Thermochimica Acta, 213 (1993) 35–46
Elsevier Science Publishers B.V., Amsterdam

Excess molar heat capacities and excess molar volumes of binary mixtures of 1,1,2-trichlorotrifluoroethane (Freon 113) with oxygenated and hydrocarbon solvents

Vladimír Dohnal[a], Dana Fenclová[a] and Miguel Costas[b]

[a] *Department of Physical Chemistry, Institute of Chemical Technology, 166 28 Prague 6 (Czech and Slovak Federal Rep.)*
[b] *Departamento de Física y Química Teórica, Facultad de Química, Universidad Nacional Autónoma de México, Mexico D.F. 04510 (Mexico)*

(Received 6 April 1992)

Abstract

Excess molar heat capacities C_p^E were determined at 298.15 K for the following thirteen mixtures with 1,1,2-trichlorotrifluoroethane (F113): +acetone (ACT), +dipropyl ether (DPE), +diisopropyl ether (DIPE), +methyl *t*-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 298.15 K were also measured for the following mixtures: F113 + DPE, +MTBE, +DIOX, +BENZ, +cC6, +22DMB, +nC7 and +24DMP. V^E data for the remaining five mixtures (those with ACT, DIPE, THF, MAC and nC6) were previously reported. The C_p^E for all oxygenated solvents is positive, whereas for the equal-structure hydrocarbon solvents (taken as homomorphs) it is almost zero or negative. This is interpreted in terms of the formation of an F113-oxygenated compound complex in the solution. Further support for the existence of this complex is given by V^E, which for the oxygenated solvents is always smaller than for the hydrocarbon compounds. The use of the homomorphs indicated that (i) the asymmetry of the C_p^E curves for F113 + DPE, +DIPE and +MTBE finds its origin in the physical contributions to C_p^E rather than in the presence of the complex, and (ii) the most probable stoichiometry of the complexes is 1:1 for MTBE, DPE and DIPE, while for DIOX the 2:1 complex is also present. The F113–oxygenated solvent complex is probably formed through a charge transfer mechanism and it is energetically weak (enthalpy of formation 2–3 kJ mol^{-1}).

INTRODUCTION

Mixtures of Freons with several types of solvents are of interest for at least two reasons. From the ecological point of view, there is an urgent need to reduce the extensive use of pure Freons in many industrial

---

Correspondence to: M. Costas, Facultad de Química, UNAM, Cd. Universitaria, México D.F. 04510, Mexico.

processes via their substitution by suitable mixtures with common, readily available, solvents. On the other hand, the detailed study of these kinds of mixtures can enhance our current understanding of solutions where specific molecular interactions lead to the formation of complexes in solution. For both purposes the acquisition of thermodynamic data is of importance. Within the framework of a long term project involving haloalkane-containing mixtures, we have previously reported and discussed vapor–liquid equilibria [1], limiting activity coefficients [2] and excess molar enthalpies [3] for 1,1,2-trichlorotrifluoroethane (Freon 113) mixed with several oxygenated and hydrocarbon solvents. These data gave some indications of the existence of weak specific interactions between Freon 113 and the oxygenated solvents, indicating that Freon 113 is not a completely inert solvent. This conclusion obtained further support when thermodynamic data for Freon 113 + methanol was analysed in the framework of several association models in which solvation was either taken into account or considered absent [4]. In this work, we further test the hypothesis of the existence of Freon 113–oxygenated solvent complexes through the measurement of heat capacity data. This property has been shown for many mixtures [5–7] to be a very useful structure indicator and, in particular, it is highly sensitive to the formation of complexes or self-associated species in solution. In order to make a more complete qualitative analysis of these data, we have also measured heat capacities for Freon 113 mixed with several hydrocarbons having chemical structure identical to that of the oxygenated compounds. These "equal-structure" hydrocarbons, when taken as homomorphs of the oxygenated solvents, allowed us to study the effect that the substitution of a methylene by an oxygen atom has on the behaviour of the excess molar heat capacities.

