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Isothermal Vapor−Liquid Equilibria for 2,2,4-Trimethylpentane + Five Chlorohydrocarbon Binary Systems at 343.15 K

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Isothermal vapor−liquid equilibria at 343.15 K for 2,2,4-trimethylpentane + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, + trichloroethylene, and + tetrachloroethylene binary systems have been determined using a recirculating still. The data were correlated by means of the Redlich−Kister equation. The excess Gibbs energies, determined from the vapor−liquid equilibrium data, present positive trends for all systems, with the maximum varying from 150 to 600 J mol^{-1}.

Introduction

The design of physical processes for liquid mixtures involving the separation of phase requires the knowledge of the conditions of equilibrium among the phases separated and the values of the activity coefficients of the components of the mixtures. For this reason, the evaluation of a good method to correlate values of the activity coefficients is of great interest.

In this paper, we report experimental data for the binary systems of 2,2,4-trimethylpentane (isooctane) (component 1) + five chlorohydrocarbons (component 2), namely, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene, and tetrachloroethylene. For these mixtures no experimental data have been published in the literature.

Experimental Section

Chemicals. All liquids were high-purity grade (≥99 mol %) Aldrich or Fluka reactives and were used as received, without further purification. Liquids were stored in dark bottles and carefully dried over molecular sieves (Union Carbide Type 4A 1/16 in. pellets). In Table 1, the physical properties of the six components are collected and compared with the literature data (*1*−*5*).

Apparatus and Procedure. An all-glass recirculatory type of still (Fritz Gmbh, Normag, Hofheim, Germany) was used for determining the vapor−liquid equilibrium (VLE) data. The equilibrium still and method of operation are well described elsewhere (*6*).

Isothermal data have been obtained at 343.15 K: both temperature T (K) and pressure P (kPa) were measured by digital instruments with an accuracy of 0.05 K and 0.05 kPa, respectively.

The experimental vapor-pressure data of all components P_i°, in the range of work temperature, were fitted to the Clausius−Clapeyron equation

$$\log(P_i^\circ/\text{kPa}) = A + B/(T/\text{K}) \tag{1}$$

by means of a least-squares procedure. Values of the vapor pressure of pure components, parameters A and B of eq 1, the mean standard deviation σ, and correlation coefficients $|R|$ of the six components are reported in Table 2.

The equilibrium vapor and liquid samples for all mixtures were analyzed by precision refractometry (Abbe refractometer, Carl-Zeiss-Jena, precision 0.0001) at 298.15 K, and the mole fractions were determined with the aid of a calibration curve prepared from n(D) vs x_1 data, as represented in Table 3.

All samples were prepared by weighing by means of a Mettler balance (model AE 160, precision 0.0001). The uncertainty in the mole fraction of samples taken from the still is estimated to be on the order of 2×10^{-3}.

Densities of pure components have been determined by using an Anton Paar density meter (model DMA 60/602, resolution of 10^{-6} g cm^{-3}) with the procedure described in ref 7.

Table 1. Sources, Purities, Densities ϱ, and Refractive Indexes n of the Chemicals Used in This Paper

		ϱ(298.15 K)/(g cm^{-3})		n(D, 298.15 K)	
compound	source	exptl	lit.	exptl	lit.
2,2,4-trimethylpentane	Aldrich (99.7%)	0.687 69	0.687 81 (*1*)	1.3892	1.38898 (*1*)
1,2-dichloroethane	Aldrich (99.8%)	1.245 68	1.246 87 (*1*) 1.245 79 (*2*)	1.4421	1.4421 (*1*)
1,1,1-trichloroethane	Fluka (99%)	1.329 73	1.329 9 (*1*) 1.331 4 (*2*)	1.4361	1.4359 (*1*)
1,1,2,2-tetrachloroethane	Aldrich (99%)	1.587 85	1.586 66 (*1*) 1.587 6 (*2*)	1.4918	1.4914 (*1*)
trichloroethylene	Aldrich (99%)	1.455 72	1.455 44 (*3*)[a]	1.4750	1.4748 (*4*)
terachloroethylene	Aldrich (99.9%)	1.613 09	1.614 82 (*1*) 1.606 82 (*5*)	1.5037	1.5032 (*1*)

[a] Interpolated from the density equation.

