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Heat Capacity, Speed of Ultrasound, and Density for 1,5-Dibromopentane + Heptane within the Temperature Range from 293.15 K to 313.15 K

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Densities for binary mixture 1,5-dibromopentane + heptane have been measured within the temperature range from 293 K to 313 K using a vibrating tube densimeter. The phase speeds of ultrasound have been measured with a pulse−echo−overlap apparatus. The heat capacities at constant pressure have been measured with a differential scanning calorimeter DSC III (Setaram). From those experimental data, the excess molar volumes, V^E, excess isobaric molar heat capacities, C_p^E, excess isentropic compressibilities, κ_s^E, excess isothermal compressibilities, κ_T^E, and excess ultrasonic speeds, u^E, were calculated.

Introduction

Dibromoalkanes are polar nonassociated liquids, in which important electrostatic intermolecular interactions occur due to nonzero permanent dipole moments and/or quadrupole moments. In addition, these are compounds characterized by the so-called intramolecular proximity effect,[1] that is, a change in the distance between two bromine atoms in the molecule provokes a change in the behavior and hence in the parameters of interaction with other molecular groups.

The knowledge of the thermophysical properties of liquid halogenoalkanes is of high interest on account of their wide usage in science and industrial processes. Those properties are crucial for the designing of chemical processes as well as for the progress of thermodynamic theories. The heat capacities, speeds of sound, and densities as functions of temperature and their derivatives render some insight in the molecular structure of liquids and provide information on intermolecular interactions.

Furthermore, polyhaloalkanes are interesting from the theoretical point of view. The correlation of their molecular structures with thermodynamic properties of polyhaloalkane mixtures is necessary for gaining systematic information on the behavior of substances with different specific groups. Therefore, a knowledge of the behavior of those mixtures constitutes a good test of the limitations and applicability of predictive methods based on the group contribution theories (e.g., DISQUAC, UNIFAC).[2−8]

It is most interesting that, for the investigated mixtures of 1,5-dibromopentane with heptane, the excess heat capacity as a function of mole fraction x is W-shaped like for mixtures of alkanes with α,ω-dichloroalkanes[11−13,17,18] and 1,2-dibromoethane.[25]

Grolier and Wilhelm et al.[9] have discovered the W-shape anomaly of the dependence of C_p^E on composition. Since then, the interest in this phenomenon is constantly growing.

Theoretical and model descriptions have been suggested by relating the W-shape effect to rotational isomerism[10−13] and evolved finally into a full interpretation accomplished by Saint-Victor and Patterson.[14] The latter interpretation is based on Guggenheim's quasi-chemical lattice theory of solutions. A comprehensive discussion of this phenomenon was carried out by Cobos.[15]

Recently, Troncoso et al.[16] have been successful in the quantitative description of the W-shaped molar excess heat capacities based on the non-random two liquid (NRTL) model.

Moreover, the systems that exhibit a W-shape dependence of excess heat capacity on composition have large excess enthalpies from (1000 to 2000) J·mol^{-1} and excess Gibbs energies from (800 to 1200) J·mol^{-1}. This rule applies also to similar systems such as 1,5-dibromopentane + hexane. The values of H^E for this system[43] are ≈1200 J·mol^{-1}.

Unfortunately, basic properties of dibromoalkanes and their mixtures with *n*-alkanes, such as heat capacities, densities, and speeds of sound are rather scarce in the literature. Systematic studies of C_p, ρ, and u can be found only for mixtures of α,ω-dichloroalkanes with alkanes.[17,18] To the best of our knowledge, for the mixtures studied in this paper, no experimental data corresponding to density, speed of sound, and heat capacity are available in the accessible literature. This prompted us to continue our earlier calorimetric study of pure halogenoalkanes[19−21] and to expand it onto C_p, ρ, and u measurements for binary mixtures containing α,ω-dibromoalkanes and aliphatic alkanes. In this work, the excess properties V^E, C_p^E, κ_s^E, κ_T^E, and u^E of the binary system 1,5-dibromopentane + heptane are presented.

Experimental Section

Chemicals. Heptane (≥99.8 %) from POCH (Polish Chemicals) was used without further purification.

1,5-Dibromopentane (Lancaster, 97 %) was purified before use by fractional distillation and the middle fraction (approximately 5 %) collected in every case. The purities of the liquid samples of 1,5-dibromopentane checked by gas−liquid chromatography (GLC) were >99 %.

