258.76	0.996 40	263.78
0.068 03	113.79	0.825 60	258.69	0.997 25	264.03
0.084 15	134.08	0.857 48	258.69	0.998 20	264.15
0.104 13	155.85	0.886 07	258.71	1.000 00	264.27
0.127 55	177.54	0.916 67	258.73		

Table 14. Experimental H^E Data for the System *cis/trans*-1-Chloro-1-propene (1) + 1,2-Propanediol (2)

323.15 K and 1.14 MPa		363.15 K and 1.34 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0448	121.00	0.0448	196.96
0.0901	249.43	0.0901	390.35
0.1359	362.67	0.1359	559.76
0.1822	460.35	0.1822	731.29
0.2290	539.85	0.2290	870.98
0.2763	593.35	0.2763	982.47
0.3242	582.06	0.3242	1065.1
0.3726	560.85	0.3727	1154.5
0.4216	534.46	0.6233	1207.1
0.4712	516.14	0.6752	1152.4
0.5213	491.06	0.7277	1105.8
0.5720	465.42	0.7809	1045.6
0.6233	436.83	0.8347	950.77
0.6752	407.88	0.8891	819.21
0.7277	379.81	0.9442	580.75
0.7809	351.54	0.9720	459.55
0.8347	320.57		
0.8891	286.17		
0.9442	251.19		
0.9720	170.57		

Table 15. Experimental $P-x$ Data for the System *cis/trans*-1-Chloro-1-propene (1) + 1,2-Dichloropropane (2) at 338.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	36.450	0.235 01	90.902	0.819 34	220.50
0.005 68	37.831	0.269 24	98.625	0.859 90	229.58
0.010 79	39.050	0.303 79	106.37	0.892 76	237.01
0.016 29	40.380	0.339 53	114.39	0.919 81	243.23
0.021 23	41.570	0.374 58	122.24	0.941 90	248.24
0.026 61	42.847	0.409 67	130.12	0.958 19	251.99
0.031 87	44.085	0.441 09	137.18	0.970 17	254.78
0.036 95	45.268	0.454 82	140.58	0.978 26	256.63
0.041 71	46.381	0.471 09	143.99	0.982 33	257.57
0.047 06	47.634	0.487 92	147.80	0.984 32	258.02
0.053 01	49.047	0.500 78	150.74	0.986 24	258.44
0.058 91	50.449	0.522 24	155.28	0.988 20	258.89
0.076 62	54.528	0.558 77	163.21	0.990 18	259.34
0.095 84	59.037	0.600 90	172.39	0.992 17	259.78
0.116 78	63.856	0.643 83	181.77	0.994 11	260.25
0.141 76	69.614	0.688 79	191.61	0.996 07	260.69
0.169 58	75.994	0.732 55	201.22	0.998 04	261.12
0.201 77	83.330	0.776 46	210.69	1.000 00	261.57

Table 16. Experimental H^E Data for the System *cis/trans*-1-Chloro-1-propene (1) + 1,2-Dichloropropane (2)

323.15 K and 1.27 MPa		363.15 K and 1.28 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0296	11.865	0.0589	11.530
0.0589	26.951	0.1166	17.228
0.1166	47.395	0.1166	21.811
0.1733	64.554	0.1733	25.249
0.2290	80.456	0.1733	30.045
0.2837	93.359	0.2290	33.911
0.3374	104.17	0.2290	36.194
0.3902	108.32	0.2837	40.287
0.4420	110.43	0.2837	41.179
0.4930	112.34	0.3374	45.297
0.5430	112.38	0.3374	43.838
0.5922	108.71	0.3902	47.510
0.6406	103.17	0.3902	45.498
0.6882	95.981	0.4420	46.242
0.7349	88.901	0.4420	44.233
0.7809	79.013	0.4929	41.732
0.8262	66.261	0.5430	38.659
0.8707	51.285	0.5922	33.406
0.9145	35.951	0.6406	27.037
0.9576	19.467	0.6881	28.176
0.9789	8.802	0.6882	21.711
		0.7349	22.368
		0.7809	15.711
		0.8262	10.557
		0.8262	9.763
		0.8707	10.099
		0.9145	6.575
		0.9576	2.838
		0.9576	2.428

