Excess Volumes and Excess Enthalpies of Binary Liquid Mixtures of *trans*-1,2-Dichloroethene and of *cis*-1,2-Dichloroethene + *n*-Alkanes or +2,2,4-Trimethylpentane

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Molar excess volumes have been determined from density measurements of the liquid mixtures of *trans*-1,2-dichloroethene and of *cis*-1,2-dichloroethene + heptane, +decane, +dodecane, +tetradecane, +hexadecane, and +2,2,4-trimethylpentane at 293.15 K and 313.15 K and atmospheric pressure. For the same mixtures the molar excess enthalpies were measured by means of a flow microcalorimeter of the Picker type at 293.15 K and atmospheric pressure.

Introduction

The measured molar excess volumes and excess enthalpies of the binary liquid mixtures of *trans*-1,2-dichloroethene and of *cis*-1,2-dichloroethene + heptane, +decane, +dodecane, +tetradecane, +hexadecane, and +2,2,4-trimethylpentane presented here may be of interest for plant design in chemical engineering. In addition, mixtures of dichloroethenes with alkanes can serve as models for polymer solutions.

The present work is also part of a systematic study on liquid mixtures in which the molecular structure of one component is changed only slightly to investigate the influence of these structural changes on the excess properties. For this reason the three compounds, 1,2-dichloroethane, *trans*-1,2-dichloroethene, and *cis*-1,2-dichloroethene, are compared, since dichloroethane exists in the two conformers, trans and gauche, that are structurally related to both dichloroethenes. Recently, the volumetric properties and the molar excess enthalpies of 1,2-dichloroethane + *n*-alkanes and +2,2,4-trimethylpentane (Hahn et al., 1993 and 1986) have been reported, which were interpreted by a quasi chemical approach. A comparison of both the thermodynamic properties is made for the corresponding mixtures with *trans*- and *cis*-1,2-dichloroethene instead of dichloroethane.

Experimental Section

trans-1,2-Dichloroethene was obtained by separation of a mixture consisting of about 75 mol % *trans*- + 25 mol % *cis*-1,2-dichloroethene available from Baker ("Baker" grade, Baker, Holland). This mixture was first kept over P_2O_5 for several days, which was continuously renewed. Then *trans*-1,2-dichloroethene was separated from the mixture by fractional distillation (over P_2O_5, under atmospheric pressure, approximately 100 plates), stored over phosphorus pentoxide, and then fractionally distilled a second time immediately before the measurements (purity better than 99.4 mol % by GLC: 100 m glass capillary; oven, 150 °C; flame ionization detector; main impurity, cis isomer).

cis-1,2-Dichloroethene was obtained together with the trans isomer by separation of the mixture (Baker, Holland). It did not undergo polymerization, but its final yield was rather low (purity 99.2 mol % by GLC, same conditions as above; main impurity, trans isomer).

The sources of the *n*-alkanes and of 2,2,4-trimethylpentane and their purification were the same as described previously by Hahn et al. (1986). For heptane, decane, dodecane, tetradecane, hexadecane, and 2,2,4-trimethylpentane purities of 99.82, 99.94, 99.67, 99.89, 99.77, and 99.92 mol %, respectively, were found, all by GLC (conditions as above; oven temperatures 80, 120, 140, 160, 180, and 80 °C, respectively).

Table 1. Densities ρ and Experimental Molar Volumes V_m of the Pure Liquids at Temperatures T and Atmospheric Pressure

compound	T/K	ρ/g cm^{-3} exptl	ρ/g cm^{-3} lit.	V_m/cm^3 mol^{-1} exptl
trans-1,2-dichloroethene	293.15	1.256 80	1.256 70[a]	77.135
	313.15	1.219 36	1.225 6[b]	79.503
cis-1,2-dichloroethene	293.15	1.288 02	1.283 7[c]	75.265
	313.15	1.254 96		77.248
2,2,4-trimethylpentane	293.15	0.691 92	0.691 93[c]	165.093
			0.691 95[d]	
	313.15	0.675 38	0.675 35[d]	169.136
heptane	293.15	0.683 74	0.683 76[c]	146.553
			0.683 69[d]	
	313.15	0.666 92	0.666 74[d]	150.249
decane	293.15	0.729 91	0.730 05[c]	194.935
			0.729 91[e]	
	313.15	0.714 76	0.714 70[e]	199.066
dodecane	293.15	0.748 83	0.748 75[d]	227.473
			0.748 83[f]	
	313.15	0.734 33	0.734 4[d]	231.964
			0.734 27[f]	
tetradecane	293.15	0.762 78	0.762 74[e]	260.091
			0.762 55[d]	
	313.15	0.748 70	0.748 62[e]	264.982
hexadecane	293.15	0.773 62	0.773 55[f]	292.710
			0.773 53[d]	
	313.15	0.759 78	0.759 72[f]	298.041
			0.759 5[d]	

[a] *TRC Source Database* (1995). [b] Extrapolated, *TRC Source Database* (1995). [c] Riddick et al. (1986). [d] *TRC Thermodynamic Tables* (1995). [e] Siddiqi et al. (1980). [f] Findenegg (1970).

