

Isothermal Compressibilities of Binary Liquid Mixtures of 1,2-Dichloroethane and of *trans*- and *cis*-1,2-Dichloroethene + *n*-Alkanes or + 2,2,4-Trimethylpentane in the Pressure Range (0.1 to 10) MPa and at 293.15 K

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Isothermal compressibilities have been determined from density measurements of the liquid mixtures of 1,2-dichloroethane, of *trans*-1,2-dichloroethene, and of *cis*-1,2-dichloroethene + heptane, + decane, + dodecane, + tetradecane, + hexadecane, and + 2,2,4-trimethylpentane at pressures from (0.1 to 10) MPa and 293.15 K. The compressibilities were calculated from a fit of the molar volumes to a modified Tait equation. The data could also be correlated surprisingly well by a new linear p - V - T relationship suggested in the literature recently. This correlation makes it possible to judge the quality of the measurements.

Introduction

Knowledge of the p - V - T properties and the derived isothermal compressibility data of liquid mixtures of 1,2-dichloroethane and of the 1,2-dichloroethenes with alkanes may be of interest for plant design in chemical engineering. Especially, such mixtures can also serve as models for monomer and polymer solutions. It has been shown that careful density measurements by means of vibrating steel capillary densimeters at elevated pressures (up to several megapascals) allow rather accurate p - V - T data of pure fluids and fluid mixtures to be determined (Svejda et al., 1990; Galicia-Luna et al., 1994). Also, these data bridge a gap between studies at atmospheric pressure and conventional high-pressure investigations. Therefore, such measurements on the binary liquid mixtures of 1,2-dichloroethane + heptane, + decane, + dodecane, + tetradecane, + hexadecane, and + 2,2,4-trimethylpentane, of *trans*-1,2-dichloroethene + the same alkanes, and of *cis*-1,2-dichloroethene + the same alkanes at pressures between (0.1 and 10) MPa and 293.15 K are reported in the present work. Isothermal compressibilities calculated from these data were also needed for theoretical studies of an equation of state that incorporates information on molecular shape (note that dichloroethane and the dichloroethenes, except for the double bond, differ only little in their molecular structure) (Svejda and Kohler, 1983). Finally, the accurate p - V - T data presented here could be used to test a new linear relationship for pure liquids and liquid mixtures, which was suggested in the literature, recently (Parasfar and Mason, 1993, 1994). This new regularity not only appeared to be useful to judge the quality of the measurements but also gives some insight into the repulsive and attractive forces in fluids.

Experimental Section

1,2-Dichloroethane had a purity of 99.999 mol %, and for the *n*-alkanes heptane, decane, dodecane, tetradecane, and hexadecane and 2,2,4-trimethylpentane purities of 99.82, 99.94, 99.67, 99.89, 99.77, and 99.92 mol %, respec-

tively, were found, all by GLC. The sources of the liquids and their purification were the same as described previously by Hahn et al. (1986).

trans-1,2-Dichloroethene from two different sources was used: either from Aldrich (pA, but not available anymore, EGA-Chemie, Germany) stored over P_2O_5 in darkness before final purification or from Baker (mixture of 75% *trans*- + 25% *cis*-1,2-dichloroethene, "Baker" grade, Baker, Holland). In the latter case the mixture was first kept over P_2O_5 for several days, while black polymerized products appeared on the surface of phosphorus pentoxide, which was continuously renewed. Then the mixture was separated by fractional distillation (over P_2O_5 , under atmospheric pressure, approximately 100 plates). In this way purities of over 90% were obtained for both isomers, which were again stored over phosphorus pentoxide in the dark. Since pure *trans*-1,2-dichloroethene would undergo polymerization quickly (mainly catalyzed by solid surfaces), the final purification was performed immediately before the measurements by further fractional distillation (leading to purities better than 99.4 mol % by GLC).

cis-1,2-Dichloroethene (pA) from Aldrich, EGA-Chemie, Germany, was used without further treatment, or it was obtained from the mixture (Baker, Holland) and purified as described above. *cis*-1,2-Dichloroethene did not undergo polymerization, but the final yield was rather low (purity 99.2 mol % by GLC).

Relative atomic masses $A_r(H) = 1.0079$, $A_r(C) = 12.011$, and $A_r(Cl) = 35.4527$ (IUPAC, 1993) were used for the calculation of molar volumes, V , from densities.

