J. Chem. Eng. Data 1986, 31, 250-252

Liquid-Phase Enthalpy of Mixing for the System 1,3-Dioxolane–Chlorobenzene in the Temperature Range 288.15–313.15 K

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The molar heat of mixing ΔH_m for the system 1,3-dioxolane (1)–chlorobenzene (2) was determined with an LKB flow microcalorimeter as a function of composition in the temperature range T = 288.15–313.15 K. ΔH_m vs. molar fraction x_1 data were correlated by means of the Redlich–Kister empirical expression $\Delta H_m = x_1x_2\sum_{k=0}^{\infty}c_k(x_1 - x_2)^k$ and the adjustable parameters were evaluated by the least-squares method. At about T = 298.15 K the mixture is athermic, whereas small hexothermal and endothermal effects are measured at temperatures below and above T = 298.15 K. A comparison with the results of vapor–liquid experiments on the same system is given.

Introduction

The present work concerns a study on the calorimetric behavior of the binary liquid mixtures of 1,3-dioxolane and chlorobenzene aiming at collecting further information on this system which the vapor–liquid equilibrium (VLE) data have revealed to be very complex, with possible association between the components (*1*).

The enthalpy of mixing of several binary systems containing 1,3-dioxolane was obtained by Inglese et al. (*2*). The mixture 1,3-dioxolane–water is noteworthy for the characteristic curve of the enthalpy of mixing showing a sign inversion with composition (*3*, *4*).

Experimental Section

Chemicals Used. The source and the purification procedure of 1,3-dioxolane and chlorobenzene are quoted in ref *1*. 1,3-Dioxolane is component 1.

Calorimetric Measurements. The molar liquid-phase enthalpy of mixing ΔH_m for the system 1,3-dioxolane–chlorobenzene was determined by means of a flow microcalorimeter (Model 2107, LKB-Produkter AB.Bromme, Sweden). For a detailed description of this apparatus, see ref *5*.

Fully automatic burets (ABU, from Radiometer, Copenhagen) were used to pump the liquids into the LKB unit; volume of cylinder = 2.5 mL.

Table I and Figure 1 show the values of ΔH_m at T = 288.15, 298.15, 298.65, 303.15, and 313.15 K, for increasing molar fractions of 1,3-dioxolane.

The accuracy of the LKB bath temperature is 0.1 K; the ambient was kept at 294.15 K over 24 h. Calibration of the equipment was achieved with reference to the very accurate heat of dilution ΔH_d of HCl in water (*6*).

For this system one also has the extensive tabulation of density vs. composition data (*6*), which is necessary to evaluate the mole fraction of the sample in the calorimetric measurement (see eq 1 and 2). HCl 1 N at T = 293.15 K (molality 0.98711) was brought, by increasing dilution with bidistilled water at T = 298.15 K, to molality 0.333. The values of ΔH_d obtained are mean values taken from two experiments and are in agreement to within 1% with the above-mentioned literature data.

All measured calorimetric data refer to 1 M unit of HCl and of 1,3-dioxolane–chlorobenzene mixture, for dilution and mixing heats, respectively.

The molar thermal effect ΔH is evaluated from the formula

$$\Delta H = I^2R(E/E_c)/n \tag{1}$$

where I and R are the electric current intensity and resistance in the electrical calibration experiment, E and E_c are the instrumental readings for measurement and electrical calibration and n is the number of moles of the reference sustance. The moles n_k of component k pumped per second into the mixing cell is given by

$$n_k = \frac{\rho_k}{M_k}v_k\frac{2.5F}{6000} \tag{2}$$

where ρ_k and M_k are density and molecular weight, v_k is the actual percent of the buret flow rate selected between two reference values (F = 1 and F = 0.1, corresponding to 2.5 and 0.25 mL/min).

The mole fraction of 1,3-dioxolane, $x_1 = n_1/n$, calculated from eq 2 has been compared with the one measured directly with an Abbe refractometer (*7*), taking the outlet mixed solution coming from the calorimetric cells, after prolonged rinsing of tubing to expel previous liquids. As an example, the results over at least 10 successive refractometer measurements were, for 1,3-dioxolane–chlorobenzene mixture at T = 298.15 K, $\bar{x}$ = 0.5246 and s = 0.0028, $\bar{x}$ and s being the average value and root-mean-square deviation, whereas the molar fraction calculated through eq 2 is 0.5231. A slightly higher discrepancy, about 0.5%, between the two $\bar{x}$'s is found for the extreme values of the molar fractions. Hence, only three significant figures were retained for x_1 in Table I. The experimental uncertainty on the ΔH values can be evaluated from eq 1 considering the contribution of all terms (assumed as independent random variables) to the sample variance $s^2(\Delta H)$ (*8*); that is

$$\frac{s^2(\Delta H)}{(\Delta H)^2} = \frac{s^2(\Sigma)}{\Sigma^2} + \frac{s^2(E)}{E^2} + \frac{\sum_{k=1}^{2}\left(\frac{\rho_k}{M_k}\Phi_k v_k\right)^2}{\sum_{k=1}^{2}\left(\frac{\rho_k}{M_k}v_k\right)^2} \tag{3}$$

where

$$\Sigma = I^2R/E_c \tag{4}$$

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Table I. Molar Liquid-Phase Enthalpy of Mixing ΔH_m (J mol^{-1}) for the System 1,3-Dioxolane (1)–Chlorobenzene (2), as a Function of the Molar Fraction x_1[a]