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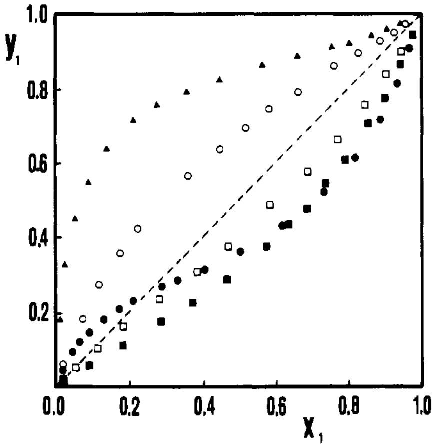

Figure 1. x_1 vs y_1 diagram at 343.15 K for the systems 2,2,4-trimethylpentane (1) + 1,2-dichloroethane (2) (●), + 1,1,1-trichloroethane (2) (■), + 1,1,2,2-tetrachloroethane (2) (▲), + trichloroethylene (2) (□), and + tetrachloroethylene (2) (○).

Table 2. Vapor Pressure $P_i°$, Parameters A and B (Eq 1), Standard Deviation $\sigma(P_i°)$, and Correlation Coefficients $|R|$ of the Pure Compounds

2,2,4-trimethylpentane		1,2-dichloroethane		1,1,1-trichloroethane	
T/K	$P_i°$/kPa	T/K	$P_i°$/kPa	T/K	$P_i°$/kPa
292.5	5.0	292.9	19.5	298.2	16.2
295.7	5.9	317.5	25.3	303.4	20.4
298.2	6.6	321.8	30.2	308.3	25.2
318.3	16.1	326.6	36.2	313.1	30.6
330.7	26.4	330.2	41.6	316.6	35.4
340.1	37.2	333.1	46.3	320.2	40.7
347.1	47.3	336.3	52.0	323.1	44.9
354.0	59.5	338.4	56.0	326.7	51.5
360.2	72.0	341.3	62.2	329.2	56.5
367.0	88.6	345.1	71.0	332.4	63.2
		348.7	79.9	336.0	71.7
		350.8	85.8	339.6	80.4
		353.2	95.9	342.7	89.1
		355.5	99.9	345.1	96.5
				345.9	99.0
$A = 6.861\ 323$		$A = 7.038\ 393$		$A = 6.896\ 059$	
$B = -1800.722$		$B = -1789.504$		$B = -1693.930$	
$\sigma(P_i°) = 0.0046$		$\sigma(P_i°) = 0.0039$		$\sigma(P_i°) = 0.0029$	
$\|R\| = 0.9999$		$\|R\| = 0.9998$		$\|R\| = 0.9999$	
1,1,2,2-tetrachloroethane		trichloroethylene		tetrachloroethylene	
T/K	$P_i°$/kPa	T/K	$P_i°$/kPa	T/K	$P_i°$/kPa
333.0	4.7	305.1	13.5	316.3	6.2
335.4	5.2	312.4	18.7	324.4	8.9
342.5	7.2	317.2	22.8	330.7	11.7
350.0	9.9	323.6	29.5	337.0	15.0
354.4	12.0	327.2	33.8	342.9	19.1
357.6	13.7	331.2	39.1	348.4	23.6
360.1	15.1	335.0	45.1	352.1	28.0
363.5	17.2	339.7	53.4	356.5	31.6
366.0	18.9	345.0	63.9	359.3	34.9
368.8	21.0	347.8	70.4	363.2	39.9
		350.9	78.0	365.2	42.7
		354.6	87.5		
		357.9	96.9		
$A = 7.404\ 794$		$A = 6.925\ 168$		$A = 7.054\ 126$	
$B = -2242.187$		$B = -1766.023$		$B = -1979.880$	
$\sigma(P_i°) = 0.0021$		$\sigma(P_i°) = 0.0021$		$\sigma(P_i°) = 0.0016$	
$\|R\| = 0.9999$		$\|R\| = 0.9999$		$\|R\| = 0.9999$	

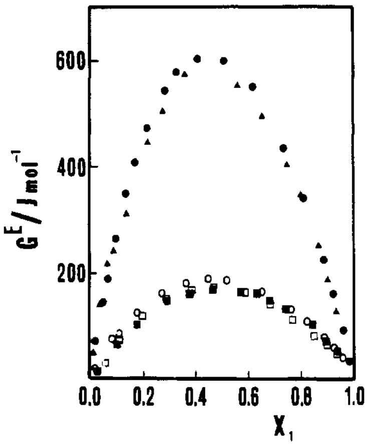

Figure 2. Calculated excess molar Gibbs energies G^E for the systems 2,2,4-trimethylpentane (1) + 1,2-dichloroethane (2) (●), + 1,1,1-trichloroethane (2) (■), + 1,1,2,2-tetrachloroethane (2) (▲), + trichloroethylene (2) (□), and + tetrachloroethylene (2) (○).

