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Temperature and Pressure Dependence of the Volumetric Properties of Binary Liquid Mixtures Containing Dihaloalkanes

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Densities of ethyl acetate + dibromomethane, + bromochloromethane, + 1,2-dichloroethane, or + 1-bromo-2-chloroethane binary mixtures were measured at 288.15, 298.15, and 308.15 K over the entire composition range. Thermal expansion coefficients and excess molar volumes were calculated. Moreover, densities at 298.15 K at pressures up to 200 bar were determined for the same mixtures. Isothermal compressibilities of the pure liquids and their mixtures were obtained. The excess molar volumes are positive, and the excess isothermal compressibilities are negative for all the studied mixtures.

KEY WORDS: density; excess volume; isothermal compressibility; thermal expansion coefficient.

1. INTRODUCTION

Thermodynamic properties for suitably chosen binary mixtures have been studied for examining some theories of mixtures and for understanding the strength and nature of the molecular interactions. In this way, we have studied the thermodynamic properties of different halogenated aliphatic compounds and their mixtures [1–7]. Mono- and poly-haloalkanes represent a class of technically important compounds, used in industry as intermediates or as final products. We present here the densities of ethyl acetate + dibromomethane, + bromochloromethane, + 1,2-dichloroethane, or + 1-bromo-2-chloroethane binary mixtures at 288.15, 298.15,

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and 308.15 K. Thermal expansion coefficients, α, and excess molar volumes, V_m^E, were calculated over the entire composition range. Moreover, densities of the same mixtures at 298.15 K at pressures up to 200 bar were determined. Isothermal compressibilities, κ_T, of the pure liquids and their mixtures were calculated. As far as we know, the only previous studies of such mixtures are those of Oswal et al. [8, 9] and Reddy et al. [10] on excess molar volumes, viscosity, and isentropic compressibilities of ethyl acetate + 1,2-dichloroethane.

2. EXPERIMENTAL

The liquids used were ethyl acetate (>99.5 mol%; water <0.05%), dibromomethane (>98.5 mol%; water <0.05%), and 1,2-dichloroethane (> 99.5 mol%; water ≤ 0.03%), obtained from Fluka AG Buchs, and bromochloromethane (> 99 mol%) and 1-bromo-2-chloroethane (> 98.0 mol%), obtained from Aldrich. All the liquids were used without further purification. The measured densities of the pure liquids are listed in Table I.

The excess molar volumes V_m^E were calculated from densities measured at 288.15, 298.15, and 308.15 K with a vibrating-tube densimeter (Anton-Paar Model DMA 60) equipped with a DMA 602 cell. The densimeter calibration was performed at atmospheric pressure by using doubly distilled and degassed water, cyclohexane, and carbon tetrachloride [11]. The vibrating-tube temperature was measured using an Anton-Paar DM 100-30 digital thermometer, and was regulated to better than ±0.01 K using a Neslab RTE-210 thermostat. The thermometer was previously checked [7] against the vapor pressure of benzene using the equation of Ambrose [12] relating temperature (T_{68}) with pressure by means of a sum of Chebyshev polynomials up to degree six (as recommended by IUPAC [13]).

Table I. Densities, ρ, of the Pure Liquids at 298.15 K

	$\rho(\mathrm{g{\cdot}cm^{-3}})$		Deviation (%)
Substance	Experimental	Literature [11, 14]	$100\{\lvert\rho_{\mathrm{exp}} - \rho_{\mathrm{lit}}\rvert/\rho_{\mathrm{exp}}\}$
dibromomethane	2.47837	2.48420	0.2
bromochloromethane	1.92488	1.92300	0.1
1,2-dichloroethane	1.24659	1.24560	0.1
1-bromo-2-chloroethane	1.72788	1.73015	0.1
ethyl acetate	0.89497	0.89400	0.1

The mixtures were prepared by weight, and the mole-fraction error was estimated to be less than $\pm 10^{-4}$. Duplicate density measurements for the pure liquids and mixtures agree to within $2 \times 10^{-5}\,\mathrm{g \cdot cm^{-3}}$. Taking into account the uncertainty in the temperature, the overall total uncertainty in density is estimated to be $\leq 3 \times 10^{-5}\,\mathrm{g \cdot cm^{-3}}$.

The densities (ρ) of the pure components and binary mixtures were measured at 298.15 K at pressures from 2 to 200 bar using the vibrating-tube densimeter with a DMA 512 high pressure cell. High pressures were generated by a liquid pump (Model LC-10 AT; Shimadzu). Pressures were measured with a pressure gauge (Gefran) calibrated with distilled water and nitrogen using another pressure gauge (Druck, Model DPI 145). The uncertainty of the measured pressures is about ±0.04%.