Molar volumes and isothermal compressibilities of the pure liquids and of the mixtures of constant composition, at pressures of (0.1, 2, 4, 6, 8, and 10) MPa and 293.15 K, were determined from densities measured in a steel capillary vibrating tube densimeter (DMA 512, Paar, Germany). The densimeter was calibrated with benzene and carbon tetrachloride, for which accurate compressibility data are available in the literature (Holder and Whalley, 1962). This procedure led to more accurate results than a calibration

Table 1. Measured Molar Volumes V of the Pure Liquids at Pressures p , Isothermal Compressibilities κ° at 0.1 MPa, Constants n Calculated with the Modified Tait Equation, and Comparison with Data from the Literature, All at 293.15 K

compound	$V/(\text{cm}^3 \text{ mol}^{-1})$						$\kappa^\circ/\text{TPa}^{-1}$	n
	$p = 0.1 \text{ MPa}$	$p = 2 \text{ MPa}$	$p = 4 \text{ MPa}$	$p = 6 \text{ MPa}$	$p = 8 \text{ MPa}$	$p = 10 \text{ MPa}$		
1,2-dichloroethane	78.967	78.854	78.736	78.621	78.507	78.394	762	10.2
lit.	78.984 ^a						787 ^a	
	78.984 ^b	78.866 ^b	78.744 ^b	78.624 ^b	78.505 ^b	78.389 ^b	785 ^b	
	78.966 ^c						780 ^d	
<i>trans</i> -1,2-dichloroethene	78.966 ^e	78.850 ^e	78.730 ^e	78.613 ^e	78.496 ^e	78.382 ^e	778 ^e	10.2
lit.	77.136	76.977	76.811	76.648	76.489	76.332	1106	8.5
	77.264 ^f							
<i>cis</i> -1,2-dichloroethene	75.266	75.127	74.983	74.843	74.705	74.572	982	10.2
lit.	75.519 ^f							
2,2,4-trimethylpentane	165.092	164.636	164.173	163.724	163.289	162.871	1468	10.2
lit.	165.085 ^g						1432 ^g	
	165.082 ^h	164.632 ^h	164.173 ^h	163.728 ^h	163.296 ^h	162.877 ^h	1456 ^h	
	165.082 ^c							
heptane	146.550	146.174	145.788	145.413	145.050	144.694	1371	9.8
lit.	146.548 ^f						1357 ⁱ	
							1373 ^j	
decane	194.936	194.553	194.160	193.775	193.398	193.028	1043	9.9
lit.	194.896 ^f						1062 ^j	
dodecane	227.484	227.073	226.651	226.238	225.833	225.435	957	10.2
lit.	227.514 ^f						963 ^j	
tetradecane	260.093	259.652	259.197	258.750	258.312	257.882	900	9.9
lit.	260.103 ^k						899 ^j	
hexadecane	292.714	292.260	291.780	291.320	290.860	290.410	829	9.4
lit.	292.734 ^l						858 ^j	

^a Malhotra et al. (1990). ^b V calculated as a function of pressure from data and correlations by Malhotra et al. (1990), but κ° calculated by eq 1 of this paper. ^c Polynomial interpolation of density data at 0.1 MPa and 278.15–338.15 K from Malhotra and Woolf (1994). ^d Polynomial interpolation of κ_T data at 0.1 MPa and 278.15–338.15 K from Malhotra and Woolf (1994), but κ° calculated by eq 1 of this paper. ^e V calculated as a function of pressure from data and correlations by Malhotra and Woolf (1994), but κ° calculated by eq 1 of this paper. ^f Riddick et al. (1986). ^g Malhotra and Woolf (1990). ^h V calculated as a function of pressure from data and correlations by Malhotra and Woolf (1990), but κ° calculated by eq 1 of this paper. ⁱ Polynomial interpolation of κ_T data at 0.1 MPa and 278.15–338.15 K from Malhotra and Woolf (1991). ^j By numerical differentiation of correlations $V_p/V_{0.1}$ vs pressure at 293.15 K from Dymond and Malhotra (1987); cf. text. ^k Siddiqi et al. (1980). ^l Findenegg (1970).

with water and nitrogen, i.e., a liquid and a gas, as normally used in the literature.