Relative atomic masses, $A_r(H) = 1.007\,94$, $A_r(C) = 12.011$, and $A_r(Cl) = 35.4527$ (IUPAC, 1995) were used for the calculation of the molar volumes V_m from densities. In Table 1, the experimental densities ρ of the pure liquids are compared with data from the literature. Due to the difficulties of separating and purifying the *trans*- and *cis*-dichloroethenes their present density data appear more reliable than those from the literature often measured some years ago. The molar volumes V_m of the pure liquids are also given in Table 1 for the convenience of the reader, if a conversion to density data of the mixtures is needed.

Molar excess volumes V^E were calculated from precise densities of the liquids measured by means of a vibrating

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Table 2. Molar Excess Volumes V^E of Binary Liquid Mixtures with *trans*-1,2-Dichloroethene as One Component at Temperatures of 293.15 K and 313.15 K and Atmospheric Pressure

	V^E/cm^3 mol^{-1}			V^E/cm^3 mol^{-1}	
x_1	293.15 K	313.15 K	x_1	293.15 K	313.15 K
trans-1,2-Dichloroethene (1) + 2,2,4-Trimethylpentane (2)					
0.092 38	0.123	0.152	0.458 83	0.382	0.441
0.151 44	0.192	0.212	0.496 17	0.385	0.456
0.202 43	0.237	0.275	0.588 60	0.384	0.445
0.259 98	0.290	0.334	0.703 18	0.338	0.399
0.288 83	0.306	0.356	0.807 47	0.253	0.304
0.329 36	0.327	0.378	0.887 80	0.162	0.191
0.403 28	0.366	0.428	0.946 03	0.083	0.100
trans-1,2-Dichloroethene (1) + Heptane (2)					
0.116 34	0.178	0.200	0.549 34	0.477	0.537
0.131 52	0.199	0.223	0.570 21	0.477	0.533
0.230 93	0.312	0.353	0.588 14	0.469	0.526
0.241 05		0.359	0.601 82	0.473	0.529
0.293 43	0.373		0.648 52	0.452	0.510
0.333 58		0.452	0.655 18	0.447	0.496
0.341 12	0.404	0.458	0.665 15	0.436	0.490
0.395 70	0.441		0.688 00	0.431	0.483
0.440 76	0.457	0.514	0.740 45	0.387	0.433
0.450 73	0.464	0.527	0.742 49	0.389	0.434
0.464 78	0.468	0.526	0.807 54	0.322	0.356
0.489 86	0.475		0.832 21	0.290	0.325
0.535 76	0.480	0.532	0.889 91	0.207	0.232
trans-1,2-Dichloroethene (1) + Decane (2)					
0.049 53	0.086	0.092	0.637 09	0.611	0.650
0.162 82	0.266	0.281	0.684 17	0.593	0.631
0.289 96	0.433	0.460	0.742 47	0.549	0.586
0.376 51	0.520	0.551	0.786 81	0.502	0.530
0.472 91	0.590	0.623	0.852 59	0.397	0.425
0.530 15	0.617	0.650	0.895 11	0.308	0.336
0.560 65	0.624	0.656	0.951 38	0.161	0.177
0.612 68	0.618	0.654			
trans-1,2-Dichloroethene (1) + Dodecane (2)					
0.072 35	0.129	0.131	0.564 76	0.663	0.673
0.121 02	0.205	0.213	0.573 58	0.666	0.675
0.163 89	0.265	0.273	0.621 85	0.659	0.672
0.256 67	0.401	0.409	0.665 84	0.648	0.662
0.281 42	0.436	0.443	0.709 29	0.628	0.641
0.308 58	0.467	0.476	0.753 22	0.590	0.604
0.393 07	0.560	0.569	0.807 08	0.528	0.538
0.448 52	0.605	0.612	0.856 72	0.442	0.457
0.496 83	0.638	0.642	0.902 81	0.331	0.342
0.538 01	0.654	0.663	0.951 93	0.186	0.200
trans-1,2-Dichloroethene (1) + Tetradecane (2)					
0.058 91	0.105	0.104	0.644 10	0.690	0.680
0.126 44	0.218	0.214	0.683 08	0.680	0.670
0.172 65	0.289	0.281	0.704 41	0.671	0.662
0.273 21	0.429	0.422	0.755 20	0.633	0.631
0.316 64	0.489	0.481	0.799 63	0.577	0.573
0.389 59	0.569	0.557	0.819 17	0.548	0.546
0.465 38	0.638	0.622	0.852 35	0.486	0.487
0.490 44	0.652	0.636	0.888 97	0.403	0.405
0.547 41	0.685	0.670	0.899 96	0.376	0.381
0.573 07	0.691	0.677	0.950 53	0.213	0.217
trans-1,2-Dichloroethene (1) + Hexadecane (2)					
0.035 11	0.007	0.066	0.539 20	0.703	0.665
0.056 60	0.104	0.098	0.599 92	0.719	0.685
0.079 55	0.140	0.127	0.646 82	0.721	0.695
0.151 12	0.256	0.239	0.687 95	0.714	0.693
0.192 49	0.329	0.316	0.694 11	0.709	0.690
0.249 16	0.411	0.388	0.754 25	0.667	0.637
0.278 29	0.448	0.434	0.797 72	0.617	0.600
0.310 84	0.489	0.466	0.857 41	0.515	0.495
0.401 98	0.589	0.569	0.897 08	0.409	0.401
0.498 12	0.677	0.642	0.950 34	0.236	0.227
0.500 43	0.672	0.645			

