Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 1993, **3(4)**, 175–176

Mendeleev
Communications

Relative Fugacity in the Benzene–Monofluorobenzene System in the Presence of Polar Solvents

Michael I. Zaretskii* and Ruben E. Serebryakov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation.
Fax: +7 095 135 5328

Experimental data for the calculation of relative fugacity values in the benzene–monofluorobenzene system in the presence of polar solvents has been obtained.

The preparation of monofluorobenzene **1** by pyrolysis of cyclopentadiene with fluorohalogenomethanes in the presence of ammonia and water vapour[1] afforded products contaminated with 2–5 mass % of benzene **2**. It is difficult to purify **1** from **2** by distillation or rectification owing to the small difference between their boiling points ($\Delta T_{bp} = 4$ °C) and the mean relative fugacity coefficient $\alpha = 1.176$[2,3]; special methods should therefore be used. A polar solvent capable of produ-

Table 1 "Polarity" parameters for some organic substances[a]

Polar solvents	Solvent polarity scales	
	E_T	π^*
DMF	43.8	0.88
N-MP	42.2	0.98
DMSO	45.0	1.00
Ethyleneglycol	56.3	0.92

[a] For **1**: $E_T = 37.0$; $\pi^* = 0.62$; for **2**: $E_T = 34.5$; $\pi^* = 0.59$.

cing solvate complexes with **1** and **2** of different stabilities was applied in those methods and led to an increase in α in the **1–2** system.

As can be revealed from NMR spectroscopic data,[4,5] some polar solvents, especially *N*,*N*-dimethylformamide (DMF), have different interactions with **1** and **2**. It is assumed that **1** and **2** are π-donors whereas DMF is a π-acceptor. IR spectroscopic data confirmed the difference between interaction of **1** and **2** with phenol (PhOH) as OH-proton donor. Two different types of **1**-PhOH complexes were established: OH ··· F and OH ··· π(F), whereas the **2**-PhOH complex is formed only due to an intramolecular hydrogen bond OH ··· π.

DMF, some lactams [*N*-methyl-2-pyrrolidinone (*N*-MP), 2-pyrrolidinone], glycols (diethyleneglycol) and dimethyl sulfoxide (DMSO) were used in the present study, based on the information reported above and the "polarity" scales of the organic substances (see Table 1; E_T is a measure of the acceptor property of the solvents,[7] π^* is a parameter of the "polarity-polarizability" scale[8]). Ethanolamine was taken as a reference.

The interaction of **1** with DMF, *N*-MP and 2-pyrrolidinone was estimated from ^{19}F NMR spectra[†] of ~0.1 mol dm^{-3} solutions of **1** and polar substances recorded in CCl_4. The chemical shift differences (Δ^{t}_{x}) were calculated using the formula: $\Delta^{t}_{x} = \delta_i - 33.78$, where δ_i (ppm) is the observed ^{19}F chemical shift in a binary mixture of **1** and the polar solvent (4–8 mass %) in CCl_4; 33.78 ppm is the ^{19}F chemical shift of **1** in pure CCl_4 (a polar solvent is absent).

The Δ^{t}_{x} values for the polar substances studied are 2.44, 2.02 and 1.82 ppm, respectively. It is therefore obvious that all three solvents interact with **1**; the strongest interaction was observed in DMF and the weakest with 2-pyrrolidinone.

Experimental studies on the vapour-liquid phase equilibrium in the three-component systems were carried out under isobaric conditions (at 760 Torr[‡]) using an Othmer apparatus with vapour-phase circulation. Equilibrium phase compositions were analysed using GLC.

Experimental data allowed us to calculate the relative fugacities of the components in the presence of polar solvent (α_s) using equation (1), where y and x represent the content of **2** (in mole fractions) in the vapour and liquid, respectively (converted into a binary mixture of the components and subjected to separation). The calculated data are presented in Table 2.

Table 2 Relative fugacity of the benzene–monofluorobenzene mixture in the presence of a polar solvent

Dipolar solvent	Solvent concentration in mixture admitted into the apparatus (mass %)	Vapour–liquid mixture boiling point / °C	Relative fugacity α_s
DMF	80.0	121	1.46
	87.5	123	1.67
	90.0	125	1.52
N-MP	90.0	136	1.85
2-Pyrrolidinone	90.0	88	1.35
Ethanolamine	90.0	94	1.69
Diethyleneglycol	70.0	85	1.41
	80.0	85	1.41
	90.0	86	1.53
DMSO	90.0	102	1.58

$$\alpha_s = \frac{y_i}{x_i}\left(\frac{1 - x_i}{1 - y_i}\right) \qquad (1)$$

The results show that DMF, *N*-MP, DMSO and ethanolamine present rather high selectivity and considerable increase in relative fugacity in the binary system studied. However, the utility of ethanolamine or diethyleneglycol is limited because of the possible formation of two liquid phases (so-called 'stratification') in the mixtures of these solvents with **1** and **2**. When DMSO is used vacuum distillation is needed for its regeneration and recovery of **1** and **2** seems to be a difficult task. DMF and *N*-MP appear to be the most appropriate extractive agents for **1** and **2** separation and will be studied more extensively.

References

1 O. M. Nefedov, A. A. Ivashchenko, S. F. Politanskii, I. D. Kushina, V. M. Yakovlev, A. V. Strashenko and E. J. Katz, USSR Pat., 572445, 1977.

2 R. E. Banks and W. K. Musgrave, *J. Chem. Soc.*, 1956, 4682.

3 D. Pena, A. Composito, C. Colin and J. Escudero, *J. Chem. Thermodyn.*, 1981, **13**, 869.

4 G. Rudakoff, R. Radeglia, P. Junghans, T. Ha-Phuong and W. Kohler, *Z. Chem.*, 1971, **11**, 307.

5 G. Rudakoff, T. Ha-Phuong, P. Junghans and R. Radeglia, *Z. Chem.*, 1972, **12**, 37.

6 K. Szczepianak and W. J. Ozwill-Thomas, *J. Chem. Soc. Faraday Trans.*, 1974, **70**, 1175.

7 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH Verlagsgesellschaft mbH, Weinheim, FRG, 1988 (in English).

8 M. J. Kamlet, J. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.

Received: Moscow, 21st December 1992
Cambridge, 17th May 1993; Com. 2/06891E

[†] The spectra were recorded by A. I. Ignatenko using a Perkin Elmer radiospectrometer (internal standard CF_3CO_2H).

[‡] 1 Torr = (101325/760) Pa.