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Vapor−Liquid Equilibria in Binary Systems Formed by Cyclohexane with Alcohols

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The modified Świętosławski ebulliometer was used for the accurate determination of vapor−liquid equilibria in binary isothermal systems formed by cyclohexane with: 2-butanol at 313.15 K, 323.15 K, 333.15 K, and 343.15 K, 2-pentanol at 333.15 K, 343.15 K, and 353.15 K, 2-methyl-2-butanol at 313.15 K, 323.15 K, 333.15 K, and 343.15 K, and 1-hexanol at 323.15 K, 333.15 K, 343.15 K, and 353.15 K. The vapor pressures of the pure substances are also given. The experimental data have been compared with literature data (if available) of those systems and correlated by means of the Redlich−Kister, NRTL, and Wilson equations.

Introduction

Reliable and accurate vapor−liquid equilibrium (VLE) data are always needed for both better understanding of the behavior of liquid mixtures and process engineering design. The literature data are not always consistent and are usually measured only at one or two different pressures (isobaric data) or temperatures (isothermal data). For many systems, there are simply the lack of the experimental data.

This work is a part of a big project concerning accurate measurement of binary isothermal VLE data for systems formed by hydrocarbons (aliphatic, cyclic, aromatic) and organic compounds containing oxygen, nitrogen, and sulfur. The aim of the project is to deliver very reliable, accurate VLE isothermal data at many different temperatures for systems which are not available in the literature as well as systems for which only one or two isotherms were measured or measured VLE are not reliable (small number of experimental points, lack of information about the purity of pure components, inconsistent data).

The purpose of this paper is to provide reliable and accurate binary VLE data for systems formed by cyclohexane with the following alcohols:
(a) 2-butanol at 313.15 K, 323.15 K, 333.15 K, and 343.15 K;
(b) 2-pentanol at 333.15 K, 343.15 K, and 353.15 K;
(c) 2-methyl-2-butanol at 313.15 K, 323.15 K, 333.15 K, and 343.15 K;
(d) 1-hexanol at 323.15 K, 333.15 K, 343.15 K, and 353.15 K.

Nineteen VLE data for the cyclohexane + 2-butanol system have already been reported in the literature. The main sources[1−4] consist both of isobaric (from (8 to 101) kPa) and of isothermal [(323.15 to 372.15) K] data. Much less (only two publications[5,6]) VLE data can be found for the cyclohexane + 2-methyl-2-butanol system, and the VLE for the cyclohexane + 1-hexanol system have been measured only in one laboratory by Svoboda et al.[7] In the literature, there are the lack of VLE data for the cyclohexane + 2-pentanol system.

Experimental Section

The modified Świętosławski ebulliometer[8] was used for determination of both VLE data of all investigated binary systems and the boiling points of the pure components. The selection of the method for VLE measurement was imposed by the physical properties of the mixtures investigated. First, the pure components were highly hygroscopic and even a small amount of water present in the sample could change considerably the results of the vapor pressure measurements. Second, the differences between the boiling temperatures of cyclohexane and other components of the investigated mixtures were big, and consequently the values of relative volatilities were high. Third, the experimental program was extensive, and due to this the method chosen should provide accurate results in a relatively short time. Moreover, the selected ebulliometric method has some other following advantages:[8]
(a) it enables accurate determination of total pressure above the samples of known composition;
(b) the measurement can be isolated from the surroundings to prevent the penetration of moisture into the sample being investigated;
(c) the time for achieving a steady state operation is short.

Since using the ebulliometer requires rapid, reliable, and accurate methods for determining pressure and temperature, in our ebulliometer system, the Systemteknik AB Temperature Meter type S1228 was used for determination of the temperature and Pfeiffer vacuum manometer TPG 251A for measurement

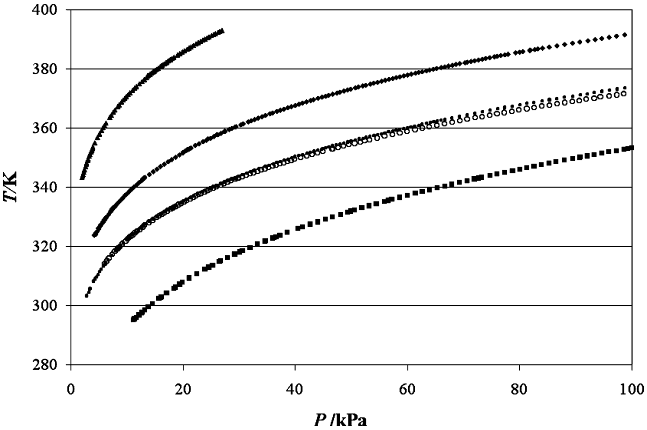

Figure 1. Experimental $T-P$ data of the all pure components investigated. ■, cyclohexane; ○, 2-butanol; ◆, 2-pentanol; ●, 2-methyl-2-butanol; ▲, 1-hexanol.