Table 3. Molar Excess Volumes V^E of Binary Liquid Mixtures with *cis*-1,2-Dichloroethene as One Component at Temperatures of 293.15 K and 313.15 K and Atmospheric Pressure

	V^E/cm^3 mol^{-1}			V^E/cm^3 mol^{-1}	
x_1	293.15 K	313.15 K	x_1	293.15 K	313.15 K
cis-1,2-Dichloroethene (1) + 2,2,4-Trimethylpentane (2)					
0.039 54	0.049	0.056	0.608 30	0.251	0.330
0.138 31	0.157	0.190	0.697 97	0.219	0.284
0.292 50	0.247	0.325	0.817 49	0.135	0.182
0.413 84	0.286	0.374	0.894 75	0.079	0.109
0.484 71	0.284	0.365			
cis-1,2-Dichloroethene (1) + Heptane (2)					
0.086 32	0.167	0.195	0.552 24	0.450	0.523
0.119 14	0.216	0.244	0.593 17	0.436	0.520
0.163 06	0.278	0.322	0.635 64	0.416	0.490
0.289 58	0.396	0.474	0.705 24	0.362	0.433
0.388 60	0.447	0.529	0.751 59	0.327	0.387
0.441 06	0.461	0.538	0.802 10	0.275	0.324
0.495 48	0.462	0.538	0.860 61	0.205	0.244
0.496 78	0.466		0.911 91	0.136	0.163
cis-1,2-Dichloroethene (1) + Decane (2)					
0.061 66	0.146	0.159	0.648 26	0.666	0.748
0.153 80	0.323	0.358	0.701 38	0.626	0.700
0.295 01	0.544	0.603	0.741 06	0.582	0.652
0.377 82	0.631	0.699	0.797 56	0.505	0.564
0.454 98	0.681	0.755	0.851 75	0.403	0.459
0.549 76	0.692	0.773	0.907 20	0.278	0.315
0.589 16	0.692	0.769			
cis-1,2-Dichloroethene (1) + Dodecane (2)					
0.104 37	0.244	0.261	0.576 27	0.778	0.848
0.135 72	0.312	0.335	0.615 23	0.774	0.843
0.219 38	0.471	0.505	0.626 73	0.772	0.840
0.307 12	0.605	0.644	0.670 70	0.753	0.811
0.321 01	0.628	0.667	0.710 49	0.717	0.775
0.412 13	0.719	0.768	0.759 82	0.655	0.712
0.420 99	0.728	0.781	0.816 25	0.563	0.614
0.499 49	0.766	0.829	0.857 39	0.474	0.520
0.525 67	0.783	0.839	0.905 75	0.346	0.380
0.552 91	0.781	0.844	0.952 86	0.190	0.216
cis-1,2-Dichloroethene (1) + Tetradecane (2)					
0.079 77	0.198	0.210	0.591 85	0.860	0.907
0.122 11	0.296	0.313	0.648 21	0.842	0.890
0.228 96	0.512	0.531	0.654 41	0.837	0.887
0.232 31	0.519	0.541	0.704 28		0.853
0.327 78	0.673	0.700	0.752 41	0.748	0.797
0.391 01	0.754	0.784	0.801 83	0.666	0.709
0.464 69	0.818	0.856	0.854 67	0.547	0.589
0.511 87		0.887	0.905 26	0.400	0.434
0.541 28	0.855	0.898	0.951 16	0.231	0.255
0.545 25	0.858	0.899			
cis-1,2-Dichloroethene (1) + Hexadecane (2)					
0.089 26	0.234	0.239	0.555 44	0.920	0.941
0.140 12	0.349	0.353	0.600 74	0.921	0.951
0.189 09	0.455	0.460	0.657 37	0.905	0.947
0.269 09	0.610	0.627	0.704 96	0.865	0.901
0.282 14	0.634	0.646	0.761 00	0.801	0.840
0.347 74	0.738	0.751	0.800 26	0.733	0.767
0.408 63	0.812	0.839	0.899 79	0.468	0.500
0.454 66	0.861	0.879	0.949 88	0.269	0.294
0.499 83	0.899	0.917			

glass tube densimeter (Model DMA 02 D, Chempro Paar, Germany) at 293.15 K and 313.15 K and at atmospheric pressure. The preparation of the samples (from carefully degassed liquids, under vacuum, with vapor space correction), their transfer to the vibrating tube (without losses by evaporation or contact to air), and the experimental setup (like measurement and control of the temperature) have been described in detail, recently (Svejda et al., 1990). Here only the uncertainties of the measurements are summarized: The temperature was controlled and accurate to ±0.002 K. The final mole fractions were accurate to 3×10^{-5}. The precision in the densities was estimated to be 3×10^{-6} g cm^{-3}, the accuracies were 2×10^{-5} g cm^{-3}, at 293.15 K, and 1×10^{-4} g cm^{-3}, at 313.15 K. The excess volume V^E was accurate to 0.003 cm^3 mol^{-1} at about equimolar composition.

