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Excess molar heat capacities and excess molar volumes of binary mixtures of 2-bromo-2-chloro-1,1,1-trifluoroethane (halothane) with oxygenated and hydrocarbon solvents

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Abstract

Excess molar heat capacities C_p^E were determined at 298.15 K for the following thirteen mixtures: 2-bromo-2-chloro-1,1,1-trifluorethane (halothane)+acetone (ACT), +dipropyl ether (DPE), +diisopropyl ether (DIPE), +methyl *tert*-butyl ether (MTBE), +tetrahydrofuran (THF), 1,4-dioxane (DIOX), +methyl acetate (MAC), +benzene (BENZ), +cyclohexane (cC6), +*n*-hexane (nC6), +2,2-dimethylbutane (22DMB), +*n*-heptane (nC7), and +2,4-dimethylpentane (24DMP). Excess molar volumes V^E at 281.15 K were also measured for the following mixtures: halothane + DPE, +DIPE + DIOX, +BENZ, +cC6, +22DMB, +nC7, and +24DMP. V^E values for the remaining five mixtures (ACT, MTBE, THF, MAC, and nC6) were previously reported. For all oxygenated solvents, C_p^E is positive and V^E negative, while for the equal-structure hydrocarbon solvents (taken as homomorphs), they are of the opposite sign. This is interpreted in terms of the formation of H-bonded complexes between the oxygen atom in the solvent molecule and the highly acidic hydrogen atom in halothane. For benzene, C_p^E and V^E are positive but small; this is consistent with the weak electron-donor character of benzene and indicates the presence of a weak halothane/BENZ complexation which most probably occurs through a charge transfer mechanism similar to that present in mixtures of fully halogenated freons, such as Freon 113, with oxygenated solvents. The use of the homomorphs indicated that (i) for halothane + DPE, +DIPE, and +MTBE, the asymmetry of the C_p^E curves and their opposite-sign curvatures at low and high halothane concentrations are mainly due to the physical contributions to C_p^E, and (ii) for halothane + ACT, +MAC, and +DIOX, the solutions contain multisolvated species.

INTRODUCTION

Mixtures of halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) with oxygenated solvents have been previously studied [1, 2] through the

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measurement of excess molar enthalpies (H^E) and vapor–liquid equilibria (VLE). The H^E and G^E values were found to be strongly negative, signalling the formation of a halothane/oxygenated-compound H-bonded complex formed between the oxygen atom in the solvent molecules and the hydrogen atom in halothane. It was also found that, for a given oxygenated solvent, the H^E value for halothane is always more negative than for chloroform [1] indicating that the acidity of the hydrogen atom in halothane is bigger than that in chloroform. In this work, we study further the halothane/oxygenated-solvent complexation through the measurement of heat capacity data which have been shown to be very useful in understanding the formation of complexes [3–5] and self-associated species [6, 7] in solution. In order to make a more complete qualitative analysis, we have also measured heat capacities for halothane mixed with several hydrocarbons whose chemical structure is identical to that of the oxygenated compounds and which are taken as their homomorphs. The quantitative analysis through several association models of all the thermodynamic data accumulated (VLE, H^E and C_p^E) for several halothane/oxygenated-solvent mixtures is presented elsewhere [8].

EXPERIMENTAL

Halothane (Spofa, stabilized with 0.01 mass% thymol) was distilled to separate the stabilizing agent. After distillation, no impurity was detected by a gas chromatographic analysis. All other materials were obtained either from Aldrich Chem. Co. or Merck Chem. Co. with stated purities between 99 and 99.99 mol.%, except for 2,2-dimethylbutane whose purity was 98 mol.%. All chemicals were used without further purification. However, before the measurements, the liquids were partially degassed.