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 of temperature and pressure and control of both quantities) have been described in great detail, recently (Svejda et al., 1990). Here only the uncertainties of the measurements are summarized: The final mole fractions were accurate to 3×10^{-5} , the relative error in the pressure, $\Delta p/p$, was estimated to be 1×10^{-4} , and the temperature was kept constant to ± 0.011 K. The measurements of the density were reproducible to better than $1 \times 10^{-5} \text{ g cm}^{-3}$, which resulted in relative errors of the derived molar volumes, $\Delta V/V$, of better than 1×10^{-4} .

Since the measurements by the densimeter DMA 512 with a steel capillary exhibited only a limited accuracy (of about 1×10^{-4}), the densities at $p^\circ = 0.1$ MPa were measured by means of a densimeter with a vibrating glass tube (DMA 02, Anton Paar, Austria) to accuracies of $5 \times 10^{-5} \text{ g cm}^{-3}$. In this way the high internal consistency of the density measurements (at various pressures) by the instrument DMA 512 (due to its good reproducibility; see above) resulted in good quality of the derivatives, $(\partial V/\partial p)_T$. This was combined with measurements by the instrument DMA 02 to obtain very accurate molar volumes V° at 0.1 MPa in order to obtain the best possible values of the isothermal compressibilities κ° [$= -1/V^\circ (\partial V^\circ/\partial p)_T$] at least at this lowest pressure p° .

These κ° values were determined by a nonlinear fit of the molar volumes to a modified Tait equation

$$V = V^\circ [1 + n\kappa^\circ(p - p^\circ)]^{-1/n} \quad (1)$$

(where n is a constant of fitting) with relative errors of $\Delta\kappa^\circ/\kappa^\circ$ of 0.01 and standard deviations of the fit better than $0.004 \text{ cm}^3 \text{ mol}^{-1}$.

Compressibilities at other pressures than 0.1 MPa (however, with reduced accuracies) can then be calculated as shown in the previous paper, too (Svejda et al., 1990).

Results

In Table 1 the molar volumes of the pure liquids measured at various pressures, the calculated isothermal compressibilities at 0.1 MPa, and the constants of fitting n (in eq 1) are shown. For some of the liquids the compressibility data published previously by this laboratory have been further improved by the present results.

Some excellent data obtained by conventional p - V - T measurements are available in the literature, especially for 1,2-dichloroethane (Malhotra et al., 1990; Malhotra and Woolf, 1994), 2,2,4-trimethylpentane (Malhotra and Woolf, 1990; Malhotra and Woolf, 1994), and heptane (Malhotra and Woolf, 1991) which are compared with the measurements in Table 1. From correlations presented by the authors the necessary data could be calculated. Otherwise the data were determined by polynomial interpolation of Woolf's measurements. Since the authors calculated the compressibility differently, their data of the molar volumes were used to determine κ° according to eq 1 of this work. The very good agreement between the measured volumes of 1,2-dichloroethane, 2,2,4-trimethylpentane, and heptane and those from the literature and the agreement between the compressibilities within the combined experimental errors are very satisfying.

Further, Dymond and Malhotra (1987) have correlated all available density data of n -alkanes from the literature

Table 2. Measured Molar Volumes V of Binary Liquid Mixtures with 1,2-Dichloroethane as One Component at Pressures p , Isothermal Compressibilities κ° at 0.1 MPa, and Constants n Calculated with the Modified Tait Equation, All at 293.15 K