Table 4. Molar Excess Enthalpies H^E of Binary Liquid Mixtures with *trans*-1,2-Dichloroethene as One Component at 293.15 K and Atmospheric Pressure

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
trans-1,2-Dichloroethene (1) + 2,2,4-Trimethylpentane (2)					
0.1328	217	0.5332	577	0.6824	545
0.1885	285	0.5517	574	0.6926	530
0.2544	391	0.5571	577	0.7357	500
0.2561	386	0.5777	583	0.7727	460
0.3253	466	0.5845	572	0.8092	417
0.4150	519	0.6055	582	0.8404	366
0.4325	544	0.6285	567	0.8988	259
0.4532	545	0.6468	563	0.9517	138
0.4584	561	0.6554	556		
0.5167	591	0.6658	547		
trans-1,2-Dichloroethene (1) + Heptane (2)					
0.0675	119	0.4157	629	0.6429	655
0.1368	238	0.4520	661	0.6534	651
0.1911	339	0.4756	662	0.6742	636
0.2074	356	0.4978	675	0.7038	607
0.2453	426	0.5334	678	0.7296	581
0.2905	465	0.5472	684	0.7761	522
0.3272	534	0.5627	689	0.8005	491
0.3520	540	0.5821	677	0.8468	408
0.3757	573	0.6074	688	0.9070	274
0.4118	630	0.6295	666	0.9624	126
trans-1,2-Dichloroethene (1) + Decane (2)					
0.0575	92	0.5312	751	0.7284	682
0.1583	266	0.5522	746	0.7393	673
0.2175	362	0.5739	732	0.7653	620
0.2316	395	0.6031	731	0.7812	604
0.2585	444	0.6102	734	0.8229	532
0.3396	554	0.6375	745	0.8478	487
0.3972	638	0.6555	735	0.8849	394
0.4202	671	0.6727	708	0.9335	252
0.4829	705	0.6923	691	0.9785	89
0.5111	722	0.6977	696		
trans-1,2-Dichloroethene (1) + Dodecane (2)					
0.0860	169	0.5654	809	0.7547	724
0.1183	209	0.5792	797	0.7676	693
0.1952	382	0.5911	811	0.7935	648
0.2543	465	0.6218	808	0.8276	586
0.2658	480	0.6370	797	0.8542	528
0.3540	630	0.6708	782	0.8799	448
0.4354	733	0.6712	796	0.9289	296
0.4463	730	0.6857	776	0.9652	159
0.5034	797	0.7145	761		
0.5297	793	0.7213	747		
trans-1,2-Dichloroethene (1) + Tetradecane (2)					
0.1129	209	0.5634	859	0.7470	786
0.1792	367	0.5851	855	0.7570	777
0.2511	476	0.6008	868	0.7570	775
0.3112	586	0.6211	876	0.7762	744
0.3404	642	0.6352	870	0.8082	688
0.3809	692	0.6675	854	0.8541	588
0.4345	756	0.6789	846	0.8757	532
0.4786	809	0.7008	832	0.9005	450
0.5019	835	0.7106	827	0.9374	312
0.5350	839	0.7314	800	0.9678	141
trans-1,2-Dichloroethene (1) + Hexadecane (2)					
0.0735	147	0.6514	921	0.8239	720
0.1541	333	0.6662	924	0.8464	674
0.1873	395	0.6915	927	0.8578	636
0.3532	699	0.7106	897	0.8776	575
0.4001	770	0.7294	872	0.8951	523
0.4326	804	0.7428	857	0.9161	444
0.5287	887	0.7510	856	0.9485	297
0.5819	932	0.7698	825	0.9795	128
0.6155	933	0.7846	810		
0.6328	923	0.8008	770		

The molar excess enthalpies H^E were measured with a dynamic flow microcalorimeter of Picker type (Setaram, France) at 293.15 K and atmospheric pressure as described in detail previously (Hahn et al., 1986). The instrument was thermostated to ±0.05 K or better and controlled by

