

Thermodynamic and Acoustic Properties of Mixtures of 1,6-Dichlorohexane with Heptane from (293 to 313) K[†]

Mirosław Chorążewski,^{*,‡} Paweł Góralski,[§] Małgorzata Hrynko,[‡] Jean-Pierre Grolier,^{||} and Emmerich Wilhelm[⊥]

Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland, Department of Physical Chemistry, University of Łódź, Pomorska 165, 90-236 Łódź, Poland, Laboratory of Thermodynamics of Solutions and Polymers, Blaise Pascal University of Clermont-Ferrand, F-63177, Aubière, France, and Institute of Physical Chemistry, University of Wien, Währinger Strasse 42, A-1090 Wien, Austria

For $\{x\text{Cl}(\text{CH}_2)_6\text{Cl} + (1-x)n\text{-C}_7\text{H}_{16}\}$, densities ρ were measured with a vibrating-tube densimeter at (293.15, 298.15, 303.15, 308.15, and 313.15) K, covering the whole composition range. From the densities the corresponding isobaric expansivities α_p and the excess molar volumes V^E were calculated. At the same temperatures, the molar heat capacities at constant pressure C_p were also measured over the whole composition range using a differential scanning calorimeter (DSC III from Setaram), and excess molar heat capacities at constant pressure C_p^E were calculated therefrom. In addition, ultrasound speeds u were determined with a pulse-echo-overlap apparatus. From these results, isentropic compressibilities κ_S , isothermal compressibilities κ_T , molar heat capacities at constant volume C_V , and internal pressures Π were obtained for this system at all five temperatures. The V^E are negative throughout; they are somewhat skewed with minima around $x = 0.6$, and they become less negative with decreasing temperature. The C_p^E are all negative and strongly asymmetric with minima around $x = 0.3$ and rather broad shoulders at larger mole fractions of 1,6-dichlorohexane. With decreasing temperature, the $C_p^E(x)$ curves become less negative with more pronounced shoulders, which behavior is reminiscent of the onset of a W-shaped composition dependence.

Introduction

Directional intermolecular forces contribute significantly to the thermodynamic properties of pure liquids and liquid mixtures. A versatile approximate statistical–mechanical method for estimating and discussing dipolar and quadrupolar contributions was presented some time ago by Pople,¹ with later contributions being due to Kalali et al.² and to Patterson.³ In pure liquids, at high densities and low temperatures, these orientational contributions lead to local structure, that is, to ordering. The presence of order lowers the Helmholtz energy as well as the internal energy and the entropy, and increasingly so at low temperatures, while the contribution to the heat capacity at constant volume of the pure liquid is positive. Extension to mixtures is fairly straightforward. The net destruction of order resulting from mixing, say, a polar liquid with a nonpolar alkane or cycloalkane,² results in *positive* contributions to the excess molar Gibbs energy G^E , to the excess molar enthalpy H^E , and to the excess molar entropy S^E , and to a *positive* contribution to the excess molar heat capacity C_p^E at constant pressure p , which may be expressed as

$$C_p^E = -\frac{2(H^E - G^E)}{T} \quad (1)$$

where T is the thermodynamic temperature. This simple relation appears to hold well for mixtures containing a weakly polar substance. However, for mixtures involving a strongly polar

substance as the second component, the experimental C_p^E is usually less negative than demanded by eq 1, which indicates that some orientations have considerably greater stability than accounted for by the angle-averaging procedure involved. One possible way of treating these nonrandom effects is based on Guggenheim's quasi-chemical theory,⁴ as first suggested by Saint-Victor and Patterson.⁵ To an excellent approximation, C_p^E may be separated into a random and a nonrandom contribution.^{5–10} While the random contribution is always negative with a parabolic composition dependence, the nonrandom contribution is always positive and has zero slope against the mole fraction axis at both ends of the composition range.¹¹ Thus, the superposition of these two contributions accounts qualitatively for the appearance of W-shaped $C_p^E(x)$ curves, as first reported by Grolier et al.¹² With decreasing temperature, the W-shape becomes more pronounced and is, in fact, indicative for approaching an upper critical solution temperature.

Initially, studies of mixtures of α,ω -dihaloethanes with hydrocarbons have primarily been motivated by interest in the influence of rotational isomerism (involving carbon–carbon single bonds) upon various thermophysical properties of such systems. For instance, the experimental results for mixtures of 1,2-dichloroethane with benzene or cyclohexane,^{13,14} respectively, were discussed in terms of stabilization of either the strongly dipolar *gauche* rotamers or the nonpolar *trans* rotamer through interaction with the hydrocarbon component. Thus in view of the above, in systems of type (α,ω -dihaloethanes + alkane or cycloalkane) either W-shaped C_p^E or a composition dependence of C_p^E indicating incipient W-shape is expected and indeed observed.^{15–18} To complement these studies and, in particular, to investigate in detail the temperature dependence of C_p^E in such systems, we report here first results obtained for the mixture of 1,6-dichlorohexane with heptane, at atmospheric pressure, from (293 to 313) K. It is, in fact, a continuation of

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* Corresponding author. E-mail: mirosław.chorazewski@us.edu.pl.

[‡] University of Silesia.

[§] University of Łódź.

^{||} Blaise Pascal University of Clermont-Ferrand.

[⊥] University of Wien.

recent studies of thermodynamic and acoustic properties of liquid mixtures of dihaloalkanes with heptane.^{19,20} We also note that systematic investigations on mixtures of type $\{x\text{Cl}(\text{CH}_2)_k\text{Cl} + (1-x)n\text{-C}_7\text{H}_{2l+2}\}$ will contribute to a better, molecular-based understanding of the so-called intramolecular *proximity effect*, which was first quantified by Kehiaian et al.^{21–23} via a group-contributive analysis of excess molar quantities (within the frame of the TOM project).