x_1	$V(\text{cm}^3 \text{mol}^{-1})$						$\kappa^\circ/\text{TPa}^{-1}$	n
	$p = 0.1 \text{ MPa}$	$p = 2 \text{ MPa}$	$p = 4 \text{ MPa}$	$p = 6 \text{ MPa}$	$p = 8 \text{ MPa}$	$p = 10 \text{ MPa}$		
1,2-Dichloroethane (1) + 2,2,4-Trimethylpentane (2)								
0.10253	156.535	156.124	155.705	155.300	154.904	154.519	1399	10.2
0.19079	149.174	148.785	148.386	148.000	147.625	147.260	1394	10.2
0.30561	139.349	139.006	138.656	138.316	137.984	137.659	1310	10.0
0.40085	131.185	130.876	130.560	130.252	129.951	129.658	1254	10.0
0.47382	124.898	124.615	124.324	124.041	123.763	123.492	1206	9.3
0.58133	115.585	115.338	115.085	114.835	114.596	114.358	1137	10.2
0.68422	106.625	106.412	106.196	105.982	105.774	105.568	1057	10.0
0.79708	96.763	96.589	96.409	96.233	96.060	95.890	955	9.4
0.89839	87.877	87.734	87.588	87.443	87.301	87.162	861	10.2
1,2-Dichloroethane (1) + Heptane (2)								
0.09261	140.625	140.271	139.909	139.556	139.213	138.878	1341	9.5
0.19838	133.820	133.486	133.145	132.812	132.489	132.173	1328	9.5
0.25858	131.170	130.853	130.529	130.213	129.904	129.603	1286	9.5
0.37908	122.007	121.726	121.438	121.157	120.883	120.614	1225	9.5
0.49074	114.317	114.067	113.809	113.559	113.314	113.073	1164	9.5
0.58593	107.777	107.553	107.324	107.099	106.879	106.663	1103	9.5
0.69805	100.060	99.868	99.669	99.474	99.283	99.046	1024	9.5
0.80676	92.510	92.347	92.179	92.013	91.851	91.692	936	9.5
0.88994	86.855	86.714	86.568	86.423	86.282	86.143	865	9.5
1,2-Dichloroethane (1) + Decane (2)								
0.07909	186.760	186.386	186.000	185.624	185.255	184.895	1066	9.9
0.19412	173.187	172.835	172.476	172.121	171.777	171.437	1077	9.5
0.25905	165.789	165.455	165.110	164.774	164.444	164.119	1071	9.1
0.36471	154.179	153.881	153.574	153.273	152.978	152.686	1025	8.6
0.48354	140.085	139.819	139.545	139.277	139.013	138.753	1006	8.6
0.59218	127.415	127.179	126.936	126.697	126.464	126.233	982	9.1
0.69459	115.422	115.214	115.000	114.789	114.582	114.379	957	9.4
0.78706	104.448	104.262	104.071	103.884	103.700	103.518	943	9.6
0.90475	90.406	90.260	90.109	89.960	89.818	89.669	856	9.0
1,2-Dichloroethane (1) + Dodecane (2)								
0.05052	220.165	219.768	219.359	218.959	218.568	218.182	957	10.2
0.19889	198.752	198.392	198.021	197.658	197.299	196.952	964	10.2
0.27762	187.291	186.951	186.603	186.259	185.921	185.592	960	9.0
0.38563	171.464	171.153	170.833	170.519	170.210	169.909	964	10.2
0.47171	158.730	158.441	158.145	157.853	157.566	157.288	966	10.2
0.57797	143.032	142.775	142.510	142.250	142.000	141.745	955	9.7
0.66121	130.581	130.349	130.111	129.877	129.645	129.421	942	9.7
0.79182	110.915	110.726	110.531	110.339	110.150	109.965	904	9.0
0.89795	94.743	94.589	94.431	94.275	94.122	93.972	857	9.0
1,2-Dichloroethane (1) + Tetradecane (2)								
0.06987	247.453	247.034	246.601	246.176	245.760	245.348	900	9.9
0.19152	226.390	226.006	225.610	225.219	224.837	224.461	900	9.5
0.27755	210.904	210.547	210.176	209.811	209.453	209.097	899	8.0
0.36718	194.857	194.525	194.182	193.843	193.510	193.181	903	8.0
0.47810	174.613	174.316	174.010	173.707	173.408	173.115	901	8.0
0.58608	155.359	155.094	154.820	154.550	154.286	154.025	902	8.0
0.68684	136.952	136.719	136.477	136.239	136.010	135.775	902	8.0
0.79030	117.868	117.672	117.467	117.264	117.067	116.872	887	8.0
0.89569	98.193	98.035	97.870	97.709	97.550	97.393	856	8.8
1,2-Dichloroethane (1) + <i>n</i> -Hexadecane (2)								
0.10652	270.420	270.000	269.552	269.122	268.700	268.280	834	9.5
0.13251	264.970	264.550	264.113	263.683	263.263	262.850	844	9.8
0.28620	232.660	232.288	231.903	231.524	231.152	230.786	849	9.4
0.36467	216.101	215.750	215.383	215.024	214.673	214.330	868	10.4
0.47019	193.748	193.431	193.103	192.783	192.465	192.153	867	9.1
0.58081	170.180	169.900	169.620	169.330	169.060	168.780	865	8.4
0.68179	148.553	148.310	148.060	147.810	147.570	147.330	868	9.3
0.78906	125.330	125.120	124.910	124.710	124.500	124.300	866	9.8
0.89373	102.494	102.330	102.160	102.000	101.840	101.680	839	9.7