The mass fraction of water, determined by the Karl Fischer method, was less than 4×10^{-8} for 1,5-dibromopentane and 3×10^{-8} for heptane. Prior to the measurements, the pure liquids

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Table 1. Comparison of the Molar Heat Capacities, Densities, and Speeds of Sound in the Pure Components at $T = 298.15$ K Obtained in This Work with Those Reported in the Literature

liquid	this work	literature
	Heptane	
C_p/(J·mol^{-1}·K^{-1})	224.72	223.0[26], 224.19[26], 224.7[27,28,29], 224.72[30], 224.78[12],224.93[26], 224.707[26]
u/(m·s^{-1})	1130.70	1129.92[31],1130.18[32], 1130.2[33], 1130.44[34], 1130.6[35],1131[36]
ρ/(kg·m^{-3})	679.69	679.42[37], 679.50[38], 679.52[25], 679.58[39], 679.60[32], 679.68[31], 679.70[40]
	1,5-Dibromopentane	
C_p/(J·mol^{-1}·K^{-1})	220.84	220.7[19]
u/(m·s^{-1})[a]	1133.60	
ρ/(kg·m^{-3})	1691.74	1692.81[19], 1699.55[43]

[a] At 293.15 K.

were dried with molecular sieves (type 3A, (1 to 2) mm beads from Lancaster) and degassed in an ultrasonic stream.

The mixtures were prepared by mass using a Sartorius RC 210D balance with an accuracy of ±2 × 10^{-5} g. Before each series of measurements, each sample was degassed in an ultrasonic cleaner.

A comparison of the molar heat capacities, densities, and speed of sound values of the pure components determined in this work with those reported in the literature is given in Table 1. Most of the data are in a satisfactory agreement. Small differences may result from differences in the purity of the chemicals, measurement techniques, and calibrations.

Apparatus and Procedure. The differential scanning calorimetry (Micro DSC III Setaram), applied in this study, is one of the modern analytical techniques often used since quantitative information can be obtained over a wide range of temperatures from small (1 mL) samples. The "continuous with reference" method was applied. The uncertainty of the measurements was estimated to be ±0.15 %. Details of the applied procedure and the calorimeter calibration have been described previously.[20]

The densities at atmospheric pressure, ρ, have been measured by a vibrating tube densimeter model Unilab MG-2. The water used for the calibration of the densimeter was redistilled over alkaline $KMnO_4$ and deaerated by multiple boiling. The densimeter was calibrated with reference to water and air taking the densities at each temperature from the literature.[22] The technique of the experimental procedure and other details were described elsewhere.[23] The uncertainty of density is 5 × 10^{-2} kg·m^{-3}, as evidenced by test measurements of liquids of known density, prepared in our laboratory. The liquids were pure organic substances and aqueous solutions of salts, purified by common methods. Their densities measured using bicapillary pycnometers in a way described in Ernst et al.[41] were treated as true values. Thus, the procedure applied was similar to that of Ashcroft et al.,[42] who discussed in detail the viscosity of liquid as a source of error in the vibrating-tube measurement.

The phase speed of the ultrasound at 4 MHz was measured with a pulse−echo−overlap apparatus designed and constructed in the Department of Physical Chemistry of the University of Silesia (electronic part and ultrasonic cell). The uncertainty of the pulse−echo−overlap apparatus is limited mainly by the calibration procedure and may be estimated on the order of 1 dm·s^{-1}. Higher accuracy is rather difficult to attain due to uncertainty in the speed of sound in reference liquids. That uncertainty is on the order of 5 cm·s^{-1} in water,[24] which is undoubtedly the best standard liquid available.

The ultrasonic apparatus was calibrated with redistilled water as the standard liquid. The speeds of sound in water, calculated from the polynomial of Marczak[24] at atmospheric pressure, were taken as true values.

Measurement Results and Discussion

The measurements of the heat capacity of the mixtures studied were carried out generally within the temperature range from 293 K to 313 K. The scanning rate was 0.1 K·min^{-1}. Thus, with varying temperature, a measuring point is recorded each 0.01 K which results in 2600 data points over the temperature range studied. For clarity, only the values obtained for every 1 K are presented in Table 2. The other experimental data, that is, the densities and speeds of sound at (293 to 313) K, are collected in Table 3 and Table 4, respectively.

The dependences of the molar heat capacities (for all the experimental data), densities, and speeds of sound on temperature were fitted to the following equation

Table 2. Experimental Molar Heat Capacities, C_p, for x 1,5-dibromopentane + (1 − x) Heptane at Temperatures T