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Table 1. Experimantal $P-T$ Data for Pure Cyclohexane, 2-Butanol, 2-Pentanol, 2-Methyl-2-butanol, and 1-Hexanol

experimental data																	
P/(kPa)	T/(K)	P/(kPa)	T/(K)	P/(kPa)	T/(K)	P/(kPa)	T/(K)	P/(kPa)	T/(K)	P/(kPa)	T/(K)	P/(kPa)	T/(K)	P/(kPa)	T/(K)	P/(kPa)	T/(K)
cyclohexane																	
11.15	295.42	22.47	310.98	46.59	330.05	72.6	343.15	13.81	299.77	34.69	321.99	58.63	336.7	87.93	349.19		
11.16	295.45	23.89	312.48	48.07	330.94	73.25	343.43	14.52	300.85	35.95	322.94	59.96	337.36	89.43	349.72		
11.17	295.46	24.56	313.15	49.32	331.68	74.73	344.05	15.71	302.63	36.27	323.15	61.39	338.06	90.64	350.18		
11.33	295.72	25.25	313.84	49.89	332.02	75.96	344.55	16.03	303.03	36.59	323.44	61.4	338.07	90.87	350.25		
11.35	295.75	26.47	315.01	50.6	332.41	77.27	345.09	16.11	303.15	37.23	323.89	62.63	338.66	92.07	350.67		
11.63	296.22	26.67	315.26	51.87	333.11	78.76	345.69	17.04	304.38	37.33	323.95	62.64	338.67	93.27	351.1		
12.15	297.08	27.88	316.32	51.92	333.15	80	346.18	17.05	304.4	38.56	324.83	63.95	339.29	94.63	351.57		
12.16	297.13	29.23	317.52	53.15	333.83	81.25	346.67	17.07	304.42	40.45	326.13	65.29	339.92	95.92	352.01		
12.17	297.14	30.09	318.32	53.19	333.86	82.56	347.18	18.33	306.05	41.25	326.68	66.63	340.54	97.23	352.45		
12.61	297.86	30.56	318.67	54.47	334.53	82.57	347.18	18.60	306.4	42.68	327.61	67.95	341.12	98.57	352.91		
12.71	297.99	31.93	319.82	55.85	335.27	83.89	347.69	19.40	307.45	43.97	328.43	69.29	341.72	99.31	353.15		
13.23	298.84	33.27	320.87	56.56	335.64	85.23	348.19	19.91	308.06	45.4	329.33	70.65	342.32	99.95	353.36		
13.8	299.75	34.59	321.91	57.19	335.96	86.49	348.66	21.12	309.5	45.43	329.35	71.93	342.88				
2-butanol																	
6.08	314.47	18.68	333.65	35.32	346.86	63.97	360.61	11.84	325.27	26.79	340.95	47.65	353.60	84.03	367.47		
6.43	315.36	19.24	334.23	36.01	347.28	65.29	361.10	12.31	325.92	27.36	341.40	48.61	354.06	85.39	367.89		
6.81	316.21	19.71	334.69	36.63	347.65	66.71	361.64	12.81	326.66	27.99	341.87	49.61	354.53	86.71	368.27		
7.45	317.61	20.20	335.19	37.31	348.06	67.99	362.10	13.16	327.32	28.63	342.34	50.63	355.00	88.05	368.68		
7.92	318.57	20.71	335.69	37.99	348.46	69.43	362.63	14.03	328.28	29.37	342.89	51.63	355.46	89.41	369.08		
8.35	319.37	21.33	336.28	38.64	348.85	70.69	363.08	14.61	329.05	29.76	343.15	52.39	355.81	90.67	369.43		
8.45	319.58	21.85	336.77	39.29	349.21	72.12	363.58	15.31	329.91	29.97	343.32	53.33	356.23	91.91	369.79		
8.77	320.18	22.35	337.23	39.95	349.59	73.36	364.00	15.79	330.49	30.67	343.81	54.63	356.80	93.33	370.20		
9.23	321.05	22.87	337.72	40.97	350.16	74.72	364.48	16.31	331.11	31.31	344.25	55.96	357.37	94.44	370.56		
9.80	322.03	23.28	338.08	42.05	350.75	76.00	364.90	16.71	331.58	31.99	344.71	57.41	357.99	96.00	370.94		
10.19	322.68	23.87	338.60	43.03	351.26	77.31	365.33	17.25	332.17	32.63	345.15	58.67	358.50	97.35	371.32		
10.48	323.15	24.43	339.07	43.96	351.74	78.65	365.76	17.87	332.81	33.33	345.60	60.03	359.06	98.59	371.65		
10.64	323.41	24.95	339.50	44.97	352.27	79.95	366.18	18.20	333.15	33.99	346.03	61.41	359.62				
11.04	324.05	25.43	339.90	46.60	353.09	81.35	366.63	18.33	333.28	34.67	346.46	62.73	360.13				
11.47	324.72	25.97	340.34	46.75	353.15	82.63	367.04										
2-pentanol																	
4.16	323.84	13.99	344.38	34.05	363.85	62.61	379.04	7.52	333.15	23.55	355.42	48.64	372.51	77.35	384.74		
4.39	324.55	14.65	345.27	34.64	364.28	63.39	379.39	7.76	333.36	24.12	355.92	49.31	372.91	77.93	384.95		
4.41	324.20	15.31	346.15	35.47	364.84	63.91	379.60	7.99	333.88	24.44	356.39	49.87	373.16	79.27	385.42		
4.67	325.09	15.96	347.02	35.95	365.13	64.60	379.89	8.33	334.61	24.84	356.55	50.71	373.58	80.00	385.65		
4.89	326.22	16.63	347.80	36.71	365.63	65.20	380.13	8.77	335.52	25.47	357.15	51.25	373.88	80.56	385.87		
4.93	325.99	17.32	348.68	37.32	366.02	65.99	380.47	9.17	336.34	26.00	357.79	52.03	374.25	81.79	386.24		