EXPERIMENTAL

All materials were obtained either from Aldrich Chemical Co. or Merck Chemical Co. with stated purities between 99 and 99.99 mol.% with the exception of 2,2-dimethylbutane, whose purity was 98 mol.%. All chemicals were used without further purification; however, before each experiment the liquids were partially degassed.

Excess molar heat capacities C_p^E were determined at 298.15 K using a Picker flow microcalorimeter (Sodev Inc., Sherbrooke, Canada) for the following thirteen mixtures: 1,1,2-trichlorotrifluoroethane (F113) + acetone (ACT), +dipropyl ether (DPE), +diisopropyl ether (DIPE), +methyl *t*-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

TABLE 1

Molar heat capacities for pure components at 298.15 K taken from ref. 10 [a]

Liquid	C_p ($J K^{-1} mol^{-1}$)	Liquid	C_p ($J K^{-1} mol^{-1}$)	Liquid	C_p ($J K^{-1} mol^{-1}$)
ACT	126.9	DIOX	151.3	nC6	195.7
DPE	221.5	MAC	141.3	22DMB	189.2
DIPE	216.1	BENZ	135.9	nC7	223.9
MTBE	187.5	cC6	156.1	24DMP	224.3
THF	124.1				

[a] For abbreviations of compounds, see text.

those described in detail in the literature [8, 9]. The calorimeter was operated in the stepwise mode: the difference in 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 the 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 the molar basis through solution densities obtained here with a vibrating-tube densimeter (Sodev Inc.) or previously [1] with a pycnometer. The error in the C_p^E determination is estimated to be less than 2%.

The measured densities were also used to calculate excess molar volumes V^E at 298.15 K for the following mixtures: F113 + DPE, +MTBE, +DIOX, +BENZ, +cC6, +22DMB, +nC7 and +24DMP. V^E data for the remaining five mixtures (those with ACT, DIPE, THF, MAC and nC6) were previously reported in ref. 1. For every mixture, the densimeter was calibrated using the densities of the pure components. The density measurements were reproducible to $\pm 1 \times 10^{-5}$ cm^{-3}. The total uncertainty in V^E is estimated to be less than 0.01 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 F113 (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

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

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

whose parameters A_i and B_i, along with the standard deviations $s(C_p^E)$ and $s(V^E)$, are given in Tables 4 and 5. These parameters were evaluated by

TABLE 2

Experimental excess molar heat capacities C_p^E at 298.15 K [a]

x_1	C_p^E (J K^{-1} mol^{-1})	x_1	C_p^E (J K^{-1} mol^{-1})
F113 (1) + ACT (2)			
0.1058	2.87	0.6088	4.22
0.2534	4.74	0.7511	3.13
0.4168	5.03	0.9011	1.37
0.5106	4.79		
F113 (1) + DPE (2)			
0.1412	0.77	0.5111	−0.03
0.2303	0.81	0.6068	−0.40
0.3167	0.72	0.8067	−0.69
0.3988	0.46	0.8962	−0.54
F113 (1) + DIPE (2)			
0.1011	0.80	0.5952	1.19
0.2468	1.60	0.7428	0.68
0.3967	1.74	0.8987	0.30
0.4907	1.53		
F113 (1) + MTBE (2)			
0.1024	1.27	0.5955	2.52
0.2488	2.42	0.7524	1.73
0.3958	2.87	0.8959	0.74
0.4982	2.83		
F113 (1) + THF (2)			
0.0986	2.78	0.6000	5.80
0.2454	5.50	0.7407	4.53
0.3934	6.49	0.8956	1.90
0.4969	6.40		
F113 (1) + DIOX (2)			
0.0991	1.76	0.5952	4.81
0.2464	3.85	0.7514	3.79
0.4022	4.89	0.8950	1.85
0.5003	4.97		
F113 (1) + MAC (2)			
0.0969	1.43	0.6001	2.33
0.2485	2.61	0.7473	1.60
0.3978	2.77	0.8955	0.74
0.5003	2.69		
F113 (1) + BENZ (2)			
0.1008	0.17	0.6044	−0.22
0.2530	0.38	0.7541	−0.40
0.4009	0.25	0.9038	−0.22
0.5040	0.02		