	x										
	0.0000	0.1006	0.1994	0.3003	0.4008	0.5004	0.5999	0.6995	0.8002	0.8990	1.0000
T/K	C_p/J·mol^{-1}·K^{-1}										
293.15	222.87	221.62	221.15	221.00	220.91	220.80	220.50	220.19	219.87	219.89	219.76
294.15	223.23	221.93	221.54	221.39	221.29	221.14	220.66	220.44	220.16	220.02	219.98
295.15	223.60	222.35	221.76	221.59	221.60	221.41	220.91	220.59	220.44	220.30	220.19
296.15	223.97	222.62	222.09	221.89	221.77	221.59	221.30	220.81	220.57	220.61	220.41
297.15	224.35	223.06	222.53	222.34	222.15	221.87	221.50	221.19	220.89	220.76	220.66
298.15	224.72	223.39	222.84	222.66	222.48	222.23	221.68	221.42	221.11	221.09	220.84
299.15	225.10	223.70	223.20	222.87	222.74	222.55	221.91	221.69	221.39	221.32	221.10
300.15	225.47	224.16	223.42	223.30	222.91	222.69	222.30	221.83	221.48	221.55	221.28
301.15	225.87	224.39	223.89	223.58	223.33	223.05	222.57	222.17	221.85	221.77	221.49
302.15	226.22	224.88	224.24	223.78	223.52	223.39	222.87	222.33	222.09	221.93	221.73
303.15	226.61	225.21	224.57	224.21	223.81	223.49	223.01	222.58	222.36	222.22	221.95
304.15	227.00	225.49	224.90	224.44	224.26	223.94	223.37	222.93	222.44	222.36	222.17
305.15	227.40	225.96	225.30	224.89	224.59	224.11	223.63	223.17	222.81	222.72	222.41
306.15	227.75	226.32	225.50	225.09	224.80	224.39	223.91	223.45	223.05	222.99	222.63
307.15	228.14	226.59	225.83	225.41	225.15	224.77	224.05	223.72	223.33	223.23	222.85
308.15	228.54	227.03	226.31	225.84	225.38	225.09	224.36	223.89	223.55	223.34	223.09
309.15	228.95	227.44	226.66	226.09	225.80	225.27	224.76	224.26	223.77	223.60	223.31
310.15	229.30	227.81	226.87	226.50	226.12	225.70	224.95	224.52	224.04	223.81	223.56
311.15	229.71	228.09	227.25	226.85	226.31	225.87	225.30	224.66	224.19	224.19	223.78
312.15	230.11	228.59	227.70	227.09	226.60	226.24	225.58	225.06	224.56	224.44	224.03
313.15	230.51	228.91	228.06	227.49	227.05	226.53	225.84	225.31	224.81	224.67	224.26

Table 3. Experimental Densities, ρ, for x 1,5-dibromopentane + (1 − x) Heptane at Temperatures T

x	T / K	ρ / kg·m^{-3}	T / K	ρ / kg·m^{-3}	T / K	ρ / kg·m^{-3}	T / K	ρ / kg·m^{-3}	T / K	ρ / kg·m^{-3}
0.0000	292.70	684.18	297.98	679.88	302.94	675.72	308.06	671.47	314.10	666.39
0.1006	292.52	779.97	298.05	775.18	303.06	770.79	308.08	766.31	314.66	760.22
0.1994	292.52	875.92	298.05	870.87	303.06	866.00	308.08	861.23	314.66	854.58
0.3003	292.52	975.53	298.05	969.84	303.06	964.71	308.08	959.36	314.66	952.58
0.4008	292.52	1075.80	298.05	1070.23	303.06	1064.63	308.08	1058.93	314.66	1052.00
0.5004	292.52	1176.68	298.05	1170.91	303.06	1165.02	308.08	1159.11	314.66	1151.72
0.5999	292.52	1278.62	298.05	1272.47	303.06	1266.37	308.08	1260.50	314.66	1252.55
0.6995	292.52	1381.60	298.05	1375.26	303.06	1368.90	308.08	1362.98	314.66	1354.65
0.8002	292.52	1487.16	298.05	1480.47	303.06	1474.36	308.08	1467.91	314.66	1459.75
0.8990	292.52	1591.59	298.05	1584.66	303.06	1578.04	308.08	1571.77	314.66	1562.81
1.0000	292.52	1699.54	298.05	1691.87	303.06	1684.89	308.08	1678.03	314.66	1668.75

Table 4. Experimental Speeds of Sound, u, for x 1,5-dibromopentane + (1 − x) Heptane at Temperatures T

x	T / K	u / m·s^{-1}	T / K	u / m·s^{-1}	T / K	u / m·s^{-1}	T / K	u / m·s^{-1}	T / K	u / m·s^{-1}
0.0000	292.84	1153.67	298.84	1127.72	303.80	1106.38	308.78	1085.10	314.87	1059.14
0.1000	292.83	1131.10	298.83	1106.79	303.86	1086.53	308.84	1066.65	314.83	1042.82
0.2000	292.65	1116.54	298.63	1093.80	303.59	1075.07	308.55	1056.44	314.61	1033.77
0.3001	292.68	1107.18	298.67	1085.68	303.63	1067.97	308.67	1050.05	314.54	1029.33
0.4000	292.56	1103.46	298.62	1082.76	303.64	1065.77	308.58	1049.12	314.67	1028.81
0.5001	292.59	1104.16	298.59	1084.55	303.64	1068.27	308.58	1052.40	314.52	1033.40
0.6000	292.76	1108.40	298.77	1089.63	303.72	1074.22	308.69	1058.86	314.75	1040.24
0.6997	292.80	1116.22	298.80	1098.06	303.78	1083.11	308.82	1068.06	314.82	1050.34
0.7999	292.73	1126.33	298.76	1108.63	303.71	1094.24	308.70	1079.81	314.68	1062.77
0.8998	292.75	1137.29	298.73	1120.22	303.67	1106.28	308.67	1092.32	314.70	1075.60
1.0000	292.38	1149.48	298.37	1133.01	303.39	1119.29	308.38	1105.79	314.36	1089.74