The measured oscillation period (τ) of the vibrating U tube was converted to density values using

$$\rho = A(\tau^2 - B) \tag{1}$$

where A and B are instrument constants determined at high pressure by using ethanol and 1,2-dichloroethane as reference fluids [11, 14]. The values of parameters A and B, determined from the calibration, are presented as a function of pressure by

$$A = 0.65419 - 0.012P + 658.10^{-7}P^2$$

$$B = 15.1475 + 131.10^{-8}P + 818.10^{-10}P^2$$

The uncertainty of the reported densities was estimated to be $10^{-4}\,\mathrm{g \cdot cm^{-3}}$.

3. RESULTS AND DISCUSSION

The calculated values of the excess molar volume V_m^{E} for the mixtures are listed in Table II and plotted against mole fraction of dihaloalkane, x, in Figs. 1 and 2. Each set of results was fitted with a polynomial of the form,

$$V_m^{\mathrm{E}}/(\mathrm{cm^3 \cdot mol^{-1}}) = x(1-x)\Sigma A_i (2x-1)^i \tag{2}$$

using an ordinary (unweighted) least-squares method.

The values of the coefficients A_i, and the standard deviations σ given by

$$\sigma(V_m^{\mathrm{E}}) = [\Sigma(V^{\mathrm{E}} - V_{\mathrm{exp}}^{\mathrm{E}})^2/(N-M)]^{1/2} \tag{3}$$

Table II. Densities and Excess Molar Volumes for the Studied Mixtures

	288.15 K		298.15 K		308.15 K	
x	ρ $(\mathrm{g{\cdot}cm^{-3}})$	V_m^{E} $(\mathrm{cm^3{\cdot}mol^{-1}})$	ρ $(\mathrm{g{\cdot}cm^{-3}})$	V_m^{E} $(\mathrm{cm^3{\cdot}mol^{-1}})$	ρ $(\mathrm{g{\cdot}cm^{-3}})$	V_m^{E} $(\mathrm{cm^3{\cdot}mol^{-1}})$
$(1-x)$ethyl acetate + (x)dibromomethane						
0.0000	0.90671	0.0000	0.89497	0.0000	0.88227	0.0000
0.0522	0.96658	0.0562	0.95436	0.0407	0.94097	0.0376
0.2014	1.14777	0.2119	1.13383	0.1900	1.11850	0.1778
0.3006	1.27779	0.2739	1.26261	0.2549	1.24598	0.2371
0.4028	1.41989	0.3562	1.40406	0.3020	1.38570	0.3044
0.4852	1.54209	0.3749	1.52500	0.3404	1.50567	0.3304
0.6012	1.72596	0.3896	1.70790	0.3391	1.68698	0.3268
0.7001	1.89561	0.3606	1.87610	0.3275	1.85424	0.2963
0.8077	2.09530	0.2962	2.07459	0.2663	2.05067	0.2587
0.8997	2.28145	0.1743	2.25957	0.1524	2.23429	0.1472
1.0000	2.50188	0.0000	2.47837	0.0000	2.45174	0.0000
$(1-x)$ethyl acetate + (x)bromochloromethane						
0.0000	0.90671	0.0000	0.89497	0.0000	0.88187	0.0000
0.0961	0.97608	0.1061	0.96362	0.1041	0.94999	0.0734
0.2333	1.08323	0.2131	1.06974	0.2042	1.05479	0.1832
0.3083	1.14577	0.2914	1.13177	0.2743	1.11641	0.2304
0.4015	1.22840	0.3630	1.21384	0.3310	1.19733	0.3083
0.5004	1.32297	0.3923	1.30802	0.3690	1.29038	0.3362
0.6040	1.43045	0.3834	1.41477	0.3601	1.39609	0.3474
0.7004	1.53894	0.3560	1.52214	0.3339	1.50246	0.3240
0.7987	1.65996	0.2730	1.64151	0.2697	1.62066	0.2587
0.9032	1.80066	0.1752	1.78071	0.1753	1.75833	0.1730
1.0000	1.94594	0.0000	1.92488	0.0000	1.90086	0.0000
$(1-x)$ethyl acetate + (x)1,2-dichloroethane						
0.0000	0.90671	0.0000	0.89497	0.0000	0.88227	0.0000
0.1036	0.93639	0.0511	0.92454	0.0423	0.91153	0.0476
0.2054	0.96698	0.0774	0.95482	0.0790	0.94170	0.0737
0.3019	0.99699	0.1144	0.98484	0.0983	0.97132	0.1019
0.4003	1.02899	0.1357	1.01664	0.1219	1.00293	0.1192
0.4963	1.06148	0.1568	1.04895	0.1433	1.03507	0.1349
0.6020	1.09883	0.1778	1.08609	0.1671	1.07198	0.1557
0.6820	1.12850	0.1741	1.11564	0.1618	1.10130	0.1526
0.8002	1.17496	0.1226	1.16178	0.1199	1.14708	0.1136
0.9001	1.21619	0.0836	1.20279	0.0850	1.18786	0.0768
1.0000	1.26013	0.0000	1.24659	0.0000	1.23127	0.0000
$(1-x)$ethyl acetate + (x)1-bromo-2-chloroethane						
0.0000	0.90671	0.0000	0.89497	0.0000	0.88227	0.0000
0.1080	0.98497	−0.0412	0.97255	−0.0435	0.95903	−0.0429
0.1985	1.05171	0.0101	1.03906	−0.0204	1.02494	−0.0258
0.2997	1.12856	0.0680	1.11549	0.0268	1.10059	0.0285

Table II. Continued.