TABLE 2 (continued)

x_1	C_p^E (J K^{-1} mol^{-1})	x_1	C_p^E (J K^{-1} mol^{-1})
F113 (1) + cC6 (2)			
0.1066	0.12	0.6008	−0.53
0.2515	0.11	0.7535	−0.63
0.4028	−0.14	0.8988	−0.47
0.5018	−0.33		
F113 (1) + nC6 (2)			
0.1022	−0.07	0.7010	−1.77
0.2458	−0.46	0.7467	−1.84
0.3886	−1.05	0.8020	−1.56
0.4939	−1.45	0.8927	−1.10
0.5985	−1.73		
F113 (1) + 22DMB (2)			
0.1004	−0.80	0.5976	−3.24
0.2540	−2.03	0.7419	−2.77
0.3798	−2.75	0.8963	−1.43
0.4988	−3.20		
F113 (1) + nC7 (2)			
0.1333	−0.70	0.5996	−3.67
0.2308	−1.47	0.6821	−3.62
0.2984	−1.96	0.7899	−3.16
0.4104	−2.85	0.8935	−1.99
0.5008	−3.29		
F113 (1) + 24DMP (2)			
0.1313	−1.17	0.6047	−4.02
0.2272	−2.03	0.6951	−3.85
0.3130	−2.75	0.7923	−3.18
0.4167	−3.45	0.8901	−2.01
0.5034	−3.89		

[a] For abbreviations of compounds, see text.

the least-squares method with equal weighting for all values. For each system, the number of parameters p and q in eqns. (1) and (2) was chosen on the basis of a statistical criterion (F-test) and the analysis of the statistical behaviour of the residuals [11].

A comparison between the C_p^E values for F113 mixed with hydrocarbon solvents and oxygenated solvents in Figs. 1 and 2 clearly shows that, although for the latter C_p^E is positive, for the hydrocarbon compounds C_p^E is almost zero or negative. Positive values for C_p^E have been attributed to the formation or order or structure in the solution as compared with the pure compounds [5]. For example, large positive C_p^E values are always found when an alcohol is mixed with an inert solvent, and they are indicative of the alcohol self-association, via H-bonding, occurring in the solution. In a similar way, the formation of H-bonded complexes in

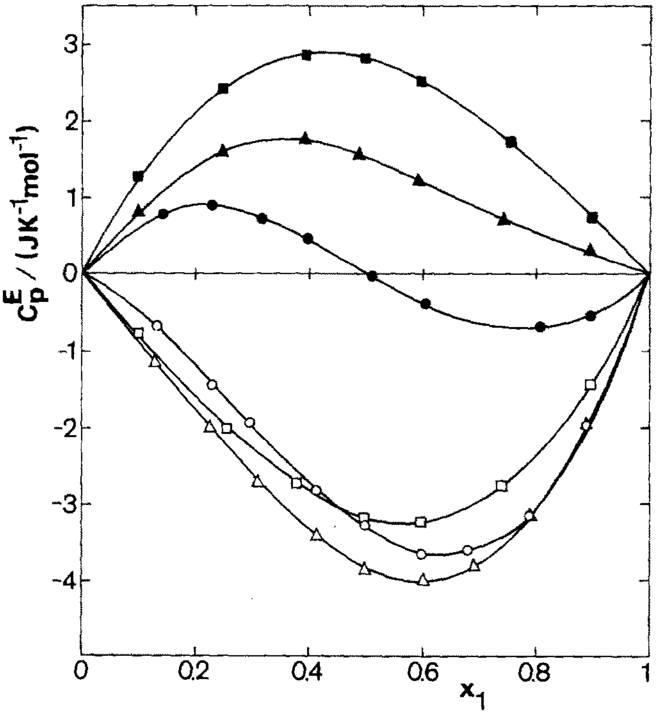

Fig. 1. Excess molar heat capacities at 298.15 K for F113 (component 1) mixed with nC7 (○), DPE (●), 24DMP (△), DIPE (▲), 22DMB (□) and MTBE (■).