Table 17. Experimental $P-x$ Data for the System *cis*-1-Chloro-1-propene (1) + Propylene Oxide (2) at 313.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	124.89	0.288 02	128.35	0.738 78	132.54
0.000 84	124.91	0.324 97	128.74	0.783 72	132.90
0.001 62	124.92	0.358 22	129.09	0.821 15	133.19
0.003 53	124.95	0.390 63	129.43	0.853 71	133.43
0.005 53	124.96	0.422 92	129.76	0.882 90	133.65
0.009 56	125.01	0.441 42	129.88	0.914 19	133.87
0.013 39	125.06	0.454 64	130.07	0.940 83	134.05
0.019 26	125.14	0.469 60	130.15	0.959 87	134.17
0.024 70	125.20	0.484 70	130.36	0.972 49	134.25
0.034 53	125.32	0.496 74	130.41	0.979 82	134.30
0.049 14	125.51	0.511 62	130.62	0.984 88	134.34
0.067 14	125.74	0.527 21	130.70	0.988 70	134.36
0.089 56	126.02	0.539 10	130.87	0.992 42	134.38
0.117 96	126.38	0.555 59	130.96	0.994 89	134.40
0.148 76	126.75	0.587 27	131.25	0.996 93	134.41
0.181 47	127.14	0.622 74	131.56	0.998 46	134.42
0.215 52	127.54	0.662 78	131.91	0.999 43	134.43
0.252 05	127.95	0.698 74	132.21	1.000 00	134.46

Table 18. Experimental H^E Data for the System *cis*-1-Chloro-1-propene (1) + Propylene Oxide (2)

303.15 K and 1.41 MPa		323.15 K and 1.41 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.1091	−23.362	0.1091	−17.805
0.2223	−42.783	0.2223	−34.057
0.4617	−72.750	0.4617	−55.027
0.7201	−64.120	0.7201	−50.335
0.8572	−38.367	0.8572	−31.822

matic valves. The liquid-phase composition is obtained by solving mass and volume balance equations which also account for the VLE. At the low system pressure of this investigation, the calculated liquid-phase compositions are identical to the feed compositions within ±0.005. The experimental uncertainties of this apparatus are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa + 0.0001 (P/Pa), and $\sigma(x_i) = 0.0001$.

The commercial isothermal flow calorimeter (model 7501, Hart Scientific) used for the determination of the H^E data was described previously by Gmehling.[25] In this apparatus,

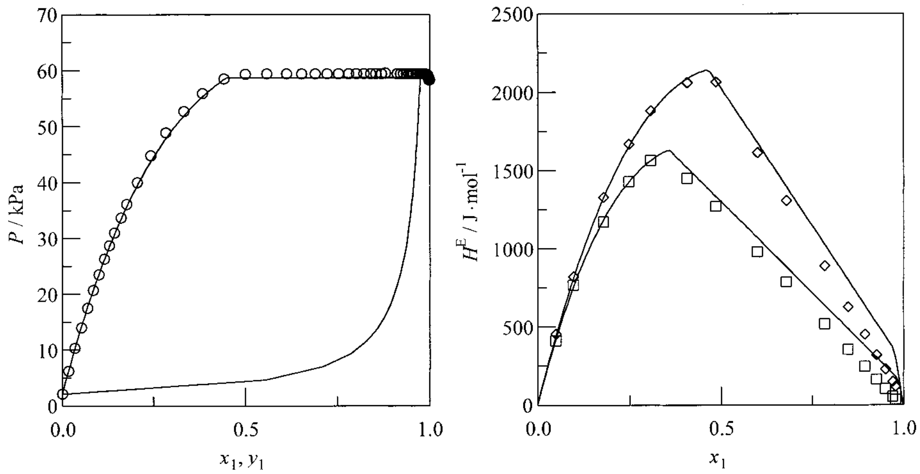

Figure 2. Experimental and calculated $P-x(y)$ and excess enthalpy data for the system water (1) + 1,2-propylene glycol diacetate (2): experimental VLE data at 358.15 K (○); experimental H^E data at 323.15 K (□) and 363.15 K (◊); NRTL (—).