Table 5. Coefficients of eq 1 with Their Standard Deviations and Mean Deviations from the Regression Line δ_i

x	a_o / c_0 J·mol^{-1}·K^{-1}	a_1 / c_1 J·mol^{-1}·K^{-1}	a_2 / c_2 J·mol^{-1}·K^{-1}	δ_y / δ_{Cp} J·mol^{-1}·K^{-1}
0.0000	222.867 ± 0.006	0.3673 ± 0.0013	0.000744 ± 0.000056	0.18
0.1006	221.624 ± 0.006	0.3489 ± 0.0005	0.000735 ± 0.000094	0.18
0.1994	221.152 ± 0.009	0.3301 ± 0.0002	0.000654 ± 0.000109	0.17
0.3003	221.030 ± 0.005	0.3073 ± 0.0002	0.000716 ± 0.000050	0.10
0.4008	220.943 ± 0.003	0.2867 ± 0.0007	0.000836 ± 0.000035	0.08
0.5004	220.829 ± 0.007	0.2684 ± 0.0016	0.000762 ± 0.000080	0.17
0.5999	220.456 ± 0.006	0.2505 ± 0.0014	0.000870 ± 0.000071	0.15
0.6995	220.165 ± 0.006	0.2369 ± 0.0013	0.000939 ± 0.000063	0.13
0.8002	219.919 ± 0.007	0.2295 ± 0.0002	0.000670 ± 0.000089	0.16
0.8990	219.896 ± 0.003	0.2227 ± 0.0006	0.000703 ± 0.000032	0.07
1.0000	219.762 ± 0.004	0.2119 ± 0.0006	0.000652 ± 0.000027	0.08
	u_0	u_1	u_2	δ_u
	m·s^{-1}	m·s^{-1}·K^{-1}	m·s^{-1}·K^{-2}	m·s^{-1}
0.0000	1152.337 ± 0.013	−4.3375 ± 0.0027	0.002171 ± 0.000122	0.01
0.1000	1129.792 ± 0.013	−4.0642 ± 0.0027	0.002413 ± 0.000119	0.01
0.2000	1114.635 ± 0.016	−3.8117 ± 0.0034	0.002069 ± 0.000156	0.02
0.3001	1105.489 ± 0.012	−3.5998 ± 0.0026	0.001794 ± 0.000117	0.01
0.4000	1101.434 ± 0.010	−3.4266 ± 0.0021	0.002399 ± 0.000095	0.01
0.5001	1102.301 ± 0.023	−3.2690 ± 0.0049	0.002105 ±0.000225	0.03
0.6000	1107.171 ± 0.007	−3.1343 ± 0.0015	0.001624 ± 0.000065	0.01
0.6997	1115.151 ± 0.010	−3.0367 ± 0.0021	0.002127 ± 0.000093	0.01
0.7999	1125.094 ± 0.014	−2.9510 ± 0.0030	0.002568 ± 0.000136	0.02
0.8998	1136.135 ± 0.022	−2.8649 ± 0.0047	0.002577 ± 0.000212	0.02
1.0000	1147.349 ± 0.012	−2.7598 ± 0.0026	0.002016 ± 0.000119	0.01
	ρ_0	ρ_1	ρ_2	δ_ρ
	kg·m^{-3}	kg·m^{-3}·K^{-1}	kg·m^{-3}·K^{-2}	kg·m^{-3}
0.0000	683.853 ± 0.033	−0.8320 ± 0.0027		0.04
0.1006	779.424 ± 0.021	−0.8520 ± 0.0046	−0.001875 ± 0.000210	0.02
0.1994	875.357 ± 0.060	−0.9122 ± 0.0131	−0.002477 ± 0.000596	0.07
0.3003	974.915 ± 0.046	−1.0382 ± 0.0036		0.06
0.4008	1075.295 ± 0.156	−1.0841 ± 0.0123		0.21
0.5004	1176.193 ± 0.170	−1.1363 ± 0.0134		0.23
0.5999	1278.058 ± 0.129	−1.1808 ± 0.0102		0.17
0.6995	1381.022 ± 0.155	−1.2192 ± 0.0122		0.21
0.8002	1486.494 ± 0.095	−1.2409 ± 0.0075		0.13
0.8990	1590.917 ± 0.149	−1.2981 ± 0.0117		0.20
1.0000	1698.681 ± 0.045	−1.3891 ± 0.0036		0.06

$$y = \sum_{i=0}^{2} a_i (T/\mathrm{K} - 293.15)^i \tag{1}$$

where y is the molar heat capacity, density, or speed of sound, T/K is the absolute temperature, and a_i are the polynomial coefficients ($a_i = c_i$ for the molar heat capacity, $a_i = \rho_i$ for the density, and $a_i = u_i$ for the speed of sound) calculated by the least-squares method. The backward stepwise rejection procedure was used to reduce the number of nonzero coefficients. The values of the coefficients and mean deviations from the regression line are collected in Table 5.

