

EXCESS ENTHALPIES OF BINARY MIXTURES CONTAINING 1,3-DIOXOLANE AND CYCLIC COMPOUNDS

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ABSTRACT

Excess molar enthalpies, H^E , of binary mixtures containing 1,3-dioxolane plus toluene, *p*-xylene, 1,2,4-trimethylbenzene, ethylbenzene, 1,4-dimethylbenzene, 1,4-dimethylcyclohexane and ethylcyclohexane were determined by means of a flow microcalorimeter. Experimental H^E values were correlated by the Redlich–Kister polynomial. The aromatic set of compounds shows calorimetric behaviour markedly different from that of corresponding aliphatic cyclic compounds.

INTRODUCTION

In continuation of earlier investigations on the thermodynamic properties of binary liquid mixtures containing 1,3-dioxolane as a common solvent, excess molar enthalpies, H^E , for the binary mixtures of 1,3-dioxolane (D) and each of the six cyclic compounds, toluene (T), *p*-xylene (XY), 1,2,4-trimethylbenzene (TMB), ethylbenzene (EB), 1,4-dimethylcyclohexane (DMCE) and ethylcyclohexane (ECE) have been determined at 298.15 K at atmospheric pressure.

Our aim in this paper is to correlate the experimental data, to stress the differing calorimetric behaviour of aromatic and saturated ring structures and to investigate the influence of lateral groups in the cyclic molecules.

A comparison with binary systems studied by other authors [1] and reference to a mixture studied by us in an earlier paper [2] will be made in the conclusions of this work.

The data reported here are not available elsewhere in the literature.

TABLE 1

Experimental densities ^a, ρ , of toluene (T), 1,2,4-trimethylbenzene (TMB), ethylbenzene (EB), 1,4-dimethylcyclohexane (DMCE) and ethylcyclohexane (ECE), coefficients A and B , correlation coefficients $|R|$ and standard deviation $\sigma(\rho)$

	T		TMB		EB		DMCE		ECE	
	T (K)	ρ (kg m ⁻³)	T (K)	ρ (kg m ⁻³)	T (K)	ρ (kg m ⁻³)	T (K)	ρ (kg m ⁻³)	T (K)	ρ (kg m ⁻³)
	288.75	870.88	290.40	877.86	292.05	867.89	293.05	776.66	291.15	789.49
	291.00	868.61	293.15	875.75	293.15	866.90	294.30	775.57	292.55	788.37
	293.75	866.33	293.75	875.29	295.05	865.25	296.95	773.43	293.15	787.88
	296.20	863.99	295.35	873.86	296.45	864.07	297.70	772.65	295.25	(787.92)
	298.15	862.04	297.10	872.50	298.15	862.49	298.05	772.46	297.20	784.63
	300.50	(862.19)	298.15	871.71	299.70	861.19	298.15	772.34	298.15	783.89
	303.15	859.85	(871.80)	869.52	301.00	860.07	298.60	771.95	300.60	(783.90)
	305.40	857.50	300.95	867.36	302.90	858.46	301.00	770.01	302.55	780.20
	307.20	855.53	303.65	867.36	303.95	857.46	301.55	769.50	304.05	779.01
		853.62	305.70	865.76	304.75	856.73	302.05	769.03	305.85	775.59
							302.40	768.75		
A	885.20		891.56		884.41		793.37		804.19	
B	-0.92402		-0.79343		-0.87671		-0.84124		-0.81454	
$ R $	0.99989		0.99992		0.99996		0.99986		0.99992	
$\sigma(\rho)$	0.09		0.05		0.04		0.05		0.05	

^a Literature values in parentheses: for T, EB and ECE, ref. 5; for TMB, ref. 6.

MATERIALS AND METHODS

1,3-Dioxolane (Fluka, purum > 99 mole%) was purified as described in ref. 3. *p*-Xylene, 1,2,4-trimethylbenzene and ethylbenzene (analytical grade 99.8%, 99.9% and 99.8%, respectively, all Kodak) were used without further purification. Also for toluene (Merck, analytical grade 99.8%), no purifica-

TABLE 2

Experimental excess molar enthalpies, H^E , for 1,3-dioxolane (1) + cyclic compound (2) systems