mixtures of chloroform with acetone [12] and 1,4-dioxane [13] are responsible for the positive C_p^E values found in these systems. Hence, in the present case the positive C_p^E values found for F113 mixed with the oxygenated solvents can be ascribed to the presence of a F113–oxygenated compound complex in the solution. More evidence for the existence of this complex can be found in Fig. 1, where C_p^E values for three different ethers (DPE, DIPE and MTBE) are contrasted with those for three hydrocarbons (nC7, 24DMP and 22DMB). Because the chemical structure of these hydrocarbons is identical with that of the ethers they can be taken as the homomorphs, their C_p^E representing the so called "physical contribution" arising from effects other than association. 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 pushes C_p^E from being negative to being positive. A similar situation is found in Fig. 2 for the pair DIOX–cC6, where C_p^E changes from being practically zero for cC6 to a large positive value for DIOX. Hence the specific interaction between Freon 113 and the oxygen atoms in the ethers is responsible for the large increase in C_p^E found in replacing the hydrocarbon solvent by the corresponding equal-structure oxygenated solvent, and gives rise to a F113–oxygenated compound complex. Further

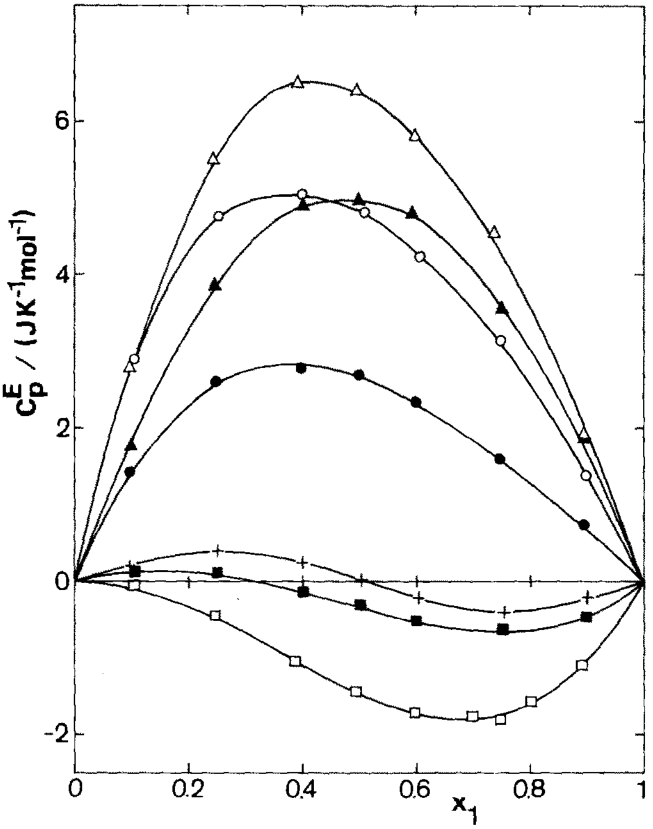

Fig. 2. Excess molar heat capacities at 298.15 K for F113 (component 1) mixed with nC6 (□), cC6 (■), BENZ (+), ACT (O), MAC (●), THF (△) and DIOX (▲).

support for the existence of this complex is found in the molar excess volumes shown in Fig. 3. Here it can be seen that V^E values for F113 mixed with the oxygenated solvents are always smaller than those for the corresponding hydrocarbon homomorphs. This reduction in V^E is consistent with the idea that complexation implies a volume contraction. Hence, although the magnitude of V^E is the result of several different (often competing) contributions [14], the reduction in V^E in going from the hydrocarbon homomorph to the corresponding oxygenated compound can be taken as an indication of complexation.