	288.15 K		298.15 K		308.15 K	
x	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})
0.3988	1.20599	0.1390	1.19241	0.1008	1.17702	0.0880
0.5008	1.28867	0.1820	1.27457	0.1471	1.25855	0.1332
0.5477	1.32776	0.1911	1.31332	0.1653	1.29696	0.1562
0.6462	1.41226	0.1863	1.39728	0.1687	1.38036	0.1567
0.7653	1.51863	0.1631	1.50313	0.1491	1.48556	0.1361
0.8030	1.55345	0.1438	1.53771	0.1360	1.51981	0.1302
0.9050	1.65002	0.0956	1.63403	0.0843	1.61555	0.0806
1.0000	1.74436	0.0000	1.72788	0.0000	1.70886	0.0000

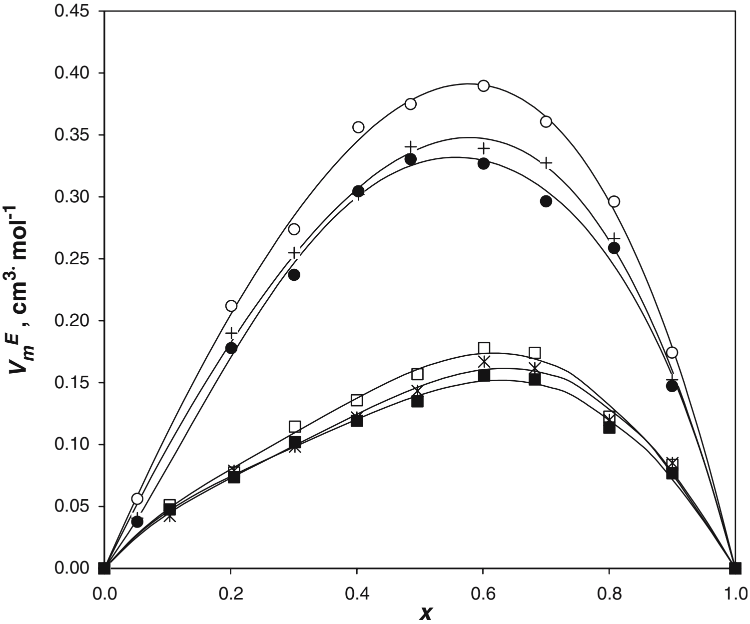

Fig. 1. Excess molar volumes, V_m^E, as a function of mole fraction: $(1-x)$ ethyl acetate + (x) dibromomethane : (○) 288.15 K, (+) 298.15 K, and (●) 308.15 K; $(1-x)$ ethyl acetate + (x) 1,2-dichloroethane: (□) 288.15 K, (*) 298.15 K, and (■) 308.15 K.

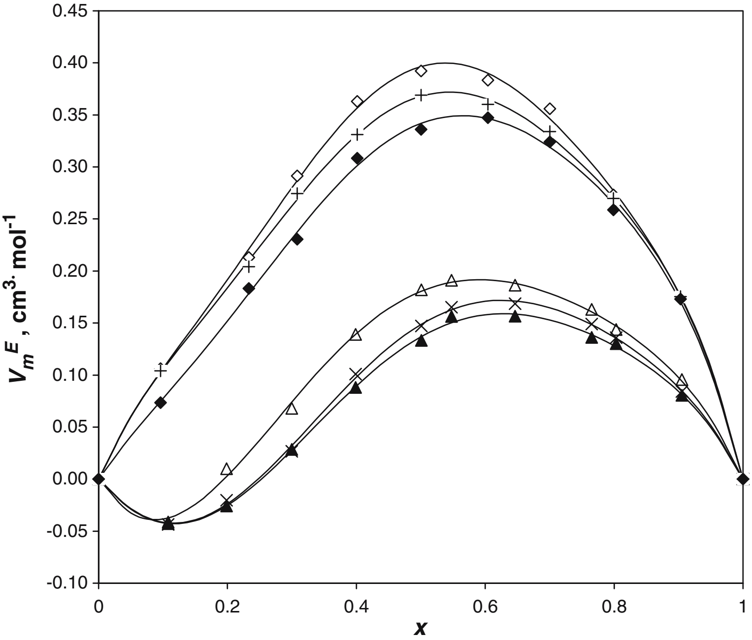

Fig. 2. Excess molar volumes, V_m^E, as a function of mole fraction: $(1-x)$ ethyl acetate + (x) bromochloromethane: (◇) 288.15 K, (+) 298.15 K, and (♦) 308.15 K; $(1-x)$ ethyl acetate + (x) 1-bromo-2-chloroethane: (△) 288.15 K, (**x**) 298.15 K, and (▲) 308.15 K.

where N is the number of experimental points and M is the number of fitting coefficients, as determined by least-squares analysis, are reported in Table III.

