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Thermophysical and Acoustical Properties of the Binary Mixtures 1,2-Dibromoethane + Heptane within the Temperature Range from 293.15 K to 313.15 K

Mirosław Chorążewski*

Institute of Chemistry, University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland

Densities for binary mixtures 1,2-dibromoethane + 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, excess isobaric molar heat capacities, excess isochoric molar heat capacities, excess molar isobaric expansions, excess molar isentropic compressions, excess molar isothermal compressions, excess ultrasonic speeds, and excess internal pressures have been calculated.

Introduction

1,2-Dibromoethane is a polar nonassociated liquid in which important electrostatic intermolecular interactions occur due to permanent dipole moments of the molecules and/or their possible higher multipoles. 1,2-Dibromoethane has attracted the attention of many researchers because of a conformational equilibrium between the nonpolar *trans* form and the polar *gauche* form due to the internal rotation around the C−C axis. As indicated by the results of ultrasonic spectroscopy measurements, near the room temperature approximately 85 % of the molecules are present in the more stable *trans* configuration.[1]

Additionally, the thermodynamic behavior of mixtures containing dibromoalkanes is of considerable interest because of their theoretical and industrial importance. The correlation of their molecular structures with thermodynamic properties of dibromoalkane 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.[2−5]

This work follows our systematic studies on heat capacities of pure halogenoalkanes[6−8] and on thermodynamic and acoustical properties of liquid mixtures containing α,ω-dibromoalkanes with heptane.[9] It is most interesting that, for the investigated mixtures of 1,2-dibromoethane with heptane, the excess heat capacity as a function of mole fraction x is W-shaped.

Grolier et al.[48] have discovered the W-shape anomaly of the dependence of excess isobaric molar heat capacities (C_p^E) on composition. Since then the interest on this phenomenon has constantly grown. Theoretical and model descriptions have been suggested by relating the W-shape effect to rotational isomerism,[10−12,22] and this has evolved finally into a full interpretation accomplished by Saint-Victor and Patterson.[54] The latter interpretation is based on the Guggenheim quasi-chemical lattice theory of solutions. A comprehensive discussion of this phenomenon was carried out by Cobos.[13]

Recently, Troncoso et al.[14] have been successful in the quantitative description of the W-shaped molar excess heat capacities basing on the 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 the system 1,2-dibromoethane + heptane. The values of H^E for this system[15] are ≈1600 J•mol^{-1}.

As a matter of fact, the basic properties of α,ω-dibromoalkanes and their mixtures with alkanes, such as heat capacities, densities, and speeds of sound are rather scarcely reported in the literature. To the best of our knowledge, for the mixtures 1,2-dibromoethane with heptane studied in this paper, no experimental data on the density, speed of sound, and heat capacity as functions of temperature are available in the accessible literature. The only literature data available for this system are the densities and heat capacities at 298.15 K.[16] In this work, the excess properties of molar volumes (V_m^E), isobaric molar heat capacities (C_p^E), isochoric molar heat capacities (C_V^E), molar isobaric expansions (E_p^E), molar isentropic compressions (K_S^E), molar isothermal compressions (K_T^E), ultrasonic speeds (u^E), and internal pressures (p_{int}^E) of the binary system 1,2-dibromoethane + heptane are reported.

Experimental Section

Chemicals. Heptane (≥ 99.8 %) from POCH (Polish Chemicals) was used without further purification. 1,2-Dibromoethane (Lancaster, 99 %) was purified before use by fractional distillation and the middle fraction (approximately 5 %) collected in every case. The purities of the liquid samples of 1,2-dibromoethane checked by gas−liquid chromatography (GLC) were > 99 %.

The mass fraction of water, determined by the Karl Fischer method, was less than 5×10^{-8} for 1,2-dibromoethane and 3×10^{-8} for heptane. Prior to the measurements, the pure liquids were dried with molecular sieves (type 3Å (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 $\pm 2 \times 10^{-5}$ g. Before each

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* E-mail: choraz3@ich.us.edu.pl.

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Table 1. Comparison of the Isobaric Molar Heat Capacities, Densities, Speeds of Sound, Isobaric Expansibilities, Isentropic Compressibilities, Isothermal Compressibilities, and Isochoric Molar Heat Capacities 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[a]	224.707,[17] 224.7.[18−20] 224.71,[48] 224.72,[21] 224.78[22]
u/m·s^{-1}	1130.70[a]	1129.81,[40] 1129.85,[46] 1129.92,[23] 1130.14,[42] 1130.18,[24] 1130.2,[25] 1130.44,[26] 1130.6,[27] 1131[28]
ρ/kg·m^{-3}	679.59	679.42,[29] 679.50,[30] 679.52,[16] 679.54,[45] 679.55,[40] 679.58,[31] 679.60,[24,42] 679.68,[23] 679.70,[32] 679.81[43]
$\alpha_p \times 10^3$/K^{-1}	1.261	1.256,[41] 1.245,[42] 1.246[45]
$\kappa_S \times 10^{12}$/Pa^{-1}	1150.96	1152.84,[40] 1152.08,[42] 1152.32[46]
$\kappa_T \times 10^{12}$/Pa^{-1}	1462.1	1485,[41] 1495,[41] 1455.1,[42] 1440,[43] 1455,[45] 1460.6[47]
C_V/J·mol^{-1}·K^{-1}	176.9	177.92,[b] 178.0[45]
		1,2-Dibromoethane
C_p/J·mol^{-1}·K^{-1}	137.04	136.4,[6] 134.7,[33,34] 136.87,[16] 134.9,[35] 136.02,[36] 135.3[d]
u/m·s^{-1}	993.73	990,[34,37] 993.9,[35] 994.2[d]
ρ/kg·m^{-3}	2168.41	2167.92,[6] 2168.7,[38] 2168.5,[39] 2169.59,[d] 2170.1,[34] 2170.2,[37] 2170.3[35]
$\alpha_p \times 10^3$/K^{-1}	0.964	0.9514,[34] 0.9665,[35] 0.956[d]
$\kappa_S \times 10^{12}$/Pa^{-1}	467.01	466.4,[35] 466.3,[d] 470.14[34]
$\kappa_T \times 10^{12}$/Pa^{-1}	642.3	607.07,[34] 645.1,[35] 640.7[d]
C_V/J·mol^{-1}·K^{-1}	99.64	97.53,[c] 98.47,[d] 104.32[e]

[a] Values from ref 9. [b] Value calculated from ref 42. [c] Value calculated from ref 35. [d] Value calculated from ref 44. [e] Value calculated from ref 34.

series of measurements, each sample was degassed in an ultrasonic cleaner.

