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Calorimetric study of binary mixtures containing chlorobenzene + linear and cyclic ethers

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Abstract

Excess molar enthalpies H^E of binary mixtures containing chlorobenzene + five ethers (oxolane, oxane, 1,4-dioxane, dimethoxymethane and 1,2-dimethoxyethane) were determined at atmospheric pressure and at 298.15 K by means of a flow microcalorimeter. Experimental H^E values were correlated by the Redlich–Kister equation and the results are interpreted in terms of molecular interactions. The influence of the structural parameters on H^E is assessed.

INTRODUCTION

This research was carried out as part of a long-term study [1–3] of the calorimetric properties of binary mixtures involving linear and cyclic ethers with the aim of investigating the nature of molecular interactions in these systems.

The present paper reports the results of the measurements for five binary mixtures formed by chlorobenzene with two linear and three cyclic ethers, namely dimethoxymethane, 1,2-dimethoxyethane, oxolane, oxane and 1,4-dioxane respectively. The chlorobenzene + 1,3-dioxolane mixture, studied in a previous paper [4], is also considered in the conclusion of this note.

The binary mixtures formed by cyclic ethers + 1-chloronaphthalene investigated in an earlier paper [1] and by cyclic ethers + benzene measured by other authors [5,6] are also considered.

We are not aware of any previous investigations of the excess enthalpies of the systems studied here, with the exception of the chlorobenzene + 1,4-dioxane mixture studied by Ruitz et al. [7] at 303.15 K.

MATERIALS AND METHODS

The samples of liquids and their methods of purification are the same as described elsewhere [3,4,8] and the densities required for evaluating fluxes and, hence, the mole fractions in the calorimetric measurements characterizing them [4] are also given in the same references.

Molar excess enthalpies were measured in an LKB flow microcalorimeter (Model 2107) as described elsewhere [9], and calorimetric measurements were performed at 298.15 ± 0.01 K (IPTS-68).

TABLE 1

Experimental molar excess enthalpies H^E for chlorobenzene(1) + linear and cyclic compound(2) systems

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
Chlorobenzene + dimethoxymethane					
0.0677	−26.1	0.3676	−104.2	0.7771	−51.1
0.1268	−47.5	0.4657	−110.8	0.8395	−33.1
0.1789	−64.4	0.5667	−105.6	0.8746	−20.2
0.2252	−76.7	0.6355	−92.6	0.9127	−10.8
0.3036	−92.2	0.7234	−69.2	0.9544	−2.7
Chlorobenzene + 1,2-dimethoxyethane					
0.0784	−166.5	0.3379	−655.3	0.7538	−532.2
0.1131	−250.3	0.4049	−709.0	0.8033	−431.5
0.1454	−327.0	0.5051	−741.6	0.8596	−311.9
0.2033	−457.5	0.6049	−704.4	0.8909	−240.0
0.2539	−539.8	0.6712	−645.7	0.9245	−159.2
				0.9608	−81.1
Chlorobenzene + oxolane					
0.0623	−166.3	0.3473	−716.5	0.7615	−479.8
0.0907	−249.0	0.4439	−762.2	0.8273	−349.0
0.1174	−321.0	0.5449	−734.8	0.8646	−277.2
0.1663	−443.5	0.6141	−679.6	0.9055	−175.5
0.2101	−536.2	0.7054	−571.4	0.9504	−85.5
0.2852	−653.0				
Chlorobenzene + oxane					
0.0741	−161.1	0.3903	−606.1	0.7935	−366.0
0.1072	−233.8	0.4899	−622.7	0.8521	−263.6
0.1380	−297.7	0.5903	−586.1	0.8848	−199.1
0.1936	−400.4	0.6576	−532.7	0.9202	−135.4
0.2425	−476.8	0.7424	−438.5	0.9584	−67.4
0.3244	−565.7				
Chlorobenzene + 1,4-dioxane					
0.0393	−16.4	0.2955	−84.4	0.7156	−104.7
0.0653	−23.4	0.3586	−99.6	0.7704	−97.4
0.1226	−37.8	0.4562	−112.7	0.8342	−79.3
0.1733	−48.7	0.5572	−115.0	0.9097	−46.1
0.2185	−60.1	0.6265	−112.6	0.9527	−24.1