The excess volumes of ethyl acetate + 1,2-dichloroethane have been measured by Oswal et al. [8, 9] at 303.15 K and by Reddy et al. [10] at 303.15 K. Our experimental results ($V_m^E = 0.1615$, $V_m^E = 0.1470$, and $V_m^E = 0.1400$ at $x = 0.5$ and 288.15, 298.15, and 308.15 K, respectively) are closer to those of Reddy et al. ($V_m^E = 0.163$ at $x = 0.5$ and 303.15 K) than to those of Oswal et al. ($V_m^E = 0.1098$ at $x = 0.5$ and 303.15 K). Our V_m^E curves and those from the other authors have the same shape.

In order to obtain the thermal expansion coefficients of the pure liquids, the measured densities for each system have been fitted to a polynomial function,

$$\rho/(g \cdot \mathrm{cm}^{-3}) = \sum_{i=1}^{N} \sum_{j=1}^{3} A_{ij} (T - T_0)^{j-1} x^{i-1} \tag{4}$$

where $T_0 = 278.15\,\mathrm{K}$.

Table III. Parameters A_i of Eq. (2) for the Mixtures and Standard Deviations $\sigma\left(V_m^{\mathrm{E}}\right)$ ($\mathrm{cm^3{\cdot}mol^{-1}}$)

System	T(K)	A_0	A_1	A_2	A_3	A_4	$\sigma\left(V_m^{\mathrm{E}}\right)$
$(1-x)C_4H_8O_2$ + $(x)CH_2Br_2$	288.15	1.527 ± 0.02	0.477 ± 0.04	0.109 ± 0.09	–	–	0.008
	298.15	1.357 ± 0.02	0.430 ± 0.04	0.109 ± 0.09	–	–	0.008
	308.15	1.311 ± 0.02	0.296 ± 0.09	0.009 ± 0.12	0.334 ± 0.25	–	0.010
$(1-x)C_4H_8O_2$ + $(x)BrClCH_2$	288.15	1.586 ± 0.02	0.360 ± 0.08	−0.781 ± 0.26	0.224 ± 0.20	1.217 ± 0.44	0.009
	298.15	1.472 ± 0.02	0.360 ± 0.05	−0.572 ± 0.16	0.244 ± 0.12	1.164 ± 0.27	0.005
	308.15	1.367 ± 0.02	0.473 ± 0.07	−0.487 ± 0.22	0.307 ± 0.18	0.833 ± 0.39	0.008
$(1-x)C_4H_8O_2$ + $(x)ClC_2H_4Cl$	288.15	0.646 ± 0.02	0.387 ± 0.07	0.064 ± 0.08	−0.295 ± 0.18	–	0.008
	298.15	0.588 ± 0.02	0.384 ± 0.06	0.134 ± 0.08	−0.233 ± 0.17	–	0.007
	308.15	0.560 ± 0.01	0.330 ± 0.05	0.145 ± 0.06	−0.235 ± 0.13	–	0.006
$(1-x)C_4H_8O_2$ + $(x)BrC_2H_4Cl$	288.15	0.722 ± 0.01	0.514 ± 0.05	−0.794 ± 0.15	0.671 ± 0.13	0.284 ± 0.27	0.005
	298.15	0.594 ± 0.01	0.750 ± 0.04	−0.866 ± 0.11	0.235 ± 0.09	0.538 ± 0.20	0.004
	308.15	0.701 ± 0.03	0.547 ± 0.01	−0.804 ± 0.10	0.274 ± 0.09	0.493 ± 0.19	0.004