Specifically, for the system $\{x\text{Cl}(\text{CH}_2)_6\text{Cl} + (1-x)n\text{-C}_7\text{H}_{16}\}$ we report here densities ρ , derived excess molar volumes V^E , isobaric expansivities α_p , molar heat capacities C_p , excess molar heat capacities C_p^E , speeds of ultrasound u , isentropic compressibilities κ_S , isothermal compressibilities κ_T , molar heat capacities at constant volume C_V , ratios of heat capacities $\gamma \equiv C_p/C_V = \kappa_T/\kappa_S$, and internal pressures Π over the whole composition range in the temperature range (293 to 313) K.

Experimental Section

Materials. Heptane was from Polish Chemicals with a stated purity of more than 99.8 % (molar basis). The 1,6-dichlorohexane was specified by the supplier (Avocado) as having a purity of 97 % and was further purified by fractional distillation. Only the middle fractions were collected, resulting in a liquid sample with a purity of more than 98 % (by gas–liquid chromatography). The mass fraction of water as determined by the Karl Fischer method was less than $3 \cdot 10^{-5}$ for heptane and less than $4 \cdot 10^{-5}$ for 1,6-dichlorohexane. Both liquids were dried with a molecular sieve (Lancaster, type 3A, beads) and stored in the dark. Prior to the experiments, they were degassed ultrasonically. Mixtures were prepared by mass using a Sartorius RC 210D balance (for heat capacity measurements) or an Ohaus AS-2000 balance and used immediately. All molar quantities are based on the relative atomic mass table of IUPAC 2005.²⁴ The possible error in the mole fraction is about 10^{-4} .

Measurements. Densities ρ were measured with a vibrating-tube densimeter (Anton Paar, model DMA 5000) operated in the static mode with an uncertainty of $5 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$, as estimated from results of measurements on standard materials for density determinations, such as highly purified and degassed water, aqueous solutions of sodium chloride, and selected organic liquids.

The density of any liquid relative to the density of pure water, ρ_w , is given by

$$\rho = \rho_w + b(\tau^2 - \tau_w^2) \quad (2)$$

where b is characteristic for a particular oscillator depending somewhat on temperature, and τ and τ_w are the periods of vibration of the tube filled with the liquid and with water, respectively. From the measured density ρ of a mixture, the excess molar volume of that mixture with mole fraction x of 1,6-dichlorohexane is obtained from

$$V^E = xM_1 \left\{ \left(\frac{1}{\rho} \right) - \left(\frac{1}{\rho_1} \right) \right\} + (1-x)M_2 \left\{ \left(\frac{1}{\rho} \right) - \left(\frac{1}{\rho_2} \right) \right\} \quad (3)$$

where M_i and ρ_i denote, respectively, the molar mass and the density of pure component $i = 1$ (1,6-C₆H₁₂Cl₂) or $i = 2$ (n-C₇H₁₆).

From the temperature dependence of the densities the isobaric expansivity α_p is obtained via

$$\alpha_p = -\rho^{-1} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (4)$$

Isobaric heat capacities were measured with a differential scanning calorimeter (Micro DSC III, from Setaram) using the “continuous with reference” method as described in detail by Góralski et al.²⁵ The uncertainty of the measurements is estimated to be about ± 0.15 %. Excess molar heat capacities were then calculated from

$$C_p^E = C_p - \{xC_{p,1} + (1-x)C_{p,2}\} \quad (5)$$

where $C_{p,i}$ is the molar heat capacity of pure component $i = 1$ or 2.

The speeds of ultrasound at 4 MHz were measured with a pulse-echo-overlap apparatus designed and constructed in the Department of Physical Chemistry of the University of Silesia. The measuring cell was thermostatted to ± 0.005 K using a Techne TU16D temperature controller. The instrument was calibrated with doubly distilled water using Marczak’s²⁶ recent speed-of-ultrasound data for water. The measurement uncertainty was estimated at $0.5 \text{ m} \cdot \text{s}^{-1}$, while the precision was an order of magnitude better.³⁸

Isentropic compressibilities were then calculated from

$$\kappa_S = \frac{1}{\rho u^2} \quad (6)$$

and isothermal compressibilities from

$$\kappa_T = \gamma \kappa_S \quad (7)$$

where

Table 1. Comparison with Selected Literature Data at $T = 298.15$ K: Densities ρ , Molar Heat Capacities at Constant Pressure C_p , Speeds of Ultrasound u , Isobaric Expansivities α_p , Isentropic Compressibilities κ_S , Isothermal Compressibilities κ_T , Molar Heat Capacities at Constant Volume C_V , Ratio of Heat Capacities $\gamma = C_p/C_V$, and Internal Pressures Π of the Pure Liquid Components

	Heptane				
	this work	literature			
$\rho/(\text{kg} \cdot \text{m}^{-3})$	679.56	679.43, ²⁷	679.50, ²⁸	679.54, ²⁹	679.60 ^{30,31}
$C_p/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	224.72 ^a	224.7, ^{32,33}	224.71, ¹²	224.72, ³¹	224.78 ²⁷
$u/(\text{m} \cdot \text{s}^{-1})$	1130.38	1129.81, ³⁴	1129.85, ³⁵	1130.14, ³¹	
		1130.18, ³⁰	1130.2, ³⁶	1130.44, ³⁷	1130.6 ³⁸
$10^3 \alpha_p/\text{K}^{-1}$	1.257	1.245, ³¹	1.246, ²⁹	1.256 ³⁹	
$10^{12} \kappa_S/\text{Pa}^{-1}$	1151.66	1152.08, ^b	1152.32, ³⁵	1152.84 ³⁴	
$10^{12} \kappa_T/\text{Pa}^{-1}$	1460.6	1438, ⁴⁰	1440, ⁴¹	1455, ^{29,31}	1485 ³⁹
$C_V/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	177.19	177.92, ^b	178.0 ²⁹		
γ	1.2682				
Π/MPa	256.5				
		1,6-Dichlorohexane			
$\rho/(\text{kg} \cdot \text{m}^{-3})$	1063.61	1063.0, ^c	1063.74, ⁴³	1064.39, ¹⁷	1064.65 ⁴⁴
$C_p/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	240.64	239.57, ¹⁷	240.39, ²⁵	240.60 ⁴³	
$u/(\text{m} \cdot \text{s}^{-1})$	1319.81	1317.28 ⁴³			
$10^3 \alpha_p/\text{K}^{-1}$	0.891	0.890 ^d			
$10^{12} \kappa_S/\text{Pa}^{-1}$	539.75	541.76 ^d			
$10^{12} \kappa_T/\text{Pa}^{-1}$	683.1	684.9 ^d			
$C_V/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	190.15	190.31 ^d			
γ	1.2655				
Π/MPa	388.8				