up to 1987 as a function of pressure, reduced temperature, and carbon chain length (their eq 2), which could be used to calculate isothermal compressibilities as the pressure derivatives (cf. eqs 2 and 3 in Malhotra and Woolf (1991)). With the critical temperatures of 540.3 K, 617.7 K, 658.2 K, 693.0 K, and 722.0 K for heptane, decane, dodecane, tetradecane, and hexadecane, respectively, from the literature (Ambrose, 1980) and by numerical differentiation the compressibilities were calculated and compared with

the present measurements in Table 1. Again a very good correspondence between the compressibility data was found.

In Tables 2–4 the measured molar volumes at various pressures, the calculated compressibilities at 0.1 MPa, and the constants of fitting n are presented for the mixtures of 1,2-dichloroethane, of *trans*-1,2-dichloroethene, and of *cis*-1,2-dichloroethene, respectively, with the alkanes. As described above it was difficult to obtain large amounts of

Table 3. Measured Molar Volumes V of Binary Liquid Mixtures with *trans*-1,2-Dichloroethene as One Component at Pressures p , Isothermal Compressibilities κ° at 0.1 MPa, and Constants n Calculated with the Modified Tait Equation, All at 293.15 K

x_1	$V/(\text{cm}^3 \text{ mol}^{-1})$						$\kappa^\circ/\text{TPa}^{-1}$	n
	$p = 0.1 \text{ MPa}$	$p = 2 \text{ MPa}$	$p = 4 \text{ MPa}$	$p = 6 \text{ MPa}$	$p = 8 \text{ MPa}$	$p = 10 \text{ MPa}$		
<i>trans</i> -1,2-Dichloroethene (1) + 2,2,4-Trimethylpentane (2)								
0.15144	151.956	151.551	151.133	150.727	150.333	149.948	1426	8.9
0.25999	142.510	142.130	141.745	141.369	141.005	140.649	1419	10.1
0.32937	136.456	136.099	135.734	135.378	135.032	134.695	1395	9.4
0.45884	125.108	124.788	124.460	124.141	123.831	123.591	1366	9.8
0.54441	117.532	117.237	116.935	116.641	116.355	116.075	1340	9.8
0.67075	106.140	105.884	105.620	105.363	105.113	104.869	1291	9.8
0.77895	96.792	96.567	96.335	96.109	95.889	95.673	1243	9.8
0.84760	90.691	90.486	90.275	90.069	89.867	89.671	1207	9.8
0.94602	81.944	81.769	81.587	81.409	81.236	81.065	1140	8.5
<i>trans</i> -1,2-Dichloroethene (1) + Heptane (2)								
0.09168	140.357	140.000	139.624	139.262	138.910	138.565	1373	8.7
0.20069	132.928	132.586	132.239	131.900	131.570	131.251	1370	10.3
0.29069	126.744	126.420	126.090	125.767	125.452	125.147	1361	9.5
0.38125	120.486	120.183	119.873	119.571	119.276	118.990	1341	9.5
0.48634	113.215	112.934	112.647	112.368	112.097	111.833	1321	10.1
0.59177	105.870	105.613	105.350	105.095	104.847	104.605	1292	10.1
0.69450	98.677	98.443	98.206	97.973	97.748	97.526	1258	10.1
0.80822	90.659	90.453	90.242	90.036	89.836	89.639	1210	10.1
0.90569	83.745	83.562	83.375	83.191	83.014	82.838	1162	10.1
<i>trans</i> -1,2-Dichloroethene (1) + Decane (2)								
0.33561	155.846	155.525	155.193	154.871	154.557	154.249	1098	10.4
0.45232	142.148	141.851	141.548	141.249	140.959	140.673	1110	10.0
0.64215	120.132	119.881	119.621	119.367	119.120	118.878	1117	10.0
0.78469	102.814	102.597	102.374	102.157	101.946	101.736	1121	9.9
<i>trans</i> -1,2-Dichloroethene (1) + Dodecane (2)								
0.20776	196.591	196.228	195.853	195.485	195.127	194.775	982	10.0
0.35101	175.220	174.887	174.543	174.209	173.881	173.558	1010	10.0
0.49360	154.009	153.711	153.404	153.105	152.812	152.525	1027	10.0
0.64349	131.384	131.123	130.854	130.592	130.336	130.085	1055	10.0
0.79817	107.946	107.725	107.499	107.275	107.059	106.847	1088	10.0
<i>trans</i> -1,2-Dichloroethene (1) + Tetradecane (2)								
0.18452	226.612	226.224	225.825	225.432	225.048	224.671	908	10.2
0.38802	189.589	189.254	188.909	188.571	188.240	187.913	938	10.2
0.51522	166.300	166.000	165.688	165.383	165.086	164.794	963	10.2
0.64807	142.045	141.780	141.508	141.241	140.980	140.725	990	10.2
0.79544	114.956	114.732	114.503	114.279	114.060	113.845	1031	10.2
<i>trans</i> -1,2-Dichloroethene (1) + Hexadecane (2)								
0.15933	258.650	258.235	257.807	257.385	256.973	256.565	851	9.9
0.32689	222.749	222.382	222.002	221.629	221.262	220.903	876	9.7
0.48546	188.712	188.390	188.060	187.730	187.410	187.098	907	9.9
0.59911	164.260	163.972	163.674	163.382	163.094	162.815	933	9.9
0.79641	121.633	121.401	121.170	120.940	120.714	120.492	996	9.7