The isentropic compressibility, κ_s, was calculated from the Newton−Laplace equation

$$\kappa_s = \frac{1}{\rho u^2} \tag{2}$$

The isothermal compressibility, κ_T, was calculated from the well-known thermodynamic relationship

$$\kappa_T = \kappa_s + \frac{T V_m {\alpha_p}^2}{C_{p,m}} \tag{3}$$

where the isobaric expansibility, α_p, was calculated using the equation

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

Excess properties were calculated using the following expression

$$Z^{\mathrm{E}} = Z - Z^{\mathrm{id}} \tag{5}$$

where Z^{E} is the excess quantity of the property Z (V_m, C_p, κ_s, κ_T, u) and Z^{id} is the corresponding ideal value.

The ideal values were calculated using the criteria redefined by Douhéret et al.[44]

$$V_m^{\mathrm{id}} = x_1 V_1{}^* + (1 - x_1) V_2{}^* \tag{6}$$

$$C_{p,m}^{\mathrm{id}} = x_1 C_{p,m,1}{}^* + (1 - x_1) C_{p,m,2}{}^* \tag{7}$$

$$\kappa_s^{\mathrm{id}} = \kappa_T^{\mathrm{id}} - \frac{T V_m^{\mathrm{id}} (\alpha_p^{\mathrm{id}})^2}{C_{p,m}^{\mathrm{id}}} \tag{8}$$

$$\kappa_T^{\mathrm{id}} = \phi_1 \kappa^*{}_{T,1} + (1 - \phi_1) \kappa^*{}_{T,2} \tag{9}$$

$$\alpha_p^{\mathrm{id}} = \phi_1 \alpha_{p,1}{}^* + (1 - \phi_1) \alpha_{p,2}{}^* \tag{10}$$

$$u^{\mathrm{id}} = \left[(\phi_1)^2 \left(\frac{C^*_{p,m,1}}{C^*_{V,m,1}}\right) \left(\frac{C_{V,m}^{\mathrm{id}}/C_{p,m}^{\mathrm{id}}}{w_1 (u_1{}^*)^2}\right) + (\phi_2)^2 \left(\frac{C^*_{p,m,2}}{C^*_{V,m,2}}\right) \left(\frac{C_{V,m}^{\mathrm{id}}/C_{p,m}^{\mathrm{id}}}{w_2 (u_2^*)^2}\right) \right]^{-1/2} \tag{11}$$

$$C_{V,m}^{\mathrm{id}} = C_{p,m}^{\mathrm{id}} \frac{\kappa_s^{\mathrm{id}}}{\kappa_T^{\mathrm{id}}} \tag{12}$$

where in eqs 9 and 10, ϕ_1 is the ideal volume fraction

$$\phi_1 = \frac{x_1 V_1{}^*}{V_m^{\mathrm{id}}} \tag{13}$$

x_1 being the mole fraction for component 1 (1,5-dibromopentane).

In eq 11, ϕ_1 is the volume fraction defined by the mass-fraction, w_1

$$\phi_1 = \frac{w_1 \rho^{\mathrm{id}}}{\rho_1{}^*} \tag{14}$$

where

$$\rho^{\mathrm{id}} = \phi_1 \rho_1{}^* + (1 - \phi_1) \rho_2{}^* \tag{15}$$

The asterisks indicate parameters of the pure components.

The results obtained in this way were fitted to polynomials of the Redlich−Kister type

$$Z^{\mathrm{E}} = x_1 (1 - x_1) \sum_{i=0}^{n} A_i (1 - 2x_1)^i \tag{16}$$

where Z^{E} is the excess function, and A_i are the polynomial coefficients ($A_i = V_i^{\mathrm{E}}$ for the excess molar volumes, $A_i = C_{p,i}^{\mathrm{E}}$ for the excess molar heat capacities, $A_i = \kappa_{s,i}^{\mathrm{E}}$ for the excess isentropic compressibilities, $A_i = \kappa_{T,i}^{\mathrm{E}}$ for the excess isothermal compressibilities, and $A_i = u_i^{\mathrm{E}}$ for the excess speeds of sound). The coefficients were determined by the multiple regression method using a stepwise rejection procedure and the F-test. The values of the coefficients and mean deviations from the regression line are collected in Table 6.