Table IV. Coefficients A_{ij} of Eq. (4) and Standard Deviations (σ)

i	$j = 1$	2	3
$(1-x)$ethyl acetate + (x)dibromomethane			
1	0.92385	−0.00105	-4.40×10^{-6}
2	1.03121	-4.47×10^{-4}	-1.73×10^{-5}
3	0.55734	-3.39×10^{-4}	5.10×10^{-6}
		$\sigma = 3.5 \times 10-3$	
$(1-x)$ethyl acetate + (x)bromochloromethane			
1	0.92381	−0.00106	-4.95×10^{-6}
2	0.61231	1.77×10^{-4}	-1.75×10^{-5}
3	0.42042	-8.02×10^{-4}	7.95×10^{-6}
		$\sigma = 2.8 \times 10^{-3}$	
$(1-x)$ethyl acetate + (x)1,2-dichloroethane			
1	0.91836	−0.00103	-4.95×10^{-6}
2	0.26931	-2.45×10^{-5}	-3.75×10^{-6}
3	0.08333	-5.75×10^{-5}	3.50×10^{-7}
		$\sigma = 4.2 \times 10^{-4}$	
$(1-x)$ethyl acetate + (x)1-bromo-2-chloroethane			
1	0.91945	−0.00102	-5.10×10^{-6}
2	0.68658	-1.83×10^{-4}	-1.03×10^{-5}
3	0.15052	-8.15×10^{-5}	3.05×10^{-6}
		$\sigma = 7.3 \times 10^{-4}$	

The coefficients A_{ij} and standard deviations are reported in Table IV.

The thermal expansion coefficients α are obtained by using the equation,

$$\alpha = -\rho^{-1}(\delta\rho/\delta T)_p \tag{5}$$

We have obtained the following values of α for the pure liquids at 298.15 K: $\alpha(\mathrm{EA}) = 1.363 \times 10^{-3}\,\mathrm{K}^{-1}$; $\alpha(\mathrm{CH_2Br_2}) = 9.845 \times 10^{-4}\,\mathrm{K}^{-1}$; $\alpha(\mathrm{CH_2BrCl}) = 1.174 \times 10^{-3}\,\mathrm{K}^{-1}$; $\alpha(\mathrm{ClC_2H_4Cl}) = 1.163 \times 10^{-3}\,\mathrm{K}^{-1}$; and $\alpha(\mathrm{BrC_2H_4Cl}) = 1.055 \times 10^{-3}\,\mathrm{K}^{-1}$. The values found in the literature for the pure liquids are α (EA) $= 1.39 \times 10^{-3}\,\mathrm{K}^{-1}$ at 293.15 K, $\alpha(\mathrm{ClC_2H_4Cl}) = 1.141 \times 10^{-3}\,\mathrm{K}^{-1}$ at 293.15 K [14], and $\alpha(\mathrm{ClC_2H_4Cl}) = 1.17 \times 10^{-3}\,\mathrm{K}^{-1}$ at 298.15 K [15]. Figure 3 shows the calculated values of α for the studied mixtures at 298.15 K.

The measured densities for the pure liquids and binary mixtures at 298.15 K and over the pressure range from 2 to 200 bar are reported in Tables V and VI. The isothermal compressibilities, $\kappa_T = -\rho^{-1}(\delta\rho/\delta P)_T$ were obtained at 298.15 K and are reported in Table VII. As far as we know, the only experimental value found in the literature for the isothermal compressibility for the studied liquid is that of Malhotra

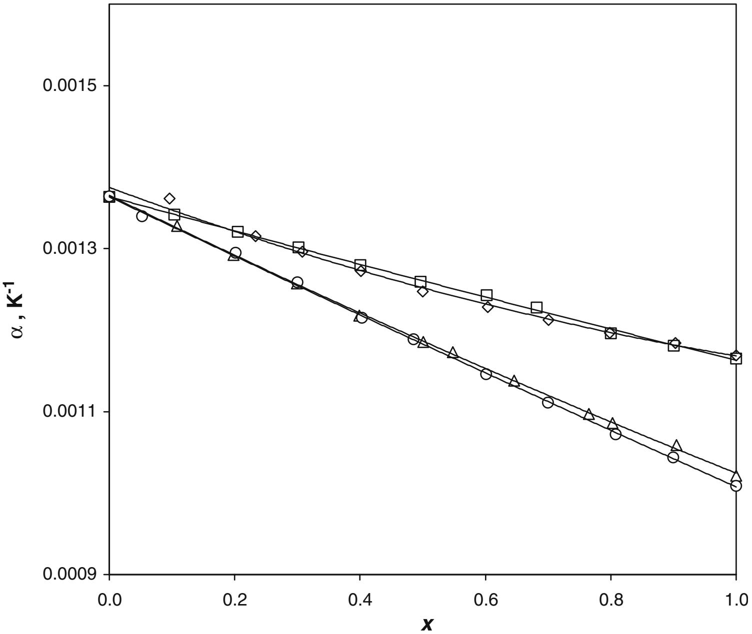

Fig. 3. Thermal expansion coefficient, α, as a function of mole fraction at 298.15 K: $(1-x)$ ethyl acetate + (x) dibromomethane (○), + (x) bromochloromethane (◇), + (x) 1,2-dichloroethane (□), and + (x) 1-bromo-2-chloroethane (△).

et al. [15] for 1,2-dichloroethane from 278.15 K ($10^4\kappa_T = 7.06\,\mathrm{MPa}^{-1}$) to 338.15 K ($10^4\kappa_T = 11.04\,\mathrm{MPa}^{-1}$).