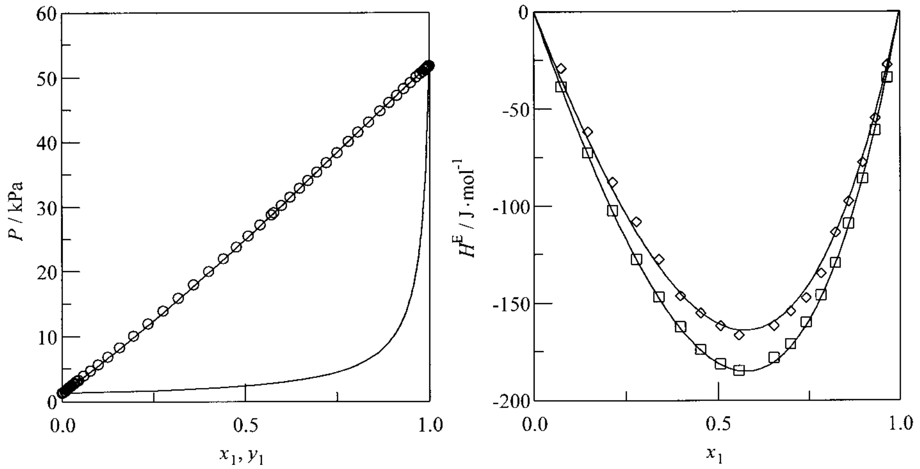

Figure 3. Experimental and calculated $P-x(y)$ and excess enthalpy data for the system 1,2-dichloropropane (1) + 1,2-propylene glycol diacetate (2): experimental VLE data at 348.15 K (○); experimental H^E data at 323.15 K (□) and 363.15 K (◊); NRTL (—).

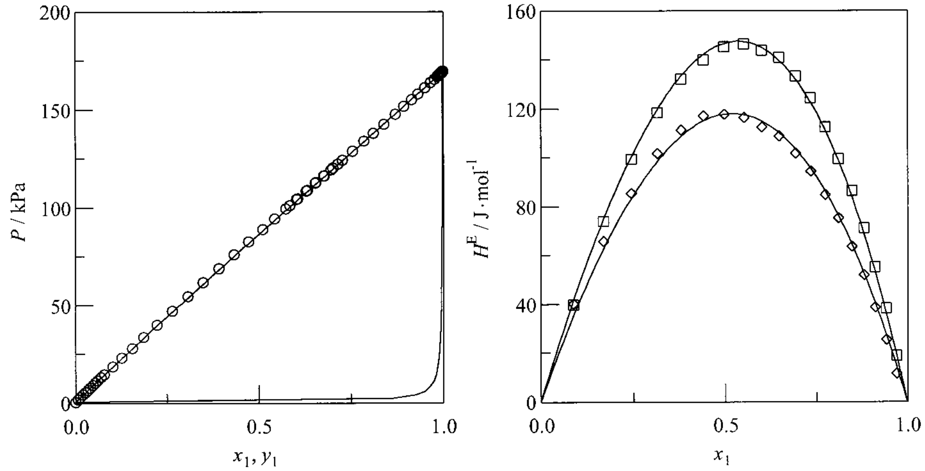

Figure 4. Experimental and calculated $P-x(y)$ and excess enthalpy data for the system *cis*/*trans*-1-chloropropene (1) + 1,2-propylene glycol diacetate (2): experimental VLE data at 323.15 K (○); experimental H^E data at 323.15 K (□) and 363.15 K (◊); NRTL (—).

two syringe pumps (model LC-2600, ISCO) provide a flow of constant composition through a thermostated calorimeter cell equipped with a pulsed heater and a Peltier cooler. The Peltier cooler is working at constant power, producing a constant heat loss from the calorimeter cell. This arrangement allows measurement of endothermal as well as exothermal heat effects. A back-pressure regulator serves to keep the pressure at a level at which evaporation and degassing effects can be prevented. The experimental uncertainties of this device are as follows: $\sigma(T) = 0.03$ K, $\sigma(H^E) = 2$ J·mol^{-1} + 0.01 (H^E/J·mol^{-1}), and $\sigma(x_i) = 0.0001$.

Results

For the components *cis*-1-chloropropene, *trans*-1-chloropropene, and 1,2-propylene glycol diacetate, the Antoine equation with the constants A_i, B_i, and C_i