Douhéret et al. discussed extensively the methods of calculation of excess ultrasound speeds and proposed a thermodynamically correct equation for expressing the ultrasonic speeds in binary ideal liquid mixtures in terms of the speeds in the pure components[44] in contrast to many other proposals based on either empirical or intuitive approaches. Somewhat later, Gliński[45] argued that an equation proposed earlier by Ernst et al.[46] is the simplest one and leads to reliable results. However, the conclusions of Gliński are based only on statistical arguments, furthermore Ernst et al. have stressed that only a rough estimate of the excess ultrasound speeds can be obtained in this way. Therefore, in this work, the excess ultrasonic speeds have been calculated using the mixing rule suggested by Douhéret et al.

The excess properties are plotted against mole fraction x of 1,5-dibromopentane in Figures from 1to 5. The excess molar volumes are negative over the entire composition range while $V_{\mathrm{m}}^{\mathrm{E}}$ values decrease with increasing temperature. A W-shaped excess heat capacity as a function of the mole fraction is observed in Figure 2 while the values of $C_{p,\mathrm{m}}^{\mathrm{E}}$ decrease with increasing temperature. Both the excess compressibilities κ_s^{E} and κ_T^{E} are negative and have a symmetric shape with minima located around the mole fraction $x = 0.5$.

Moreover, for the mixtures under test, the excess compressibilities and $V_{\mathrm{m}}^{\mathrm{E}}$ have the same signs. The dependence of κ_s^{E} on mole fraction is similar to that of u^{E}, but the signs are opposite. The excess speeds of sound are positive within the whole composition range and increase with increasing temperature. The excess ultrasound speed is a function of the product of two thermodynamic quantities $(\rho\kappa_s)^{-1/2} = V_{\mathrm{m}}^{1/2}(M\kappa_s)^{-1/2}$. It is therefore difficult to interpret the ultrasound speed-like thermodynamic quantities, that is, in terms of molecular structure, molecular space filling, or molecular interactions. However, the sign of $u^{\mathrm{E}} = u - u^{\mathrm{id}} = V_{\mathrm{m}}^{1/2}/(M\kappa_s)^{1/2} - (V_{\mathrm{m}}^{\mathrm{id}})^{1/2}/(M\kappa_s^{\mathrm{id}})^{1/2}$, related in a simple way to those of V^{E} and $\kappa_s{}^{\mathrm{E}}$:u^{E} is positive provided that the inequality $V_{\mathrm{m}}/V_{\mathrm{m}}^{\mathrm{id}} > \kappa_s/\kappa_s^{\mathrm{id}}$ is fulfilled, as in the case of the mixtures under test.

The compressibility of a liquid results from the combination of various factors: the size and shape of the molecules, the

Table 6. Coefficients of eq 16 with Their Standard Deviations and Mean Deviations from the Regression Line δ_i