5.20	327.15	17.95	349.38	37.95	366.40	66.63	380.71	9.19	336.37	26.2	357.76	52.55	374.47	81.88	386.32		
5.27	326.99	18.63	350.16	38.64	366.86	67.31	381.00	9.59	337.20	26.75	358.23	53.37	374.85	82.68	386.54		
5.43	327.64	19.31	350.93	39.31	367.24	68.01	381.26	9.95	337.85	27.32	358.88	53.95	375.15	83.23	386.77		
5.64	328.23	19.96	351.64	39.97	367.65	68.67	381.53	10.43	338.74	27.45	358.83	54.67	375.45	84.05	386.96		
5.71	328.19	20.00	351.88	40.64	368.06	69.31	381.77	10.81	339.44	27.45	359.01	55.37	375.83	85.27	387.37		
5.91	329.05	20.43	352.34	41.27	368.44	70.21	382.08	11.21	340.10	28.19	359.53	56.01	376.13	86.61	387.79		
5.95	329.11	20.65	352.60	41.96	368.85	70.63	382.28	11.67	340.82	28.67	359.91	56.71	376.47	88.00	388.23		
6.04	329.11	20.72	352.70	42.73	369.32	71.31	382.55	12.11	341.54	29.25	360.35	57.36	376.74	89.39	388.66		
6.16	329.66	20.83	352.77	43.23	369.58	71.95	382.78	12.52	342.20	29.41	360.49	58.00	377.07	90.69	389.07		
6.33	329.90	20.96	352.90	44.05	370.05	72.65	383.05	12.77	342.83	30.29	361.13	58.64	377.33	92.16	389.51		
6.71	330.86	21.12	353.05	44.75	370.46	73.35	383.29	12.97	342.88	30.68	361.45	59.32	377.65	93.44	389.90		
7.08	331.78	21.19	353.10	45.40	370.74	73.93	383.53	13.00	343.15	31.59	362.10	59.97	377.91	94.61	390.26		
7.17	332.29	21.20	353.15	45.91	371.08	74.63	383.77	13.07	343.26	32.13	362.49	60.67	378.22	95.95	390.66		
7.31	332.61	21.40	353.35	46.64	371.47	75.48	384.09	13.11	343.30	32.73	362.93	61.40	378.56	97.27	391.05		
7.40	332.55	22.16	354.12	47.45	371.82	75.99	384.26	13.16	343.38	33.35	363.38	61.97	378.81	98.71	391.46		
7.43	332.92	22.83	354.72	47.93	372.15	76.63	384.50										
2-methyl-2-butanol																	
2.81	303.29	17.29	332.46	39.32	350.08	61.27	360.83	8.61	319.86	27.97	342.4	49.95	355.74	78.63	367.53		
2.85	303.47	17.87	333.15	39.96	350.49	61.99	361.11	8.84	320.32	28.67	342.92	50.75	356.09	79.97	368.02		
3.16	304.67	17.99	333.26	40.64	350.83	62.61	361.40	9.36	321.32	28.95	343.15	51.36	356.45	81.28	368.44		
3.40	305.75	18.65	333.99	41.31	351.20	63.35	361.72	9.99	322.44	29.31	343.42	52.00	356.69	82.53	368.83		
3.43	305.90	19.32	334.70	42.08	351.67	64.04	362.01	10.41	323.15	30.01	343.94	52.61	356.99	83.93	369.31		
4.08	308.35	20.03	335.46	42.65	351.95	64.67	362.24	10.49	323.28	30.67	344.47	53.32	357.35	85.28	369.73		
4.31	309.12	20.67	336.05	43.35	352.30	65.35	362.54	11.03	324.11	31.35	344.91	54.03	357.67	86.63	370.15		
4.55	309.86	21.31	336.68	44.00	352.73	66.00	362.84	11.51	324.91	32.07	345.39	54.67	357.96	87.97	370.56		
4.80	310.61	21.96	337.31	44.65	353.02	66.71	363.07	12.03	325.71	32.67	345.78	55.35	358.25	89.39	370.99		
5.15	311.64	22.63	337.97	44.87	353.15	67.92	363.56	12.55	326.45	33.48	346.35	55.95	358.47	90.76	371.39		
5.43	312.47	23.47	338.69	45.35	353.44	69.21	364.15	13.05	327.18	34.67	347.18	56.63	358.85	91.99	371.77		
5.77	313.38	23.97	339.15	45.97	353.73	70.64	364.62	13.36	327.63	35.32	347.57	57.33	359.15	93.31	372.16		
6.08	314.17	24.67	339.68	46.63	354.09	71.99	365.21	13.97	328.41	36.07	348.07	58.00	359.48	94.67	372.56		
6.59	315.44	25.35	340.31	47.28	354.41	73.37	365.73	14.65	329.33	36.71	348.49	58.59	359.68	95.99	372.95		
7.31	317.09	26.00	340.83	47.95	354.72	74.75	366.16	15.31	330.15	37.36	348.88	59.27	360.01	97.39	373.34		
7.99	318.64	26.67	341.39	48.65	355.11	76.05	366.67	15.97	330.98	38.01	349.27	59.95	360.21	98.71	373.73		
8.36	319.37	27.33	341.90	49.31	355.43	77.28	367.11	16.67	331.80	38.64	349.64	60.59	360.53				
1-hexanol																	
2.04	343.46	5.79	360.34	13.53	377.22	19.05	384.87	3.44	351.39	9.67	370.24	16.15	381.15	23.60	389.89		
2.16	344.20	6.04	361.12	13.71	377.83	19.47	385.37	3.64	352.20	9.95	370.83	16.37	381.45	23.95	390.23		
2.23	344.59	6.29	361.86	13.85	378.01	19.91	385.86	3.73	352.64	10.27	371.45	16.71	381.89	24.36	390.65		
2.35	345.36	6.99	363.85	14.15	378.37	20.31	386.32	3.83	353.01	10.59	372.10	16.97	382.25	24.67	390.93		