D + T		D + XY		D + TMB	
x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)
0.0598	22.3	0.0687	58.9	0.0368	62.5
0.1129	42.1	0.1286	107.9	0.0721	121.8
0.1603	62.2	0.1813	157.7	0.1029	164.3
0.2029	80.8	0.2279	201.8	0.1328	208.3
0.2764	112.0	0.3070	258.4	0.1867	264.4
0.3374	133.6	0.3713	301.6	0.2343	312.2
0.4331	158.7	0.4700	346.5	0.3146	366.4
0.5045	171.9	0.5414	357.1	0.3796	389.2
0.6044	176.7	0.6392	347.4	0.4786	404.1
0.6962	165.4	0.7266	308.6	0.5793	376.7
0.7534	146.5	0.7799	272.5	0.6474	344.3
0.8209	119.2	0.8417	212.0	0.7336	284.8
0.8594	97.4	0.8764	173.5	0.7860	238.0
0.9016	67.0	0.9140	123.5	0.8463	177.4
0.9245	49.2	0.9341	94.3	0.8802	136.7
0.9483	34.2	0.9551	61.9	0.9168	95.4
0.9735	17.0	0.9770	33.0	0.9566	50.9
D + EB		D + DMCE		D + ECE	
x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)	x_1	H^E (J mol ⁻¹)
0.0683	80.0	0.0796	486.1	0.0731	457.6
0.1278	146.6	0.1475	853.6	0.1457	855.3
0.1803	210.5	0.2061	1131.0	0.2037	1126.2
0.2267	255.7	0.2571	1257.9	0.2543	1305.9
0.3055	319.7	0.3418	1475.5	0.3463	1591.6
0.3697	348.8	0.4091	1585.7	0.4055	1720.3
0.4680	391.0	0.5095	1665.2	0.5058	1806.4
0.5397	400.6	0.5806	1640.3	0.5770	1784.8
0.6376	390.1	0.6750	1527.7	0.6718	1650.8
0.7252	346.9	0.7570	1325.4	0.7543	1434.9
0.7787	305.3	0.8060	1151.4	0.8037	1267.0
0.8408	242.8	0.8617	893.2	0.8599	994.8
0.8756	197.1	0.8926	717.3	0.8912	788.8
0.9135	135.8	0.9257	506.7	0.9247	542.1
0.9337	108.7	0.9433	391.8	0.9425	402.5
0.9548	69.3	0.9614	253.8	0.9609	264.8

tion was carried out. Ethylcyclohexane (Aldrich, purity > 99%) was further purified by azeotropic distillation with 2-ethoxyethanol. 1,4-Dimethylcyclohexane (Fluka, analytical grade, 99%) is a mixture of *cis*- and *trans*-isomers; density measurements revealed that the *cis*-*trans* molar ratio was about 2.2.

The densities, ρ , of the pure components, required for evaluating fluxes and hence mole fractions in the calorimetric measurements [4], were determined with a two-capillary glass pycnometer (volume, 31.41 ml at 298.15 K), calibrated with distilled mercury, and are shown in Table 1. Density values of MCE, D and XY do not appear in this table because they are reported in earlier papers [2,4,7] while those of T, TMB, EB, DMCE and ECE, determined at atmospheric pressure, were fitted by the equation

$$\rho(\text{kg m}^{-3}) = A + B(T(\text{K}) - 273.15) \quad (1)$$

Coefficients A and B , correlation coefficients $|R|$ and sample standard deviation $\sigma(\rho)$, obtained by a least-squares analysis, are given in Table 1.

Molar excess enthalpies were determined using an LKB flow microcalorimeter (Model 2107) described in ref. 8. Fully automatic burettes (ABU) (Radiometer, Copenhagen, Denmark), were used to pump the pure liquids into the flow-mixing cell. Details of the electrical calibration and analytical measurements are given in ref. 4. The calorimetric experiments were performed at 298.15 ± 0.01 K (IPTS-68).

The microcalorimeter was electrically calibrated before use and the calibration was subsequently checked using the well-known standard cyclohexane-hexane mixture [9]. Agreement with the literature data was less than 0.5% in the central range of molar composition.

The six isothermal sets of calorimetric data in Table 2 were correlated by the Redlich-Kister expression

$$H^E = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \quad (2)$$

where x_1 and x_2 are the molar fractions of D (component 1) and cyclic compounds (component 2), and the parameters a_k are obtained by the

TABLE 3

Coefficients, a_k , and standard deviations, $\sigma(H^E)$, determined by the least-squares method

System	a_0	a_1	a_2	a_3	a_4	a_5	σ
D+T	685.7	298.2	-18.9	-142.0	-209.1		1.7
D+XY	1406.6	453.4	-108.7	-120.0	-200.7		2.7
D+TMB	1607.2	-304.6	-109.5				2.6
D+EB	1579.8	291.7	312.1	-604.3			3.1
D+DMCE	6596.6	658.6	1846.7	-327.4	-1801.6		9.3
D+ECE	7178.1	606.1	974.9	5229.9	-1555.7	-7244.1	11.9