The compounds of the homologous series of α,ω-dihalogenoalkanes are difficult to study due to their instability. They are sensitive to the light and temperature. Thus, the decomposition of the 1,2-dibromoethane is the major source of errors. The instability of 1,2-dibromoethane is also the main reason that there are only a few papers in the literature concerning the properties of the 1,2-dibromoethane as a function of temperature.

In order to minimize the errors, the compounds were kept in the dark glass flasks. The flasks were wrapped in an aluminum foil and stored in the desiccator. The solutions were used immediately after they were prepared. The measuring cells have been filled in the drybox.

A comparison of the molar heat capacities, densities, speed of sound, isobaric expansibilities, isentropic compressibilities, isothermal compressibilities, and isochoric molar heat capacities 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 satisfactory agreement. Small differences may result from differences in the purity of the chemicals, measurement techniques, and calibrations.

Apparatus and Procedure. Isobaric heat capacities were measured in a micro DSC III scanning calorimeter from Setaram, using the "continuous with reference" method. The uncertainty of the measurements was estimated to be ± 0.15 %. Details of the applied procedure and the calorimeter calibration have been described previously.[7]

The measurements of the densities (ρ) of the pure components and the binary mixtures were carried out using an Anton−Paar densitometer (model DMA 5000) operated in static mode with an uncertainty of 5×10^{-2} kg·m^{-3}. The water used for the calibration of the densimeter was re-distilled over alkaline $KMnO_4$ and deaerated by multiple boiling. The apparatus was also tested with the density of known molality of aqueous NaCl.

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 vessel was immersed in a water bath. The temperature was stabilized within the limits ± 0.005 K by a Techne TU16D temperature controller of proportional integrating differential type. The main thermostat was cooled by a MLW MK cryostat connected with a MLW U10 thermostat in a cascade arrangement. In order to achieve a homogeneous temperature distribution, the main thermostat was additionally equipped with a two-paddle mixer. The temperature was measured with an Ertco Hart 850 platinum resistance thermometer with an uncertainty of ± 0.05 K and a resolution of 0.001 K. The temperature fluctuations did not exceed ± 0.005 K in a 30 min period of measurement and did not exceed ± 0.01 K during 1 day. 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,[49] which is undoubtedly the best standard liquid available. The ultrasonic apparatus was calibrated with re-distilled water as the standard liquid. The speeds of sound in water, calculated from the polynomial of Marczak[49] at atmospheric pressure, were taken as true values.

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 K to 313 K, are shown in Tables 3 and 4, respectively.

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

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

where y is the molar heat capacity, density, or speed of sound; T/K is the absolute temperature; 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. In order to calculate C_V^E, E_p^E, K_S^E, K_T^E, u^E, and p_{int}^E and to obtain a consistent presentation of the measurement results, "new" (calculated) density and speed of sound values have been generated (i.e., those for mole fractions at which the heat capacities were measured). To this end, polynomials of the 4th order (ρ or $u = \sum_{i=0}^{4} a_i \cdot x^i$) describing the density and speed of sound isotherms were used.

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

	C_p/J·mol^{-1}·K^{-1}										
T/K	x = 0.0000[a]	x = 0.1016	x = 0.2016	x = 0.2989	x = 0.3977	x = 0.4996	x = 0.5991	x = 0.6928	x = 0.8022	x = 0.9003	x = 1.0000
293.15	222.87	213.58	204.39	196.15	187.73	179.31	170.59	162.47	153.18	144.90	136.87
294.15	223.23	213.90	204.73	196.48	188.03	179.43	170.80	162.60	153.26	144.94	136.90
295.15	223.60	214.26	204.92	196.66	188.20	179.65	170.96	162.81	153.40	145.07	136.95
296.15	223.97	214.59	205.30	196.95	188.51	179.89	171.13	162.90	153.53	145.16	136.99
297.15	224.35	214.90	205.51	197.29	188.66	180.09	171.23	163.05	153.63	145.24	137.02
298.15	224.72	215.25	205.83	197.53	188.94	180.26	171.40	163.18	153.72	145.27	137.04
299.15	225.10	215.55	206.18	197.72	189.11	180.39	171.55	163.24	153.84	145.33	137.09
300.15	225.47	215.90	206.45	198.00	189.43	180.66	171.77	163.47	153.91	145.40	137.11
301.15	225.87	216.32	206.71	198.31	189.64	180.79	171.90	163.50	153.98	145.47	137.15
302.15	226.22	216.60	207.03	198.60	189.82	181.03	172.01	163.71	154.13	145.60	137.20
303.15	226.61	216.95	207.33	198.77	190.01	181.17	172.23	163.89	154.24	145.65	137.25
304.15	227.00	217.33	207.57	199.17	190.33	181.40	172.31	163.94	154.32	145.75	137.29
305.15	227.40	217.70	207.95	199.39	190.62	181.54	172.49	164.06	154.37	145.77	137.32
306.15	227.75	218.07	208.28	199.58	190.75	181.72	172.71	164.29	154.55	145.83	137.39
307.15	228.14	218.39	208.47	199.90	191.03	181.95	172.88	164.40	154.60	145.96	137.42
308.15	228.54	218.69	208.80	200.20	191.31	182.17	173.00	164.48	154.68	146.01	137.49
309.15	228.95	219.10	209.10	200.37	191.50	182.37	173.19	164.70	154.79	146.13	137.53
310.15	229.30	219.41	209.50	200.65	191.66	182.48	173.29	164.80	154.90	146.20	137.60
311.15	229.71	219.69	209.78	200.99	191.91	182.68	173.50	164.88	155.00	146.21	137.65
312.15	230.11	220.11	210.10	201.15	192.12	182.91	173.69	165.06	155.16	146.30	137.71
313.15	230.51	220.35	210.39	201.51	192.42	183.06	173.84	165.16	155.25	146.43	137.77

[a] Values from ref 9.