Table 4. Measured Molar Volumes V of Binary Liquid Mixtures with *cis*-1,2-Dichloroethene as One Component at Approximately Equimolar Composition and Pressures p , Isothermal Compressibilities κ° at 0.1 MPa, and Constants n Calculated with the Modified Tait Equation, All at 293.15 K

x_1	$V/(\text{cm}^3 \text{ mol}^{-1})$						$\kappa^\circ/\text{TPa}^{-1}$	n
	$p = 0.1 \text{ MPa}$	$p = 2 \text{ MPa}$	$p = 4 \text{ MPa}$	$p = 6 \text{ MPa}$	$p = 8 \text{ MPa}$	$p = 10 \text{ MPa}$		
<i>cis</i> -1,2-Dichloroethene (1) + 2,2,4-Trimethylpentane (2)								
0.50595	120.152	119.858	119.559	119.266	118.983	118.706	1306	10.7
<i>cis</i> -1,2-Dichloroethene (1) + Heptane (2)								
0.47692	109.478	109.219	108.955	108.699	108.448	108.204	1261	11.1
<i>cis</i> -1,2-Dichloroethene (1) + Decane (2)								
0.50152	135.679	135.405	135.122	134.845	134.577	134.313	1078	10.5
<i>cis</i> -1,2-Dichloroethene (1) + Dodecane (2)								
0.50441	152.460	152.183	151.897	151.619	151.345	151.075	965	10.1
<i>cis</i> -1,2-Dichloroethene (1) + Tetradecane (2)								
0.53313	174.232	173.925	173.609	173.300	173.000	172.698	934	10.2
<i>cis</i> -1,2-Dichloroethene (1) + Hexadecane (2)								
0.51759	188.294	187.980	187.654	187.335	187.023	186.714	887	9.8

pure liquid *cis*-1,2-dichloroethene. Therefore, in Table 4 only measurements at equimolar composition can be presented. There are no other compressibility data of these mixtures available in the literature, but the results at least allow a comparison with the other systems.

On comparison with data for mixtures from the literature it was found (but not further shown here) that the compressibilities κ° at 0.1 MPa of the system 1,2-dichloroethane + 2,2,4-trimethylpentane did agree within the combined experimental errors with the measurements of Malhotra

and Woolf (1994), if their data were properly interpolated by polynomials.

All polynomial interpolations and numerical differentiations were carried out by the program MATHEMATICA (Wolfram, 1992).

Finally, the measurements were used to test a new regularity introduced by Parsafar and Mason (1993, 1994), who suggested that $[(pV/RT) - 1]V^2$ was linear with $1/V^2$ for pure liquids and liquid mixtures at least in the pressure and temperature range applied in the present work. The p - V - T results for the pure liquids and for some equimolar mixtures (with 2,2,4-trimethylpentane, heptane, dodecane, and hexadecane, which were tested) could be fitted to that linear relationship surprisingly well with coefficients of determination R^2 (which are the square of the correlation coefficients) of ~ 0.9999 or better, in full accordance with the authors. Only in a few cases a slightly worse fit was obtained. For pure 1,2-dichloroethane, $R^2 = 0.9997$, for *trans*-1,2-dichloroethene + dodecane, $R^2 = 0.996$, and for *cis*-1,2-dichloroethene + hexadecane $R^2 = 0.98$ were found. However, since the linear relationship held in the majority of cases, a worse coefficient of determination was taken to indicate that the quality of the measured values was somewhat poorer.