The "excess" compressibility, defined as

$$\kappa^{\mathrm{E}} = -V^{-1}(\delta V^{\mathrm{E}}/\delta P)_T = \kappa - \phi_1\kappa_1 - \phi_2\kappa_2 \qquad (6)$$

where ϕ_1 and ϕ_2 are the volume fractions, is widely used. The values of κ^E of the studied systems are plotted against x in Fig. 4.

As shown in Fig. 3 and Table VII, dibromomethane gives the smallest values of the thermal expansion coefficient and isothermal compressibility, and bromochloromethane and 1,2-dichloroethane show similar α and κ_T values. Moreover, except for 1-bromo-2-chloroethane, the density of these haloalkanes change in the opposite direction to that of isothermal compressibility, showing that any increase in the density of the haloalkane could decrease the intermolecular free space and thereby the ability to be compressed.

Table V. Densities as a Function of Pressure for the Pure Liquids at 298.15 K

CH_2Br_2		$BrClCH_2$		ClC_2H_4Cl		BrC_2H_4Cl		$C_4H_8O_2$	
P (bar)	ρ (g·cm^{-3})	*P* (bar)	ρ (g·cm^{-3})	*P* (bar)	ρ (g·cm^{-3})	*P* (bar)	ρ (g·cm^{-3})	*P* (bar)	ρ (g·cm^{-3})
193	2.50884	196	1.95316	197	1.26429	194	1.74948	195	0.91259
192	2.50869	178	1.95026	177	1.26237	176	1.74712	176	0.91084
177	2.50574	157	1.94701	157	1.26048	156	1.74452	160	0.90945
159	2.50249	139	1.94425	139	1.25884	139	1.74249	138	0.90754
158	2.50233	118	1.94079	120	1.25696	117	1.73960	117	0.90554
137	2.49859	98	1.93783	101	1.25518	96	1.73717	99	0.90388
118	2.49498	88	1.93636	89	1.25400	87	1.73613	89	0.90288
98	2.49258	80	1.93488	80	1.25307	80	1.73510	80	0.90212
88	2.49092	70	1.93343	71	1.25227	68	1.73374	70	0.90111
80	2.48954	59	1.93203	61	1.25122	60	1.73277	60	0.90019
69	2.48782	49	1.93051	51	1.25032	48	1.73135	51	0.89922
59	2.48626	38	1.92877	41	1.24953	41	1.73057	40	0.89820
50	2.48484	29	1.92762	31	1.24851	29	1.72914	29	0.89710
41	2.48350	21	1.92624	20	1.24741	20	1.72817	21	0.89614
30	2.48188	10	1.92464	11	1.24654	9	1.72694	11	0.89518
21	2.48041	5	1.92388	5	1.24602	5	1.72648	6	0.89465
10	2.47890	2	1.92354	2	1.24568	2	1.72608	2	0.89420
6	2.47835	–	–	–	–	–	–	–	–
3	2.47792	–	–	–	–	–	–	–	–
2	2.47756	–	–	–	–	–	–	–	–

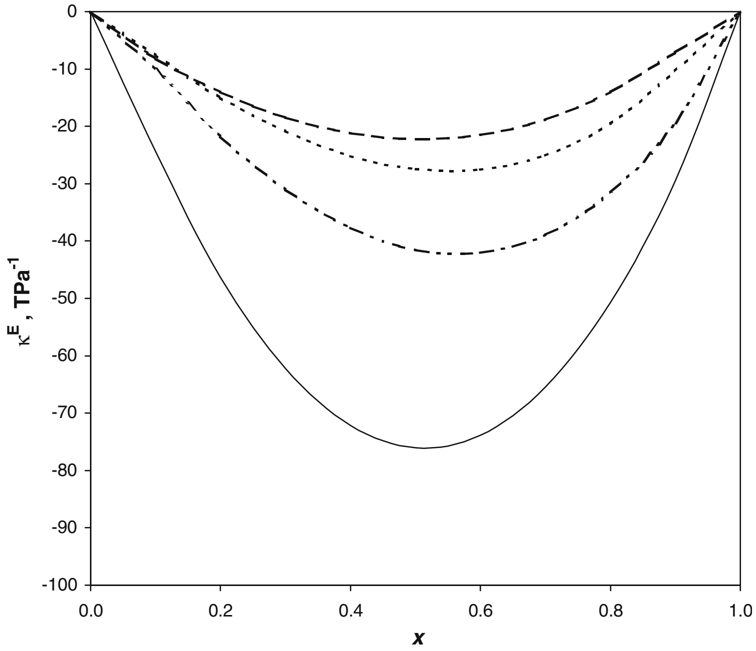

Fig. 4. Excess isothermal compressibility, κ^{E} as a function of mole fraction at 298.15 K: $(1-x)$ ethyl acetate + (x) dibromomethane (– – — – – — – –), + (x) bromochloromethane (– – – – – – – –), + (x) 1,2-dichloroethane (— — — — —), and + (x) 1-bromo-2-chloroethane (——————).