Table 3. Experimental Densities, ρ, for x 1,2-Dibromoethane + (1 − x) Heptane at Temperatures T

	ρ/kg·m^{-3}				
x	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
0.0000	683.82	679.59	675.31	671.02	666.68
0.1018	776.01	771.16	766.40	761.38	756.39
0.2052	878.46	872.98	867.72	862.14	856.68
0.2931	973.90	968.00	962.23	956.31	950.37
0.3754	1070.54	1064.30	1058.00	1051.80	1045.35
0.3919	1091.09	1084.74	1078.36	1071.93	1065.57
0.5009	1234.71	1227.73	1220.93	1213.97	1207.14
0.5993	1379.31	1372.04	1364.69	1357.19	1349.51
0.6916	1530.51	1522.49	1514.35	1506.30	1498.20
0.7886	1707.97	1699.34	1690.56	1681.76	1673.14
0.8919	1922.00	1912.55	1903.13	1893.55	1884.12
1.0000	2178.77	2168.41	2157.94	2147.47	2136.96

Table 4. Experimental Speeds of Sound, u, for x 1,2-Dibromoethane + (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[a]	292.84	1153.67	298.84	1127.72	303.80	1106.38	308.78	1085.10	314.87	1059.14
0.1024	292.64	1112.12	298.56	1087.95	303.59	1067.66	308.62	1047.39	314.59	1023.62
0.2000	292.62	1079.50	298.58	1056.48	303.61	1037.19	308.65	1017.99	314.56	995.72
0.2986	292.64	1050.76	298.69	1028.57	303.65	1010.63	308.62	992.63	314.61	971.18
0.4002	292.68	1027.19	298.60	1006.69	303.54	989.74	308.58	972.63	314.58	952.25
0.4996	292.70	1009.41	298.59	990.17	303.66	973.72	309.57	954.55	314.59	938.54
0.6005	292.60	996.77	298.59	978.03	303.62	962.51	308.59	947.22	314.59	928.96
0.6997	292.66	989.87	298.60	972.29	303.61	957.60	308.57	943.03	314.55	925.53
0.8004	292.68	989.25	298.68	972.17	303.78	957.87	308.59	944.46	314.58	927.74
0.9061	292.70	995.84	298.56	980.00	303.57	966.53	308.44	953.47	314.52	937.35
1.0000	292.84	1007.52	299.17	991.14	303.37	980.18	308.75	966.56	314.45	952.00

[a] Values from ref 9.

The isentropic compressibility (κ_S) was calculated from the Newton−Laplace equation:

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

and K_S was calculated from

$$K_S = V_m \kappa_S \tag{3}$$

The isothermal compressibility (κ_T) and molar isothermal compression (K_T) were calculated from the well-known thermodynamic relationship:

$$\kappa_T = \kappa_S + \frac{T V_m \alpha_p^2}{C_{p,m}} \tag{4}$$

$$K_T = V_m \kappa_T \tag{5}$$

where the isobaric expansibility (α_p) was calculated by analytical differentiation of the density fitting equation:

$$\alpha_p = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{6}$$

The temperature dependence of the "new" densities, calculated as mentioned above, were described again by eq 1. Linear dependences were achieved for each mole fraction and the α_p values calculated analytically from eq 6.

The molar isobaric expansion (E_p) was calculated from

$$E_p = \alpha_p V_m \tag{7}$$

Excess properties were calculated using the following expression:

$$Z^E = Z - Z^{id} \tag{8}$$

where Z^E is the excess quantity of the property Z (V_m, C_p, C_V, E_p, K_S, K_T, u, p_{int}) and Z^{id} is the corresponding ideal value.

The ideal values were calculated using the criteria redefined by Douhéret et al.:[50]

$$V_m^{id} = x_1 V_1^* + (1 - x_1) V_2^* \tag{9}$$

$$C_{p,m}^{id} = x_1 C_{p,m,1}^* + (1 - x_1) C_{p,m,2}^* \tag{10}$$

$$\kappa_S^{id} = \kappa_T^{id} - \frac{T V_m^{id} (\alpha_p^{id})^2}{C_{p,m}^{id}} \tag{11}$$

$$K_S^{id} = V_m^{id} \kappa_S^{id} \tag{12}$$

$$\kappa_T^{id} = \phi_1 \kappa_{T,1}^* + (1 - \phi_1) \kappa_{T,2}^* \tag{13}$$

$$K_T^{id} = V_m^{id} \kappa_T^{id} \tag{14}$$

$$\alpha_p^{id} = \phi_1 \alpha_{p,1}^* + (1 - \phi_1) \alpha_{p,2}^* \tag{15}$$

$$E_p^{id} = V_m^{id} \alpha_p^{id} \tag{16}$$

$$u^{id} = \left[(\phi_1)^2 \left(\frac{C_{p,m,1}^*}{C_{V,m,1}^*} \right) \left(\frac{C_{V,m}^{id}/C_{p,m}^{id}}{w_1 (u_1^*)^2} \right) + (\phi_2)^2 \left(\frac{C_{p,m,2}^*}{C_{V,m,2}^*} \right) \left(\frac{C_{V,m}^{id}/C_{p,m}^{id}}{w_2 (u_2^*)^2} \right) \right]^{-1/2} \tag{17}$$

$$C_{V,m}^{id} = C_{p,m}^{id} \frac{\kappa_S^{id}}{\kappa_T^{id}} \tag{18}$$

where in eqs 13 and 15, ϕ_1 is the ideal volume fraction:

$$\phi_1 = \frac{x_1 V_1^*}{V_m^{id}} \tag{19}$$

x_1 being the mole fraction for component 1 (1,2-dibromoethane). In eq 17, ϕ_1 is the volume fraction defined by the mass fraction, w_1:

$$\phi_1 = \frac{w_1 \rho^{id}}{\rho_1^*} \tag{20}$$

where

$$\rho^{id} = \phi_1 \rho_1^* + (1 - \phi_1) \rho_2^* \tag{21}$$

The excess internal pressures were calculated from the equation of Marczak:[51]

$$p_{int}^E = \psi_1 p_{int,1}^* + (1 - \psi_1) p_{int,2}^* \tag{22}$$

where

$$p_{int,i}^* = \frac{T \alpha_{p,i}^*}{\kappa_{T,i}^*} \tag{23}$$

is the internal pressures, and

$$\psi_1 = \frac{x_1 K_{T,1}^*}{x_1 K_{T,1}^* + (1 - x_1) K_{T,2}^*} \tag{24}$$

is called the "compression fraction" where $K_{T,i}^*$ is the molar isothermal compression and x_i is the mole fractions of the pure ith component, respectively. The asterisks indicate parameters of the pure components.