^a Value from ref 19. ^b Value calculated from ref 31. ^c Value calculated from ref 42. ^d Value calculated from ref 43.

Table 2. Experimental Molar Heat Capacities at Constant Pressure $C_p(T,x)$ as a Function of Mole Fraction x for { x 1,6-Dichlorohexane + (1 - x) Heptane} at Temperatures 293.15 $\leq T/K \leq$ 313.15

T/K	$C_p/(J \cdot K^{-1} \cdot mol^{-1})$										
	$x = 0.0000^a$	$x = 0.1033$	$x = 0.2005$	$x = 0.3004$	$x = 0.3970$	$x = 0.5025$	$x = 0.5978$	$x = 0.7012$	$x = 0.7975$	$x = 0.8993$	$x = 1.0000$
293.15	222.87	224.18	225.58	226.93	228.73	230.53	232.22	233.79	235.58	237.46	239.21
294.15	223.42	224.47	225.71	227.22	229.08	230.89	232.55	234.00	235.86	237.73	239.50
295.15	223.60	224.85	226.27	227.61	229.51	231.34	232.94	234.33	236.23	238.10	239.69
296.15	223.97	225.28	226.73	227.98	229.89	231.84	233.25	234.73	236.51	238.39	240.02
297.15	224.35	225.70	227.04	228.31	230.27	231.98	233.48	235.05	236.81	238.57	240.35
298.15	224.72	226.02	227.35	228.65	230.41	232.13	233.77	235.36	237.10	238.92	240.64
299.15	225.10	226.42	227.84	228.96	230.75	232.24	234.00	235.65	237.33	239.06	240.85
300.15	225.47	226.82	228.08	229.21	231.06	232.49	234.22	236.05	237.68	239.39	241.15
301.15	225.87	227.16	228.49	229.61	231.57	232.94	234.60	236.34	238.04	239.79	241.46
302.15	226.22	227.48	228.83	230.00	231.80	233.35	234.96	236.63	238.29	240.08	241.80
303.15	226.61	227.86	229.13	230.36	232.08	233.73	235.31	236.93	238.61	240.37	242.06
304.15	227.00	228.19	229.46	230.70	232.56	234.04	235.48	237.20	238.86	240.64	242.34
305.15	227.40	228.57	229.83	230.91	232.74	234.33	235.88	237.53	239.21	240.92	242.62
306.15	227.75	228.88	230.10	231.36	233.13	234.40	236.03	237.84	239.44	241.20	242.83
307.15	228.14	229.30	230.51	231.65	233.51	235.07	236.50	238.18	239.76	241.48	243.21
308.15	228.54	229.71	230.91	232.08	233.76	235.33	236.85	238.49	240.12	241.83	243.49
309.15	228.95	230.05	231.19	232.35	234.03	235.45	237.17	238.74	240.37	242.06	243.73
310.15	229.30	230.40	231.55	232.73	234.35	235.77	237.52	239.07	240.64	242.36	244.00
311.15	229.71	230.86	231.97	233.11	234.88	236.41	237.89	239.43	241.08	242.73	244.35
312.15	230.11	231.16	232.33	233.45	235.01	236.75	238.16	239.72	241.32	243.02	244.68
313.15	230.51	231.55	232.68	233.79	235.43	236.93	238.39	240.06	241.64	243.28	244.91

^a C_p values for pure liquid heptane were taken from Chorążewski et al.¹⁹

Table 3. Experimental Densities $\rho(T,x)$ as a Function of Mole Fraction x for { x 1,6-Dichlorohexane + (1 - x) Heptane} at Temperatures $T/K = 293.15, 298.15, 303.15, 308.15,$ and 313.15

x	$\rho/(kg \cdot m^{-3})$				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.0000	683.79	679.56	675.30	671.02	666.71
0.0998	722.22	717.96	713.61	709.34	704.96
0.1999	760.97	756.72	752.30	748.07	743.68
0.2998	799.74	795.42	791.00	786.58	782.17
0.4001	838.66	834.33	830.00	825.61	821.26
0.5001	877.38	873.04	868.59	864.37	859.93
0.6002	916.12	911.75	907.23	902.95	898.61
0.7000	954.46	950.12	945.63	941.10	936.70
0.8002	992.78	988.40	983.71	979.09	974.58
0.9001	1030.70	1026.11	1021.49	1016.82	1012.12
1.0000	1068.33	1063.61	1058.87	1054.14	1049.39

$$\gamma = 1 + \frac{TM\alpha_p^2 u^2}{C_p} \quad (8)$$

and

$$M = xM_1 + (1 - x)M_2 \quad (9)$$

Finally, the molar heat capacities C_V at constant volume $V = (M/\rho)$ were obtained from

$$C_V = \frac{C_p}{\gamma} \quad (10)$$

and internal pressures Π from

$$\Pi \cong \frac{T\alpha_p}{\kappa_T} \quad (11)$$

thereby neglecting the term $-P_o$, since the vapor pressure is *very much* smaller than $T\alpha_p/\kappa_T$.