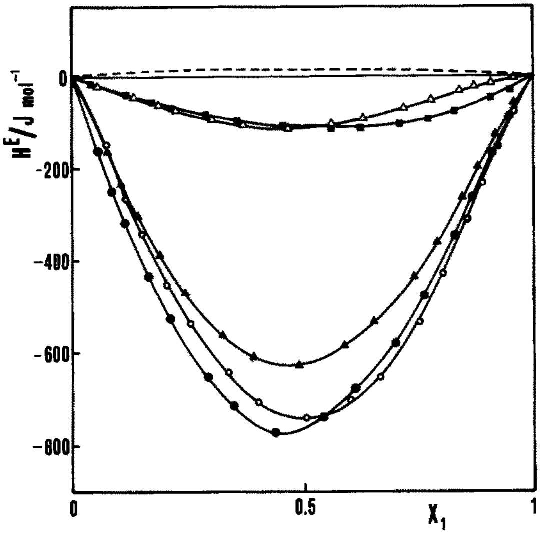

Fig. 1. Excess molar enthalpies H^E at 298.15 K of chlorobenzene (1)+linear and cyclic ethers (2) vs. x_1, the mole fraction of chlorobenzene. △, dimethoxymethane; ○, 1,2-dimethoxyethane; ●, oxolane; ▲, oxane; - - -, 1,3-dioxolane; ■, 1,4-dioxane. Curves calculated by eqn. (1) with coefficients of Table 2.

The Redlich–Kister smoothing polynomial

$$H^E = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \qquad (1)$$

where x_1 and x_2 are the mole fractions of chlorobenzene (component 1) and ether (component 2) respectively, and a_k are the adjustable parameters, was fitted to each set of results by the method of least-squares, with all points weighted equally.

Table 1 and Fig. 1 report the experimental data, while parameters a_k, based on the lowest values of standard deviation

$$\sigma(H^E) = |\phi/(N-n)|^{0.5} \qquad (2)$$

where ϕ is the objective function, N is the number of experimental points and n the number of parameters, are listed in Table 2.

TABLE 2

Coefficients a_k and standard deviation $\sigma(H^E)$ determined by the least-squares method for chlorobenzene(1)+linear and cyclic ethers(2)

Component 2	a_0	a_1	a_2	a_3	σ
Dimethoxymethane	−441.1	76.1	236.2	148.9	0.9
1,2-Dimethoxyethane	−2943.0	1225.0			3.5
Oxolane	−3011.7	563.8	1039.7		3.2
Oxane	−2482.7	308.7	742.3		1.6
1,4-Dioxane	−458.9	−52.8	−610.4	740.3	0.9

DISCUSSION OF THE RESULTS

Figure 1 shows that all the mixtures considered in this paper show an exothermic calorimetric effect. Diethers, 1,3-dioxolane and 1,4-dioxane, show more negative enthalpies of mixing than the corresponding monoethers, oxolane and oxane, because the double oxygen atom leads to stronger interactions with chlorobenzene. The same trend has been observed when these compounds are mixed with benzene [5,6] whereas 1-chloronaphthalene behaves differently when mixed with oxane and 1,4-dioxane, probably due to the steric effects of the second benzenic ring on the interaction between the ether and the planar 1-chloronaphthalene.

For the linear diethers, 1,2-dimethoxyethane has a more negative H^E value than dimethoxymethane in the binary mixture with chlorobenzene because the first molecule is less rigid and may overlap easily with the chlorobenzene molecule, giving rise to stronger interactions and a large value of the energy term E_{12} contributing to H^E, if we consider that approximately [10]

$$H^E \alpha E_{11} + E_{22} - 2E_{12} \tag{3}$$

where E_{ij} is the energy interaction between molecules i and j.

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