Table 1.. Continued

experimental data															
P/(kPa)	*T*/(K)	*P*/(kPa)	*T*/(K)	*P*/(kPa)	*T*/(K)	*P*/(kPa)	*T*/(K)	*P*/(kPa)	*T*/(K)	*P*/(kPa)	*T*/(K)	*P*/(kPa)	*T*/(K)	*P*/(kPa)	*T*/(K)
2.47	346.17	7.27	364.61	14.40	378.72	20.79	386.84	3.89	353.32	11.05	373.00	17.21	382.56	25.13	391.40
2.67	347.27	7.64	365.59	14.65	379.10	21.15	387.23	3.96	353.82	11.43	373.67	17.44	382.85	25.51	391.76
2.79	348.10	7.92	366.29	14.91	379.46	21.48	387.63	4.31	355.21	11.73	374.19	17.69	383.18	25.83	392.06
2.85	348.35	8.40	367.45	15.12	379.75	21.91	388.10	4.79	357.02	12.27	375.14	17.84	383.34	26.31	392.51
3.04	349.38	8.67	368.05	15.37	380.06	22.37	388.59	5.15	358.22	12.73	375.93	18.09	383.67	26.59	392.78
3.11	349.75	9.08	368.99	15.61	380.41	22.79	389.05	5.51	359.42	13.15	376.59	18.43	384.08	27.00	393.15
3.32	350.75	9.40	369.67	15.95	380.87	23.20	389.48								

Table 2. Parameters of the Antoine Equation (Equation 5) Together with Calculated (T_b^c) and Literature (NIST, T_b^l) Values of Boiling Points for All Investigated Substances

	Antoine parameters			T_b^c	T_b^l	Δ*T*	rmsd(*P*)
compound	*A*	*B*	*C*	K	K	K	kPa
cyclohexane	5.6641	1033.631	−71.351	353.89	353.9 ± 0.2	−0.01	0.204
2-butanol	5.8479	928.321	−130.917	372.53	372.0 ± 1.0	0.53	0.349
2-pentanol	5.6760	931.131	−139.043	392.74	392.0 ± 1.0	0.74	1.011
2-methyl-2-butanol	5.3203	744.494	−150.173	374.79	375.1 ± 0.9	−0.31	0.563
1-hexanol	5.3941	899.201	−166.275	431.65	430.0 ± 2.0	1.65	0.125

of the total pressure. The accuracy of measurements in the case of the temperature was about 0.01 K (the thermometer resolution, 0.001 K) and in the case of pressure about 10 Pa (the pressure gauge resolution, 1 Pa). Both instruments are subject to drift to obtain the absolute values of temperature and pressure, which is why they were frequently recalibrated by the determination of the vapor pressure of water or benzene as a function of temperature.

The ebulliometric measurements have been carried out in the following ways:

(1) for pure substances: simultaneous determination of pressure, *P*, and temperature, *T*;
(2) for mixtures: simultaneous determination of *P*, *T*, and *x* (*P*, *T*, *x* method).