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

$$Z^E = x_1 (1 - x_1) \sum_{i=0}^{n} A_i (1 - 2x_1)^i \tag{25}$$

where Z^E is the excess function, and A_i are the polynomial coefficients ($A_i = V_{m,i}^E$ for the excess molar volumes, $A_i = C_{p,i}^E$ for the excess isobaric molar heat capacities, $A_i = C_{V,i}^E$ for the excess isochoric molar heat capacities, $A_i = E_{p,i}^E$ for the excess molar isobaric expansions, $A_i = K_{s,i}^E$ for the excess molar isentropic compressions, $A_i = K_{T,i}^E$ for the excess molar isothermal compressions, $A_i = u_i^E$ for the excess speeds of sound, and $A_i = p_{int,i}^E$ for the excess internal pressures). 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.[50] 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 in contrast to many other proposals based on either empirical or intuitive approaches. Somewhat later Gliński[52] argued that an equation proposed earlier by Ernst et al.[53] 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 1,2-dibromoethane in Figures 1 to 8. Additionally in Figures 9 and 10 the molar excess volumes and excess isobaric molar heat capacity at 298.15 K have been compared with literature data,[16] respectively. The only literature existing data for the studded system are from Lainez et al.,[16] thus the following remarks ought to be made. It was impractical to carry on the proper statistical analysis (e.g., determination of the residual errors, deviation plot) if the only set of the available literature data is at one temperature. According to the instability of 1,2-dibromoethane (see the Chemicals section), the observed deviation in Figures 9 and 10 may be attribute to the measurements difficulty and can be regarded as small. The absolute values of excess molar volumes and excess molar heat capacities are small, and the relative errors are magnified.

As shown in Figure 1 the values of V^E have been found to be positive throughout the entire range of x, which indicates

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

	a_o	a_1	a_2	δ_y
x	c_0/J·mol^{-1}·K^{-1}	c_1/J·mol^{-1}·K^{-2}	c_2/J·mol^{-1}·K^{-3}	δ_{Cp}/J·mol^{-1}·K^{-1}
0.0000[a]	222.867 ± 0.006	0.3673 ± 0.0013	0.000744 ± 0.000056	0.18
0.1016	213.514 ± 0.011	0.3439 ± 0.0030		0.19
0.2016	204.355 ± 0.003	0.2994 ± 0.0056		0.08
0.2989	196.176 ± 0.011	0.2648 ± 0.0019		0.20
0.3977	187.752 ± 0.018	0.2331 ± 0.0022		0.17
0.4996	179.298 ± 0.019	0.1894 ± 0.0031		0.19
0.5991	170.611 ± 0.004	0.1600 ± 0.0010		0.09
0.6928	162.490 ± 0.023	0.1343 ± 0.0029		0.20
0.8022	153.187 ± 0.005	0.1022 ± 0.0012		0.12
0.9003	144.889 ± 0.005	0.0758 ± 0.0013		0.10
1.0000	136.877 ± 0.006	0.0294 ± 0.0011	0.000731 ± 0.000044	0.05

	a_o	a_1	a_2	δ_y
x	u_0/m·s^{-1}	u_1/m·s^{-1}·K^{-1}	u_2/m·s^{-1}·K^{-2}	δ_u/m·s^{-1}
0.0000[a]	1152.337 ± 0.013	−4.3375 ± 0.0027	0.002171 ± 0.000122	0.01
0.1024	1110.023 ± 0.044	−4.0937 ± 0.0096	0.002964 ± 0.000436	0.05
0.2000	1077.449 ± 0.021	−3.8803 ± 0.0046	0.002870 ± 0.000211	0.02
0.2986	1048.856 ± 0.045	−3.6699 ± 0.0096	0.002297 ± 0.000436	0.05
0.4002	1025.537 ± 0.042	−3.4667 ± 0.0090	0.002221 ± 0.000408	0.05
0.4996	1007.944 ± 0.044	−3.2791 ± 0.0098	0.001869 ± 0.000443	0.05
0.6005	995.024 ± 0.024	−3.1345 ± 0.0052	0.002490 ± 0.000236	0.03
0.6997	988.411 ± 0.028	−2.9578 ± 0.0060	0.000919 ± 0.000275	0.03
0.8004	987.880 ± 0.059	−2.8424 ± 0.0127	0.001734 ± 0.000577	0.06
0.9061	994.630 ± 0.019	−2.7161 ± 0.0040	0.001668 ± 0.000183	0.02
1.0000	1006.708 ± 0.068	−2.6045 ± 0.0142	0.001726 ± 0.000596	0.07

	a_o	a_1	a_2	δ_y
x	ρ_0/kg·m^{-3}	ρ_1/kg·m^{-3}·K^{-1}	ρ_2/kg·m^{-3}·K^{-2}	δ_ρ/kg·m^{-3}
0.0000	683.853 ± 0.026	−0.8571 ± 0.0021		0.03
0.1018	775.994 ± 0.050	−0.9501 ± 0.0117	−0.001506 ± 0.000563	0.05
0.2052	878.479 ± 0.063	−1.0882 ± 0.0052		0.08
0.2931	973.910 ± 0.042	−1.1748 ± 0.0034		0.05
0.3754	1070.577 ± 0.052	−1.2579 ± 0.0043		0.07
0.3919	1091.104 ± 0.020	−1.2767 ± 0.0016		0.03
0.5009	1234.677 ± 0.038	−1.3779 ± 0.0031		0.05
0.5993	1379.295 ± 0.023	−1.4328 ± 0.0054	−0.002794 ± 0.000257	0.02
0.6916	1530.534 ± 0.023	−1.6163 ± 0.0019		0.03
0.7886	1708.000 ± 0.046	−1.7446 ± 0.0038		0.06
0.8919	1922.021 ± 0.035	−1.8950 ± 0.0028		0.04
1.0000	2178.824 ± 0.038	−2.0912 ± 0.0031		0.05

[a] Values from ref 9.

that the addition of heptane decreases the attractive van der Waals interactions between the molecules of the polar component. This effect is more pronounced at lower temperatures at which the dipole interactions are stronger. The excess volumes show a point of interest: they are crossing each other within a narrow concentration interval in the vicinity of the mole fraction $x \approx 0.4$ of 1,2-dibromoethane. It is worthy of notice that the single crossing point of the excess volume isotherms appear practically at the same concentrations at which the excess molar isobaric expansion values change their sign from positive to negative ones (see Figure 4). These facts seem to suggest the formation of a stable, temperature independent (or almost temperature independent) structure in the vicinity of $x \approx 0.4$.

A W-shape of the excess heat capacity plotted as a function of the mole fraction is observed in Figures 2 and 3. A comprehensive interpretation of this phenomenon, based on the Guggenheim quasi-chemical lattice theory of solutions, was suggested by Saint-Victor and Patterson.[54] The W-shaped curves have two regions of negative curvature separated by a region of a positive one. This is a consequence of two opposite contributions: a positive contribution to C_p^E (the so-called non-random contribution) transferring into a parabolic negative curve (the so-called random contribution).