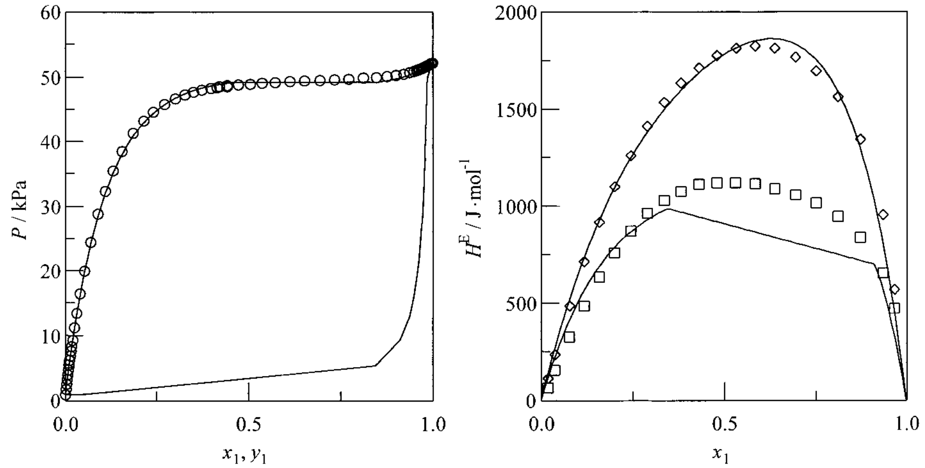

Figure 5. Experimental and calculated $P-x(y)$ and excess enthalpy data for the system 1,2-dichloropropane (1) + 1,2-propanediol (2): experimental VLE data at 348.15 K (○); experimental H^E data at 323.15 K (□) and 363.15 K (◇); NRTL (—).

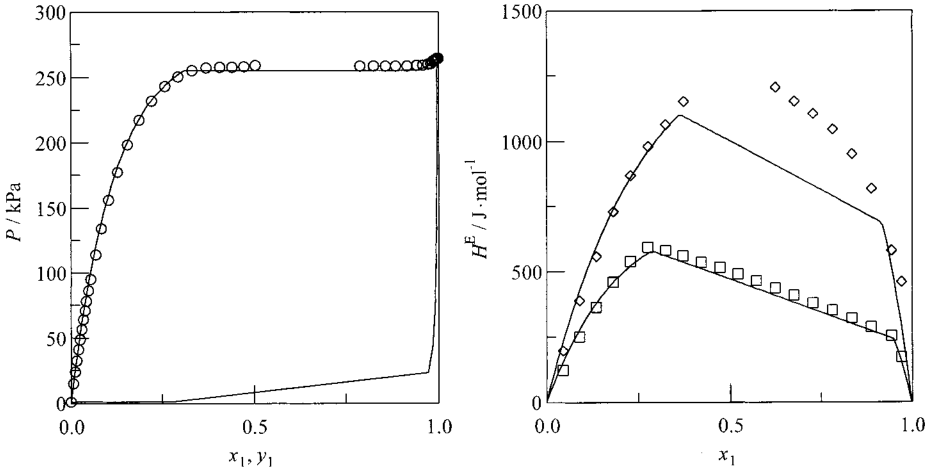

Figure 6. Experimental and calculated $P-x(y)$ and excess enthalpy data for the system *cis/trans*-1-chloropropene (1) + 1,2-propanediol (2): experimental VLE data at 338.15 K (○); experimental H^E data at 323.15 K (□) and 363.15 K (◇); NRTL (—).

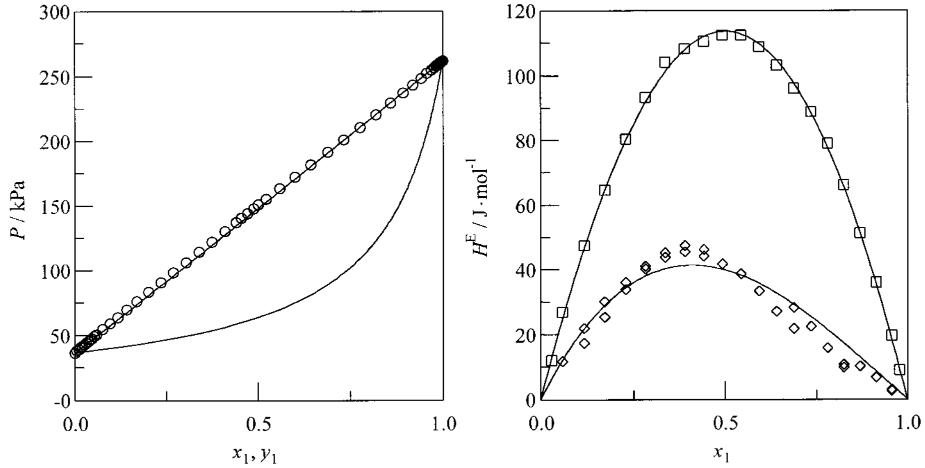

Figure 7. Experimental and calculated $P-x(y)$ and excess enthalpy data for the system *cis/trans*-1-chloropropene (1) + 1,2-dichloropropane (2): experimental VLE data at 338.15 K (○); experimental H^E data at 323.15 K (□) and 363.15 K (◇); NRTL (—).

$$\log(P_i^{s}/\mathrm{kPa}) = A_i - \frac{B_i}{C_i + T/\mathrm{K}} \qquad (2)$$

was fitted to the experimental vapor pressures (Tables 1−3). The results are graphically shown in Figure 1. For the other components, the coefficients stored in the Dortmund Data Bank (DDB) were used for the calculations. The constants for all components are given in Table 4 together with the liquid density at 298.15 K, which was also taken from the DDB or measured using a vibrating tube densimeter (model DMA 02 D, Anton Paar).