The excess heat capacity data for F113 + hydrocarbon solvents (C_p^E(homomorph)) in Figs. 1 and 2 can be used to gain some insight into the stoichiometry of the F113–oxygenated solvent complexes. Assuming that C_p^E(homomorph) is a good approximation for the physical contributions to C_p^E in the F113 + oxygenated solvent mixtures, then [C_p^E(oxygenate) − C_p^E(homomorph)] is a measure of C_p^E(complexation), i.e. the excess heat capacity due to the formation of the complex. It is clear from Fig. 1 and the values of the A_i constants in Table 4 that, for the

TABLE 3

Experimental excess molar volumes V^E at 298.15 K [a]

x_1	V^E (cm^3 mol^{-1})	x_1	V^E (cm^3 mol^{-1})
F113 (1) + DPE (2)			
0.1412	0.171	0.7050	0.325
0.2303	0.267	0.8067	0.255
0.5111	0.394	0.8962	0.147
0.6068	0.386		
F113 (1) + MTBE (2)			
0.1024	0.077	0.4982	0.209
0.2488	0.169	0.7524	0.146
0.3958	0.207	0.8959	0.079
F113 (1) + DIOX (2)			
0.0991	−0.050	0.5952	−0.162
0.2464	−0.110	0.7514	−0.122
0.4022	−0.164	0.8950	−0.059
0.5003	−0.177		
F113 (1) + BENZ (2)			
0.1008	0.194	0.6044	0.506
0.2530	0.414	0.7541	0.393
0.4009	0.504	0.9038	0.186
0.5040	0.523		
F113 (1) + cC6 (2)			
0.1066	0.256	0.6008	0.630
0.2515	0.513	0.7535	0.477
0.4028	0.641		
0.5018	0.669		
*F*113 (1) + 22*DMB* (2)			
0.0995	0.248	0.6003	0.639
0.2484	0.536	0.7509	0.480
0.3966	0.670	0.8985	0.227
0.4987	0.690		
F113 (1) + nC7 (2)			
0.1333	0.429	0.6821	0.863
0.4104	0.924	0.7899	0.689
0.5008	0.959	0.8935	0.404
0.5996	0.948		
F113 (1) + 24DMP (2)			
0.1313	0.371	0.5034	0.818
0.2272	0.582	0.6047	0.798
0.3130	0.692	0.6951	0.694
0.4167	0.793	0.8996	0.287

[a] For abbreviations of compounds, see text.

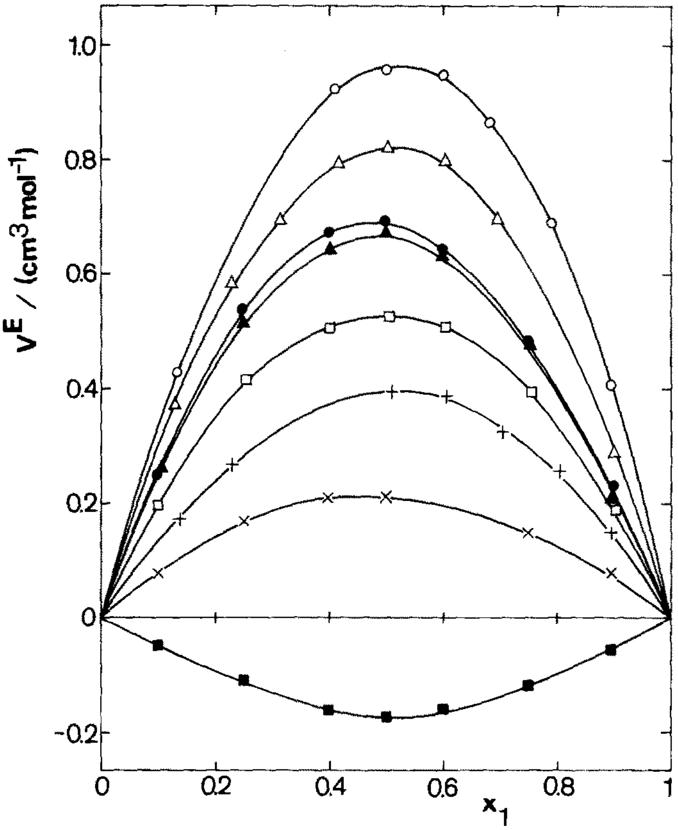

Fig. 3. Excess molar volumes at 298.15 K for F113 (component 1) mixed with nC7 (○), 22DMB (●), 24DMP (△), cC6 (▲), BENZ (□), DIOX (■), DPE (+) and MTBE (×).