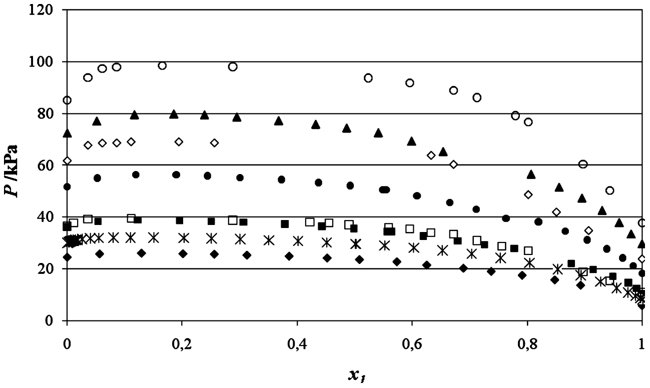

Figure 2. Comparison of the experimental isothermal *P*−*x* data with the literature data for the 2-butanol (1) + cyclohexane (2) system. This work: ♦, *T* = 313.15 K; ■, *T* = 323.15 K; ●, *T* = 333.15 K; ▲, *T* = 343.15 K; *, ref 1, *T* = 318.15 K; □, ref 2, *T* = 323.15 K; ◇, ref 2, *T* = 338.15 K; ○, ref 2, *T* = 348.15 K.

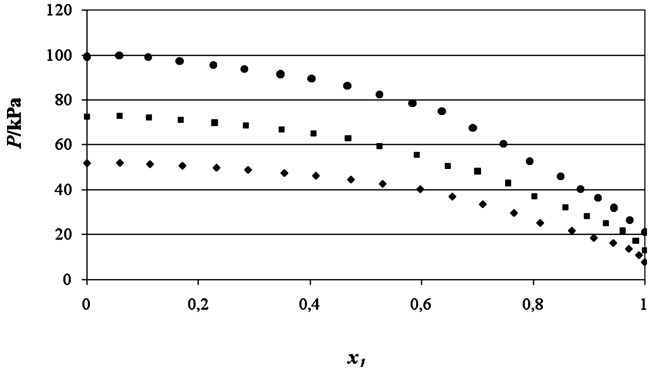

Figure 3. Experimental isothermal *P*−*x* data for the 2-pentanol (1) + cyclohexane (2) system. This work: ♦, *T* = 333.15 K; ■, *T* = 343.15 K; ●, *T* = 353.15 K.

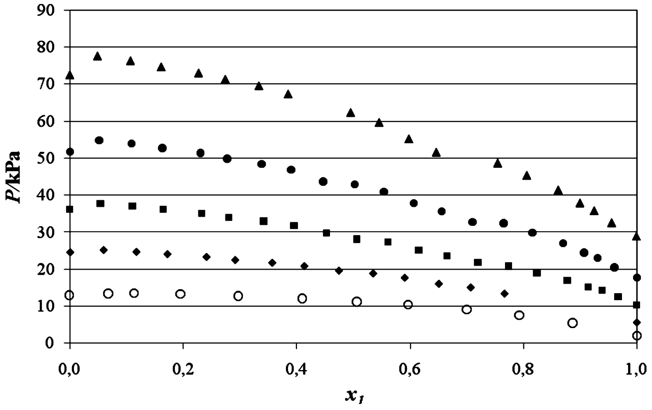

Figure 4. Comparison of the experimental isothermal *P*−*x* data with the literature data for the 2-methyl-2-butanol (1) + cyclohexane (2) system. This work: ♦, *T* = 313.15 K; ■, *T* = 323.15 K; ●, *T* = 333.15 K; ▲, *T* = 343.15 K; ○, ref 6, *T* = 298.15 K.

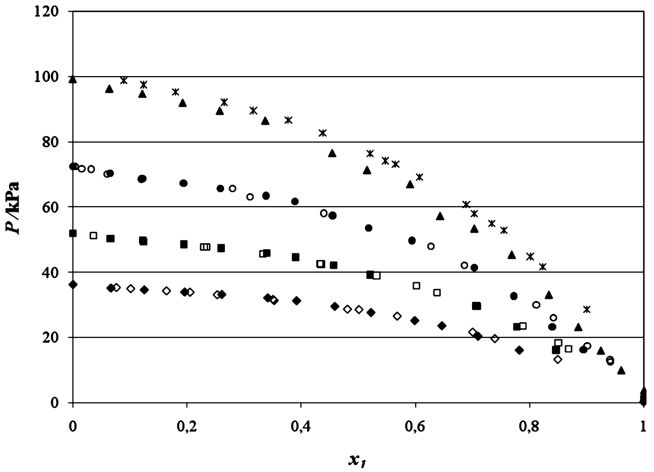

Figure 5. Comparison of the experimental isothermal *P*−*x* data with the literature data for the 2-methyl-2-butanol (1) + cyclohexane (2) system. This work: ♦, *T* = 323.15 K; ■, *T* = 333.15 K; ●, *T* = 343.15 K; ▲, *T* = 353.15 K; ◇, ref 7, *T* = 323.15 K; □, ref 7, *T* = 333.15 K; ○, ref 7, *T* = 343.15 K; *, ref 7, *T* = 354.65 K.