The excess molar volumes V_m^{E} for all the studied mixtures are positive and increase in the following sequence: ethyl acetate + 1-bromo-2-chloroethane < + 1,2-dichloroethane < + dibromomethane < + bromochloromethane. On the other hand, the excess isothermal compressibilities, κ^{E}, are negative, and the ethyl acetate + 1-bromo-2-chloroethane and ethyl acetate + 1,2-dichloroethane mixtures show the largest and smallest deviations from ideality, respectively.

Taking into account the V_m^{E} of the corresponding dihaloalkane + n-alkane [16] and ethylacetate + n-alkane mixtures [17], we can conclude that the contribution to $V^{\mathrm{E};m}$ due to the strong halogen atom-carboxylate group specific interaction is more important than the geometrical ("free volume") effects in the mixture. Moreover, experimental values of excess enthalpies H_m^{E} of these type of mixtures from the literature [18, 19] seem to confirm the existence of a strong (exothermic) halogen atom carboxylate group specific interaction (H_m^{E} of 1,2-dichloroethane + n-hexane is 1595 J·mol^{-1} at $x=0.5$, and of 1,2-dichloroethane + ethylacetate is

Table VI. Densities for the Studied Mixtures at 298.15 K

$x = 0.2995$		$x = 0.5013$		$x = 0.6994$	
P (bar)	ρ (g·cm^{-3})	P (bar)	ρ (g·cm^{-3})	P (bar)	ρ (g·cm^{-3})
$(1-x)$ethyl acetate + (x)dibromomethane					
201	1.28419	198	1.57640	198	1.90309
179	1.28150	176	1.57334	178	1.90002
158	1.27896	158	1.57087	159	1.89708
140	1.27689	138	1.56824	140	1.89437
121	1.27455	120	1.56567	123	1.89162
98	1.27189	100	1.56292	104	1.88873
89	1.27084	86	1.56102	100	1.88823
80	1.26958	79	1.56000	91	1.88700
68	1.26829	67	1.55840	81	1.88533
59	1.26724	60	1.55743	70	1.88378
48	1.26579	47	1.55568	60	1.88225
37	1.26458	39	1.55465	52	1.88121
29	1.26367	29	1.55329	42	1.87975
21	1.26247	19	1.55183	29	1.87802
11	1.26134	11	1.55084	22	1.87685
5	1.26063	6	1.55003	12	1.87551
2	1.26020	2	1.54945	6	1.87473
–	–	–	–	2	1.87405
$(1-x)$ethyl acetate + (x)bromochloromethane					
200	1.14092	199	1.32419	194	1.54059
177	1.13839	176	1.32138	192	1.54032
157	1.13618	159	1.31923	177	1.53820
138	1.13416	139	1.31683	159	1.53570
118	1.13184	121	1.31457	138	1.53298
99	1.12986	98	1.31174	119	1.53029
90	1.12874	88	1.31044	98	1.52742
79	1.12744	78	1.30922	87	1.52586
69	1.12638	70	1.30807	79	1.52470
61	1.12553	60	1.30693	68	1.52333
51	1.12432	49	1.30564	58	1.52203
40	1.12304	40	1.30449	51	1.52108
31	1.12197	30	1.30321	40	1.51964
20	1.12079	21	1.30196	31	1.51835
11	1.11969	12	1.30097	19	1.51663
6	1.11903	6	1.30017	12	1.51577
2	1.11850	2	1.29953	7	1.51504
–	–	–	–	2	1.51436
$(1-x)$ethyl acetate + (x)1,2-dichloroethane					
194	1.00251	199	1.06599	196	1.13910
179	1.00114	180	1.06425	177	1.13732
159	0.99926	159	1.06230	156	1.13523