three ethers in Fig. 1, C_p^E(complexation) is practically symmetrical. Hence the asymmetry of C_p^E curves for F113–ether in Fig. 1 is caused, not by the presence of the complex, but rather by the physical contribution. If an association model could be applied (see below), this symmetry would imply that the F113–ether (MTBE, DPE or DIPE) complex is a 1:1 complex. Contrasting with this situation, Fig. 2 and the A_1 constants in Table 4 show that C_p^E(complexation) for 1,4-dioxane is asymmetrical and skewed to high F113 concentration; hence the F113–DIOX mixture contains most probably both 1:1 and 2:1 complexes.

Considering the chemical structure of both F113 and the oxygenated compounds, their complexation probably involves a charge transfer mechanism. Here the oxygen atoms are electron donors and the strongly electronegative halogen atoms which form the surface of a F113 molecule act as electron acceptors. A similar electron donor–acceptor complexation has been considered to explain the non-inert behavior of carbon tetrachloride in several solvents [16]. In this context, it is interesting to note that, in Figs. 1 and 3, C_p^E and V^E for F113 + BENZ are, respectively,

TABLE 4

Parameters A_i and standard deviations $s(C_p^E)$ for representation of excess molar heat capacities at 298.15 K by eqn. (1) [a]

F113 (1) +	A_0	A_1	A_2	A_3	$s(C_p^E)$ ($J K^{-1} mol^{-1}$)
ACT	19.29	−8.72	6.10		0.06
DPE	0.13	−8.10	0.82		0.02
DIPE	6.04	−6.08	0.03	4.11	0.01
MTBE	11.26	−3.69	−0.60		0.01
THF	25.87	−6.56			0.10
DIOX	20.15				0.06
MAC	10.62	−5.28	2.27		0.04
BENZ	0.12	−5.01	−0.70	3.50	0.00_4
cC6	−1.31	−4.00	−0.74		0.02
nC6	−5.93	−6.80			0.04
22DMB	−12.76	−3.94	0.91		0.02
nC7	−13.32	−9.61			0.03
24DMP	−15.37	−6.91			0.02

[a] For abbreviations of compounds, see text.

bigger and smaller than for F113 + cC6, indicating a weak Freon 113–benzene complexation consistent with the weak electron donor character of benzene [15]. Support for the charge transfer mechanism has been found [17] through quantum mechanical calculations performed with the so called AM1 method [18]. These calculations indicated that such a complex is energetically stable and that its enthalpy of formation is only 2–3 kJ mol^{-1}. It is precisely the weakness of this interaction which complicates a possible quantitative analysis of the data presented here and in refs. 1–3 through an association model. The difficulties arises from the

TABLE 5

Parameters B_i and standard deviations $s(V^E)$ for representation of excess molar volumes at 298.15 K by eqn. (2) [a]

F113 (1) +	B_0	B_1	B_2	$s(V^E)$ ($cm^3 mol^{-1}$)
DPE	1.5597	0.1078		0.007
MTBE	0.8430	−0.0734		0.006
DIOX	−0.6893	−0.0404	0.2015	0.004
BENZ	2.1184			0.006
cC6	2.6523	−0.1226		0.005
22DMB	2.7490	−0.2658	−0.1680	0.006
nC7	3.8536	0.3416	0.2177	0.005
24DMP	3.2747			0.009

[a] For abbreviations of compounds, see text.

fact that the physical contributions to the excess thermodynamic quantities are not small, and in fact they might, in some cases, be dominant. Association models can, however, be applied to thermodynamic data for some other Freon mixtures where the enthalpy of complexation is large. For example, for 2-bromo-2-chloro-1,1,1-trifluoroethane (halothane) mixed with oxygenated solvents, the presence of a highly acidic hydrogen atom in the Freon molecule causes the formation of H-bonded complexes in solution [19–21]. The enthalpy of formation of these complexes is in the range 10–15 kJ mol^{-1}, and hence complexation dominates over the physical contributions, allowing the successful application of association models [22].