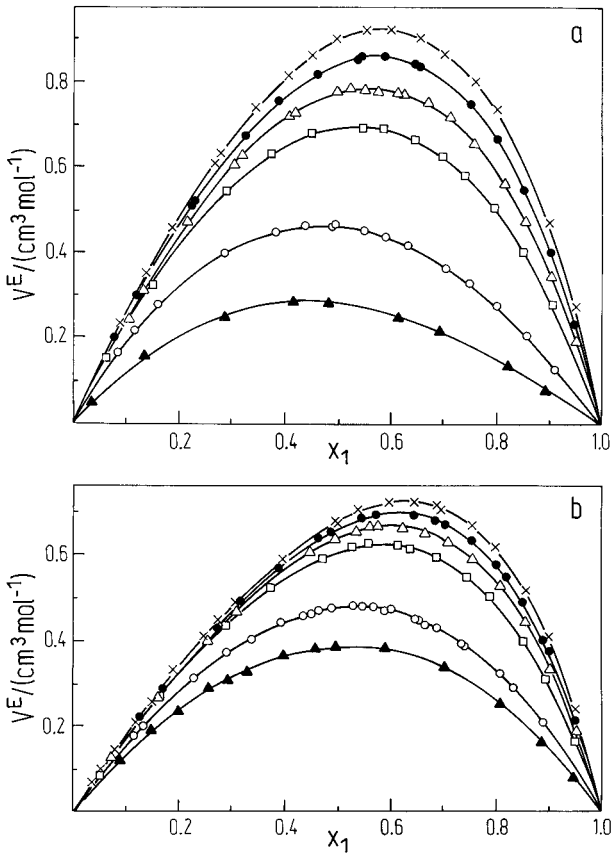

Figure 1. Molar excess volume V^E versus mole fraction x_1 of the binary liquid mixtures: (a) *cis*-1,2-dichloroethene (1) + *n*-alkanes (2) or +2,2,4-trimethylpentane (2); (b) *trans*-1,2-dichloroethene (1) + *n*-alkanes (2) or +2,2,4-trimethylpentane (2) (both at 293.15 K and atmospheric pressure). Key: (▲) 2,2,4-trimethylpentane; (○) heptane; (□) decane; (△) dodecane; (●) tetradecane; (×) hexadecane.

Table 5. Molar Excess Enthalpies H^E of Binary Liquid Mixtures with *cis*-1,2-Dichloroethene as One Component at 293.15 K and Atmospheric Pressure

x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
cis-1,2-Dichloroethene (1) + 2,2,4-Trimethylpentane (2)					
0.2119	596	0.5812	946	0.8061	649
0.3627	873	0.6622	878	0.8696	484
0.4911	952	0.7314	785	0.9434	237
cis-1,2-Dichloroethene (1) + Heptane (2)					
0.0572	203	0.4595	1024	0.7579	767
0.2014	620	0.5694	1006	0.8409	572
0.3465	912	0.6673	925	0.9317	273
cis-1,2-Dichloroethene (1) + Decane (2)					
0.2397	715	0.6225	1087	0.8301	737
0.4025	1059	0.6996	999	0.8863	546
0.5330	1131	0.7635	883	0.9492	277
cis-1,2-Dichloroethene (1) + Dodecane (2)					
0.2693	804	0.6609	1177	0.8510	799
0.4431	1185	0.7327	1081	0.9026	582
0.5743	1249	0.7922	969	0.9588	284
cis-1,2-Dichloroethene (1) + Tetradecane (2)					
0.3157	958	0.7166	1321	0.8831	811
0.5126	1369	0.7787	1207	0.9230	583
0.6380	1404	0.8323	1028	0.9690	275
cis-1,2-Dichloroethene (1) + Hexadecane (2)					
0.3151	991	0.7140	1479	0.8823	953
0.5093	1387	0.7791	1363	0.9221	703
0.6348	1505	0.8308	1181	0.9676	334

calibrated Pt-100 thermoresistors. It was checked against literature data of the system benzene + cyclohexane (Elliott and Wormald, 1976) and exhibited a precision of better

Table 6. Coefficients A_i, Standard (σ) and Maximum (δ) Deviations of the Redlich−Kister Equation (Eq 1) for the Experimental Excess Data at Temperature T (for V^E All A_i, σ, and δ in the Units cm³ mol⁻¹; for H^E All A_i, σ, and δ in the Units J mol⁻¹)