Results and Discussion

Densities, molar heat capacities at constant pressure, and speeds of ultrasound obtained in this work at 298.15 K, as well as the derived isobaric expansivities, isentropic compressibilities, isothermal compressibilities, molar heat capacities at constant volume, ratios of the heat capacities, and internal pressures of the pure liquids at 298.15 K are given in Table 1. In general, agreement with reliable values from the literature is satisfactory.

Heat capacity measurements on the pure liquids and the mixtures were carried out from somewhat below 293 K to somewhat above 313 K at a scanning rate of 0.1 K \cdot min⁻¹. The

Table 4. Experimental Speeds of Ultrasound $u(T,x)$ at 4 MHz as a Function of Mole Fraction x for { x 1,6-Dichlorohexane + (1 - x) Heptane} at Various Temperatures in the Range 292.49 $\leq T/K \leq$ 313.45

x	T	u	T	u	T	u	T	u	T	u
	K	m \cdot s ⁻¹	K	m \cdot s ⁻¹	K	m \cdot s ⁻¹	K	m \cdot s ⁻¹	K	m \cdot s ⁻¹
0.0000	292.70	1154.11	298.00	1131.06	302.98	1109.45	308.06	1087.42	313.45	1064.29
0.1014	292.92	1167.57	298.21	1145.47	303.20	1124.68	308.18	1103.97	313.25	1082.87
0.1999	292.81	1181.63	298.21	1159.37	303.20	1138.92	308.19	1118.59	313.28	1098.01
0.3004	292.49	1199.10	298.17	1176.14	303.15	1156.10	308.13	1136.24	313.21	1116.15
0.4000	292.91	1215.33	298.20	1194.95	303.19	1175.46	308.17	1156.12	313.26	1136.54
0.4999	292.79	1234.95	298.17	1214.49	303.14	1195.51	308.13	1176.55	313.22	1157.34
0.6004	292.81	1254.97	298.21	1235.23	303.20	1216.82	308.18	1198.30	313.28	1179.51
0.6998	292.56	1276.92	298.16	1256.20	303.14	1237.89	308.12	1219.79	313.21	1201.40
0.8001	292.80	1297.03	298.20	1277.52	303.19	1259.56	308.18	1241.65	313.26	1223.62
0.8957	292.80	1316.31	298.16	1297.10	303.14	1279.45	308.12	1261.91	313.21	1244.05
1.0000	293.01	1337.76	298.18	1319.69	303.15	1302.36	308.14	1284.96	313.23	1267.39

Table 5. Temperature Dependence of Densities, Molar Heat Capacities at Constant Pressure, and Speeds of Ultrasound (at 4 MHz), Respectively, of Mixtures {*x* 1,6-Dichlorohexane + (1 - *x*) Heptane} at Experimental Mole Fractions *x*: Coefficients *a_i* of Equation 12 with their Standard Deviations and Mean Deviations δ_Q from the Regression Curve

<i>x</i>	<i>a</i> ₀	<i>a</i> ₁	<i>a</i> ₂	δ_Q
$Q(T,x) = \rho(\text{kg}\cdot\text{mol}^{-1})$				
0.0000	683.816 ± 0.022	-0.8540 ± 0.0018		0.03
0.0998	722.247 ± 0.024	-0.8629 ± 0.0019		0.03
0.1999	760.997 ± 0.039	-0.8649 ± 0.0032		0.05
0.2998	799.775 ± 0.026	-0.8793 ± 0.0021		0.03
0.4001	838.671 ± 0.017	-0.8703 ± 0.0014		0.02
0.5001	877.376 ± 0.045	-0.8714 ± 0.0037		0.06
0.6002	916.095 ± 0.051	-0.8764 ± 0.0042		0.07
0.7000	954.507 ± 0.044	-0.8909 ± 0.0036		0.06
0.8002	992.854 ± 0.064	-0.9144 ± 0.0052		0.08
0.9001	1030.698 ± 0.003	-0.9132 ± 0.0008	-0.000794 ± 0.000041	0.00
1.0000	1068.342 ± 0.007	-0.9474 ± 0.0005		0.01
$Q(T,x) = C_p(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$				
0.0000 ^a	222.867 ± 0.006	0.3673 ± 0.0013	0.000744 ± 0.000056	0.18
0.1033	224.175 ± 0.002	0.3689 ± 0.0002		0.05
0.2005	225.578 ± 0.003	0.3552 ± 0.0002		0.06
0.3004	226.931 ± 0.006	0.3430 ± 0.0004		0.13
0.3970	228.731 ± 0.008	0.3352 ± 0.0006		0.19
0.5025	230.528 ± 0.008	0.3199 ± 0.0006		0.17
0.5978	232.224 ± 0.007	0.3084 ± 0.0005		0.16
0.7012	233.789 ± 0.003	0.3137 ± 0.0002		0.05
0.7975	235.583 ± 0.002	0.3027 ± 0.0002		0.05
0.8993	237.464 ± 0.004	0.2909 ± 0.0003		0.09
1.0000	239.212 ± 0.0	0.2851 ± 0.0002		0.05
$Q(T,x) = u(\text{m}\cdot\text{s}^{-1})$				
0.0000	1152.168 ± 0.026	-4.3669 ± 0.0060	0.001811 ± 0.000289	0.03
0.1014	1166.594 ± 0.009	-4.1763 ± 0.0022	0.000578 ± 0.000107	0.01
0.1999	1180.220 ± 0.008	-4.1319 ± 0.0019	0.002319 ± 0.000094	0.01
0.3004	1196.419 ± 0.022	-4.0573 ± 0.0051	0.002800 ± 0.000251	0.02
0.4000	1214.408 ± 0.062	-3.8749 ± 0.0051		0.08
0.4999	1233.534 ± 0.050	-3.7998 ± 0.0041		0.06
0.6004	1253.749 ± 0.059	-3.6646 ± 0.0138	-0.001280 ± 0.000665	0.06
0.6998	1274.729 ± 0.017	-3.7124 ± 0.0041	0.002826 ± 0.000200	0.02
0.8001	1295.776 ± 0.027	-3.6289 ± 0.0062	0.001999 ± 0.000301	0.03
0.8957	1315.049 ± 0.024	-3.5897 ± 0.0055	0.002545 ± 0.000692	0.03
1.0000	1337.219 ± 0.050	-3.4814 ± 0.0041		0.06