Excess heat capacities C_p^E were determined at 298.15 K with a Picker flow microcalorimeter (Sodev Inc., Sherbrooke, Canada) for the following thirteen mixtures: 2-bromo-2-chloro-1,1,1-trifluoroethane (halothane)+acetone (ACT), +dipropyl ether (DPE), +diisopropyl ether (DIPE), +methyl *tert*-butyl ether (MTBE), +tetrahydrofuran (THF), +1,4-dioxane (DIOX), +methyl acetate (MAC), +benzene (BENZ), +cyclohexane (cC6), +*n*-hexane (nC6), +2,2-dimethylbutane (22DMB), +*n*-heptane (nC7), and +2,4-dimethylpentane (24DMP). The procedures used were those described in detail in the literature [9, 10]. The calorimeter was operated in the stepwise mode: the difference in the isobaric volumetric heat capacity between successive solutions was measured, proceeding through the concentration range from one pure liquid to the other. For all systems, the oxygenated or hydrocarbon solvent was used as the reference liquid. Molar heat capacities for the pure liquids are shown in Table 1. The volumetric heat capacities were transformed to molar

TABLE 1

Molar heat capacities (C_p, $\mathrm{J\,K^{-1}\,mol^{-1}}$) for pure components at 298.15 K taken from ref. 11

Liquid	C_p	Liquid	C_p	Liquid	C_p
ACT	126.0	DIOX	150.7	nC6	195.6
DPE	221.5	MAC	142.0	22DMB	189.2
DIPE	216.1	BENZ	136.1	nC7	223.9
MTBE	187.5	cC6	155.7	24DMP	224.3
THF	123.9				

basis through solution densities obtained here with a vibrating-tube densimeter (Sodev Inc.) or previously with a pycnometer [2] or a dilatometer [12]. The error in the C_p^E determination is estimated to be less than 2%.

The measured densities were used to calculate excess molar volumes V^E at 298.15 K for the following mixtures: halothane + DPE, +DIPE, +DIOX, +BENZ, +cC6, +22DMB, +nC7, and +24DMP. V^E for the remaining five mixtures (ACT, MTBE, THF, MAC, and nC6) were previously reported [2, 12]. For every mixture, the densimeter was calibrated using the densities of the pure components. The density measurements were reproducible to $\pm 1 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$. The total uncertainty in V^E is estimated to be less than $0.01\,\mathrm{cm^3\,mol^{-1}}$.

RESULTS AND DISCUSSION

The experimental values of the excess molar heat capacities are given in Table 2 and plotted against mole fraction of halothane (component 1) in Figs. 1 and 2. The excess molar volumes are reported in Table 3 and shown in Fig. 3. For each mixture, the results were correlated with the Redlich–Kister equations

$$C_p^E\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = x_1(1-x_1)\sum_{i=0}^{p} A_i(2x_1-1)^i \tag{1}$$

$$V^E\,(\mathrm{cm^3\,mol^{-1}}) = x_1(1-x_1)\sum_{i=0}^{q} B_i(2x_1-1)^i \tag{2}$$

whose parameters A_i and B_i, evaluated by the method of least-squares with equal weighting of all values, are given along with the standard deviations $s(C_p^E)$ and $s(V^E)$ in Tables 4 and 5. For each system, the number of parameters p and q in eqns. (1) and (2) were chosen on the basis of a statistical criterion (F-test) and the analysis of the statistical behavior of the residuals [13].

In Fig. 1, the C_p^E values for three ethers (DPE, DIPE and MTPE) are

TABLE 2

Experimental excess molar heat capacities (C_p^E, J K^{-1} mol^{-1}) at 298.15 K

x_1	C_p^E	x_1	C_p^E
Halothane(1) + ACT(2)			
0.1005	1.95	0.6000	5.78
0.2010	3.43	0.6970	5.02
0.2991	4.51	0.7946	3.59
0.3972	5.42	0.8991	1.89
0.4989	5.92		
Halothane(1) + DPE(2)			
0.1188	3.93	0.6022	6.83
0.2039	6.29	0.6992	4.60
0.3176	8.45	0.8030	2.35
0.4173	9.00	0.8989	0.85
0.5144	8.28		
Halothane(1) + DIPE(2)			
0.1051	4.64	0.6004	11.18
0.2014	8.53	0.7034	7.47
0.3026	11.84	0.8006	4.21
0.3926	13.66	0.8979	1.76
0.4979	13.52		
Halothane(1) + MTBE(2)			
0.1057	3.10	0.6019	9.30
0.2041	5.82	0.7012	6.70
0.2987	8.60	0.7996	4.08
0.3992	10.58	0.8940	1.98
0.4972	10.90		
Halothane(1) + THF(2)			
0.1061	3.32	0.5934	8.16
0.1981	5.70	0.6984	6.02
0.2958	7.82	0.7937	3.93
0.3947	9.19	0.8902	1.91
0.4990	9.43		
Halothane(1) + DIOX(2)			
0.1038	1.20	0.6022	6.99
0.1989	2.49	0.7011	6.49
0.2980	4.38	0.7982	4.86
0.3978	5.63	0.8920	2.51
0.4986	6.60		