The experimental $P-x$ and H^E data for the investigated systems are listed in Tables 5−20. For all systems the data were correlated simultaneously to obtain temperature-

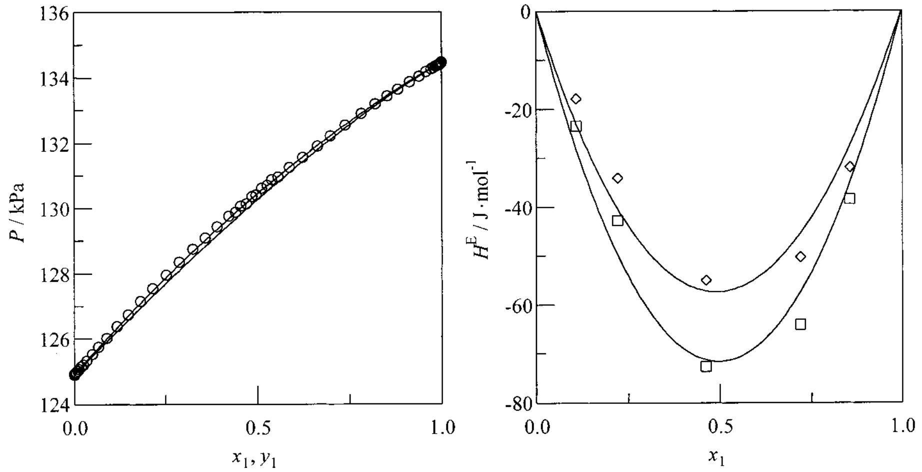

Figure 8. Experimental and calculated $P-x(y)$ and excess enthalpy data for the system *cis*-1-chloropropene (1) + propylene oxide (2): experimental VLE data at 313.15 K (○); experimental H^E data at 303.15 K (□) and 323.15 K (◇); NRTL (—).

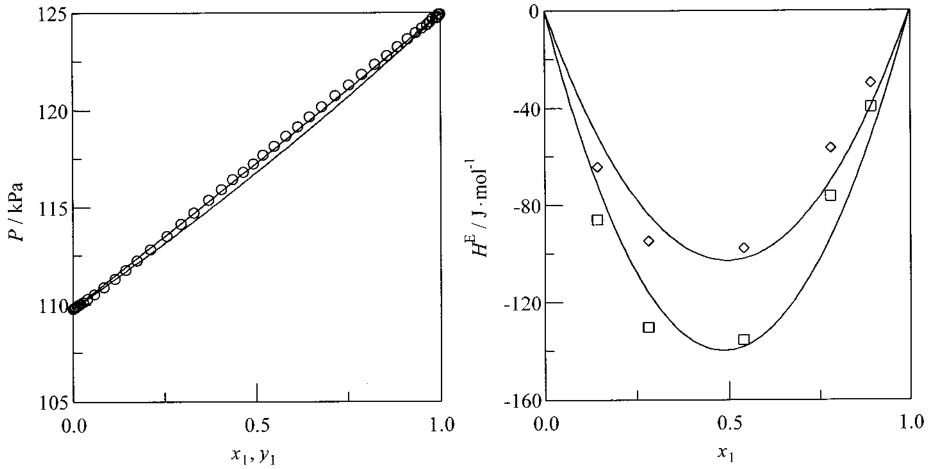

Figure 9. Experimental and calculated $P-x(y)$ and excess enthalpy data for the system propylene oxide (1) + *trans*-1-chloropropene (2): experimental VLE data at 313.15 K (○); experimental H^E data at 303.15 K (□) and 323.15 K (◇); NRTL (—).