^a *C_p* values for pure liquid heptane were taken from Chorążewski et al.¹⁹

measured heat capacity was recorded for each successive temperature 0.01 K apart, resulting in about 2600 data points for the temperature range studied. For the sake of clarity, Table 2 contains only values of *C_p* from (293.15 to 313.15) K at intervals of 1 K. The remaining experimentally determined data, that is, densities and speeds of ultrasound at, roughly, (293.15, 298.15, 303.15, 308.15, and 313.15) K, are shown in Tables 3 and 4, respectively. For the mixtures, no literature results could be found for comparison.

Table 6. Interpolated Densities $\rho(T,x)$ and Speeds of Sound $u(T,x)$ as a Function of Mole Fraction *x* at Which the Heat Capacities Were Measured for {*x* 1,6-Dichlorohexane + (1 - *x*) Heptane} at Temperatures *T*/K = 293.15, 298.15, 303.15, 308.15, and 313.15

<i>x</i>	$\rho(\text{kg}\cdot\text{m}^{-3})$					$u(\text{m}\cdot\text{s}^{-1})$				
	<i>T</i> = 293.15 K	<i>T</i> = 298.15 K	<i>T</i> = 303.15 K	<i>T</i> = 308.15 K	<i>T</i> = 313.15 K	<i>T</i> = 293.15 K	<i>T</i> = 298.15 K	<i>T</i> = 303.15 K	<i>T</i> = 308.15 K	<i>T</i> = 313.15 K
0.0000	683.79	679.56	675.3	671.02	666.71	1152.17	1130.38	1108.68	1087.07	1065.55
0.1033	723.58	719.33	714.97	710.65	706.34	1166.64	1124.73	1103.88	1103.88	1083.12
0.2005	761.20	756.92	752.53	748.21	743.82	1180.59	1160.06	1139.63	1119.28	1099.04
0.3004	799.95	795.64	791.24	786.94	782.50	1196.45	1176.40	1156.43	1136.54	1116.73
0.3970	837.45	833.13	828.73	824.43	820.00	1213.58	1194.04	1174.55	1155.10	1135.70
0.5025	878.34	874.00	869.58	865.26	860.90	1234.02	1215.05	1196.09	1177.13	1158.17
0.5978	915.16	910.82	906.35	901.97	897.64	1253.49	1234.95	1216.41	1197.87	1179.32
0.7012	954.93	950.57	946.02	941.55	937.17	1275.02	1256.77	1238.57	1220.41	1202.30
0.7975	991.75	987.34	982.72	978.14	973.61	1294.99	1276.87	1258.87	1240.99	1223.22
0.8993	1030.41	1025.87	1021.18	1016.50	1011.78	1315.96	1298.00	1280.19	1262.53	1245.03
1.0000	1068.33	1063.61	1058.87	1054.14	1049.39	1337.22	1319.81	1302.40	1285.00	1267.59

For the pure liquids as well as the mixtures (with mole fraction *x* of 1,6-dichlorohexane), the temperature dependences of the measured densities, molar heat capacities at constant pressure (considering *all* experimental data points) and speeds of ultrasound at each experimental mole fraction were represented satisfactorily by fitting the data with smoothing functions of the form

$$Q(T,x) = \sum_{i=0}^2 a_i \tau^i \quad (12)$$

by the method of unweighted least-squares. Here, $\tau = T/\text{K} - 293.15$, *Q* denotes either $\rho(\text{kg}\cdot\text{m}^{-3})$, $C_p(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$, or $u(\text{m}\cdot\text{s}^{-1})$, and the *a_i* are the corresponding polynomial coefficients. The backward stepwise rejection procedure was used to reduce the number of nonzero coefficients. These coefficients and the mean deviations δ_Q from the respective regression curve are given in Table 5.

To obtain consistent results through the use of eqs 6 to 11, for the derived isobaric expansivities $\alpha_p(T,x)/\text{K}^{-1}$, isentropic compressibilities $\kappa_S(T,x)/\text{Pa}^{-1}$, isothermal compressibilities $\kappa_T(T,x)/\text{Pa}^{-1}$, molar heat capacities at constant volume $C_V(T,x)/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$, ratios of heat capacities $\gamma(T,x)$, and internal pressures $\Pi(T,x)/\text{MPa}$, for each of the temperatures (293.15, 298.15, 303.15, 308.15, and 313.15) K, the densities and speeds of ultrasound (as obtained from the results given in Table 5) were smoothed with respect to composition. Using the best fitting polynomials in *x*, “interpolated” values of these two properties at the mole fractions for which the heat capacities were measured have been thus obtained at each temperature. The interpolated quantities at mole fractions for which the heat capacities were measured have been then used to obtain all properties contained in Table 6. The derived quantities are given in Table 7.