Hence, C_p^E is a value that clearly indicates the degree of non-randomness in the mixture. The values of C_p^E decrease and W-shape becomes less pronounced with increasing temperature. As can be seen in Figure 2, the randomness, being predominant within the composition ranges 0 to 0.4 and 0.6 to 1, results from the disruption of the molecular order of the dilute component (i.e., the molecules of the dilute component; the solute) are separated and randomly distributed in the component of higher concentration (the solvent). However, for compositions ranging from $x = 0.4$ to $x = 0.6$, a positive contribution to C_p^E is observed (non-randomness) that results from the possible attractive van der Waals molecular interactions: attractions between permanent dipoles (Keesom's effects), between permanent and induced dipoles (Debye's effects), and dispersive interactions (London's effects). Higher multipoles can also play some role. This situation becomes more pronounced with decreasing temperature, probably because the Keesom effects increase. The W-shape of the C_V^E curves (Figure 3) is a consequence of a strong influence of the isobaric heat capacity on the isochoric one. C_V^E is a thermodynamic function more sensible to the molecular order of the liquid than C_p^E, hence the W-shape becomes less pronounced at higher temperatures (i.e., 313.15 K).

Table 6. Coefficients of Equation 25 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	$V^E_{m,0}\times 10^6$	$V^E_{m,1}\times 10^6$	$V^E_{m,2}\times 10^6$	$V^E_{m,3}\times 10^6$	$V^E_{m,4}\times 10^6$	$V^E_{m,5}\times 10^6$	$\delta V^E_m\times 10^6$
K	$\mathrm{m^3\cdot mol^{-1}}$	$\mathrm{m^3\cdot mol^{-1}}$	$\mathrm{m^3\cdot mol^{-1}}$	$\mathrm{m^3\cdot mol^{-1}}$	$\mathrm{m^3\cdot mol^{-1}}$	$\mathrm{m^3\cdot mol^{-1}}$	$\mathrm{m^3\cdot mol^{-1}}$
293.15	1.578 ± 0.013	0.959 ± 0.050	0.200 ± 0.065	0.354 ± 0.138			0.006
298.15	1.536 ± 0.012	1.123 ± 0.062	0.617 ± 0.141	0.898 ± 0.422	−0.385 ± 0.252	−0.832 ± 0.583	0.005
303.15	1.493 ± 0.018	1.369 ± 0.037	0.415 ± 0.088				0.008
308.15	1.435 ± 0.014	1.510 ± 0.040	0.800 ± 0.070			0.718 ± 0.207	0.007
313.15	1.383 ± 0.020	1.567 ± 0.077	0.944 ± 0.099	0.796 ± 0.212			0.009

	A_0	A_1	A_2	A_3	A_4	A_5	δZ^E
T	$C^E_{p,0}$	$C^E_{p,1}$	$C^E_{p,2}$	$C^E_{p,3}$	$C^E_{p,4}$	$C^E_{p,5}$	δC^E_p
K	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$
293.15	−2.74 ± 0.20	−0.36 ± 1.06	−11.91 ± 2.20	−11.28 ± 6.85	9.43 ± 3.87	17.50 ± 9.15	0.07
298.15	−2.91 ± 0.16		−11.71 ± 1.80	−14.02 ± 2.47	10.54 ± 3.16	20.82 ± 4.56	0.06
303.15	−3.24 ± 0.15		−11.54 ± 1.64	−14.71 ± 2.25	11.07 ± 2.87	21.73 ± 4.15	0.05
308.15	−3.72 ± 0.14		−11.40 ± 1.56	−15.41 ± 2.15	11.05 ± 2.74	22.64 ± 3.96	0.05
313.15	−4.35 ± 0.14		−11.30 ± 1.57	−16.12 ± 2.16	10.45 ± 2.76	23.57 ± 3.99	0.05

	A_0	A_1	A_2	A_3	A_4	A_5	δZ^E
T	$C^E_{V,0}$	$C^E_{V,1}$	$C^E_{V,2}$				δC^E_V
K	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$				$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$
293.15	−9.12 ± 0.15	−9.41 ± 0.31	−17.88 ± 0.71				0.07
298.15	−9.64 ± 0.15	−9.29 ± 0.31	−17.34 ± 0.71				0.07
303.15	−10.29 ± 0.16	−9.10 ± 0.32	−17.07 ± 0.74				0.07
308.15	−11.10 ± 0.17	−8.97 ± 0.33	−17.23 ± 0.77				0.07
313.15	−12.05 ± 0.17	−8.84 ± 0.35	−17.69 ± 0.80				0.08

	A_0	A_1	A_2	A_3	A_4	A_5	δZ^E
T	$E^E_{p,0}\times 10^9$	$E^E_{p,1}\times 10^9$	$E^E_{p,2}\times 10^9$	$E^E_{p,3}\times 10^9$	$E^E_{p,4}\times 10^9$	$E^E_{p,5}\times 10^9$	$\partial E^E_p\times 10^9$
K	$\mathrm{m^3\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{m^3\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{m^3\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{m^3\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{m^3\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{m^3\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{m^3\cdot mol^{-1}\cdot K^{-1}}$
293.15	−7.16 ± 0.05	28.99 ± 0.28	14.23 ± 0.58	4.31 ± 1.81	12.29 ± 1.02	10.95 ± 2.42	0.02
298.15	−7.39 ± 0.05	29.74 ± 0.29	14.72 ± 0.60	4.46 ± 1.85	12.58 ± 1.05	11.17 ± 2.48	0.02
303.15	−7.72 ± 0.05	30.25 ± 0.29	15.05 ± 0.60	4.58 ± 1.86	12.66 ± 1.05	11.24 ± 2.49	0.02
308.15	−8.00 ± 0.06	30.98 ± 0.30	15.51 ± 0.63	4.70 ± 1.96	13.25 ± 1.11	11.80 ± 2.62	0.02
313.15	−8.34 ± 0.06	31.75 ± 0.31	16.02 ± 0.64	4.86 ± 1.99	13.50 ± 1.13	12.08 ± 2.67	0.02

