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Note

Enthalpies of mixing of some binary mixtures of thiazole

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Molar excess enthalpies H^E of two sets of binary mixtures have been measured as a function of composition. The first set studied at 298.15 K is formed by solutions of thiazole in cyclohexane, benzene and thiophene. The second set studied at 318.15 K is formed by solutions of thiazole in hexafluorobenzene, oxazole and pyridine.

The values of H^E for the cyclohexane solutions were large and positive while those of solutions of thiazole in the aromatic compounds were slightly positive or negative. The last results support the presence of weak specific interactions between the unlike molecules.

EXPERIMENTAL

The calorimeter used was a C.R.M.T., it is isobaric and isothermic and it operates in the absence of vapour phase. Details of the apparatus, experimental method and calculation procedures have been described earlier[1,2].

Heats of mixing were determined at 298.15 and 318.15 K, all temperatures were measured with a calibrated platinum resistance thermometer in terms of IPTS-68.

The calorimeter was tested on reliability and precision by measuring the heat of mixing of the system benzene + carbon tetrachloride at 318.15 K. The agreement between our results and those published[3] was satisfactory bearing in mind the average experimental uncertainty in H^E of ±1%.

The samples of thiazole, oxazole (obtained from UGILOR) pyridine and thiophene were dried, distilled through 20 plates spinning band column stored over molecular sieve 4 Å out of contact with air in the dark. The hexafluorobenzene obtained from the Imperial Smelting Corp. was distilled and stored over molecular sieve 5 Å. The benzene and cyclohexane (Merck) for spectrophotometry were sufficiently pure for our purposes and were only dried over molecular sieve 4 Å.

Gas chromatography or freezing temperature measurements[4] showed that all samples used were better than 99 mol % pure.

Both components were not degassed before use.

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RESULTS

For the systems thiazole + hexafluorobenzene, thiazole + oxazole and thiazole + pyridine the enthalpies of mixing at 318.15 K were fitted by a least squares method in the equation:

$$H^{E} = x_1(1-x_1)\sum_{i=1}^{n} A_i(1-2x_1)^{i-1} \tag{1}$$

The values of the parameters A_i are given in Table 1. The experimental data are compiled in Table 2 with the standard deviation σ. Excess enthalpies of mixing of cyclohexane, benzene and thiophene with thiazole were measured[5] at 298.15 K, they are listed in Table 3.

For each system x_1 represents the mole fraction of thiazole.

DISCUSSION

The heats of mixing are small and positive for the systems thiazole + hexafluorobenzene, thiazole + benzene, thiazole + oxazole and thiazole + thiophene. Those for the system thiazole + pyridine are small and negative while those for the thiazole + cyclohexane mixture are large and positive.

The positive and large H^E value for the last binary mixture can be attributed to the dipolar association of thiazole[5,6] and to the dispersive forces between the unlike molecules. The presence of both π–π and n–π interactions between the azaaromatic molecules[5,6,8] can explain the more important values of excess enthalpies beyond that of the homomorphic system thiophene + cyclohexane[5]. For instance at 318.15 K in the system thiazole + cyclohexane:

$$\text{for } x_1 \simeq x_2,\ H^E = 1740\ \text{J mol}^{-1};\ (\bar{H}^E)^{\infty} = 10.2\ \text{kJ mol}^{-1}$$

in the system thiophene + cyclohexane:

$$\text{for } x_1 \simeq x_2,\ H^E = 995.8\ \text{J mol}^{-1};\ (\bar{H}^E)^{\infty} = 4.1\ \text{kJ mol}^{-1}$$

The difference in the H^E values of the studied systems may be taken as fair evidence of the contributions of specific interactions between thiazole and aromatic components.

The ability of aromatic molecules to form complexes with various substances is well known[8–18].

The thermodynamic studies of the mixtures pyridine + C_6H_6[9–12,17] and pyridines + C_6F_6[12,13,18] were interpreted recently in terms of a specific interaction between the unlike molecules. Our results confirm that pyridine is a better electron donor π than other aromatic molecules studied. In order to obtain information about the specific interactions, the partial molar excess enthalpie of mixing of thiazole at infinite dilution $(\bar{H}^E)^{\infty}$ has been calculated (Table 4). The evolution of $(\bar{H}^E)^{\infty}$ for the thiazole mixtures is: $C_6H_{12} > C_6F_6 > C_6H_6 >$ oxazole > thiophene > pyridine. This is

TABLE 1

VALUES OF THE LEAST SQUARES PARAMETERS IN EQN (1)

Mixture	A_1	A_2	A_3	σ (*J mol*$^{-1}$)	σ_m* (*J mol*$^{-1}$)
Thiazole + C_6F_6	3978.6	−1149.3	53	8	12
Thiazole + oxazole	973.3	247.9	−15	5.4	9
Thiazole + pyridine	−239.3	−60.5	−8.5	1.2	2.3

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*$\sigma_m = \max(H^E_{calc} - H^E)$.