	A_0	A_1	A_2	A_3	A_4	A_5	δZ^E
T	$V_0^E \times 10^6$	$V_1^E \times 10^6$	$V_2^E \times 10^6$	$V_3^E \times 10^6$	$V_4^E \times 10^6$		$\delta V^E \times 10^6$
K	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$		$m^3 \cdot mol^{-1}$
293.15	−2.214 ±0.016		0.844 ± 0.073	1.028 ± 0.082			0.007
298.15	−2.368 ± 0.021	0.135 ± 0.085	0.363 ± 0.099	0.524 ± 0.220			0.009
303.15	−2.529 ± 0.021	0.235 ± 0.110		0.313 ± 0.286			0.012
308.15	−2.747 ± 0.038	0.321 ± 0.126	0.445 ± 0.422	0.353 ± 0.328	−1.048 ± 0.744		0.014
313.15	−2.948 ± 0.039	0.393 ± 0.129	0.548 ± 0.433	0.650 ± 0.337	−1.213 ± 0.763		0.014
	$C_{p,0}^E$	$C_{p,1}^E$	$C_{p,2}^E$	$C_{p,3}^E$	$C_{p,4}^E$		δC_p^E
	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$		$J \cdot mol^{-1} \cdot K^{-1}$
293.15	−2.08 ± 0.06	−1.15 ± 0.21	−9.51 ± 0.70	−6.23 ± 0.55	4.96 ± 1.24		0.02
298.15	−2.50 ± 0.07	−0.88 ± 0.22	−9.35 ± 0.73	−6.53 ± 0.56	5.28 ± 1.28		0.02
303.15	−2.89 ± 0.07	−0.67 ± 0.22	−9.26 ± 0.74	−6.74 ± 0.57	5.63 ± 1.30		0.02
308.15	−3.26 ± 0.07	−0.54 ± 0.23	−9.24 ± 0.76	−6.86 ± 0.59	6.01 ± 1.34		0.03
313.15	−3.60 ± 0.08	−0.47 ± 0.26	−9.29 ± 0.87	−6.88 ± 0.68	6.42 ± 1.54		0.03
	$\kappa_{s,0}^E \times 10^{10}$	$\kappa_{s,1}^E \times 10^{10}$	$\kappa_{s,2}^E \times 10^{10}$	$\kappa_{s,3}^E \times 10^{10}$			$\delta \kappa_s^E \times 10^{10}$
	Pa^{-1}	Pa^{-1}	Pa^{-1}	Pa^{-1}			Pa^{-1}
293.15	−3.914 ± 0.002	−0.175 ± 0.009	−0.215 ± 0.010	−0.110 ± 0.023			0.001
298.15	−4.221 ± 0.003	−0.219 ± 0.010	−0.242 ± 0.012	−0.149 ± 0.027			0.001
303.15	−4.554±0.003	−0.272±0.012	−0.265±0.014	−0.174±0.032			0.001
308.15	−4.918 ± 0.003	−0.332 ± 0.013	−0.280 ± 0.016	−0.181 ± 0.035			0.001
313.15	−5.316 ± 0.003	−0.403 ± 0.014	−0.289 ± 0.016	−0.167 ± 0.036			0.002
	$\kappa_{T,0}^E \times 10^{10}$	$\kappa_{T,1}^E \times 10^{10}$	$\kappa_{T,2}^E \times 10^{10}$	$\kappa_{T,3}^E \times 10^{10}$	$\kappa_{T,4}^E \times 10^{10}$		$\delta \kappa_T^E \times 10^{10}$
	Pa^{-1}	Pa^{-1}	Pa^{-1}	Pa^{-1}	Pa^{-1}		Pa^{-1}
293.15	−4.845 ± 0.031	0.176 ± 0.146		−0.772 ± 0.380	−2.462 ± 0.300		0.016
298.15	−5.169 ± 0.032			−0.524 ± 0.198	−2.562 ± 0.309		0.017
303.15	−5.521 ± 0.033			−0.666 ± 0.198	−2.647 ± 0.309		0.017
308.15	−5.903 ± 0.032			−0.807 ± 0.200	−2.715 ± 0.311		0.017
313.15	−6.318 ± 0.033			−0.945 ± 0.203	−2.765 ± 0.316		0.017
	u_0^E	u_1^E	u_2^E	u_3^E	u_4^E	u_5^E	δu^E
	$m \cdot s^{-1}$	$m \cdot s^{-1}$	$m \cdot s^{-1}$	$m \cdot s^{-1}$	$m \cdot s^{-1}$	$m \cdot s^{-1}$	$m \cdot s^{-1}$
293.15	271.56 ± 0.04	−108.91 ± 0.24	68.86 ± 0.50	−10.84 ± 1.47	21.07 ± 0.88	−9.92 ± 2.10	0.02
298.15	277.35 ± 0.04	−111.54 ± 0.20	70.20 ± 0.41	−12.14 ± 1.30	20.00 ± 0.72	−9.58 ± 1.73	0.01
303.15	283.31 ± 0.03	−114.35 ± 0.17	71.68 ± 0.35	−13.49 ± 1.11	19.52 ± 0.62	−9.58 ± 1.48	0.01
308.15	289.45 ± 0.03	−117.34 ± 0.16	73.32 ± 0.32	−14.91 ± 1.02	19.66 ± 0.57	−9.92 ± 1.37	0.01
313.15	295.77 ± 0.03	−120.52 ± 0.16	75.12 ± 0.33	−16.39 ± 1.03	20.42 ± 0.57	−10.63 ± 1.37	0.01

intermolecular interaction energy, and the molecular structure (correlation of molecular orientations). Negative values of κ_s^E mean that the real mixture is less compressible than the corresponding ideal one and suggest that V_m^E values increase with increasing pressure.

Negative values of V_m^E are due to a closer geometrical packing and strong interactions between the haloalkane and heptane molecules and result from the predominance of dipole−dipole and dipole−induced dipole interactions. In other words, negative values of excess compressibilities of a given system are attributed to a closer approach of the unlike molecules leading to a reduction in both the volume and compressibility. Generally, negative values of the excess isentropic compressibility are observed when the two unlike components of a binary mixture undergo specific interactions leading to the formation of either H-bonds or charge-transfer complexes, however those interactions are impossible in 1,5-dibromopentane + heptane.

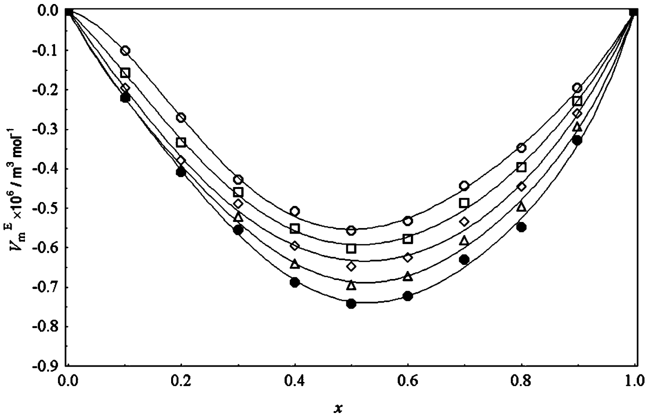

Figure 1. Excess molar volumes V_m^E for {x 1,5-dibromopentane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 16.