	A_0	A_1	A_2	A_3	A_4	A_5	δZ^E
T	$K^E_{S,0}\times 10^{13}$	$K^E_{S,1}\times 10^{13}$	$K^E_{S,2}\times 10^{13}$	$K^E_{S,3}\times 10^{13}$			$\partial K^E_S\times 10^{13}$
K	$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$	$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$	$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$	$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$			$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$
293.15	−0.304 ± 0.000	0.073 ± 0.002		0.022 ± 0.004			0.000
298.15	−0.330 ± 0.000	0.080 ± 0.002		0.025 ± 0.004			0.000
303.15	−0.361 ± 0.000	0.085 ± 0.001	0.006 ± 0.002	0.027 ± 0.004			0.000
308.15	−0.395 ± 0.000	0.092 ± 0.002	0.013 ± 0.002	0.032 ± 0.005			0.000
313.15	−0.432 ± 0.000	0.098 ± 0.002	0.018 ± 0.002	0.035 ± 0.005			0.000

	A_0	A_1	A_2	A_3	A_4	A_5	δZ^E
T	$K^E_{T,0}\times 10^{13}$	$K^E_{T,1}\times 10^{13}$	$K^E_{T,2}\times 10^{13}$	$K^E_{T,3}\times 10^{13}$			$\partial K^E_T\times 10^{13}$
K	$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$	$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$	$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$	$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$			$\mathrm{m^3\cdot Pa^{-1}\cdot mol^{-1}}$
293.15	−0.331 ± 0.001	0.193 ± 0.004	0.122 ± 0.005	0.087 ± 0.010			0.000
298.15	−0.360 ± 0.001	0.207 ± 0.004	0.133 ± 0.005	0.093 ± 0.011			0.000
303.15	−0.392 ± 0.001	0.217 ± 0.004	0.140 ± 0.005	0.097 ± 0.010			0.000
308.15	−0.427 ± 0.001	0.230 ± 0.005	0.153 ± 0.005	0.107 ± 0.012			0.001
313.15	−0.465 ± 0.001	0.243 ± 0.005	0.166 ± 0.006	0.114 ± 0.013			0.001

	A_0	A_1	A_2	A_3	A_4	A_5	δZ^E
T	u^E_0	u^E_1	u^E_2	u^E_3	u^E_4	u^E_5	δu^E
K	$\mathrm{m\cdot s^{-1}}$	$\mathrm{m\cdot s^{-1}}$	$\mathrm{m\cdot s^{-1}}$	$\mathrm{m\cdot s^{-1}}$	$\mathrm{m\cdot s^{-1}}$	$\mathrm{m\cdot s^{-1}}$	$\mathrm{m\cdot s^{-1}}$
293.15	167.66 ± 0.07	−118.50 ± 0.36	85.74 ± 0.74	−49.66 ± 2.31	46.94 ± 1.31	−32.24 ± 3.09	0.02
298.15	170.81 ± 0.07	−121.70 ± 0.38	86.94 ± 0.79	−51.13 ± 2.44	48.80 ± 1.38	−33.47 ± 3.26	0.03
303.15	174.10 ± 0.08	−124.77 ± 0.40	88.43 ± 0.83	−52.66 ± 2.58	50.83 ± 1.46	−34.77 ± 3.45	0.03
308.15	177.55 ± 0.08	−127.71 ± 0.43	90.21 ± 0.88	−54.27 ± 2.74	53.04 ± 1.55	−36.13 ± 3.67	0.03
313.15	181.16 ± 0.09	−130.56 ± 0.45	92.29 ± 0.94	−55.97 ± 2.92	55.45 ± 1.65	−37.60 ± 3.91	0.03

	A_0	A_1	A_2	A_3	A_4	A_5	δZ^E
T	$p^E_{int,0}\times 10^{-5}$	$p^E_{int,1}\times 10^{-5}$	$p^E_{int,2}\times 10^{-5}$	$p^E_{int,3}\times 10^{-5}$	$p^E_{int,4}\times 10^{-5}$		$\delta p^E_{int}\times 10^{-5}$
K	Pa	Pa	Pa	Pa	Pa		Pa
293.15	644.24 ± 1.41	−375.73 ± 4.60	511.48 ± 15.64	−490.89 ± 11.98	499.52 ± 27.46		0.51
298.15	663.89 ± 1.49	−402.21 ± 4.86	526.93 ± 16.51	−513.95 ± 12.65	518.44 ± 28.99		0.54
303.15	684.11 ± 1.58	−427.01 ± 5.15	543.57 ± 17.47	−536.78 ± 13.39	536.08 ± 30.68		0.57
308.15	704.22 ± 1.67	−452.12 ± 5.43	561.17 ± 18.43	−560.31 ± 14.13	550.06 ± 32.37		0.60
313.15	724.93 ± 1.75	−477.15 ± 5.71	580.08 ± 19.40	−583.98 ± 14.86	564.10 ± 34.06		0.63

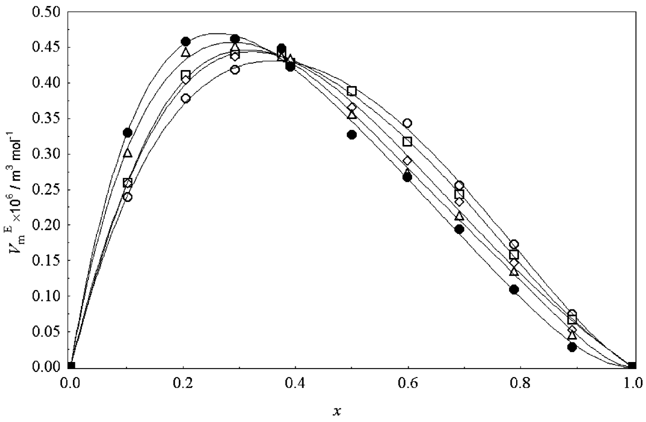

Figure 1. Excess molar volumes V_m^E for {x 1,2-dibromoethane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 25.

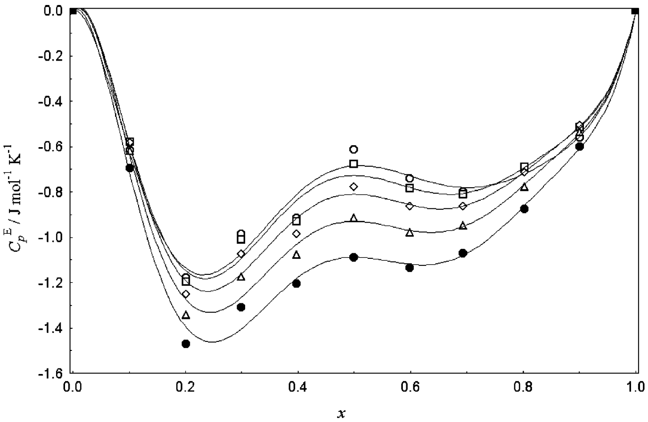

Figure 2. Excess isobaric molar heat capacities C_p^E for {x 1,2-dibromoethane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 25.