TABLE 2—contd.

x_1	C_p^E	x_1	C_p^E
Halothane(1) + MAC(2)			
0.1016	1.36	0.6012	4.62
0.1977	2.47	0.6932	3.92
0.2948	3.44	0.7918	2.76
0.3974	4.35	0.8859	1.53
0.4958	4.81		
Halothane(1) + BENZ(2)			
0.1098	1.19	0.5972	2.28
0.2015	1.93	0.6986	1.75
0.2958	2.48	0.7994	1.20
0.3953	2.73	0.8961	0.61
0.5023	2.62		
Halothane(1) − cC6(2)			
0.1070	−0.33	0.6032	−1.16
0.2003	−0.47	0.7009	−1.16
0.3033	−0.71	0.8996	−0.58
0.3989	−0.84		
0.5029	−0.97		
Halothane(1) + nC6(2)			
0.1048	−0.59	0.6030	−2.78
0.1973	−1.11	0.6991	−2.58
0.2934	−1.62	0.7956	−2.23
0.3944	−2.13	0.8948	−1.54
0.4956	−2.49		
Halothane(1) + 22DBM(2)			
0.1063	−0.83	0.5974	−3.05
0.2660	−1.98	0.7454	−2.64
0.4218	−2.72	0.8960	−1.41
0.5096	−2.97		
Halothane(1) + nC7(2)			
0.1227	−0.83	0.5979	−3.31
0.2269	−1.62	0.6932	−3.35
0.3118	−2.08	0.7961	−2.98
0.4106	−2.60	0.8975	−1.90
0.5015	−3.01		
Halothane(1) + 24DMP(2)			
0.1157	−0.95	0.6112	−3.32
0.2871	−2.32	0.7538	−2.88
0.4148	−2.95	0.9003	−1.54
0.4991	−3.26		

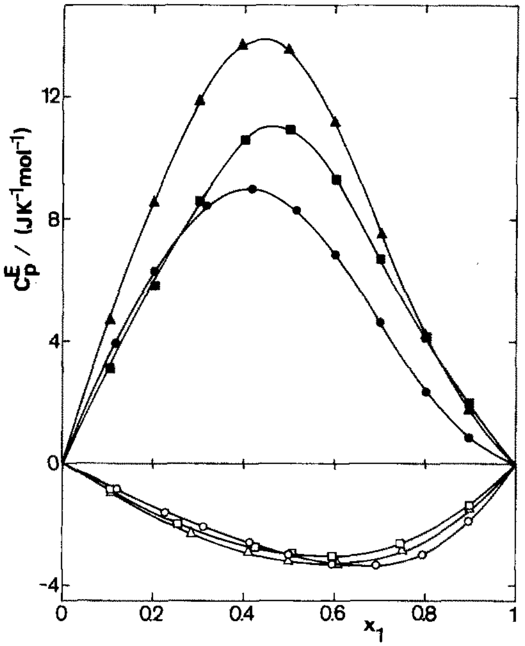

Fig. 1. Excess molar heat capacities at 298.15 K for halothane (component 1) mixed with nC7 (○), DPE (●), 24DMP (△), DIPE (▲), 22DMB (□), and MTBE (■).