The examined samples were prepared by introducing a known mass of one substance to the ebulliometer and adding known masses of the other component. The equilibrium composition of the liquid phase in the ebulliometer can be calculated from the composition of the introduced sample by means of the material balance equation.[8] For one mole of the sample, the liquid, L, and vapor, V, streams leaving the equilibrium chamber fulfill the equation

$$V + L = 1 \tag{1}$$

The mole fraction of component i in the sample, q_i, is related to the mole fraction of this component in the liquid phase, x_i, and in the vapor phase, y_i, by the equation

$$q_i = Vy_i + Lx_i \tag{2}$$

If we define the coefficient of evaporation, f

$$f = \frac{V}{L} \tag{3}$$

and compare eqs 1 and 2, the relation enabling the calculation of liquid phase composition by a iterative procedure is obtained

$$x_i = q_i \frac{1 + f}{1 + (y_i/x_i)f} \tag{4}$$

The coefficient f is fairly constant[8] over the range of temperatures and pressures applied in usual ebulliometric measurements. The above experimental procedures as well as a detailed description of the ebulliometer were reported previously.[8]

All reagents used in the investigations were supplied by Fluka with a guaranteed mass fraction greater than 0.9995 determined by GLC analysis. The remaining moisture was removed by sorption on molecular sieves AJ (Wolfen Zeosorb), and to prevent further contamination, each sample was introduced into

Table 3. Vapor−Liquid Equilibrium Measurements for the 2-Butanol (1) + Cyclohexane (2) System at (313.15 to 343.15) K, the 2-Pentanol (1) + Cyclohexane (2) System at (333.15 to 353.15) K, the 2-Methyl-2-butanol (1) + Cyclohexane (2) System at (313.15 to 343.15) K, and the 1-Hexanol (1) + Cyclohexane (2) System at (323.15 to 353.15) K