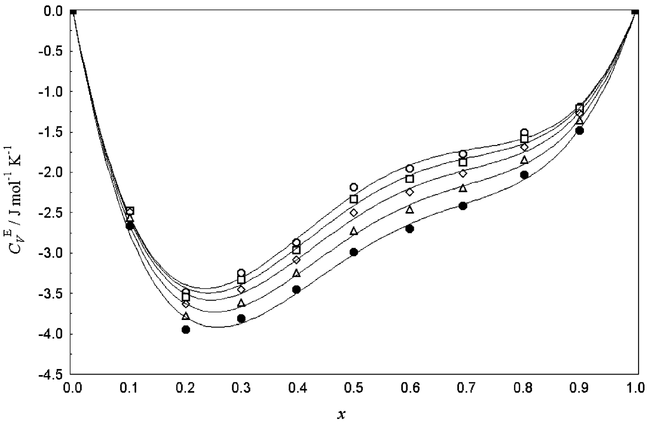

Figure 3. Excess isochoric molar heat capacities C_V^E for {x 1,2-dibromoethane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 25.

Both the excess molar compressions K_S^E and K_T^E are in principle negative and a little asymmetric with minima shifted to higher mole fractions of 1,2-dibromoethane. The values of K_S^E and K_T^E decrease with increasing temperature (Figures 5 and 6). The dependence of K_S^E and K_T^E on the mole fraction is similar to that of u^E, but the signs are opposite. The minima of the excess molar compressions are located around the mole fraction $x = 0.6$. On the other hand, for the mixtures under test, the excess molar compressions and V_m^E have opposite signs.

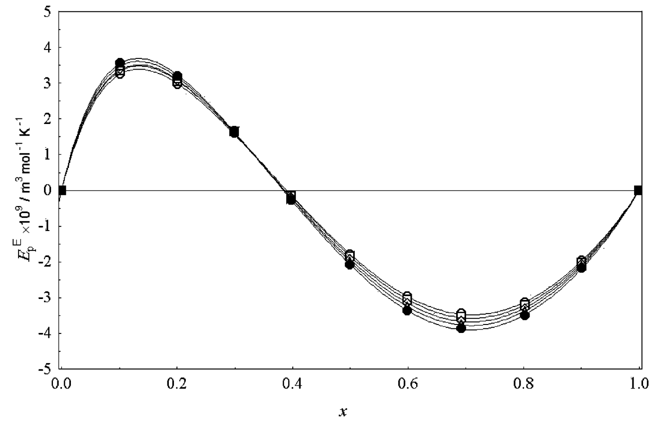

Figure 4. Excess molar isobaric expansions E_p^E for {x 1,2-dibromoethane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 25.

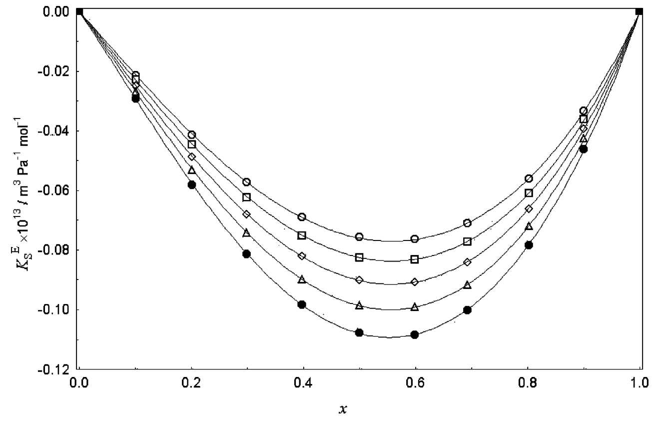

Figure 5. Excess molar isentropic compressions K_S^E for {x 1,2-dibromoethane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 25.

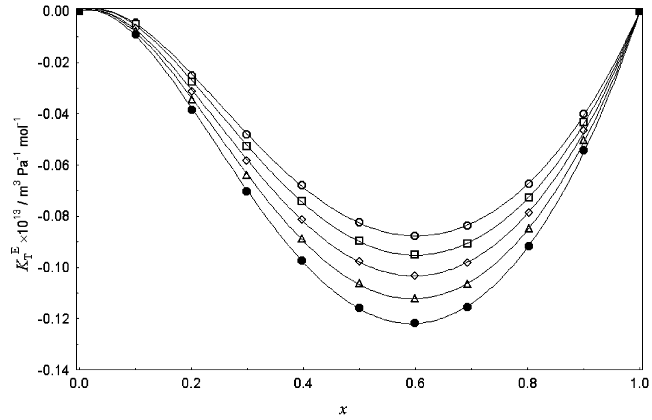

Figure 6. Excess molar isothermal compressions K_T^E for {x 1,2-dibromoethane + (1 - x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 25.

The excess speeds of sound and excess internal pressure are positive for the whole composition range and have an asymmetric shape with maxima shifted toward higher mole fractions of 1,2-dibromoethane. The values of u^E and p_{int}^E increase with increasing temperature (Figures 7 and 8).

The excess ultrasound speed is a function of the product of two thermodynamic quantities $(\rho\kappa_S)^{-1/2} = V_m^{1/2}(M\kappa_S)^{-1/2}$. It is therefore difficult to interpret the ultrasound speed like thermodynamic quantities (i.e., in terms of molecular structure, molecular space filling, or molecular interactions). The positive

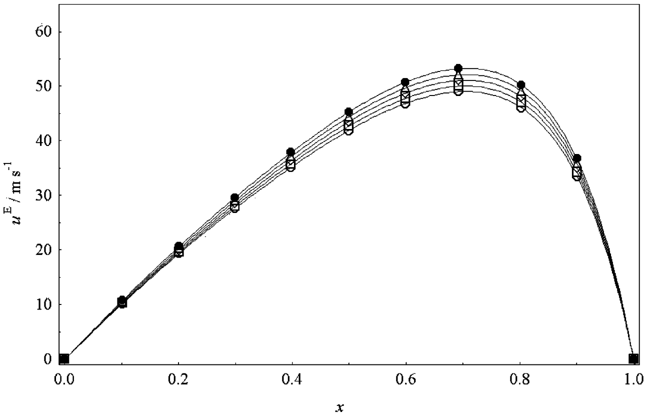

Figure 7. Excess speeds of sound u^E for {x 1,2-dibromoethane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 25.