excess property	T/K	A_0	A_1	A_2	A_3	σ	δ
trans-1,2-Dichloroethene (1) + 2,2,4-Trimethylpentane (2)							
V^E	293.15	1.548	0.129	0.014		0.003	0.006
V^E	313.15	1.807	0.193	0.040		0.006	0.011
H^E	293.15	2285	537	68	181	6.5	15.8
trans-1,2-Dichloroethene (1) + Heptane (2)							
V^E	293.15	1.899	0.260	0.021		0.003	0.007
V^E	313.15	2.131	0.278	0.006		0.003	0.006
H^E	293.15	2687	705	−215	131	8.6	20.2
trans-1,2-Dichloroethene (1) + Decane (2)							
V^E	293.15	2.409	0.850	0.276		0.003	0.005
V^E	313.15	2.541	0.918	0.374		0.004	0.007
H^E	293.15	2879	1063	−59	457	8.6	17.6
trans-1,2-Dichloroethene (1) + Dodecane (2)							
V^E	293.15	2.541	1.098	0.425		0.006	0.009
V^E	313.15	2.573	1.133	0.534		0.006	0.015
H^E	293.15	3111	1276	170	275	8.4	17.0
trans-1,2-Dichloroethene (1) + Tetradecane (2)							
V^E	293.15	2.623	1.286	0.634		0.006	0.011
V^E	313.15	2.563	1.306	0.733		0.008	0.014
H^E	293.15	3289	1497	384	423	8.6	26.4
trans-1,2-Dichloroethene (1) + Hexadecane (2)							
V^E	293.15	2.699	1.462	0.731		0.016	0.019
V^E	313.15	2.575	1.425	0.806		0.009	0.016
H^E	293.15	3501	1628	692	616	6.7	18.2
cis-1,2-Dichloroethene (1) + 2,2,4-Trimethylpentane (2)							
V^E	293.15	1.127	−0.267	−0.088		0.005	0.007
V^E	313.15	1.472	−0.290	−0.160		0.004	0.006
H^E	293.15	3834	225	0.997	668	4.2	5.3
cis-1,2-Dichloroethene (1) + Heptane (2)							
V^E	293.15	1.843	−0.225	0.064		0.003	0.005
V^E	313.15	2.165	−0.234	0.083		0.004	0.008
H^E	293.15	4107	182	−150	260	6.5	8.0
cis-1,2-Dichloroethene (1) + Decane (2)							
V^E	293.15	2.771	0.472	0.175		0.004	0.006
V^E	313.15	3.081	0.572	0.231		0.004	0.006
H^E	293.15	4515	477	−369	1688	5.7	10.0
cis-1,2-Dichloroethene (1) + Dodecane (2)							
V^E	293.15	3.082	0.802	0.392		0.005	0.008
V^E	313.15	3.317	0.936	0.468		0.005	0.012
H^E	293.15	4933	1042	−570	2473	8.1	8.8
cis-1,2-Dichloroethene (1) + Tetradecane (2)							
V^E	239.15	3.350	1.095	0.508		0.006	0.010
V^E	313.15	3.506	1.234	0.659		0.006	0.015
H^E	293.15	5418	2337	−240	1768	6.8	9.0
cis-1,2-Dichloroethene (1) + Hexadecane (2)							
V^E	293.15	3.568	1.316	0.644		0.008	0.018
V^E	313.15	3.660	1.469	0.810		0.011	0.026
H^E	293.15	5504	3111	1879	428	8.5	15.0

than 2.5% at the maximum value of H^E, and the mole fraction had an accuracy of 1×10^{-4}.

Results

In Tables 2 and 3 the molar excess volumes V^E and in Tables 4 and 5 the molar excess enthalpies H^E are summarized at various mole fractions x_1 of the mixtures. Only a minimum number of measurements were carried out with the cis isomer, because of the difficulty in obtaining larger amounts of this liquid with sufficient purity. All excess properties have been fitted to Redlich−Kister type polynomials:

$$Z^E_{calc} = x_1 x_2 [\sum_{i=0}^{k} A_i (x_1 - x_2)^i] \quad (1)$$

where $Z^E = V^E/\text{cm}^3\ \text{mol}^{-1}$ and $H^E/\text{J mol}^{-1}$.

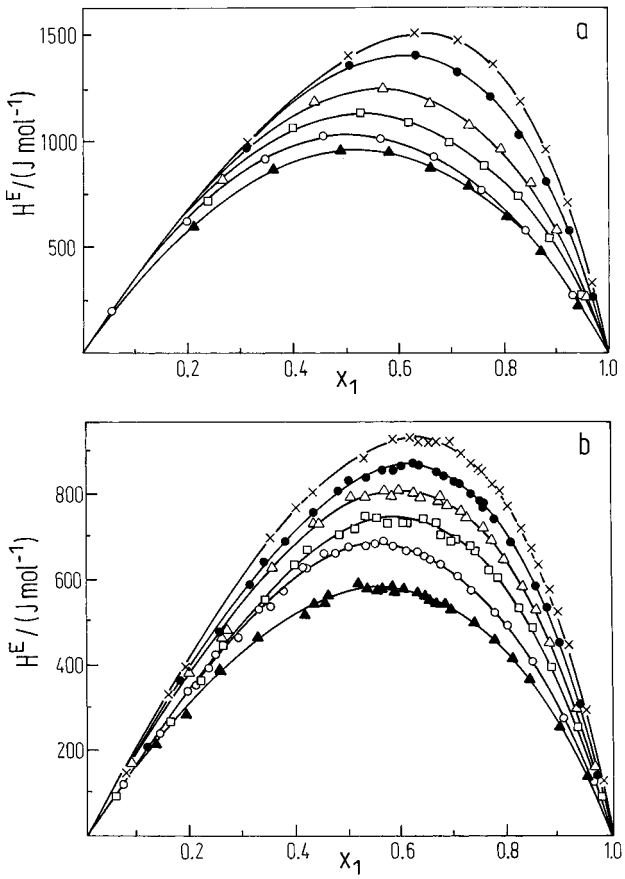

Figure 2. Molar excess enthalpy H^E versus mole fraction x_1 of the binary liquid mixtures: (a) *cis*-1,2-dichloroethene (1) + *n*-alkanes (2) or +2,2,4-trimethylpentane (2); (b) *trans*-1,2-dichloroethene (1) + *n*-alkanes (2) or +2,2,4-trimethylpentane (2) (both at 293.15 K and atmospheric pressure). Symbols are given in the legend for Figure 1.