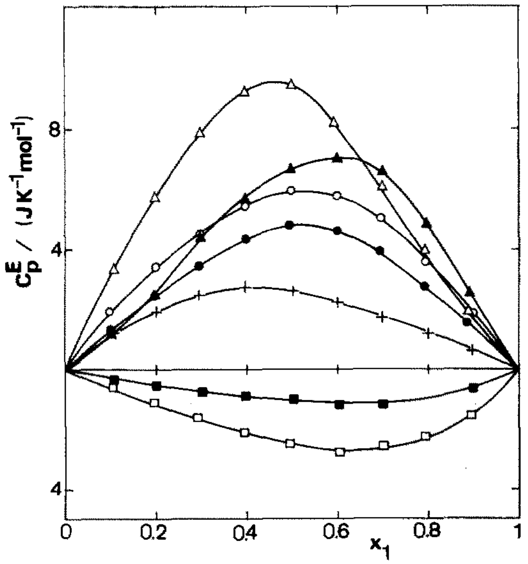

Fig. 2. Excess molar heat capacities at 298.15 K for halothane (component 1) mixed with nC6 (□), cC6 (■), BENZ (+), ACT (○), MAC (●), THF (△), and DIOX (▲).

TABLE 3

Experimental excess molar volumes (V^E, cm^3 mol^{-1}) at 298.15 K

x_1	V^E	x_1	V^E
Halothane(1) + DPE(2)			
0.1188	−0.348	0.6022	−0.775
0.3176	−0.684	0.6992	−0.680
0.4173	−0.784	0.8030	−0.488
0.5144	−0.794		
Halothane(1) + DIPE(2)			
0.1051	−0.560	0.6004	−1.479
0.2014	−1.001	0.7034	−1.215
0.3026	−1.368	0.8006	−0.862
0.3926	−1.561	0.8979	−0.452
Halotahne(1) + DIOX(2)			
0.1038	−0.102	0.6022	−0.694
0.1989	−0.212	0.7011	−0.705
0.2980	−0.342	0.7982	−0.599
0.3978	−0.483	0.8920	−0.398
0.4986	−0.600		
Halothane(1) + BENZ(2)			
0.1076	0.110	0.4981	0.188
0.1098	0.107	0.5023	0.186
0.2015	0.169	0.5972	0.166
0.3085	0.195	0.6986	0.124
0.3953	0.201	0.8917	0.046
Halothane(1) + cC6(2)			
0.1070	0.394	0.6032	1.003
0.2003	0.681	0.7009	0.874
0.3033	0.875	0.7991	0.670
0.3989	1.026	0.8996	0.386
0.5029	1.067		
Halothane(1) + 22DMB(2)			
0.1063	0.374	0.6981	0.598
0.1933	0.535	0.7454	0.543
0.4218	0.745	0.8960	0.279
0.5196	0.699	0.9094	0.266
0.5974	0.699		
Halothane(1) + nC7(2)			
0.2269	0.792	0.6932	0.999
0.3118	0.963	0.7961	0.778
0.4106	1.113	0.8975	0.455
0.5015	1.159		
Halothane(1) + 24DMP(2)			
0.2497	0.689	0.6112	0.886
0.2871	0.725	0.7538	0.677
0.4148	0.885	0.9003	0.355
0.4914	0.924		

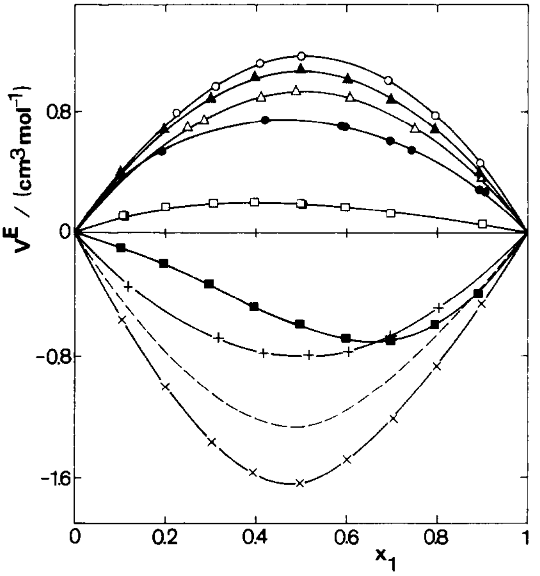

Fig. 3. Excess molar volumes at 298.15 K for halothane (component 1) mixed with nC7 (○), 22DMB (●), 24DMP (△), cC6 (▲), BENZ (□), DIOX (■), DPE (+) and DIPE (×). Data for MTBE (broken line) are from ref. 2.