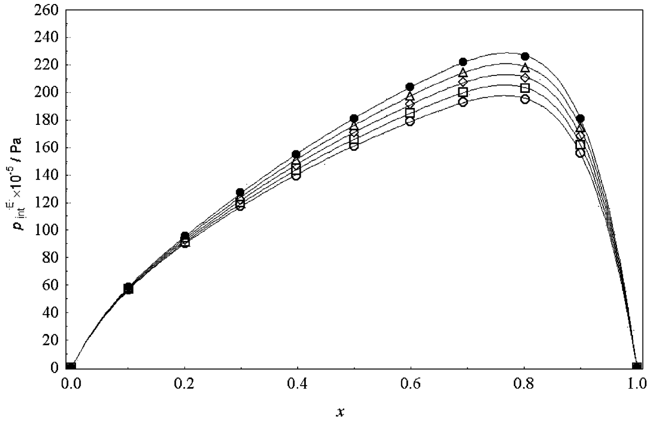

Figure 8. Excess internal pressures p_{int}^E for {x 1,2-dibromoethane + (1 − x) heptane} at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; —, values calculated from eq 25.

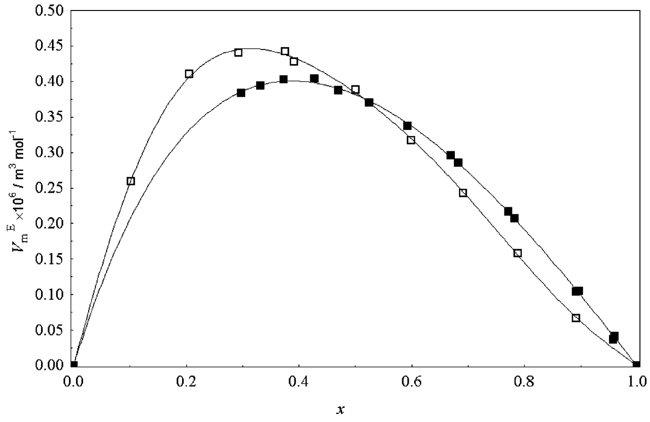

Figure 9. Excess molar volumes V_m^E for {x 1,2-dibromoethane + (1 − x) heptane} at 298.15 K; □, experimental points from this work; ■, literature data;[16] —, values calculated from eq 25.

excess ultrasound speed results from a simple relationship between $u^E = V_m^{1/2}/(M\kappa_S)^{1/2} - (V_m^{id})^{1/2}/(M\kappa_S^{id})^{1/2}$, the excess molar volume (V_m^E), and the excess adiabatic compressibility coefficient (κ_S^E): if $u^E > 0$, the inequality $V_m/\kappa_S > V_m^{id}/\kappa_S^{id} = V_m/V_m^{id} > \kappa_S/\kappa_S^{id}$ must be fulfilled. For the system under test, the excess volumes are positive ($V_m > V_m^{id}$; i.e., $V_m/V_m^{id} > 1$) and excess adiabatic compressibilities are negative ($\kappa_S < \kappa_S^{id}$; i.e., $\kappa_S/\kappa_S^{id} < 1$). Thus, the excess speed is positive.

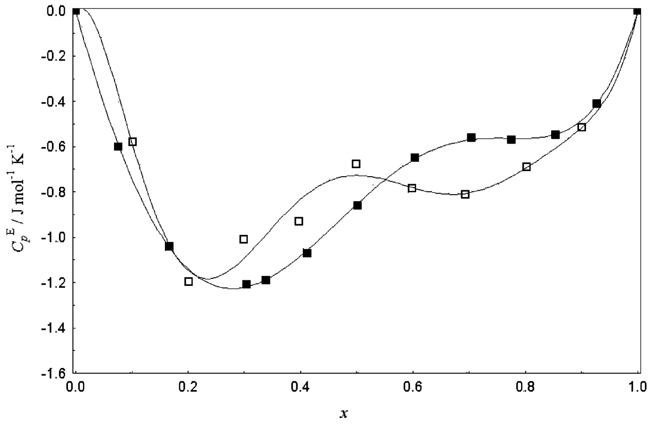

Figure 10. Excess isobaric molar heat capacities C_p^E for {x 1,2-dibromoethane + (1 − x) heptane} at 298.15 K; □, experimental points from this work; ■, literature data;[16] —, values calculated from eq 25.

The compressibility of a liquid results from the combination of various factors: the size and shape of the molecules, the intermolecular interaction energy, and the molecular structure (correlation of molecular orientations). However, some explanation of the opposite signs of V_m^E and K_S^E and K_T^E for the mixtures of 1,2-dibromoethane with heptane should be given. Negative values of K_S^E mean that the mixture is less compressible than the corresponding ideal mixture and suggest that the V_m^E values increase with increasing pressure. Generally, negative values of the excess molar isentropic compression are observed when two unlike components of a mixture undergo specific interactions leading to the formation of either H-bonds or charge-transfer complexes, but those interactions are impossible in 1,2-dibromoethane + heptane.

Heptane and α,ω-dibromoalkanes are different regarding their chemical nature; thus, the interactional contribution to the excess molar volumes of their binary mixtures should be significant. It should be noticed that in both the types of the pure substances, that is, in the nonpolar heptane and in the polar α,ω-dibromoalkanes, there exists some molecular order; hence, the structure breaking effects in both the components during mixing have to be taken into account. Positive values of V_m^E result from the predominance of positive contributions, that is, the destruction of dispersive interactions and/or the dipolar order of at least one of the pure components (breaking down dipole−dipole interactions in 1,2-dibromoethane), or from the reduction of the orientational order of long-chain linear heptane. The expansion of volume, on the other hand, is caused generally by factors such as unfavorable geometric fitting or steric effects, which hinder the molecules from approaching each other. In addition, the destruction of the molecular order is favored as the temperature increases and thereby V_m^E increases too.

The internal pressure $p_{int} = (\partial U/\partial V)_T = (\partial U_m/\partial V_m)_T$ is a measure of the energy that must be supplied to increase the volume of the liquid by one unit at constant temperature. It is therefore related to internal forces in the liquid phase and thereby to molecular interactions. The excesses found are asymmetric with maxima shifted toward higher concentrations of the polar component, where dipole interactions should be more pronounced. It is worthy of notice that a similar shift of the maximum appears in the system bromoform + octane.[51]

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