Table 19. Experimental $P-x$ Data for the System Propylene Oxide (1) + *trans*-1-Chloro-1-propene (2) at 313.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	109.76	0.256 52	113.52	0.789 87	121.84
0.000 93	109.77	0.295 65	114.15	0.823 69	122.34
0.001 84	109.79	0.330 78	114.72	0.856 08	122.79
0.002 98	109.80	0.370 12	115.36	0.886 36	123.23
0.004 78	109.83	0.405 14	115.93	0.913 95	123.65
0.007 25	109.85	0.436 48	116.43	0.935 29	123.95
0.011 23	109.91	0.464 78	116.79	0.952 05	124.17
0.015 94	109.96	0.492 47	117.23	0.965 22	124.36
0.020 87	110.02	0.519 61	117.68	0.973 76	124.51
0.028 09	110.11	0.549 89	118.15	0.981 38	124.66
0.041 16	110.28	0.581 84	118.66	0.990 79	124.69
0.058 29	110.51	0.614 34	119.16	0.994 56	124.76
0.084 64	110.87	0.646 95	119.67	0.996 39	124.88
0.115 45	111.31	0.680 41	120.18	0.998 33	124.89
0.144 81	111.76	0.717 49	120.76	0.999 17	124.87
0.176 23	112.24	0.753 67	121.28	1.000 00	124.90
0.212 68	112.83				

Table 20. Experimental H^E Data for the System Propylene Oxide (1) + *trans*-1-Chloro-1-propene (2)

303.15 K and 1.31 MPa		323.15 K and 1.34 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.1439	−85.983	0.1440	−64.289
0.2818	−130.39	0.2818	−94.556
0.5407	−135.73	0.5407	−97.671
0.7793	−76.429	0.7793	−56.347
0.8918	−39.465	0.8918	−29.653

dependent NRTL[26] interaction parameters. The following expression was used to describe the temperature dependence of the interaction parameters:

$$\Delta g_{ij}/\mathrm{J{\cdot}mol^{-1}} = a_{ij} + b_{ij}(T/\mathrm{K}) + c_{ij}(T/\mathrm{K})^2 \qquad (3)$$

The fitted parameters are given in Table 21. In the regression procedure, the coefficient A_i of the Antoine equation was adjusted to the experimental vapor pressures in order to eliminate systematic experimental errors for the calculation of the required excess Gibbs energies. The experimental data are presented in Figures 2−9 together with the values calculated by the NRTL model. For most of the systems, an excellent agreement between experimental and calculated values was achieved. The systems 1,2 dichloropropane + 1,2-propylene glycol diacetate (Figure 3), cis/*trans*-1-chloropropene + 1,2-propylene glycol diacetate (Figure 4), cis/*trans*-1-chloropropene + 1,2 dichloropropane (Figure 7), *cis*-1-chloropropene + propylene oxide (Figure 8), and propylene oxide + *trans*-1-chloropropene (Figure 9) show nearly ideal behavior (Raoult's law), and only small values for the heats of mixing (<200 J·mol^{-1}) are observed. Small deviations between the experiments and calculations may occur when liquid−liquid demixing is described. For the system 1,2-dichloropropane + 1,2-propanediol (Figure 5), a miscibility gap is calculated at

Table 21. Temperature-Dependent NRTL Interaction Parameters Fitted Simultaneously to Isothermal $P-x$ and H^E Data

component 1	component 2	i	j	a_{ij}/J·mol^{-1}	b_{ij}/J·mol^{-1}·K^{-1}	c_{ij}/J·mol^{-1}·K^{-2}
water	1,2-propylene glycol diacetate	1	2	9051.99	4.3637	
		2	1	10257.37	−24.5235	
				$\alpha_{12} = 0.3610$		
1,2-dichloropropane	1,2-propylene glycol diacetate	1	2	1387.66	−1.6063	
		2	1	−1554.47	0.8105	
				$\alpha_{12} = 0.4700$		
cis/*trans*-1-chloropropene	1,2-propylene glycol diacetate	1	2	2675.09	−8.1715	0.002 536 46
		2	1	−841.48	−0.3133	0.007 849 58
				$\alpha_{12} = 0.4700$		
1,2-dichloropropane	1,2-propanediol	1	2	−1491.59	61.6263	−0.113 287 27
		2	1	6634.61	−8.3330	0.000 352 83
				$\alpha_{12} = 0.4092$		
cis/*trans*-1-chloropropene	1,2-propanediol	1	2	−12472.69	115.3731	−0.166 324 82
		2	1	−1823.14	33.9504	−0.054 600 90
				$\alpha_{12} = 0.3780$		
cis/*trans*-1-chloropropene	1,2-dichloropropane	1	2	3870.72	−3.3565	−0.022 947 35
		2	1	1940.32	−29.7094	0.069 259 30
				$\alpha_{12} = 0.2975$		
cis-1-chloropropene	propylene oxide	1	2	2375.89	−5.9907	
		2	1	−2462.32	6.5163	
				$\alpha_{12} = 0.2000$		
propylene oxide	*trans*-1-chloropropene	1	2	−2622.04	7.3015	
		2	1	2452.20	−6.7128	
				$\alpha_{12} = 0.4700$		