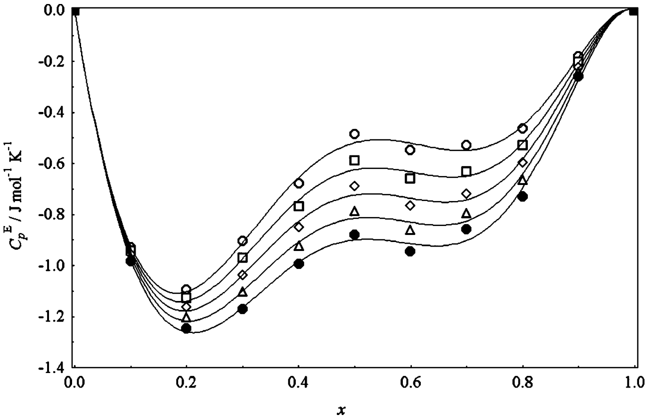

Figure 2. Excess molar heat capacities C_p^E for {x 1,5-dibromopentane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 16.

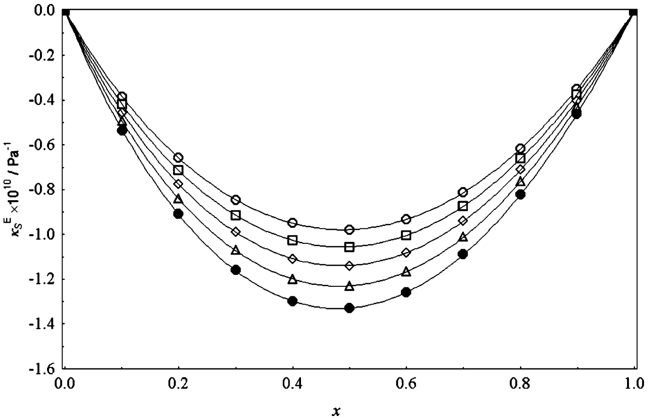

Figure 3. Excess isentropic compressibilities κ_s^E for {x 1,5-dibromopentane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 16.

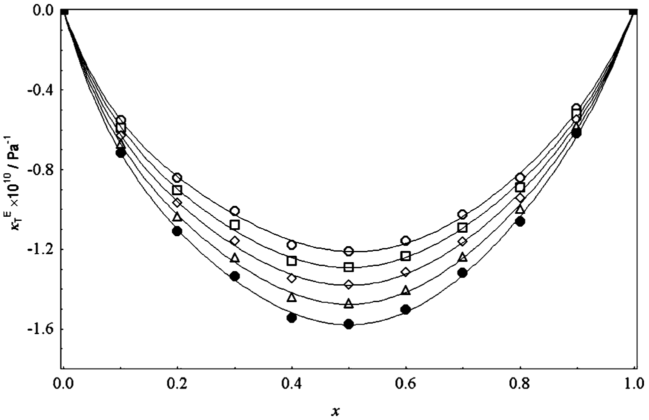

Figure 4. Excess isothermal compressibilities κ_T^E for {x 1,5-dibromopentane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 16.

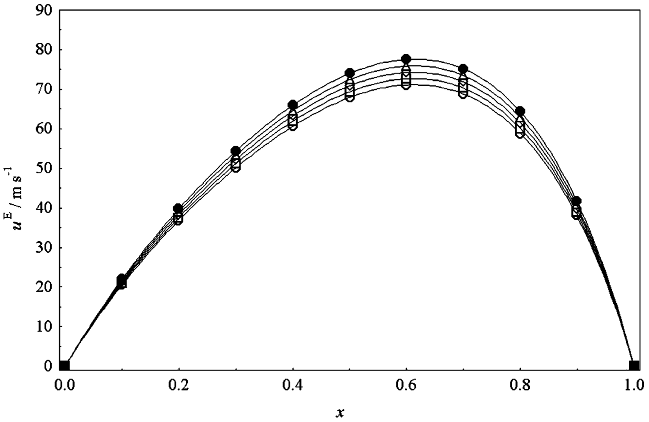

Figure 5. Excess speeds of sound u^E for {x 1,5-dibromopentane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 16.

Heptane and α,ω-dibromoalkanes are different regarding their chemical nature, thus the contribution of intermolecular interactions to the excess molar volumes of their mixtures should be significant. It should be noticed that, in both the pure components, that is, in the nonpolar heptane and in the polar α,ω-dibromoalkanes, there exists some molecular order. Hence, besides van der Waals effects, that is, dispersion forces and the dipole−dipole and dipole−induced dipole interactions leading to negative excess volumes, also structure variations, that is, structure-breaking and structure-making effects accompanying the mixing of the components, have to be taken into account.

The study of thermodynamic properties of mixtures of α,ω-dibromoalkanes with hydrocarbons will be continued in our laboratories.

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