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Molecular Interaction of Fluorobenzenes with Polar Solvents

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The free energies of complexation of fluorobenzenes with seven polar solvents have been estimated using NMR spectroscopy.

The preparation of difluorobenzenes **1** either by buta-1,3-diene–CF_2Cl_2 co-pyrolysis[1,2] or by direct fluorination of monofluorobenzene **2**[3,4] involves the problem of separating the generated mixtures of *ortho*-, *meta*- and *para*-isomeric **1** and **2**. This problem arises because of the proximity of their boiling points. Thus, the differences in boiling points (Δb.p) for the pairs *m*-**1**, *p*-**1** and *m*-**1**, **2** are only 5.5 and 3 °C, respectively. For that reason special methods of separation are necessary, in particular those based on the employment of organic solvents.

In this connection we have studied the interaction of **1** and **2** with seven polar solvents taken from various classes of organic compound. This set comprised γ-butyrolactone, 2-pyrrolidinone, *N*-methyl-2-pyrrolidinone (*N*-MP), *N,N*-dimethylformamide (DMF), hexamethylphosphotriamide (HMPA),

Table 1. Free energies of complexation of fluorobenzenes with polar solvents

Polar solvents	ΔG_c at 25±2 °C (kJ mol^{-1})^a			
	o-**1**	*m*-**1**	*p*-**1**	**2**
γ-Butyrolactone	0.82±0.02 (4.56±0.31)	0.52±0.04 (2.48±0.24)	−4.69±0.08 (−0.63±0.04)	0.78±0.03 (1.58±0.16)
2-Pyrrolidinone	1.67±0.17 (4.56±0.46)	−0.3±0.02 (2.48±0.25)	−1.21±0.12 (0.32±0.03)	−0.65±0.2 (−0.28±0.01)
N-MP	2.91±0.29	0.89±0.05	−0.52±0.05	1.40±0.08
DMF	1.11±0.06	0.35±0.02	−1.31±0.07	1.53±0.15
HMPA	2.76±0.28	0.85±0.09	−0.04±0.004	2.34±0.23
TMU	1.61±0.08	1.07±0.05	−3.00±0.15	2.68±0.13
Cyclohexanone	4.13±0.38	−1.96±0.08	−4.58±0.40	0.05±0.002

[a] At 60±3 °C.

tetramethylurea (TMU) and cyclohexanone, their common feature being the ability to form solvates. Their association with each of the fluorinated benzenes was studied by means of ^{19}F NMR spectroscopy. The respective binary mixtures, dissolved in CCl_4, were analysed using a Bruker AC 200p radiospectrometer at a ^{19}F operating frequency 188.31 MHz with Freon 113 as internal standard. The accuracy of the δ_F measurements was in the 3–5% range.

The resulting concentrations of polar solvents (C_{ps}) were varied from 0.04–2.0 mol dm^{-3}, whereas those of the fluoro compounds (C_i) were set at 0.02 mol dm^{-3}. At such a concentration, especially when $C_{ps} >> C_i$, the possibility of self-association of the fluorobenzenes in the non-solvating CCl_4 is likely to be negligible.

In all cases a satisfactory linear dependence of C_{ps}/Δ^t_x values (where Δ^t_x is the recorded variation of δ_F) on C_{ps} was observed over the studied range of concentrations. That type of relationship implies the formation of an equimolar complex of the two solutes.

Using the Beneshi–Gildebrand equation and the values of Δ^t_xobserved in the cases when $C_{ps} >> C_i$, the stability constants of the complexes (K_c,/dm^3 mol^{-1}) were determined for all the pairs of solutes.

The free energies of complexation (ΔG_c/kJ mol^{-1}) were obtained from the well-known equation $\Delta G_c = -RT \ln K_c$.

The stability of solvate complexes is known to depend upon the nature of the complexation and the temperature. For the studied binary systems in question two types of complex, the hydrogen-bonded and the π-bonded, are plausible. In some of these systems, if not in all, both mechanisms of complexation may be operating concomitantly. Among the fluoro compounds studied in this work, the greatest ability to interact with polar solvents was displayed by *p*-**1** ($\Delta G_c = -4.69$ kJ mol^{-1} for the system with γ-butyrolactone and −4.58 kJ mol^{-1} for the systems with cyclohexanone). On the other hand, the interaction of *m*-**1** with the same two solvents was relatively weak ($\Delta G_c = 0.52$ and −1.96 kJ mol^{-1}, respectively). The weakest interactions with the polar solvents were observed for **2** and *o*-**1**, the only exception being the interaction of **2** with 2-pyrrolidinone.

As expected, when the temperature was raised to 60 °C the absolute values of ΔG_c diminished. However, even at this temperature the difference in the free energies of complexation of *p*-**1** and *m*-**1** with γ-butyrolactone remained considerable. This observation suggests that γ-butyrolactone could be used as a selective solvent to separate *p*-**1** and *m*-**1** by means of low-pressure extractive distillation.

Similar conclusions can be made concerning 2-pyrrolidinone (see Table 1) which appears to be very effective in separating *m*-**1** and, using the same low-pressure extractive distillation technique

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