experimental data															
P/(kPa)	x_1	P/(kPa)	x_1	P/(kPa)	x_1	P/(kPa)	x_1	P/(kPa)	x_1	P/(kPa)	x_1	P/(kPa)	x_1	P/(kPa)	x_1
2-butanol (1) + cyclohexane (2)															
$T = 313.15$ K		$T = 323.15$ K		$T = 333.15$ K		$T = 343.15$ K		$T = 313.15$ K		$T = 323.15$ K		$T = 333.15$ K		$T = 343.15$ K	
24.56	0.0000	36.27	0.0000	51.92	0.0000	72.63	0.0000	20.31	0.6891	32.71	0.6198	48.33	0.6082	69.51	0.5989
25.85	0.0562	38.41	0.0537	55.16	0.0523	77.27	0.0513	19.07	0.7373	30.91	0.6792	45.63	0.6652	65.47	0.6539
26.11	0.129	38.97	0.1226	56.47	0.1196	79.72	0.1168	17.53	0.7913	29.35	0.7262	43.12	0.7113	61.27	0.6987
25.91	0.2011	38.80	0.1950	56.44	0.1897	80.01	0.1852	15.77	0.848	27.99	0.7776	39.60	0.7634	56.69	0.8069
25.72	0.2559	38.52	0.2502	56.07	0.2440	79.65	0.2388	13.73	0.893	22.17	0.8768	38.21	0.8195	51.65	0.8556
25.35	0.3124	38.05	0.3063	55.40	0.3001	78.83	0.2949	5.83	1.0000	19.68	0.9149	34.49	0.8665	47.45	0.8954
24.95	0.386	37.43	0.3785	54.60	0.3726	77.43	0.3677			17.09	0.9493	31.19	0.9048	42.71	0.9304
24.28	0.452	36.57	0.4431	53.47	0.4372	76.05	0.4321			14.67	0.9759	27.64	0.9385	38.01	0.9601
23.67	0.5083	35.71	0.4986	52.27	0.4917	74.59	0.4860			12.55	0.9903	24.16	0.9665	33.60	0.9808
22.79	0.5734	34.47	0.5571	50.72	0.5482	72.77	0.5411			10.48	1.0000	21.00	0.9848	29.76	1.0000
21.47	0.6253	34.49	0.5635	50.72	0.5544	72.72	0.5470					18.20	1.0000		
2-pentanol (1) + cyclohexane (2)															
$T = 333.15$ K		$T = 343.15$ K		$T = 353.15$ K				$T = 333.15$ K		$T = 343.15$ K		$T = 353.15$ K			
51.92	0.0000	72.63	0.0000	99.31	0.0000			37.00	0.6548	50.53	0.6465	75.08	0.6363		
52.00	0.0588	72.83	0.0580	99.79	0.0575			33.59	0.7094	48.23	0.7002	67.56	0.6917		
51.52	0.1128	72.16	0.1109	99.12	0.1096			29.67	0.7653	42.96	0.7554	60.55	0.7469		
50.77	0.1709	71.04	0.1681	97.48	0.1660			25.24	0.8125	37.15	0.8022	52.64	0.7939		
49.91	0.2320	69.89	0.2286	95.52	0.2261			21.73	0.8692	32.20	0.8581	45.95	0.8491		
48.91	0.2887	68.60	0.2849	93.73	0.2823			18.55	0.9084	28.17	0.8961	40.36	0.8852		
47.51	0.3536	66.73	0.3494	91.56	0.3466			16.27	0.9434	25.07	0.9302	36.39	0.9166		
46.33	0.4103	65.11	0.4057	89.63	0.4025			13.64	0.9713	21.67	0.9599	31.92	0.9451		
44.60	0.4730	62.85	0.4678	86.47	0.4665			10.79	0.9895	17.35	0.9838	26.57	0.9730		
42.68	0.5301	59.45	0.5241	82.53	0.5243			7.68	1.0000	13.08	1.0000	21.20	1.0000		
40.27	0.5974	55.56	0.5917	78.52	0.5834										
2-methyl-2-butanol (1) + cyclohexane (2)															
$T = 313.15$ K		$T = 323.15$ K		$T = 333.15$ K		$T = 343.15$ K		$T = 313.15$ K		$T = 323.15$ K		$T = 333.15$ K		$T = 343.15$ K	
24.56	0.0000	36.27	0.0000	51.92	0.0000	72.63	0.0000	16.11	0.6505	25.19	0.6160	38.00	0.6069	51.68	0.6466
25.19	0.0591	37.76	0.0542	54.91	0.0513	77.71	0.0488	15.09	0.7068	23.67	0.6658	35.71	0.6558	48.77	0.7552
24.67	0.1169	37.11	0.1106	54.00	0.1087	76.43	0.1071	13.47	0.7665	21.89	0.7202	32.88	0.7099	45.43	0.8065
24.07	0.1715	36.21	0.1647	52.81	0.1627	74.77	0.1612	5.69	1.0000	20.91	0.7748	32.55	0.7651	41.47	0.8620
23.33	0.2407	35.21	0.2325	51.52	0.2295	73.12	0.2273			18.95	0.8244	30.00	0.8158	37.97	0.9003
22.49	0.2913	34.11	0.2810	49.99	0.2772	71.43	0.2743			16.97	0.8777	27.11	0.8699	35.89	0.9254
21.76	0.3565	33.01	0.3424	48.60	0.3377	69.63	0.3337			15.28	0.9149	24.53	0.9069	32.63	0.9563
20.85	0.4133	31.76	0.3956	46.93	0.3902	67.43	0.3853			14.40	0.9392	23.17	0.9311	28.95	1.0000
19.63	0.4742	29.79	0.4526	43.76	0.4465	62.45	0.4956			12.53	0.9675	20.61	0.9604		
18.87	0.5346	28.16	0.5062	43.08	0.5023	59.75	0.5458			10.41	1.0000	17.87	1.0000		
17.73	0.5904	27.43	0.5615	41.09	0.5534	55.33	0.5984								
1-hexanol (1) + cyclohexane (2)															
$T = 323.15$ K		$T = 333.15$ K		$T = 343.15$ K		$T = 353.15$ K		$T = 323.15$ K		$T = 333.15$ K		$T = 343.15$ K		$T = 353.15$ K	
36.27	0.0000	51.92	0.0000	72.63	0.0000	99.31	0.0000	25.25	0.5989	29.73	0.7066	49.95	0.5939	57.33	0.6430
35.19	0.0663	50.27	0.0656	70.53	0.0647	96.36	0.0641	23.71	0.6464	23.25	0.7781	41.71	0.7029	53.49	0.7028
34.65	0.1248	49.47	0.1239	68.89	0.1227	94.76	0.1218	20.49	0.7097	16.21	0.8465	32.93	0.7728	45.45	0.7684
33.99	0.1956	48.56	0.1946	67.52	0.1934	92.01	0.1924	16.27	0.7821	1.01	1.0000	23.48	0.8395	33.20	0.8334
33.24	0.2607	47.45	0.2596	65.91	0.2583	89.57	0.2573	0.45	1.0000			16.40	0.8944	23.28	0.8849
32.20	0.3411	45.87	0.3398	63.71	0.3382	86.57	0.3369					2.04	1.0000	16.08	0.9243
31.33	0.3917	44.59	0.3903	61.91	0.3885	76.60	0.4541							10.07	0.9600
29.57	0.4587	42.20	0.4570	57.60	0.4549	71.43	0.5151							3.87	1.0000
27.72	0.5221	39.28	0.5203	53.81	0.5178	67.05	0.5905								

Table 4. Parameters for the Hayden−O'Connell Correlation[a]

compound	T_c/K	P_c/kPa	μ/D	RD/Å	η
cyclohexane	554.00	4000.70	0.00	3.561	0.00
2-butanol	536.00	4200.00	1.66	3.182	0.2580
2-pentanol	560.30	3700.10	1.70	3.634	0.2435
2-methyl-2-butanol	543.70	3700.10	1.68	3.641	0.2476
1-hexanol	611.00	4000.50	1.80	4.198	0.2496

[a] T_c, critical temperature; P_c, critical pressure; μ, dipole moment; RD, mean redius of gyration; η, association parameter.

the ebulliometer by direct distillation, made just before each measurement.