Excess molar volumes $V^E(T,x)$ were calculated from eq 3 and excess molar heat capacities at constant pressure $C_p^E(T,x)$ from eq 5. Numerical values of calculated excess quantities are collected in Table 8. The excess molar volumes obtained for *T*/K = 293.15, 298.15, 303.15, 308.15, and 313.15 were fitted for each temperature to Redlich–Kister type smoothing functions

$$V^E(T,x) = x(1-x) \sum_{i=0}^n A_i (1-2x)^i \quad (13)$$

The corresponding coefficients *A_i* and the mean deviations δV^E from the regression curves are collected in Table 9, while graphical representations are provided by Figure 1. Additionally,

Table 7. Calculated Isobaric Expansivities α_p , Isentropic Compressibilities κ_S , Isothermal Compressibilities κ_T , Molar Heat Capacities at Constant Volume C_V , Ratio of Heat Capacities $\gamma = C_p/C_V$, and Internal Pressures Π for $\{x$ 1,6-Dichlorohexane + $(1 - x)$ Heptane $\}$ at Temperatures $T/K = 293.15, 298.15, 303.15, 308.15,$ and 313.15

x	$10^3 \alpha_p/K^{-1}$				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.0000	1.249	1.257	1.265	1.273	1.281
0.1033	1.193	1.200	1.207	1.214	1.222
0.2005	1.142	1.149	1.156	1.162	1.169
0.3004	1.090	1.096	1.102	1.108	1.115
0.3970	1.041	1.047	1.052	1.058	1.063
0.5025	0.994	0.999	1.004	1.009	1.014
0.5978	0.959	0.964	0.969	0.973	0.978
0.7012	0.933	0.937	0.942	0.946	0.951
0.7975	0.917	0.921	0.926	0.930	0.934
0.8993	0.905	0.909	0.913	0.917	0.922
1.0000	0.887	0.891	0.895	0.899	0.903
x	$10^{12} \kappa_S/\text{Pa}^{-1}$				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.0000	1101.66	1151.66	1204.74	1261.10	1321.03
0.1033	1015.41	1059.19	1105.66	1154.77	1206.79
0.2005	942.55	981.72	1023.18	1066.83	1113.04
0.3004	873.27	908.18	945.05	983.76	1024.76
0.3970	810.78	841.88	874.67	909.09	945.49
0.5025	747.64	774.99	803.83	834.08	865.97
0.5978	695.44	719.90	745.67	772.66	801.00
0.7012	644.16	666.05	689.06	713.09	738.17
0.7975	601.26	621.21	642.11	663.84	686.45
0.8993	560.41	578.57	597.52	617.17	637.61
1.0000	523.47	539.75	556.76	574.51	593.07
x	$10^{12} \kappa_T/\text{Pa}^{-1}$				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.0000	1402.3	1460.6	1522.2	1587.2	1656.0
0.1033	1287.6	1338.7	1392.7	1449.5	1509.4
0.2005	1190.3	1236.0	1284.3	1334.8	1388.1
0.3004	1097.2	1138.0	1180.8	1225.6	1272.9
0.3970	1013.2	1049.4	1087.5	1127.3	1169.2
0.5025	930.3	962.2	995.8	1030.8	1067.6
0.5978	864.2	892.9	923.0	954.4	987.1
0.7012	802.6	828.4	855.4	883.4	912.6
0.7975	753.3	776.9	801.6	827.2	853.8
0.8993	707.1	728.8	751.5	774.9	799.2
1.0000	663.4	683.1	703.6	724.9	747.1
x	$C_V/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.0000	175.09	177.19	179.36	181.59	183.88
0.1033	176.78	178.83	180.90	183.00	185.13
0.2005	178.62	180.58	182.55	184.55	186.58
0.3004	180.61	182.48	184.36	186.29	188.22
0.3970	183.04	184.84	186.66	188.51	190.38
0.5025	185.27	186.96	188.67	190.42	192.19
0.5978	186.87	188.48	190.10	191.76	193.44
0.7012	187.63	189.24	190.86	192.50	194.18
0.7975	188.04	189.58	191.13	192.69	194.28
0.8993	188.20	189.66	191.12	192.61	194.10
1.0000	188.76	190.15	191.55	192.97	194.43
x	γ				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.0000	1.2729	1.2682	1.2635	1.2586	1.2536
0.1033	1.2681	1.2639	1.2596	1.2553	1.2508
0.2005	1.2629	1.2591	1.2552	1.2512	1.2471
0.3004	1.2565	1.2530	1.2495	1.2458	1.2421
0.3970	1.2496	1.2465	1.2434	1.2400	1.2367
0.5025	1.2443	1.2416	1.2388	1.2358	1.2328
0.5978	1.2427	1.2403	1.2378	1.2352	1.2324
0.7012	1.2460	1.2437	1.2414	1.2389	1.2363
0.7975	1.2528	1.2506	1.2484	1.2462	1.2438
0.8993	1.2618	1.2597	1.2577	1.2556	1.2534
1.0000	1.2672	1.2655	1.2637	1.2618	1.2597
x	Π/MPa				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.0000	261.1	256.5	251.8	247.1	242.2
0.1033	271.6	267.2	262.8	258.2	253.5
0.2005	281.4	277.1	272.8	268.3	263.8
0.3004	291.3	287.2	283.0	278.7	274.2
0.3970	301.3	297.4	293.3	289.1	284.8
0.5025	313.1	309.4	305.5	301.5	297.4
0.5978	325.4	321.8	318.1	314.2	310.2
0.7012	340.7	337.3	333.7	330.0	326.2
0.7975	357.0	353.6	350.1	346.5	342.8
0.8993	375.1	371.8	368.3	364.8	361.1
1.0000	391.9	388.8	385.5	382.1	378.4

in Figure 2 the molar excess volumes at 298.15 K have been compared with literature data.⁴⁴