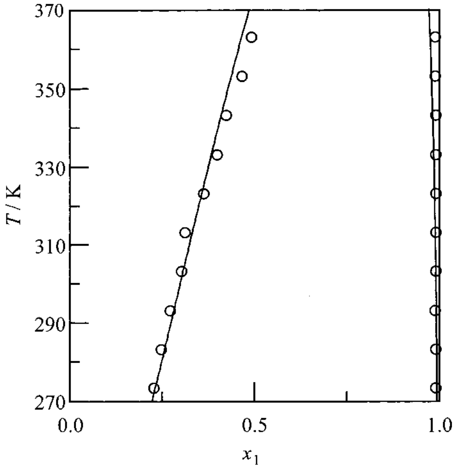

Figure 10. Experimental and predicted LLE behavior of the system water (1) + 1,2-propylene glycol diacetate (2): experimental data of Stephenson[20] (○); NRTL (—).

323 and 348 K, although the experimental data indicate a homogeneous mixture over the entire concentration range. For the system cis/*trans*-1-chloropropene + 1,2-propanediol (Figure 6), a miscibility gap is calculated at 323 K, which is in agreement with the experimental data. However, at higher temperature the calculated miscibility gap is larger than observed experimentally. For the system water (1) + 1,2-propylene glycol diacetate (2), liquid−liquid equilibrium (LLE) data are available in the literature. They are shown in Figure 10 together with the results using the fitted NRTL parameters. The LLE behavior is also indicated by the VLE and H^E data (Figure 2) measured in this work. This system exhibits heteroazeotropic behavior. From the experimental $P-x$ data at 358.15 K, the azeotropic conditions were derived to $y_{1,\text{az}} = 0.974$ and $P_{\text{az}} = 59.41$ kPa using a flexible Legendre polynomial.[27]

Conclusions

$P-x$, vapor pressure, and H^E data were measured by means of a static VLE apparatus and a flow calorimeter, respectively. From these data, temperature-dependent NRTL interaction parameters were established. As can be seen from the different diagrams, good agreement between experimental and calculated values is obtained. The comparison with experimental data from the literature proves the reliability of the data measured in this work. Because of these results, the parameters given in Table 21 can be recommended to be used for the simulation of the separation steps in the chlorohydrin process for propylene oxide production.

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Literature Cited

(1) Amaya, K.; Fujishiro, R. Heat of Mixing of Mono- and Dipropylene Glycol with Water. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 940−943.

(2) Bougard, J.; Jadot, R. Thermodynamic Study of Some Binary Systems. *Proceedings of 2nd World Congress of Chemical Engineering*, Montreal, 1981; pp 93−100.

(3) Chu, L. T.; Hirsch, W.; Fried, V. Isothermal Vapor−Liquid Equilibria for the Water + 1,2-Propanediol System. *AIChE Symp. Ser.* **1989**, *271*, 6−10.

(4) Cui, Z.; Li, Z.; Gao, Z.; Zhang, R.; Li, J. Vapor−Liquid Equilibrium for Water−1,2-Propanediol Binary System at 101.325 kPa. *J. Chem. Eng. Chin. Univ.* **1994**, *8*, 374−378.

(5) Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. *Azeotropic Data*; VCH: Weinheim, Germany, 1994.

(6) Gross, P. M. The Determination of the Solubility of Slightly Soluble Liquids in Water and the Solubilities of the Dichloroethanes and -propanes. *J. Am. Chem. Soc.* **1929**, *51*, 2362−2366.

(7) Jelinek, K.; Lesek, F.; Sivokova, M. Vapor−Liquid Equilibrium in Binary Water−1,2 Propylene Glycol, Water−Diethylene Glycol and Water−1,4-Butanediol Systems. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2650−2656.

(8) Jones, W. F.; Tamplin, W. F. Physical Properties of Propylene Glycol. In *Glycols*; Curme, G. O., Johnston, F., Eds.; Reinhold: New York, 1952; pp 210−240.