Table 3. Refractive Indexes n at 298.15 K for 2,2,4-Trimethylpentane (1) + Chlorohydrocarbons (2) as a Function of the Mole Fraction x_1

x_1	n(D, 298.15 K)	x_1	n(D, 298.15 K)	x_1	n(D, 298.15 K)
1,2-Dichloroethane		1,1,1-Trichloroethane		1,1,2,2-Tetrachloroethane	
0.0450	1.4380	0.0116	1.4351	0.0098	1.4912
0.0885	1.4335	0.0828	1.4295	0.0642	1.4830
0.1309	1.4294	0.1501	1.4247	0.0768	1.4811
0.1551	1.4272	0.1827	1.4224	0.1228	1.4747
0.1952	1.4238	0.2013	1.4213	0.2124	1.4628
0.2229	1.4215	0.2220	1.4200	0.2404	1.4594
0.2465	1.4197	0.2727	1.4169	0.2764	1.4550
0.2890	1.4168	0.2905	1.4159	0.3002	1.4522
0.2939	1.4164	0.3386	1.4135	0.3420	1.4471
0.3115	1.4152	0.3595	1.4124	0.3900	1.4416
0.3766	1.4111	0.3948	1.4107	0.4371	1.4367
0.4083	1.4095	0.4045	1.4201	0.5159	1.4291
0.4884	1.4053	0.4432	1.4084	0.5770	1.4230
0.5209	1.4038	0.4973	1.4060	0.6159	1.4193
0.6436	1.3988	0.6754	1.3990	0.6599	1.4155
0.7100	1.3966	0.7624	1.3961	0.7568	1.4075
0.7771	1.3946	0.8195	1.3945	0.8872	1.3976
0.9694	1.3905	0.9812	1.3903	0.9728	1.3917

x_1	n(D, 298.15 K)	x_1	n(D, 298.15 K)
Trichloroethylene		Tetrachloroethylene	
0.0100	1.4742	0.0089	1.5021
0.0586	1.4669	0.0729	1.4918
0.1015	1.4610	0.1490	1.4797
0.1278	1.4576	0.1613	1.4780
0.2138	1.4472	0.2044	1.4717
0.2486	1.4432	0.2382	1.4671
0.2768	1.4402	0.2994	1.4588
0.2874	1.4391	0.3226	1.4559
0.3176	1.4361	0.3510	1.4523
0.3487	1.4321	0.3744	1.4494
0.3826	1.4299	0.4137	1.4446
0.4100	1.4275	0.4338	1.4422
0.4122	1.4272	0.5137	1.4335
0.5461	1.4164	0.5487	1.4297
0.5817	1.4138	0.5846	1.4260
0.6286	1.4106	0.6887	1.4158
0.7098	1.4053	0.7490	1.4104
0.8191	1.3989	0.8658	1.4003
0.9761	1.3910	0.9836	1.3911

Results and Discussion

Table 4 presents the experimental isothermal vapor–liquid equilibrium data with their activity coefficients and Figure 1 the composition diagram x_1 vs y_1. The activity coefficients appearing in Table 4 were evaluated by the formula

$$\gamma_i = \frac{P y_i}{P_i x_i} \qquad (2)$$

with P_i the "corrected vapor pressure" of component i (*8*),

Table 4. Experimental Vapor–Liquid Equilibrium Data for the Binary Systems at 343.15 K: Experimental Liquid Mole Fraction x_1, Vapor Mole Fraction y_1, Vapor Pressure P, and Activity Coefficients γ_i