Table 8. Numerical Values of Excess Molar Volumes $V^E(T,x)$ and Excess Molar Heat Capacities $C_p^E(T,x)$ as a Function of Mole Fraction x for $\{x$ 1,6-Dichlorohexane + $(1 - x)$ Heptane $\}$ at Temperatures $T/K = 293.15, 298.15, 303.15, 308.15,$ and 313.15

x	$V^E \cdot 10^6/(\text{m}^3 \cdot \text{mol}^{-1})$				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.0998	-0.075	-0.090	-0.097	-0.121	-0.133
0.1999	-0.177	-0.213	-0.226	-0.279	-0.306
0.2998	-0.259	-0.298	-0.327	-0.358	-0.398
0.4001	-0.331	-0.380	-0.437	-0.484	-0.546
0.5001	-0.364	-0.420	-0.463	-0.546	-0.600
0.6002	-0.384	-0.438	-0.476	-0.552	-0.626
0.7000	-0.347	-0.408	-0.453	-0.490	-0.554
0.8002	-0.273	-0.327	-0.341	-0.365	-0.409
0.9001	-0.157	-0.179	-0.201	-0.215	-0.226
x	$C_p^E/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$				
	$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.1033	-0.380	-0.346	-0.346	-0.378	-0.444
0.2005	-0.566	-0.559	-0.581	-0.634	-0.716
0.3004	-0.845	-0.856	-0.893	-0.956	-1.045
0.3970	-0.625	-0.634	-0.665	-0.718	-0.794
0.5025	-0.552	-0.591	-0.649	-0.726	-0.821
0.5978	-0.414	-0.470	-0.541	-0.627	-0.728
0.7012	-0.539	-0.524	-0.521	-0.528	-0.547
0.7975	-0.319	-0.319	-0.326	-0.340	-0.362
0.8993	-0.102	-0.117	-0.135	-0.157	-0.183

Because of the relatively small number of data points for $C_p^E(T,x)$, no smoothing function is provided for this property. The data points of excess molar heat capacities at constant pressure $C_p^E(T,x)$ calculated as indicated above for each temperature are plotted against x in Figure 3 (parts a, b, and c). In these figures only smoothing curves as a help to the eye have been drawn through the data points. No literature results could be found for comparison.

The excess molar volumes are all negative and somewhat skewed toward the 1,6-dichlorohexane side. They become more negative with increasing temperature. We note that V^E of $\{x$ 1,2-dichloroethane + $(1 - x)$ heptane $\}$ at 298.15 K is positive and quite symmetric [$V^E(x = 0.5) = 0.918 \text{ cm}^3 \cdot \text{mol}^{-1}$],¹⁶ while V^E of $\{x$ 1,4-dichloroethane + $(1 - x)$ heptane $\}$ is much smaller and S-shaped.¹⁸ V^E of $\{x$ 1,6-dichlorohexane + $(1 - x)$ octane $\}$ is also small and S-shaped, but positive excess volumes are only observed for $x \leq 0.157$.¹⁷ As far as the temperature dependence of the excess volume is concerned, results obtained for $\{x$ 1,5-dibromopentane + $(1 - x)$ heptane $\}$ also show a decrease of V^E with increasing temperature¹⁹ [at 298.15 K, $V^E(x = 0.5) = -0.592 \text{ cm}^3 \cdot \text{mol}^{-1}$].

Definitely the most interesting aspect of this work concerns the variation of the excess molar heat capacity at constant pressure with composition and with temperature. The shapes of the curves C_p^E versus x are strikingly similar to the W-shaped/almost W-shaped curves found previously within the series (1,2-dichloroethane + an n -alkane)¹⁶ and (1,4-dichlorobutane + an n -alkane)¹⁸ and for (1,6-dichlorohexane + n -octane).¹⁷ As can be seen in Figures 3, the minima are situated around $x = 0.3$, while very broad shoulders are observed at higher mole fractions. With decreasing temperature, the $C_p^E(x)$ curves become less negative with more pronounced shoulders, which their behavior is reminiscent of the onset of W-shaped composition dependence. The discussion of the C_p^E is most profitably conducted along the lines indicated in the Introduction.¹⁰ Using the Patterson approximation (which is based on Guggenheim's quasi-chemical theory⁴), the (almost) W-shape results from the superposition of a negative, parabolic random contribution due to the destruction of polar order existing in 1,6-dichlorohexane by adding the nonpolar heptane and a nonrandom contribution

Table 9. Coefficients of Equation 13 with Their Standard Deviations and Mean Deviations from the Regression Curve δV^E

T/K	A_0	A_1	A_2	A_3	A_4	δV^E
			$Q^E(T,x) = V^E \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$			
293.15	-1.471 ± 0.008	0.524 ± 0.019			0.445 ± 0.079	0.004
298.15	-1.700 ± 0.010	0.613 ± 0.024			0.395 ± 0.097	0.005
303.15	-1.877 ± 0.021	0.645 ± 0.049			0.590 ± 0.199	0.011
308.15	-2.160 ± 0.036	0.613 ± 0.071	0.485 ± 0.165			0.016
313.15	-2.425 ± 0.042	0.700 ± 0.083	0.633 ± 0.191			0.018

which is always positive with zero slopes against the x axis at both ends of the composition range. With decreasing temperature, the nonrandom contribution increases rapidly, thus making the W-shape more pronounced. However, it is important to note that many of the mixtures showing W-shaped C_p^E curves are fairly close to liquid–liquid phase separation with an upper critical solution temperature T_{UC} . When the T_{UC} is approached from the homogeneous region at constant pressure and constant critical composition x_c , the heat capacity along this path diverges weakly according to

$$C_p^E(x_c) = C_p^E(x_c, \text{non-diverging}) + A_c t^{-\alpha} \quad (14)$$

where A_c is the critical amplitude, $t \equiv |(T - T_{UC})/T_{UC}|$ is the reduced distance from T_{UC} , and $\alpha = 0.11$ is a universal critical exponent. Evidently, the quasi-chemical approximation under-

estimates the nonrandom contribution to C_p^E , and increasingly so at low temperatures, and becomes qualitatively incorrect in the vicinity of T_{UC} . Thus, experiments should be performed at