Results and Discussion

Vapor pressures of the investigated five pure substances were determined as a function of temperatures, and the results are given in Table 1 and Figure 1. The obtained $P-T$ data were further correlated by the Antoine equation[9] (eq 5), and the calculated normal boiling points were compared with the values given by NIST.[10]

$$\log P = A - \frac{B}{T + C} \tag{5}$$

where P is vapor pressure (kPa); T is temperature (K); and A, B, and C are Antoine's constants.

The parameters of the Antoine equation (eq 5) together with calculated and literature values of boiling point for all investigated substances are given in Table 2. As seen from both tables, no discrepancies between data reported in the literature and measured in this work were found.

The simultaneous (P, T, x) method without withdrawal of samples[8] was applied in this experiment. The ebulliometer was filled with a known amount of one pure compound, and a sample of a second component was added after the steady state was reached. For each experimental determination, the temperature and pressure in the apparatus and the total concentration of the sample were recorded. This procedure was repeated until the concentration of the second component reached a value higher than 0.5 mol fraction. Then the ebulliometer was filled with a known amount of second pure compound, and the same procedure as for component one was repeated.

The vapor pressures of mixtures of different compositions were determined, and the equilibrium compositions of the liquid and vapor phases were calculated by the method described previously[8] using a value of 0.30 for *f*.

The obtained results, experimental data of temperature, pressure, and liquid phase composition, are given in Table 3 and Figures 2 to 5.

The obtained experimental data were compared with the available literature data[1,2,6,7] (see Figures 2 and 5) and correlated using the Redlich−Kister,[11] NRTL,[12] and Wilson[13] equations. The minimization objective function was defined as the difference between the measured and calculated total pressures, and for each equation the adjustable parameters were calculated using the Levenberg−Marquardt algorithm.[14] For computation of vapor phase nonideality, the Hayden−O'Connell correlation[15] was used. The necessary auxiliary data are given in Table 4.

The results of the correlation ($D(P)$ and $DR(P)$, the absolute and relative root mean square deviations of total pressure, respectively) for all investigated equations are shown in Table 5.

$$D(P) = \left[\frac{\sum_{i=1}^{n} (P_i^{\text{exp}} - P_i^{\text{cal}})^2}{n - m}\right]^{0.5} \tag{6}$$

$$DR(P) = \left[\frac{\sum_{i=1}^{n} \left(\frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}}\right)^2}{n - m}\right]^{0.5} \tag{7}$$

where P_i^{exp} and P_i^{cal} are the experimental and calculated total pressures, respectively; n is the number of experimental data points; and m is the number of adjustable parameters.

The experimental VLE data for 2-butanol + cyclohexane, 1-hexanol + cyclohexane, and 2-methyl-2-butanol + cyclohexane systems agree very well with the literature (Figures 2, 4, and 5).

The correlation results (Table 5) show that, depending on the equation used, the relative root mean square deviation of total pressure varied from 0.45 % to 3.52 %. The best correlation results, for all investigated systems ($RD(P)$ = (0.45 to 2.63) %, Table 5), have been obtained for the Redlich−Kister[11] equation with four adjustable parameters. The worst (almost twice) results have been obtained for both the NRTL[12] and Wilson[13] equation. It is worth noticing that the difference between results given by these equations is very small which means that the equations based on the local composition concept can not be used for accurate correlation of these systems. The obtained results confirmed the opinion that in the case of highly

Table 5. Results of Correlation ($D(P)$ and $DR(P)$, the Absolute and Relative Root Mean Square Deviations of Total Pressure, Respectively) of the Experimental VLE Isothermal Data for All the Systems Investigated

		equation					
		NRTL[12]		Wilson[13]		Redlich−Kister[11] (4 parameters)	
system	T/K	$D(P)$/kPa	$DR(P)$/%	$D(P)$/kPa	$DR(P)$/%	$D(P)$/kPa	$DR(P)$/%
2-butanol + cyclohexane	313.15	0.172	0.745	0.221	0.956	0.106	0.459
	323.15	0.319	1.907	0.705	2.980	0.287	1.627
	333.15	0.537	1.360	0.838	2.554	0.343	0.837
	343.15	0.482	0.731	0.846	1.540	0.372	0.598
2-pentanol + cyclohexane	333.15	0.713	2.853	0.879	3.517	0.657	2.629
	343.15	0.660	2.395	0.926	3.011	0.629	2.045
	353.15	0.718	1.423	0.896	1.525	0.626	1.010
2-methyl-2-butanol + cyclohexane	313.15	0.291	1.351	0.498	2.268	0.217	1.017
	323.15	0.485	1.726	0.723	3.425	0.358	1.236
	333.15	0.858	2.256	0.994	3.106	0.658	1.568
	343.15	1.240	2.278	1.328	2.718	0.917	1.458
1-hexanol + cyclohexane	323.15	0.320	1.218	0.367	1.394	0.136	0.453
	333.15	0.638	2.274	0.663	2.380	0.171	0.471
	343.15	0.731	2.570	0.785	2.996	0.444	1.493
	353.15	1.291	2.562	1.296	2.572	0.909	1.804

associating systems the good correlation can be achieved only by the use of models providing an extra term and taking into account association (usually an extra adjustable parameter).[16]

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