TABLE 2

EXCESS ENTHALPY H^E OF THIAZOLE(1) AT 318.15 K

x_1	H^E (*exp.*) (*J mol*$^{-1}$)	H^E (*calc.*) (*J mol*$^{-1}$)	x_1	H^E (*exp.*) (*J mol*$^{-1}$)	H^E (*calc.*) (*J mol*$^{-1}$)
Thiazole(1) + C_6F_6(2)					
0.083	229.2	232.6	0.694	929.3	941.0
0.1574	428.4	424.4	0.709	916.2	921.9
0.258	668.0	657.4	0.7735	807.9	810.0
0.4831	986.8	983.8	0.891	477.8	477.0
0.5981	1018.0	1011.0	0.9087	413.1	410.7
			$\sigma^* = 8$ J mol^{-1}		
			$\sigma_m = 12$ J mol^{-1}		
Thiazole(1) + oxazole(2)					
0.0616	70.5	69.5	0.6405	214.3	208.3
0.1160	118.2	120.2	0.6432	216.0	207.4
0.3766	240.5	243.0	0.6764	202.5	194.3
0.3802	240.7	243.6	0.6875	188.4	189.6
0.3922	239.7	244.9	0.7914	139.5	129.8
0.502	241.1	243.1	0.9	70.7	70.6
0.5673	233.1	230.8			
			$\sigma = 5.4$ J mol^{-1}		
			$\sigma_m = 9$ J mol^{-1}		
Thiazole(1) + pyridine(2)					
0.1013	−26.8	−26.7	0.5527	−58.7	−57.6
0.1727	−39.7	−40.4	0.5772	−55.3	−56.1
0.2603	−52.8	−52.8	0.6852	−46.6	−46.7
0.402	−61.9	−60.4	0.8851	−20.5	−20.1
0.5003	−61.3	−59.1	0.9282	−12.7	−12.9
0.5486	−55.4	−57.7			
			$\sigma = 1.2$ J mol^{-1}		
			$\sigma_m = 2.3$ J mol^{-1}		

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*$\sigma = (\Sigma H^E\,(\text{exp.}) - H^E\,(\text{calc.})/m-n)^{1/2}$, where m = number of measurement, n = number of parameters into eqn (1).

TABLE 3

EXCESS ENTHALPY H^E OF THIAZOLE(1) AT 298.15 K

x_1	H^E (*exp.*) (*J mol*$^{-1}$)	x_1	H^E (*exp.*) (*J mol*$^{-1}$)
Thiazole + cyclohexane			
0.014	100.8	0.3484	1665.2
0.020	200.4	0.3958	1690.3
0.030	289.9	0.4510	1723.8
0.060	534.7	0.5020	1707.1
0.138	1000.0	0.6984	1380.7
0.2442	1384.9	0.990	63.6
Thiazole + benzene			
0.005	5.8	0.3749	238.9
0.0145	16.5	0.5074	256.9
0.0145	16.8	0.5844	245.6
0.0730	73.6	0.7117	205.8
0.1065	101.7	0.810	154.4
0.1895	160.2		
Thiazole + thiophene			
0.0296	11.9	0.4526	86.2
0.0988	33.5	0.5022	86.6
0.2481	66.1	0.6813	68.6
0.3604	82	0.8727	33.9

TABLE 4

PARTIAL MOLAR EXCESS ENTHALPIE AT INFINITE DILUTION $(\bar{H}^E)^\infty$ OF THIAZOLE AT 318.15 K

System	$(H^E)^\infty$ (*kJ mol*$^{-1}$)
Thiazole + cyclohexane	10.2
Thiazole + hexafluorobenzene	2.8
Thiazole + benzene	1.2
Thiazole + thiophene	0.4
Thiazole + pyridine	−0.3

due to the decrease of dispersive forces and arises from specific interactions between the unlike molecules.

Like Otin et al.[15] we can assume that the partial molar excess enthalpy of thiazole at infinite dilution is made up of different contributions for example:

(a) in cyclohexane:

$$(\bar{H}^E)^\infty = (\bar{h}^E)^\infty_{disp} + (\bar{h}^E)^\infty_{auto}$$

(b) in aromatic solvants:

$$(\bar{H}^E)^\infty = (\bar{h}^E)^\infty_{disp} + (\bar{h}^E)^\infty_{auto} + (\bar{h}^E)^\infty_{spec}$$

where $(\bar{h}^{E})^{\infty}_{disp}$ = dispersion contribution;

$(\bar{h}^{E})^{\infty}_{auto}$ = autoassociation contribution;

$(\bar{h}^{E})^{\infty}_{spec}$ = contribution due to specific forces.

The term due to dispersion forces can be calculated by different methods[14,15,19,20].

Theoretical interpretation will be presented at the completion of this series of measurements.

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