The coefficients A_i are summarized in Table 6, together with the standard deviation σ defined as

$$\sigma^2 = \sum_N [Z^E - Z^E_{calc}]^2/(N - m) \quad (2)$$

where Z^E is the experimental excess property, N is the number of data points, and m is the number of coefficients A_i, and the maximum deviation δ is

$$\delta = \max|Z^E - Z^E_{calc}| \quad (3)$$

The coefficients A_i and the deviations σ and δ are given in the same units as the corresponding excess properties.

Discussion

All mixtures of *trans*- and *cis*-1,2-dichloroethene with the *n*-alkanes and 2,2,4-trimethylpentane exhibited positive molar excess volumes and enthalpies, which increased with the length of the alkane chain while the maxima where shifted toward higher concentrations of the chloro compound in systems containing the longer alkanes, as shown in Figures 1 and 2. Also the excess volumes increased at the higher temperature of 313.15 K, except for the mixtures of *trans*-1,2-dichloroethene + tetradecane or +hexadecane (cf. Figure 3). All excess properties of mixtures with 2,2,4-trimethylpentane were smaller than those with heptane. Apparently, 2,2,4-trimethylpentane behaves very similarly to hexane in liquid mixtures with a polar partner.

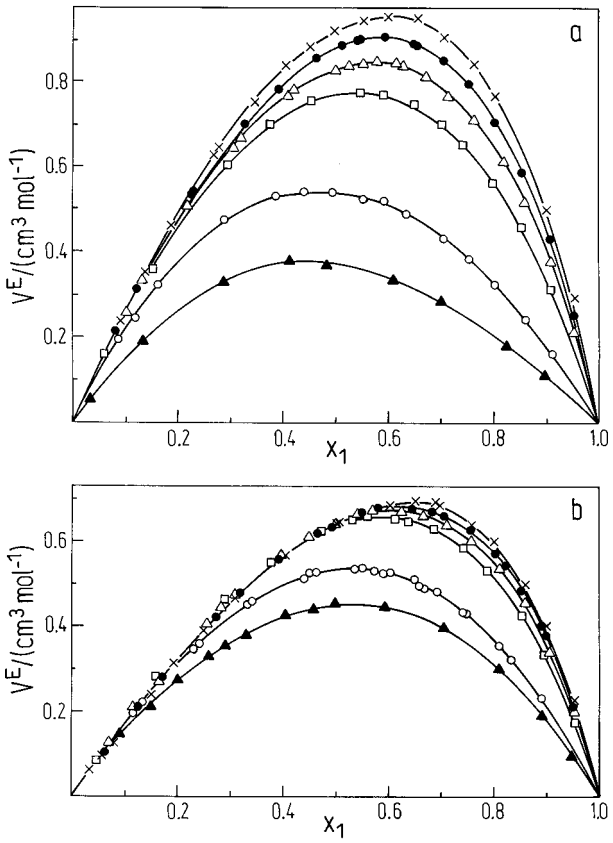

Figure 3. Molar excess volume V^E versus mole fraction x_1 of the binary liquid mixtures: (a) *cis*-1,2-dichloroethene (1) + *n*-alkanes (2) or +2,2,4-trimethylpentane (2); (b) *trans*-1,2-dichloroethene (1) + *n*-alkanes (2) or +2,2,4-trimethylpentane (2) (both at 313.15 K and atmospheric pressure). Symbols are given in the legend for Figure 1.