contrasted with those for three hydrocarbons (nC7, 24DMP and 22DMB). Because the chemical structure of these hydrocarbons is identical to that of the ethers, they can be taken as their homomorphs. The comparison between these two sets of C_p^E values shows that the substitution of a methylene group in the hydrocarbon solvent by an oxygen atom shifts the

TABLE 4

Parameters A_i and standard deviations ($s(C_p^E)$, J K^{-1} mol^{-1}) for representation of excess molar heat capacities at 298.15 K by eqn. (1)

Halothane(1)+	A_0	A_1	A_2	A_3	A_4	$s(C_p^E)$
ACT	23.53	3.63	−4.73	−7.36		0.06
DPE	33.92	−22.81	−23.00	8.44	9.69	0.02
DIPE	53.92	−26.83	−52.87	12.70	34.90	0.05
MTBE	43.47	−12.51	−48.75	9.00	35.47	0.07
THF	37.33	−11.94	−29.46	3.85	21.77	0.08
DIOX	26.59	14.45	−4.35	−9.07	−12.42	0.12
MAC	19.21	2.74	−11.77	−4.60	8.02	0.03
BENZ	10.47	−4.77	−1.96	2.22		0.02
cC6	−4.25	−2.42				0.07
nC6	−10.25	−5.84				0.07
2DMB	−11.87	−4.01				0.02
nC7	−11.97	−7.71	−6.27	−0.87	4.72	0.02
24DMP	−13.06	−4.67				0.03

TABLE 5

Parameters B_i and standard deviations ($s(V^E)$, $cm^3\ mol^{-1}$) for representation of excess molar volumes at 298.15 K by eqn. (2)

Halothane(1)+	B_0	B_1	B_2	B_3	B_4	$s(V^E)$
DPE	−3.2001					0.012
DIPE	−6.4133	0.8810	1.6029	−0.4531		0.006
DIOX	−2.4354	−2.1926	−0.3011	0.4559		0.005
BENZ	0.7518	−0.4164	0.0810			0.003
cC6	4.2139					0.011
22DMB	2.9820	−0.3752	−0.0728	−0.2435	1.4590	0.007
nC7	4.6293	0.2722				0.007
24DMB	3.6695					0.016

C_p^E values from negative to positive. A similar situation is found in Fig. 2 for DIOX and its homomorph cC6. Positive values for C_p^E have been ascribed to the formation of order or structure in the solution as compared to the pure compounds [14]. For example, the large positive C_p^E values found in mixtures of chloroform with acetone [15] and 1,4-dioxane [16] are due to the formation of H-bonded complexes which produce a highly structured solution. Hence, the positive C_p^E values for halothane mixed with the oxygenated solvents in Figs. 1 and 2 are clear consequence of the presence of H-bonded complexes in the solutions. For the present systems, the H-bonds are formed between the oxygen atom in the solvent molecules and the acidic hydrogen atom in halothane, their enthalpies of formation being in the range 10–15 kJ mol^{-1} [8]. In Figs. 1 and 2, when the solvent molecules are incapable of H-bonding, namely the hydrocarbon solvents, the C_p^E values are negative. An exception is given by benzene in Fig. 2 whose C_p^E is positive but smaller than for the other oxygenated solvents. This result is consistent with the weak electron-donor character of benzene [17] and indicates the presence of a weak halothane/BENZ complexation which must occur through a charge transfer mechanism similar to that present in mixtures of Freon 113 (1,1,2-trichlorotrifluoroethane) with oxygenated solvents [5].