ACKNOWLEDGEMENTS

We thank the Prague Institute of Chemical Technology, the Dirección de Intercambio Académico UNAM, the Facultad de Química UNAM and the Programa de Apoyo a Proyectos de Investigatión y de Innovación Docente of UNAM (Grant No. IN-014189-IF) for financial support. We also thank Dr. Michal Bureš for kindly performing the AM1 calculations and Mrs. Ana Maria López for her technical assistance.

REFERENCES

1 D. Fenclová and V. Dohnal, J. Chem. Thermodyn., 23 (1991) 911.
2 D. Fenclová and V. Dohnal, Fluid Phase Equilib., submitted for publication.
3 V. Dohnal and D. Patterson, J. Chem. Thermodyn., 21 (1989) 727.
4 D. Fenclová, V. Dohnal, M. Costas and D. Patterson, Fluid Phase Equilib., 57 (1990) 119.
5 M. Costas and D. Patterson, Thermochim. Acta, 120 (1987) 161.
6 M. Costas, Z. Yao and D. Patterson, J. Chem. Soc., Faraday Trans. 1, 85 (1989) 2211.
7 D.D. Desphande, D. Patterson, L. Andreoli-Ball, M. Costas and L.M. Trejo, J. Chem. Soc., Faraday Trans., 87 (1991) 1133.
8 J.L. Fortier, G.C. Benson and P. Picker, J. Chem. Thermodyn., 8 (1976) 289.
9 J.L. Fortier and G.C. Benson, J. Chem. Thermodyn., 8 (1976) 411.
10 CDATA: database of thermodynamic and transport properties for chemistry and engineering, Department of Physical Chemistry, Prague Institute of Chemical Technology, 1991.
11 J.R. Green and D. Margerison, Statistical Treatment of Experimental Data, Elsevier, Amsterdam, 1978.
12 A. Apelblat, A. Tamir and M. Wagner, Fluid Phase Equilib., 4 (1980) 220.
13 L. Barta, Z.S. Kooner, L.G. Hepler, G. Roux-Desgranges and J.P.E. Grolier, Can. J. Chem., 67 (1989) 1225.
14 M. Costas and D. Patterson, J. Solution Chem., 11 (1982) 807.
15 M.J. Kamlet, J.L.M. Abbound, M.H. Abraham and R.W. Taft, J. Org. Chem., 48 (1983) 2877.
16 (a) J.P. Sheridan, D.E. Martire and Y.B. Tewari, J. Am. Chem. Soc., 94 (1972) 3294; (b) D.F. Gray, I.D. Watson and A.G. Williamson, Aust. J. Chem., 21 (1968) 379; (c) A.N. Sharpe and S. Walker, J. Chem. Soc., (1964) 2340.
17 M. Bureš, personal communication, 1992.

18 M.J.S. Dewar, E.G. Zoebisch, E.F. Healy and J.J.P. Stewart, J. Am. Chem. Soc., 107 (1985) 3902.
19 D. Fenclová and V. Dohnal, J. Chem. Thermodyn., submitted for publication.
20 M. Costas, S. Pérez-Casas, V. Dohnal and D. Fenclová, Thermochim. Acta, 213 (1993) 23.
21 V. Dohnal, M. Costas and D. Fenclová, Thermochim. Acta, in press.
22 V. Dohnal, M. Costas, D. Fenclová and M. Bureš, J. Chem. Soc., Faraday Trans., submitted for publication.