Therefore, the linear regularity test suggested by Parsafar and Mason (1993) seems to be a very sensitive tool to judge the quality of p - V - T measurements at least for liquids in the pressure and temperature range given by the authors.

Discussion

The measurements by means of a vibrating steel capillary densimeter at elevated pressures presented in this work confirm that it is possible to obtain by this method p - V - T and compressibility values of as good a quality as those obtained by conventional p - V - T techniques which require considerable effort.

Regarding the linear regularity test applied to the results of this work, it should be noted that the intercept and slope of the fitted straight lines are also proportional to the average attractive and to the repulsive part of the intermolecular potential of the liquid(s), respectively (Parsafar and Mason, 1993). In the present study *trans*- and *cis*-1,2-dichloroethene exhibited an almost identical repulsive part of the potential, while the attractive part of the *cis*-isomer was a bit larger by about 4%. In the mixtures, the attractive parts of the potentials were found to be larger than the geometric means between the attractive parts of the corresponding pure components, indicating additional interactions over simple London dispersion forces. These

examples may suffice to demonstrate the interesting theoretical implications of the new linear relationship. Further studies are in progress.

Literature Cited

- Ambrose, D. Vapour-Liquid Critical Properties. National Physical Laboratory Report; Teddington, U.K., 1980.
- Dymond, J. H.; Malhotra, R. Densities of n-Alkanes and Their Mixtures at Elevated Pressures. *Int. J. Thermophys.* **1987**, *8*, 541–555.
- Findenegg, G. H. Dichte und Ausdehnungskoeffizient einiger flüssiger Alkane. *Monatsh. Chem.* **1970**, *101*, 1081–1088.
- Galicia-Luna, L. A.; Richon, D.; Renon, H. New Loading Technique for a Vibrating Tube Densimeter and Measurements of Liquid Densities up to 39.5 MPa for Binary and Ternary Mixtures of the Carbon Dioxide-Methanol-Propane System. *J. Chem. Eng. Data* **1994**, *39*, 424–431.
- 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.
- Holder, G. A.; Whalley, E. Compressibility of Liquids. *Trans. Faraday Soc.* **1962**, *58*, 2095–2107.
- IUPAC Commission on Atomic Weights and Isotopic Abundances. Atomic Weights of the Elements 1991. *J. Phys. Chem. Ref. Data* **1993**, *22*, 1571–1584.
- Malhotra, R.; Woolf, L. A. Thermodynamic Properties of 2,2,4-Trimethylpentane. *Int. J. Thermophys.* **1990**, *11*, 1059–1073.
- Malhotra, R.; Woolf, L. A. Volume ratios $\{V_{(p)}/V_{(0.1 \text{ MPa})}\}$ for n-heptane at temperatures from 278 K to 338 K for pressures up to 400 MPa. *J. Chem. Thermodyn.* **1991**, *23*, 49–57.
- Malhotra, R.; Woolf, L. A. (p , V_m , T , x) measurements for liquid mixtures of 1,2-dichloroethane with 2,2,4-trimethylpentane. *Fluid Phase Equilib.* **1994**, *94*, 227–251.
- Malhotra, R.; Price, W. E.; Woolf, L. A.; Eastale, A. J. Thermodynamic and Transport Properties of 1,2-Dichloroethane. *Int. J. Thermophys.* **1990**, *11*, 835–861.
- Parsafar, G.; Mason, E. A. Linear Isotherms for Dense Fluids: A New Regularity. *J. Phys. Chem.* **1993**, *97*, 9048–9053.
- Parsafar, G.; Mason, E. A. Linear Isotherms for Dense Fluids: Extension to Mixtures. *J. Phys. Chem.* **1994**, *98*, 1962–1967.
- Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry, Vol. II. Organic Solvents*, 4th ed.; Wiley: New York, 1986.
- 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.; Kohler, F. A generalized van der Waals equation of state I. Treatment of molecular shape in terms of the Boublik-Nezbeda equation. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 672–680.
- 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.
- Wolfram, S. *MATHEMATICA: A System for Doing Mathematics by Computer*, Version 2.1; Commercial Product by Wolfram Research Inc.: Champaign, IL, 1992.

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