The effect of changing the hydrocarbon solvent with the corresponding equal-structure oxygenated solvent is also appreciated in the excess molar volumes displayed in Fig. 3. Here, it can be seen that for all four pairs nC7/DPE, 22DMB/MTBE, 24DMP/DIPE and cC6/DIOX, V^E values for halothane mixed with the hydrocarbons are positive while those for the oxygenated solvents are negative. Although V^E values are the result of several different and often competing contributions [18], the change of sign seen in Fig. 3 complies with the idea that H-bonding in the solution implies a volume contraction. In this context, it is interesting to note that in Fig. 3 the V^E values for halothane + benzene are between those for the oxygenated and saturated hydrocarbon solvents. As with C_p^E data in Fig. 2, this behavior is consistent with the presence of a weak halothane/benzene complex.

For halothane + DPE, +DIPE, and +MTBE, the C_p^E curves in Fig. 1 are asymmetrical and display a negative curvature at low halothane concentrations and a positive one at high concentrations. If for each of these mixtures, C_p^E for halothane + the respective homomorphic hydrocarbon system is assumed to represent the so called "physical contribution" arising from effects other than association, the excess heat capacity resulting from the formation of H-bonds, C_p^E (complexation), is given by [C_p^E (oxygenated) − C_p^E(homomorph)]. Using the A_i constants in Table 4, C_p^E (complexation) curves for the three ethers in Fig. 1 are seen to be nearly symmetrical, the positive curvature at high halothane concentrations disappearing or being much less pronounced than in Fig. 1. Hence, the particular concentration behavior of C_p^E in Fig. 1 is mainly due to the physical contributions. The results in Fig. 2 indicate that C_p^E for halothane + ACT, +MAC, and +DIOX are also asymmetrical but with their maxima occurring at high halothane concentrations. For these oxygenated solvents, consideration of the physical contribution (A_i constants for DIOX and cC6 in Table 4) shows that the concentration dependence of C_p^E (complexation) is even more asymmetrical, indicating the presence of multisolvated species in solution.

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REFERENCES

1 M. Costas, S. Perez-Casas, V. Dohnal and D. Fenclová, Thermochim. Acta, 213 (1993) 23.
2 D. Fenclová and V. Dohnal, J. Chem. Thermodyn., in press.
3 M. Costas, Z. Yao and D. Patterson, J. Chem. Soc. Faraday Trans. 1, 84 (1989) 119.
4 D.D. Desphande, D. Patterson, L. Andreoli-Ball, M. Costas and L.M. Trejo, J. Chem. Soc. Faraday Trans., 87 (1991) 1133.
5 V. Dohnal, D. Fenclová and M. Costas, Thermochim. Acta, 213 (1993) 35.
6 L. Andreoli-Ball, D. Patterson, M. Costas and M. Caceres-Alonso, J. Chem. Soc. Faraday Trans. 1, 84 (1988) 3991.
7 S. Perez-Casas, L.M. Trejo and M. Costas, J. Chem. Soc. Faraday Trans., 87 (1991) 1733.
8 V. Dohnal, M. Costas, D. Fenclová and M. Bureš, J. Chem. Soc. Faraday Trans., submitted.
9 J.L. Fortier, G.C. Benson and P. Picker, J. Chem. Thermodyn., 8 (1976) 289.

10 J.L. Fortier and G.C. Benson, J. Chem. Thermodyn., 8 (1976) 411.
11 CDATA, Database of Thermodynamic and Transport Properties for Chemistry and Engineering, Department of Physical Chemistry, Prague Insitute of Chemical Technology, 1991.
12 L. Hnědkovský and I. Cibulka, J. Chem. Thermodyn., 18 (1986) 331.
13 J.R. Green and D. Margerison, Statistical Treatment of Experimental Data, Elsevier, Amsterdam, 1978.
14 M. Costas and D. Patterson, Thermochim. Acta, 120 (1987) 161.
15 A. Apelblat, A. Tamir and M. Wagner, Fluid Phase Equilib., 4 (1980) 220.
16 L. Barta, Z. S. Kooner, L. G. Hepler, G. Roux-Desgranges and J.P.E. Grolier, Can. J. Chem., 67 (1989) 1225.
17 M.J. Kamlet, J.L.M. Abbound, M.H. Abraham and R.W. Taft, J. Org. Chem., 48 (1983) 2877.
18 M. Costas and D. Patterson, J. Solution Chem., 11 (1982) 807.