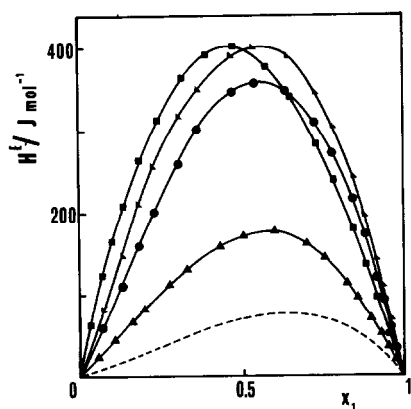


Fig. 1. Excess molar enthalpies, H^E , at 298.15 K, of 1,3-dioxolane (1)+ aromatic compound (2) vs. x_1 , the mole fraction of 1,3-dioxolane. Experimental results: — — —, benzene [1]; \blacktriangle , toluene; \blacktriangle , ethylbenzene; \bullet , *p*-xylene; \blacksquare , trimethylbenzene. Curves calculated by eqn. (2) with coefficients of Table 2.

least-squares method, with the following objective function to be brought to a minimum

$$\phi = \sum_{j=1}^{n_H} \eta_j^2 \quad (3)$$

$$\eta_j = \frac{H^E}{x_1 x_2} - \sum_{k \geq 0} a_k (x_1 - x_2)^k \quad (4)$$

where n_H is the number of calorimetric experimental points of each set of data.

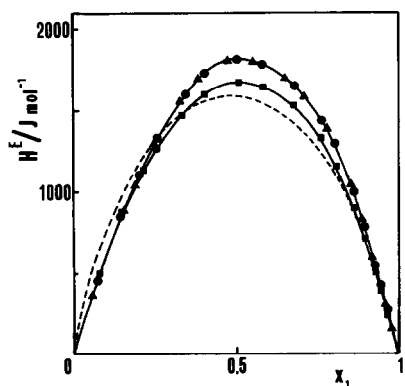


Fig. 2. Excess molar enthalpies, H^E , at 298.15 K, of 1,3-dioxolane (1)+ aliphatic cyclic compounds (2) vs. x_1 , the mole fraction of 1,3-dioxolane. Experimental results: — — —, cyclohexane [1]; \bullet , ethylcyclohexane; \blacktriangle , methylcyclohexane [2]; \blacksquare , 1,4 dimethyl-cyclohexane. Curves calculated by eqn. (2) with coefficients of Table 2.

The a_k values and the standard deviation $\sigma(H^E)$ defined as

$$\sigma(H^E) = |\phi/(N - n)|^{0.5} \quad (5)$$

with N being the number of experimental points and n the number of parameters, are reported in Table 3. In Figs. 1 and 2 the calculated curves are compared with the experimental data.

DISCUSSION OF THE RESULTS

From Figs. 1 and 2 it can be seen that all the mixtures discussed in this paper exhibit positive H^E values. Cyclic aliphatic compounds have nearly symmetric H^E vs. composition curves, whereas the curves for aromatic compounds seem to indicate a shift of skewness towards 1,3-dioxolane-rich compositions with increasing aromatic character of the compounds.

Cyclic aromatic compounds have H^E values lower than those of the aliphatic set and are more sensitive to the lateral groups (CH_3 or C_2H_5). These results can be explained, almost qualitatively, if H^E may be considered, to a first approximation, proportional to $E_{11} + E_{22} - 2E_{12}$, where E_{ij} represents the energy of molecular interactions between molecules i and j .

In fact, the electrons of the aromatic ring can interact with the 1,3-dioxolane molecule, with two negatively charged O atoms and a positively charged C atom between them, giving an increased value of E_{12} with respect to the aliphatic ring. The steric effect of the lateral groups and their negative effect on aromaticity may explain the increased H^E , because of the lowering of E_{12} in the presence of CH_3 and C_2H_5 .

In contrast, in aliphatic cyclic compounds, E_{11} and E_{22} interactions seem to prevail and relatively large H^E values are observed, with maximum values in the range 1600–1800 J mol^{-1} .

Furthermore, H^E should increase with increasing E_{22} , which is confirmed, with the exception of MCE, by the values of vaporization heats of the compounds (see Table 4) which are proportional, to a first approximation, to the energy, E_{22} , required to break the main molecular interactions in the liquid structure of aliphatic cyclic molecules [10].

TABLE 4

Vaporization heats, λ , of aliphatic cyclic compounds

Compound	λ (cal mol ⁻¹)	Maximum value of H^E (J mol ⁻¹)
Cyclohexane	7861 [5]	1590
MCE	8451 [5]	1810
DMCE	9050 [5]	1670
ECE	9720 [5]	1810

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