Table VI. Continued

$x = 0.2995$		$x = 0.5013$		$x = 0.6994$	
P (bar)	ρ (g·cm^{-3})	P (bar)	ρ (g·cm^{-3})	P (bar)	ρ (g·cm^{-3})
138	0.99735	138	1.06029	137	1.13350
117	0.99534	119	1.05845	120	1.13177
99	0.99371	98	1.05647	99	1.12984
86	0.99231	90	1.05576	88	1.12876
78	0.99151	78	1.05457	80	1.12794
69	0.99062	71	1.05382	70	1.12684
59	0.98964	61	1.05293	61	1.12611
50	0.98882	48	1.05157	48	1.12491
40	0.98778	39	1.05082	40	1.12404
29	0.98678	32	1.05004	30	1.12299
23	0.98602	21	1.04905	21	1.12219
12	0.98501	11	1.04797	12	1.12121
5	0.98427	6	1.04736	6	1.12072
2	0.98388	2	1.04697	2	1.12018
$(1-x)$ethyl acetate + (x)1-bromo-2-chloroethane					
197	1.13676	198	1.30025	192	1.46486
177	1.13448	179	1.29820	174	1.46258
159	1.13271	155	1.29542	159	1.46086
138	1.13067	137	1.29344	140	1.45857
117	1.12838	120	1.29148	120	1.45629
101	1.12671	101	1.28928	103	1.45422
86	1.12517	87	1.28786	88	1.45250
79	1.12437	80	1.28692	77	1.45109
71	1.12321	70	1.28584	70	1.45032
58	1.12217	59	1.28480	58	1.44898
50	1.12132	50	1.28371	51	1.44815
40	1.12019	40	1.28256	41	1.44707
30	1.11913	30	1.28150	29	1.44574
21	1.11811	21	1.28034	21	1.44465
12	1.11705	12	1.27948	11	1.44360
5	1.11635	7	1.27885	6	1.44312
2	1.11591	2	1.27827	2	1.44243

$-450\,\mathrm{J\cdot mol^{-1}}$ at 298.15 K). In any case, the explanation of the volumetric behavior of the studied mixtures is difficult with only this kind of measurements, given the variety and complexity of the interaction and geometric effects present in the pure dihaloalkanes, such as conformational equilibrium, orientational order, self-association, etc.

Table VII. Isothermal Compressibilities κ_T (in TPa^{-1}) for the Mixtures at 298.15 K

	x				
System	0.00	0.30	0.50	0.70	1.00
$(1-x)$ $C_4H_8O_2$ + (x) CH_2Br_2	1165	991	870	747	561
$(1-x)$ $C_4H_8O_2$ + (x) $BrClCH_2$	1165	1048	967	882	749
$(1-x)$ $C_4H_8O_2$ + (x) ClC_2H_4Cl	1165	1042	962	882	762
$(1-x)$ $C_4H_8O_2$ + (x) BrC_2H_4Cl	1165	979	876	791	700

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REFERENCES

1. M. Artal, J. Muñoz Embid, S. Otín, and I. Velasco, *J. Chem. Thermodyn.* **27**:191 (1995).
2. M. Artal, J. Muñoz Embid, S. Otín, and I. Velasco, *J. Chem. Thermodyn.* **27**:399 (1995).
3. M. Artal, J. Muñoz Embid, I. Velasco, and S. Otín, *J. Chem. Thermodyn.* **27**:475 (1995).
4. M. Artal, J. Muñoz Embid, I. Velasco, and S. Otín, *J. Sol. Chem.* **29**:355 (1997).
5. J. Boquera, M. Artal, I. Velasco, and S. Otín, *J. Chem. Thermodyn.* **30**:161 (1998).
6. M. Artal, J. Muñoz Embid, S. Otín, and I. Velasco, *Fluid Phase Equilib.* **154**:223 (1999).
7. C. Jarne, M. Artal, J. Muñoz Embid, I. Velasco, and S. Otín, *Can. J. Chem.* **77**:2046 (1999).
8. S. L. Oswal, I. N. Patel, S. P. Modi, and S. A. Barad, *Int. J. Thermophys.* **21**:681 (2000).
9. S. L. Oswal and I. N. Patel, *Indian J. Chem.* **29**:870 (1990).
10. D. V. B. Reddy, K. Ramajaneyulu, and A. Krishnaiah, *Indian J. Pure Appl. Phys.* **28**:107 (1990).
11. TRC Thermodynamics Tables of Non-Hydrocarbons. Thermodynamics Research Center, The Texas A & M University System, College Station, Texas (1994).
12. D. Ambrose, *Pure Appl. Chem.* **49**:1437 (1977).
13. K. N. Marsh. IUPAC Recommended Reference Materials for the Realization of Physicochemical Properties (Blackwell, Oxford, 1987).
14. J. A. Riddick, W. B. Bunger, and T. K. Sakano. *Organic Solvents* (John Wiley, New York, 1986).
15. R. Malhotra and L. A. Wolf, *Fluid Phase Equilib.* **94**:227 (1994).
16. J. Valero, M. C. Bueno, P. Pérez, M. Gracia, and C. Gutiérrez Losa, *Int. DATA Ser., Selected Data on Mixtures, Ser. A* **27**:297 (1999).
17. P. Lillo, L. Mussari, and M. A. Postigo, *J. Solution Chem.* **29**:183 (2000).
18. I. Baños, J. Valero, M. Gracia, and C. Gutiérrez Losa, *Ber. Bunsenges. Phys. Chem.* **87**:866 (1983).
19. G. Avedis, A. H. Roux, and J. -P. Grolier, *Int. DATA Ser., Selected Data on Mixtures, Ser. A* **1**:16 (1990).