P/kPa	x_1	y_1	γ_1	γ_2	P/kPa	x_1	y_1	γ_1	γ_2
2,2,4-Trimethylpentane (1) + 1,2-Dichloroethane (2)									
66.3	0.000	0.000			71.8	0.403	0.314	1.32	1.25
68.2	0.025	0.045	3.11	1.00	70.0	0.502	0.362	1.19	1.36
69.8	0.053	0.092	2.87	1.00	67.0	0.622	0.432	1.10	1.50
70.9	0.068	0.122	2.75	1.01	61.8	0.734	0.520	1.06	1.65
71.6	0.098	0.145	2.53	1.01	57.4	0.815	0.608	1.03	1.79
72.5	0.138	0.179	2.27	1.03	52.2	0.888	0.714	1.01	1.98
72.8	0.175	0.204	2.05	1.05	48.1	0.932	0.816	1.00	2.13
73.1	0.214	0.226	1.87	1.07	45.5	0.966	0.880	1.01	2.28
72.7	0.297	0.264	1.57	1.14	41.7	1.000	1.000		
72.6	0.332	0.284	1.47	1.17					
2,2,4-Trimethylpentane (1) + 1,1,1-Trichloroethane (2)									
90.8	0.000	0.000			61.7	0.684	0.475	1.01	1.12
90.0	0.024	0.016	1.38	1.00	58.4	0.735	0.540	1.00	1.13
87.7	0.093	0.057	1.25	1.01	55.2	0.789	0.608	1.00	1.15
84.1	0.185	0.110	1.15	1.02	51.3	0.850	0.704	1.00	1.16
80.3	0.290	0.174	1.09	1.04	48.4	0.900	0.776	1.00	1.15
76.5	0.376	0.229	1.06	1.05	45.4	0.940	0.865	1.00	1.13
72.5	0.470	0.290	1.04	1.06	43.0	0.975	0.945	1.00	1.09
67.2	0.576	0.376	1.02	1.08	41.7	1.000	1.000		
64.0	0.635	0.435	1.01	1.10					
2,2,4-Trimethylpentane (1) + 1,1,2,2-Tetrachloroethane (2)									
7.2	0.000	0.000			28.7	0.449	0.825	1.30	1.22
9.0	0.015	0.182	2.85	1.00	31.4	0.564	0.858	1.18	1.36
11.0	0.030	0.327	2.69	1.00	33.5	0.663	0.885	1.10	1.51
13.2	0.060	0.450	2.44	1.01	35.5	0.753	0.912	1.05	1.68
15.2	0.094	0.544	2.21	1.01	36.5	0.802	0.926	1.03	1.79
18.1	0.144	0.635	1.97	1.03	37.9	0.865	0.948	1.02	1.95
21.8	0.215	0.710	1.74	1.06	38.9	0.906	0.962	1.01	2.07
24.2	0.281	0.754	1.58	1.09	39.8	0.941	0.975	1.00	2.20
26.7	0.361	0.789	1.43	1.14	41.7	1.000	1.000		
2,2,4-Trimethylpentane (1) + Trichloroethylene (2)									
50.9	0.000	0.000			52.5	0.589	0.487	1.04	1.10
59.8	0.025	0.023	1.32	1.00	50.4	0.684	0.575	1.03	1.13
59.6	0.056	0.050	1.30	1.00	48.3	0.769	0.664	1.02	1.16
59.4	0.114	0.101	1.26	1.00	46.2	0.844	0.756	1.01	1.20
58.9	0.188	0.160	1.21	1.01	44.6	0.900	0.838	1.00	1.24
57.8	0.285	0.234	1.14	1.03	43.4	0.944	0.898	1.00	1.29
56.3	0.388	0.310	1.09	1.05	41.7	1.000	1.000		
55.1	0.470	0.376	1.07	1.07					
2,2,4-Trimethylpentane (1) + Tetrachloroethylene (2)									
19.2	0.000	0.000			34.0	0.580	0.745	1.05	1.11
20.1	0.021	0.062	1.44	1.00	35.;5	0.665	0.785	1.03	1.13
22.1	0.078	0.185	1.33	1.00	37.4	0.762	0.860	1.02	1.17
23.4	0.121	0.275	1.28	1.01	38.4	0.827	0.894	1.01	1.21
25.1	0.180	0.361	1.22	1.02	39.3	0.884	0.928	1.01	1.26
27.5	0.276	0.474	1.16	1.03	40.0	0.926	0.952	1.00	1.31
29.6	0.364	0.564	1.12	1.05	40.6	0.956	0.972	1.00	1.35
31.4	0.450	0.635	1.09	1.07	41.7	1.000	1.000		
32.8	0.520	0.691	1.07	1.09					

obtained from the virial coefficients, evaluated by making use of the Whol formula. The same formula was used for other mixtures containing 2,2,4-trimethylpentane (*9*). Further details are given in ref 10.