(9) Kolodziej, E. J.; Jin, Z.-L.; Greenkorn, R. A. Vapor−Liquid Equilibrium in Binary Mixtures of Propylene Oxide with 1,2-Dichloropropane and with *tert*-Butanol. *AIChE Symp. Ser.* **1985**, *81*, 80−85.

(10) Kracht, C.; Ulbig, P.; Schulz, S. Measurement and Correlation of Excess Molar Enthalpies for (Ethanediol, or 1,2-Propanediol, or 1,2-Butanediol + Water) at the Temperatures (285.65, 298.15, 308.15, 323.15, and 338.15) K. *J. Chem. Thermodyn.* **1999**, *31*, 1113−1127.

(11) Lecat, M. *Tables Azeotropiques*, 2nd ed.; Monograph l'auteur: Bruxelles, 1949.

(12) Matsumoto, Y.; Touhara, H.; Nakanishi, K.; Watanabe, N. Molar Excess Enthalpies for Water + Ethanediol, + 1,2-Propanediol, and + 1,3-Propanediol at 298.15 K. *J. Chem. Thermodyn.* **1977**, *9*, 801−805.

(13) Morcom, K. W.; Smith, R. W. Thermodynamic Study of Water and Propylene Oxide Solutions. *J. Chem. Eng. Data* **1971**, *16*, 197−200.

(14) Sokolov, N. M.; Tsygankova, L. N.; Zhavoronkov, N. M. The Liquid−Vapor Equilibrium in the Water−Ethylene Glycol and Water−1,2-Proylene Glycol Systems at Various Pressures. *Teor. Osn. Khim. Tekhnol.* **1971**, *5*, 900−904.

(15) Srinivasa, B.; Parande, M. G.; Naik, R. V. Liquid−Liquid Equilibrium for the Propylene Oxide + Water + Propylene Dichloride System. *J. Chem. Eng. Data* **1995**, *40*, 927−930.

(16) Stephenson, R. M. Mutual Solubilities: Water−Ketones, Water−Ethers and Water−Gasoline−Alcohols. *J. Chem. Eng. Data* **1992**, *37*, 80−95.

(17) Verlinde, J. R.; Verbeeck, R. M. H.; Thun, H. P. Density and Vapour Pressure of the Propylene Glycol−Water System from 15 to 50 °C. *Bull. Soc. Chim. Belg.* **1975**, *84*, 1119−1130.

(18) Wickert, J. N.; Tamplin, W. S.; Shank R. L. Phase Equilibria in the System Propylene Oxide−Water. *Chem. Eng. Prog. Symp. Ser.* **1952**, *48*, 92−96.

(19) Wilson, L. C.; Wilding, W. V.; Wilson, G. M. Vapor−Liquid Equilibrium Measurements on Four Binary Mixtures. *AIChE Symp. Ser.* **1989**, *271*, 25−43.

(20) Stephenson, R. M. Mutual Solubilities: Water−Glycol Ethers and Water−Glycol Esters. *J. Chem. Eng. Data* **1993**, *38*, 134−138.

(21) Fischer, K.; Gmehling, J. $P-x$ and γ^{∞} Data for the Different Binary Butanol−Water Systems at 50 °C. *J. Chem. Eng. Data* **1994**, *39*, 309−315.

(22) Gibbs, R. E.; Van Ness, H. C. Vapor−Liquid Equilibria from Total-Pressure Measurements. A New Apparatus. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 410−413.

(23) Rarey, J.; Gmehling, J. Computer-Operated Differential Static Apparatus for the Measurement of Vapor−Liquid Equilibrium Data. *Fluid Phase Equilib.* **1993**, *83*, 279−287.

(24) Horstmann, S.; Gardeler, H.; Bölts, R.; Zudkevitch, D.; Gmehling, J. Vapor−Liquid Equilibria and Excess Enthalpy Data for the Binary Systems 2-Methyltetrahydrofuran with 2,2,4-Trimethylpentane (Isooctane), Ethanol, Toluene, Cyclohexane and Methylcyclohexane. *J. Chem. Eng. Data* **1999**, *44*, 959−964.

(25) Gmehling, J. Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters. *J. Chem. Eng. Data* **1993**, *38*, 143−146.

(26) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

(27) Kolbe, B. Description of the Thermodynamic Properties of Liquid Mixtures Over a Wide Temperature and Pressure Range on the Example of the System Ethanol/Water. Dissertation, University of Dortmund, Dortmund, Germany, 1983.

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