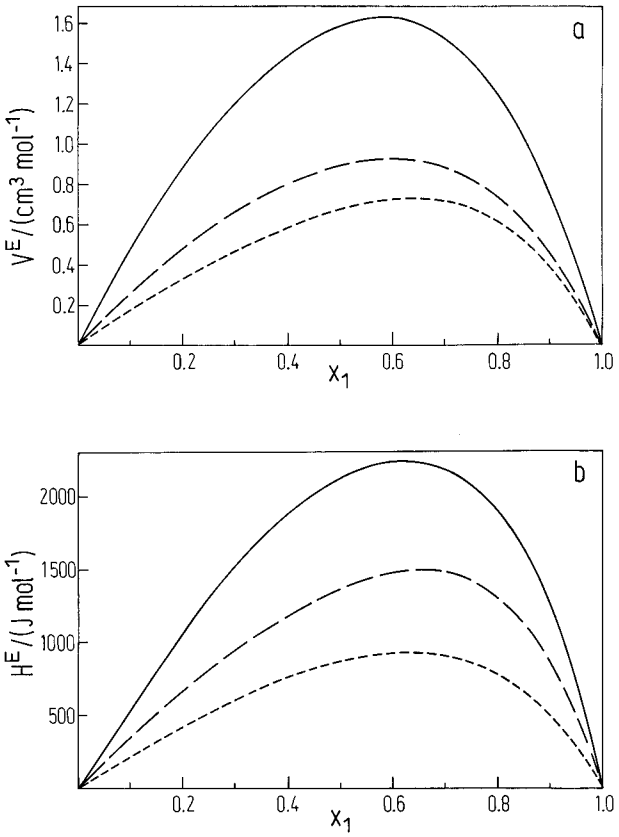

Figure 4. Comparison of (a) the molar excess volume V^E and (b) the molar excess enthalpy H^E versus mole fraction x_1 of the three binary liquid mixtures of (—) 1,2-dichloroethane (1) (Hahn et al., 1993 and 1986), of (– – –) *cis*-1,2-dichloroethene (1), and of (- - -) *trans*-1,2-dichloroethene (1) + hexadecane (2) (all at 293.15 K and atmospheric pressure). Shown are the corresponding Redlich–Kister curves.

A strong analogy between the mixing behavior of the present systems with the dichloroethenes and the mixtures with dichloroethane (Hahn et al., 1993 and 1986) exists. All three dichloro compounds are polar liquids, whose internal order is expected to be disrupted by the mixing process. On the other hand these compounds themselves may also cause a conformational change and/or a decrease in order, especially in the long-chained *n*-alkanes on mixing. Therefore, the average distance of the molecules in the mixtures will be larger than in the more ordered pure liquids and energy is necessary to break the order during the mixing, resulting in the observed positive excess volumes and enthalpies.

However, the measured values of the excess properties are rather different in the three cases. For 1,2-dichloroethane, with a dipole moment of 2.55 D of its gauche conformer (Wada, 1954), which is present in amounts up to 60% in the alkane mixtures (Hahn et al., 1993), there are unusually large positive excess volumes (up to 1.6 $cm^3\ mol^{-1}$) and excess enthalpies (up to 2000 J mol^{-1}). For *cis*-1,2-dichloroethene, exhibiting a smaller dipole moment of 1.76 D (Riddick et al., 1986), these excess values are reduced, correspondingly. Finally, the mixtures with *trans*-1,2-dichloroethene, which has no dipole moment but interacts only locally by its C–Cl bonds and the double bond in addition to its dispersion interaction, show the smallest V^E and H^E values. In Figure 4 this behavior is documented for the mixtures of the three dichloro compounds with hexadecane, where these effects are largest.

Literature Cited

Elliott, K.; Wormald, C. J. A precision differential flow calorimeter. The excess enthalpy of benzene + cyclohexane between 280.15 K and 393.15 K. *J. Chem. Thermodyn.* **1976**, *8*, 881–893.

Findenegg, G. H. Density and expansion coefficient of some liquid alkanes. *Monatsh. Chem.* **1970**, *101*, 1081–1088 (in German).

Hahn, G.; Svejda, P.; Kehiaian, H. V. Excess Enthalpies of the Liquid Systems: 1,2-Dichloroethane + n-Alkanes or + 2,2,4-Trimethylpentane. *Fluid Phase Equilib.* **1986**, *28*, 309–323.

Hahn, G.; Svejda, P.; Dallos, A. Volumetric and dielectric properties of the binary liquid systems: 1,2-dichloroethane + n-alkanes or + 2,2,4-trimethylpentane. *Fluid Phase Equilib.* **1993**, *86*, 293–313.

IUPAC Commission on Atomic Weights and Isotopic Abundances. Atomic Weights of the Elements 1993. *J. Phys. Chem. Ref. Data* **1995**, *24*, 1561–1576.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Techniques of Chemistry; Wiley: New York, 1986; Vol. II.

Siddiqi, M. A.; Götze, G.; Kohler, F. Excess volumes of mixtures of cycloalkanes and methylcycloalkanes. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 529–536.

Svejda, P.; Siddiqi, M. A.; Hahn, G.; Christoph, N. Excess Volume, Isothermal Compressibility, and Excess Enthalpy of the Binary Liquid System 2,2,2-Trifluoroethanol + 2,5,8,11,14-Pentaoxapentadecane. *J. Chem. Eng. Data* **1990**, *35*, 47–49.

TRC Data Bases for Chemistry and Engineering. *TRC Thermodynamic Tables, Vers. 2.0*; Thermodynamics Research Center of the Texas Engineering Experiment Station, The Texas A & M University System: College Station, TX 77843-3111, 1995.

TRC Source Database, Vers. 1.4; Thermodynamics Research Center of the Texas Engineering Experiment Station, The Texas A & M University System: College Station, TX 77843-3111, 1995.

Wada, A. Influence of Solvent upon the Energy Difference between Rotational Isomers. *J. Chem. Phys.* **1954**, *22*, 198–202.

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