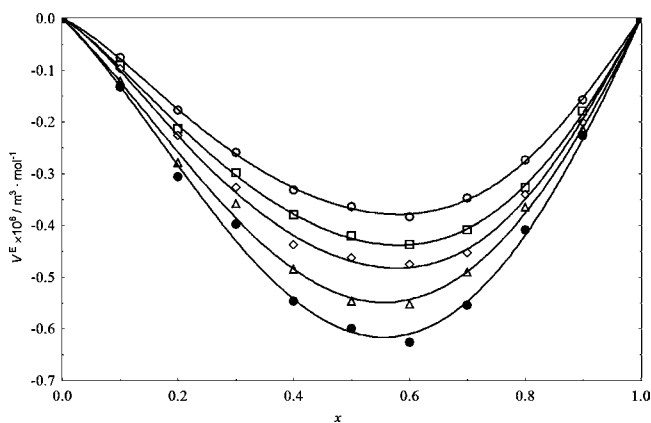


Figure 1. Excess molar volumes V_m^E for $\{x$ 1,6-dichlorohexane + $(1-x)$ heptane} at \circ , 293.15 K; \square , 298.15 K; \diamond , 303.15 K; \triangle , 308.15 K; \bullet , 313.15 K; —, values calculated from eq 13.

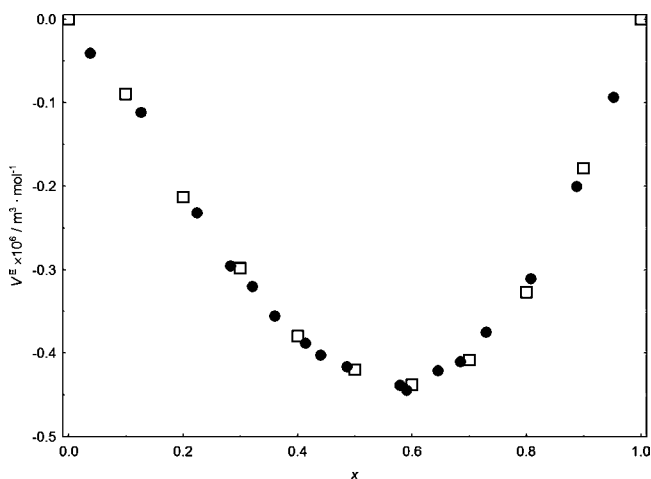


Figure 2. Excess molar volumes V_m^E for $\{x$ 1,6-dichlorohexane + $(1-x)$ heptane} at 298.15 K; \square , experimental points from this work; \bullet , literature data.⁴⁴

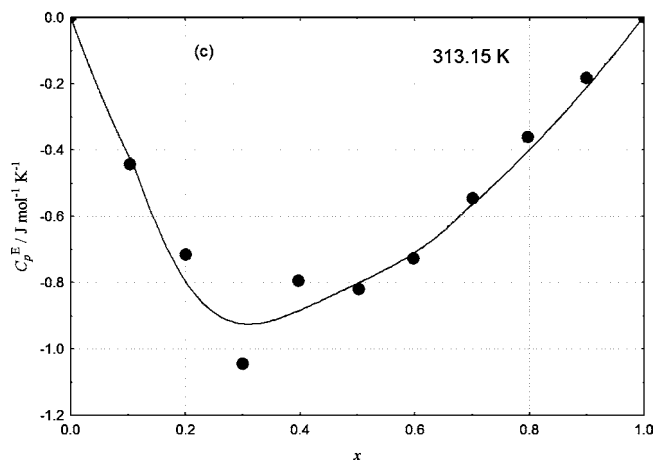
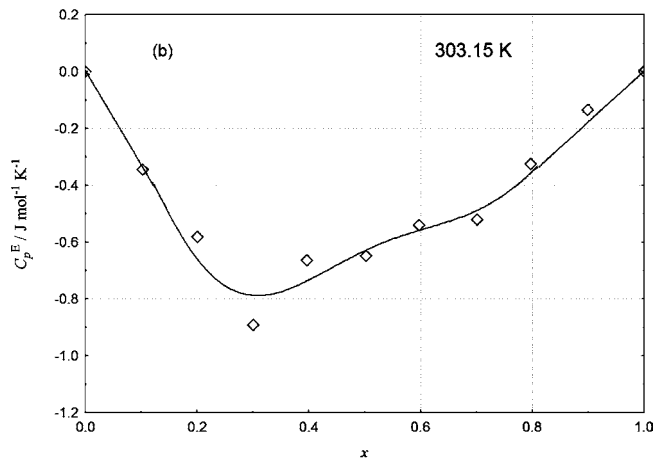
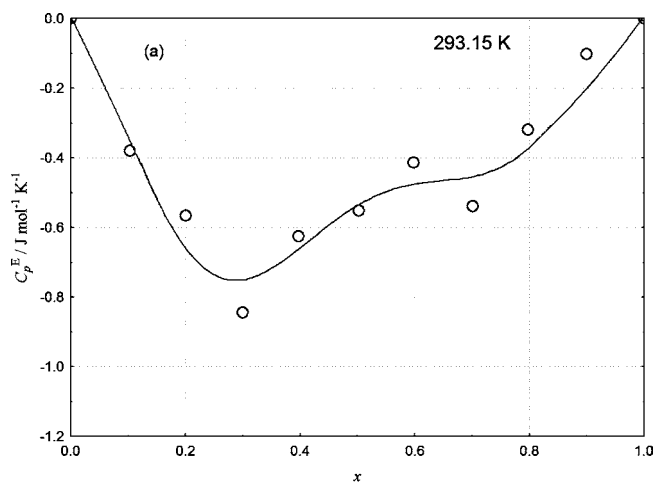


Figure 3. Excess isobaric molar heat capacities C_p^E for $\{x$ 1,6-dichlorohexane + $(1-x)$ heptane} at \circ , 293.15 K; \diamond , 303.15 K; \bullet , 313.15 K.

lower temperatures well below 293 K and are indeed planned for the future.

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