The area test (*8*) was used to check the thermodynamic consistency of the isothermal VLE data; thus

$$I = \int_0^1 (\ln \gamma_1/\gamma_2 + V^E/RT\ \mathrm{d}P/\mathrm{d}x_1)\ \mathrm{d}x_1 = 0 \qquad (3)$$

where V^E is the molar excess volume. The contribution to I given by V^E is generally neglected. However, our recent volumetric data on the same mixtures of this paper (*12*) allowed direct calculation of $V^E/RT\ \mathrm{d}P/\mathrm{d}x_1$, which is on the order of $\le 10^{-5}$, whereas the order of magnitude of I is $\ge 10^{-3}$.

The values of the integral I were compared with the uncertainty δI on the integral, obtained from variance analysis (*13*). Thermodynamic consistency of VLE data is assumed when $|I|$ and δI are of the same order, or

$$\delta I \ge |I|$$

All mixtures fulfilled this criterion of the area test.

The experimental data were correlated by means of the five-parameter Redlich–Kister equations.

The objective function ϕ, the same reported in ref 11, was used in the least-squares procedure, leading to the adjustable parameters

$$\phi = \ln(\gamma_1/\gamma_2)_{\text{exptl}} - \ln(\gamma_1/\gamma_2)_{\text{calcd}} \qquad (4)$$

with $(\gamma_1)_{\text{expll}}$ taken from eq 2 and $(\gamma_1)_{\text{calcd}}$ from the Redlich–Kister expressions.

Table 5 collects the adjustable parameters a_k and the standard deviations σ.

The excess molar Gibbs energies G^E shown in Figure 2 were calculated through the definition

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (5)$$

with γ_i given by the Redlich–Kister expressions.

As can be seen from Table 4, all mixtures have positive deviations from the Raoult law. The systems of 2,2,4-trimethylpentane with 1,1,1-trichloroethane, trichloroethylene, or tetrachloroethylene are nearly ideal, with γ_i never exceeding 1.5. Instead, the systems of 2,2,4-trimethylpentane with 1,1,2,2-tetrachloroethane or 1,2-dichloroethane are strongly nonideal, with γ_i up to 3. The same results are reflected by Figure 2 showing a marked gap between the G^E values for the two sets of mixtures.

The presence of an azeotrope for the mixture 2,2,4-trimethylpentane + 1,2-dichloroethane, showing the larger values of γ_i, is stressed by Figure 1.

In the context of a qualitative molecular interpretation of these results (such as the quasi-chemical approximation), the excess energy G^E may be related to the interaction energies E_{ij} through

$$G^E \propto E_{11} + E_{22} - 2E_{12}$$

E_{ij} being the interaction energy between molecules i and j.

This formula predicts positive values of G^E when the interaction energies between unlike molecules are smaller than those of pure compounds and may explain the G^E trends in Figure 2, with a maximum of 600 J mol^{-1} for 1,2-di- and 1,1,2,2-tetrachloroalkanes and of about 200 J mol^{-1} for 1,1,1-trichloroethane and unsaturated chloro compounds. In fact, the electronegative C1 atoms in 1,2-di- and 1,1,2,2-tetrachloroalkanes will induce a strong acid character to the neighbor H atoms with consequent E_{22} interactions stronger than those between the same chloroalkanes and 2,2,4-trimethylpentane (compound 1).

Table 5. Least-Squares Parameters a_k of the Polynomial Redlich–Kister Equation for Binary Systems Containing 2,2,4-Trimethylpentane (1) + Chlorohydrocarbons (2)

mixture	a_0	a_1	a_2	a_3	a_4	$\sigma(G^E)$
2,2,4-trimethylpentane						
+1,2-dichloroethane	0.9647	−0.2474	0.1188	0.0968	−0.03333	0.050
+1,1,1-trichloroethane	0.2087	−0.0622	0.0377	−0.0920	−0.0421	0.040
+1,2,2,2-tetrachloroethane	0.9203	−0.0522	0.0167	−0.0166	0.0727	0.081
+trichloroethylene	0.2691	−0.0337	0.0467	0.0462	−0.0179	0.0021
+tetrachloroethylene	0.2979	−0.0226	0.0486	0.0063	0.0354	0.035

This effect will be weakened in the case of the asymmetric molecule of 1,1,1-trichloroethane, since the H and Cl atoms are not placed on the same C atom, whereas unsaturated chlorocompounds will show low E_{22} values due to their molecular symmetry and small dipole moments.

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