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EXCESS ENTHALPIES AND EXCESS VOLUMES OF BINARY MIXTURES CONTAINING TETRAHYDROFURAN

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ABSTRACT

Heat of mixing data at 318.15 K are reported for the binary systems made up of tetrahydrofuran (THF) with pyridine and with thiazole.

The volumes of mixing at 298.15 K and atmospheric pressure have also been measured for the following binary mixtures: THF+pyridine, THF+thiazole THF+benzene, THF+cyclohexane, THF+hexafluorobenzene.

INTRODUCTION

The present work forms part of a programme which studies the thermodynamic behaviour of some binary systems in which specific interactions between the unlike molecules can occur[1–3].

Previous studies[4] suggest that a weak interaction occurs between cyclic ethers and aromatic hydrocarbons. Since no thermodynamic measurements exist for mixtures of azaaromatic bases with ether molecules, we have chosen in a first step to measure the enthalpies and the volume of mixing of the systems: tetrahydrofuran (THF)+thiazole, and THF+pyridine. The excess volumes of mixing V^E for the mixtures THF+benzene, THF+cyclohexane and THF+hexafluorobenzene were also studied. Our results were compared with published results[4–7].

EXPERIMENTAL

The excess enthalpies H^E were measured with a C.R.M.T. calorimeter. The apparatus is isobaric and isothermic and operates in the absence of vapour phase. Details of the apparatus, experimental method and calculation procedure have been described earlier[8,9].

After electrical calibration 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[10] was satisfactory bearing in mind the average experimental uncertainty in H^E of $\pm 1\%$.

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Excess volumes V^E were calculated from densities of mixtures measured over the entire range of composition. For the mixture THF+thiazole the densities were obtained with a Sprengel–Ostwald pycnometer. For the other systems the densities were determined by means of an automatic digital densitometer Anton Paar. The operation of the densitometer has been described previously[11,12].

The apparatus before each measurement was calibrated with some standard samples. The densities of pure components agreed in a number of cases with the literature values to better than 5.10^{-5} g cm^{-3}. We have studied the system benzene+C_6H_{12} which has been suggested as a standard for dilatometry[13].

Our results tabulated in Table 1 are in agreement with those of the literature[14,15]. The samples of thiazole (synthesised in the laboratory) and pyridine were dried, distilled through 20 plates spinning band column and stored over molecular sieve 4 Å. Benzene and cyclohexane Merck for spectrophotometry were sufficiently pure for our purposes and were only dried over molecular sieve 5 Å. Tetrahydrofuran "pure grade" was treated to remove peroxides, dried with calcium chloride and then sodium. It was then fractionally distilled twice from sodium.

TABLE 1

EXCESS VOLUMES OF BENZENE (1)+CYCLOHEXANE (2) AT 298.15 K

x_1	V^E (*exp.*) (*10^{-9} m^3 mol^{-1}*)	V^E (*calc.*) (*10^{-9} m^3 mol^{-1}*)
0.10864	266.5	264.5
0.16183	367.2	368.6
0.82341	580.9	584.6
0.49678	650	654.7
0.63301	601.9	599.3
0.68311	558	555
0.68749	552.4	550.6
0.78103	435.9	436.8
0.79235	419.4	416.2
0.88004	264.6	264
0.92378	173.7	175

The freezing temperature measurement or gas chromatography showed that all materials were at least 99.5 moles per cent pure.

RESULTS AND DISCUSSION

The experimental results are compiled in Tables 2 and 3.

When the composition range studied was sufficiently large the measurements were fitted by a least square method in the equation:

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

(the quantity fitted was $X^E/x_1(1-x_1)$ not X^E).

TABLE 2

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

x_1	H^E (*exp.*) ($J\ mol^{-1}$)	H^E (*calc.*) ($J\ mol^{-1}$)
THF (1) + pyridine (2)		
0.1286	97.5	96.9
0.1723	123	123.7
0.3389	198	194
0.4362	205.5	210
0.4478	208.3	211
0.5040	207.5	210.8
0.6551	186.4	181.6
0.6870	174.4	170.6
0.8112	113.5	114
0.8752	77.3	78
0.8819	74	74
THF (1) + thiazole (2)		
0.1273	−155	−159.4
0.18391	−225	−222
0.2113	−255	−250
0.2602	−301.5	−294.5
0.3044	−324	−332
0.3169	−340	−341
0.545	−422	−423
0.6989	−371.6	−372.3
0.8315	−255.8	−253
0.8634	−210	−214
0.8801	−194	−191.8

TABLE 3

EXCESS VOLUMES V^E OF TETRAHYDROFURAN (1) AT 298.15 K

x_1	V^E (*exp.*) ($10^{-9}\ m^3\ mol^{-1}$)	V^E (*calc.*) ($10^{-9}\ m^3\ mol^{-1}$)
THF (1) + pyridine (2)		
0.13146	−133	−132
0.18633	−177	−177
0.27963	−236	−238
0.386	−282	−282.5
0.44613	−293	−295
0.52501	−298	−299.5
0.61066	−286	−286
0.64736	−280	−274.7
0.70879	−249	−248
0.83429	−164	−165.4
THF (1) + thiazole (2)		
0.1027	−170	−164
0.1863	−270	−273.9

(*Continued on p. 382*)

