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Solvent effect on the partial molar volume and solution enthalpy of ferrocene

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A small distinction of solution enthalpy and partial molar volume in eighteen solvents of different polarity corresponds to the inaccessibility of capsulated charges inside of ferrocene for the interaction with surrounding molecules.

The chemical, physical and biopharmaceutical properties of ferrocene have been intensively studied.[1–4] In the framework of our systematic studies of salt effects on reaction rates, partial molar volumes and enthalpies of solution in organic solvents,[5–7] we examined here the properties of ferrocene in 18 solvents.†

The enthalpies of solution of ferrocene were measured at 25 °C in a differential calorimeter.[9] The accuracy of the calorimetric measurements was verified by determining the enthalpy of dissolution of dry potassium chloride in water at 25 °C. Experimental value, 4.18±0.01 kcal mol^{-1}; published[10] value, 4.185±0.002 kcal mol^{-1}. For all solutions two to six measurements of sequentially dissolving ferrocene samples in 150 cm^3 of a solvent were carried out. The concentration dependence of the heat of solution should be excluded due to the constancy of the effects in the test range of concentrations (4×10^{-3}–2×10^{-2} mol dm^{-3}). The error of the measurements did not exceed ±2%.

An Anton Paar Model DSA 5000M vibrating-tube densimeter was used for the density measurements at 25±0.002 °C in the range of 0.02–0.2 mol dm^{-3}. The concentration dependence of the molar volumes of ferrocene was not observed. The molar volumes of ferrocene in solutions (V_{FC}) were calculated from the densities of three to five solutions using the additivity equation

$$(1000 + m_A M_A)/d = 1000/d_0 + m_A V_{FC}. \quad (1)$$

Here, d_0 and d are the solvent and solution densities, respectively; m_A is the molality of solution; and M_A is the molar mass of ferrocene. The slope of $[(1000 + m_A M_A)/d]$ as a function of m_A is V_{FC}. The correlation coefficient is > 0.999 (Table 1).

The large exothermicity of solution of electrolytes in *n*-donor solvents is usually accompanied by a considerable volume electrostriction up to the negative values of partial molar volumes.[5,6] The endothermic value of the heat of ferrocene solution is defined mainly by the melting heat of ferrocene. Small differences in the heats of solution of ferrocene correlate with small differences in the heat of benzene solution (Table 1, $r = 0.88$, $n = 17$). Note that the enthalpy of ferrocene ($C_{10}H_{10}Fe$) sublimation (17.49 kcal mol^{-1})[13] is close to that of naphthalene ($C_{10}H_8$) (17.42 kcal mol^{-1}).[14] The molar volume of liquid dicyclopentadiene (134 cm^3 mol^{-1}) is practically the same as that of ferrocene in solution (Table 1).

A comparison of these results (Table 1) with the drastical difference of the solvent effect on the heats of solution and partial molar volumes of salt solutions[5–7] corresponds to the inaccessi-

† The solvents were purified by known methods.[8] Ferrocene (Aldrich) was recrystallized from hexane–ethanol (3:1), dried and sublimated at 70 °C in a vacuum at 100 Pa (mp 173–174 °C, lit.,[1–3] 174 °C).

Table 1 Sample weight of ferrocene (*a*/mg), heat effect of solution (*h*/cal), enthalpy of solution of ferrocene ($\Delta_{sol}H_{FC}$/kcal mol^{-1}), benzene ($\Delta_{sol}H_{BZ}$/kcal mol^{-1}) and partial molar volume of ferrocene (V_{FC}/cm^3 mol^{-1}) in various solvents at 25 °C.

Solvent	*a*	*h*	$\Delta_{sol}H_{FC}$	$\Delta_{sol}H_{BZ}$[11]	V_{FC}
1,2-Dichloro-	95.5	1.997	3.89		
ethane	96.1	2.040	3.95 (3.92±0.03)	0.15	137.41±0.05
n-Hexane	82.7	2.054	4.62		
	87.7	2.159	4.58 (4.60±0.02)	0.78	128.68±0.27
Toluene	95.1	1.697	3.32		
	92.6	1.618	3.25 (3.29±0.04)	0.06	133.37±0.08
Acetonitrile	91.3	2.381	4.85		
	89.4	2.413	5.02 (4.93±0.08)	0.63	135.33±0.31
Carbon	89.2	1.525	3.18		
tetrachloride	110.1	2.060	3.48		
	108.8	2.117	3.62		
	152.1	2.805	3.43		
	128.6	2.288	3.31 (3.40±0.13)	0.11	133.43±0.02
Acetone	—	—	4.01[12]	0.11	130.52±0.27
Chlorobenzene	113.4	1.939	3.18		
	147.1	2.444	3.09		
	125.2	2.167	3.22 (3.16±0.05)	0.0	134.51±0.03
Ethyl acetate	130.9	2.731	3.88		
	114.6	2.458	3.99		
	125.4	2.629	3.90 (3.92±0.05)	0.10	132.82±0.39
Benzene	92.7	1.699	3.41		
	92.8	1.696	3.40 (3.40±0.01)	0	133.76±0.12
			3.65[12]		
Ethanol	—	—	4.93[12]	0.40	131.19±0.13
Cyclohexanone	117.4	2.304	3.65		
	111.4	2.156	3.60		
	137.6	2.745	3.71		
	133.1	2.612	3.65 (3.65±0.03)	—	136.29±0.51
DMSO	45.7	1.054	4.29		
	71.2	1.722	4.50		
	73.1	1.784	4.54		
	76.5	1.875	4.56 (4.47±0.10)	0.65	136.50±0.07
1,4-Dioxane	91.2	1.726	3.52		
	101.9	1.896	3.46 (3.49±0.03)	0.03	134.73±0.17
n-Octane	152.8	3.918	4.77		
	140.3	3.455	4.58		
	106.9	2.580	4.49		
	99.5	2.381	4.45	0.19	134.55±0.19
Chloroform	87.3	1.380	2.94		
	93.5	1.382	2.75 (2.84±0.10)	–0.50	133.52±0.31
Cyclohexane	—	—	4.52[12]	0.75	136.92±0.34
2,2,4-Tri-	60.0	1.432	4.44		
methylpentane	80.9	2.000	4.60		
	71.5	1.811	4.71		
	82.4	2.051	4.63 (4.59±0.08)	0.79	130.53±0.16
o-Xylene	89.4	1.605	3.34		
	93.1	1.642	3.28 (3.31±0.03)	0.19	134.98±0.48

bility of charges capsulated inside ferrocene to interaction with solvent molecules.

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