TABLE 3 (*Continued*)

x_1	V^E (*exp.*) ($10^{-9}\ m^3\ mol^{-1}$)	V^E (*calc.*) ($10^{-9}\ m^3\ mol^{-1}$)
THF (1) + thiazole (2)		
0.2557	−335	−344.9
0.3141	−390	−390
0.4622	−436.5	−443
0.5025	−433.6	−441.9
0.6960	−353.8	−350.3
0.7411	−323.4	−310.8
0.8513	−187.8	−192
0.9197	−100.8	−106.4
THF (1) + cyclohexane (2)		
0.17042	344.7	338.6
0.20086	373.5	380
0.29101	469.6	472.7
0.34744	513.5	510.2
0.42095	537	537.2
0.45482	537.6	541.9
0.5578	530	527.6
0.5613	526	526.4
0.6444	484.6	484
0.6885	451.7	451
0.71951	424.7	423.5
0.7796	361.7	359.6
0.80627	326.5	326.8
0.87495	228.3	229.2
0.89658	194	194.5
THF (1) + hexafluorobenzene (2)		
0.37513	1110	
0.56984	1195	
0.65714	1140	
0.70185	1118	
0.76745	951.7	
0.81885	808	
0.84847	706	
THF (1) + benzene (2)		
0.15329	−115	−116.6
0.19779	−145.4	−145.4
0.26788	−186.6	−185.0
0.32216	−211.6	−210
0.39155	−238	−234.5
0.44521	−250	−247
0.4844	−252	−252.3
0.50456	−250.8	−253.8
0.57595	−249.5	−251.8
0.60266	−248	−248
0.65935	−233	−235.0
0.74762	−199.6	−199.6
0.79929	−170.8	−170.8
0.84869	−136	−137
0.89029	−105	−104.6

Where x_1 represents the mole fraction of the first named compound in the tables and X^E is H^E (J mol^{-1}) or $V^E/(10^{-9}$ m^3 mol$^{-1})$. The parameters A_i and the standard deviation σ defined by: $\sigma = (\Sigma(H^E_{\text{exp.}} - H^E_{\text{calc.}})^2/m-n)^{1/2}$, where m = number of measurements, n = number of parameters into eqn (1) are given in Table 4.

TABLE 4

VALUES OF THE LEAST SQUARES PARAMETERS IN EQN (1)

Mixture	A_1	A_2	A_3	σ *(J mol^{-1})*
A. *Excess enthalpy H^E*				
THF+pyridine	844	−98.8	−96.4	3.5
THF+thiazole	−1684.4	−256	+106	4.5
B. *Volume of mixing V^E*				
				σ *(10^{-9} m^3 mol^{-1})*
Benzene+cyclohexane	2619.9	−149.6	−7.9	3
THF+cyclohexane	2163	−229.3	186	3.3
THF+benzene	−1014.1	−122.6	64	2
THF+pyridine	−1200	−24.5	44.7	2.5
THF+thiazole	−1768.7	198.4	228	8

Generally it was found that three parameters in eqn (1) were sufficient to reproduce the experimental values. The standard deviations were comparable with the estimated precision of the two apparatus.

A comparison of our data with those recorded in the literature is only possible for the V^E of mixture THF+cyclohexane measured at 298.15 K by Arm and Bankay[7]. The values reported are slightly lower than our results for example for $x_1 = 0.5$

$$V^E = 540.7 \pm 0.003 \cdot 10^{-9} \text{ m}^3 \text{ mol}^{-1} \text{ (this work)}$$

$$V^E = 520 \pm 0.01 \cdot 10^{-9} \text{ m}^3 \text{ mol}^{-1} \text{ (ref. 7)}$$

The excess values of all the mixtures studied together with the literature values of H^E for the further systems: THF+cyclohexane[5,18] THF+benzene[6] are shown in Table 5 for $x_1 = 0.5$.

A marked decrease in X^E occurs in every case on changing from cyclohexane to aromatic compounds. The excess values of mixing shift in the negative direction in the order: cyclohexane, benzene, pyridine, thiazole. The enthalpies of mixing and the volumes of mixing vary qualitatively in the same way.

The electron donor ability of ether molecules is well known[4,5,16–20]. The present results confirm the existence of moderate interaction between the unlike molecules, and that thiazole is a better electron acceptor than other aromatic molecules studied. We have also measured the volumes of mixing of the system THF+hexa-

TABLE 5

EXCESS VALUES OF SOME BINARY MIXTURES OF THF (1) FOR $x_1 = 0.5$

System	H^E *(J mol^{-1})*	V^E *(10^{-9} m^3 mol^{-1}) at 298.15 K*
THF + cyclohexane	720[c] 745[a] at 298.15 K	541[d]
THF + hexafluorobenzene		1216[d]
THF + benzene	350[b] at 298.15 K	
THF + pyridine	207[d] at 318.15 K	−300[d]
THF + thiazole	−421[d] at 318.15 K	−442[d]

[a] Ref. 5, [b] ref. 6, [c] ref. 18, [d] this work.

fluorobenzene. We thought that the substitution of precedent compounds by a stronger acceptor might enhance the donor–acceptor interaction.

The values of V^E in Table 5 are large and positive. This comportment signaled by Andrews and coll.[4] is probably caracteristic of mixtures containing hexafluorobenzene.

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