T = 288.15 K		T = 298.15 K		T = 298.65 K		T = 303.15 K		T = 313.15 K	
x_1	$-\Delta H_m$	x_1	$-\Delta H_m$	x_1	ΔH_m	x_1	ΔH_m	x_1	ΔH_m
0.044	2.7	0.109	2.7	0.109	1.6	0.109	11.1	0.044	11.8
0.109	8.2	0.109	3.0	0.459	3.7	0.109	16.1	0.108	23.7
0.196	17.3	0.196	5.2	0.594	4.2	0.328	19.2	0.195	33.6
0.328	26.9	0.328	10.9	0.898	1.1	0.422	19.7	0.327	37.8
0.423	29.4	0.422	12.8			0.422	20.1	0.421	39.9
0.523	28.3	0.523	11.8			0.513	20.3	0.522	38.9
0.595	26.5	0.523	12.0			0.594	19.7	0.522	38.5
0.746	17.0	0.594	9.4			0.745	18.7	0.594	37.7
0.815	12.8	0.745	5.1			0.898	11.4	0.745	29.9
0.898	5.5	0.814	2.0			0.959	4.6	0.814	26.7
0.959	2.8	0.898	0.1					0.897	16.2
		0.959	0.1					0.959	6.4
$c_0 = -118.1 \pm 0.6$		$c_0 = -47.4 \pm 0.2$		$c_0 = 15.9 \pm 0.2$		$c_0 = 80.9 \pm 0.4$		$c_0 = 156.5 \pm 0.8$	
$c_1 = 37.0 \pm 1.8$		$c_1 = 27.8 \pm 0.8$		$c_1 = -1.4 \pm 0.4$		$c_1 = 1.2 \pm 0.9$		$c_1 = -12.0 \pm 3.0$	
$c_2 = 66.2 \pm 1.2$		$c_2 = 52.7 \pm 0.6$		$c_2 = -3.2 \pm 0.6$		$c_2 = 56.1 \pm 1.6$		$c_2 = 84.8 \pm 2.4$	
$c_3 = -42.6 \pm 2.7$		$c_3 = -19.9 \pm 1.5$						$c_3 = -60.5 \pm 5.1$	
$\sigma = 0.51$		$\sigma = 0.42$		$\sigma = 0.41$		$\sigma = 0.49$		$\sigma = 0.58$	

[a] The c_k's are the calculated parameters of the Redlich–Kister correlating expression. σ is the root-mean-square deviation. c_k (k = 0, 1, 2, 3) in J mol^{-1}; σ in J mol^{-1}.

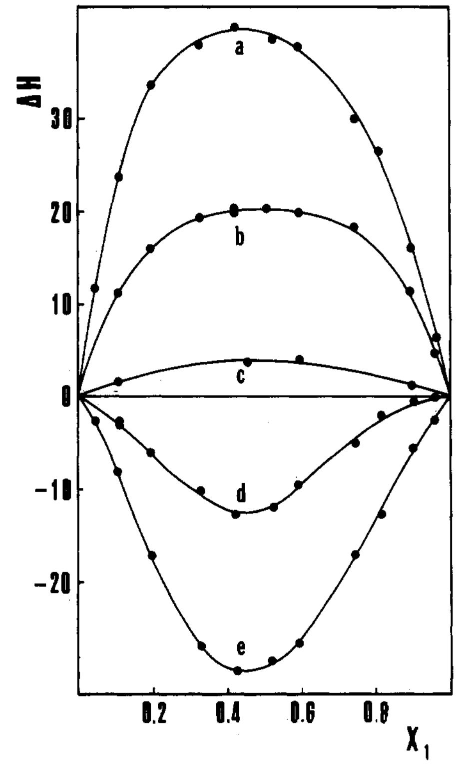

Figure 1. Molar heat of mixing ΔH_m (J mol^{-1}) for the system 1,3-dioxolane (1)–chlorobenzene (2) as a function of the molar fraction x_1, in the temperature range T = 288.15–313.15 K. Fitted curves are calculated with the parameters of Table I. a, b, c, d, e: curves at T = 288.15, 298.15, 298.65, 303.15, and 313.15 K.

and Φ_k is obtained from the buret specification as

$$10^3\Phi_k = 3 + 2.222(1 - F) + \frac{0.7 - 0.611(1 - F)}{\nu_k t} \qquad (5)$$

with

$$\nu_k = 2.5F v_k/6000 \qquad (6)$$

and t the time (s) during which a constant rate of heat evolved or adsorbed is recorded. From the technical specifications of the LKB apparatus we have for the first term of eq 3 $s^2(\Sigma)/\Sigma^2 \simeq 10^{-4}$, and the second term of eq 3, after analysis of several repeated measurements, resulted in the order of 10^{-5}.

Following the same procedure, the sample variance of the mole fraction of 1,3-dioxolane, when evaluated from eq 2, is given by

$$s^2(x_1) = x_1^2(1 - x_1)^2(\Phi_1^2 + \Phi_2^2) \qquad (7)$$

Calculation of estimated uncertainties on ΔH_m and x_1 through eq 3 and 7 gave for 1,3-dioxolane–chlorobenzene mixtures these results: $s(\Delta H) \simeq 0.1$ and $s(x_1) \simeq 10^{-3}$.

Density Measurements of Pure Components. The densities of pure liquid components ρ_1 and ρ_2 appearing in eq 2 and 3 were determined as functions of temperature with a glass two-capillary pycnometer calibrated with distilled mercury (pycnometer volume = 31.41 mL at T = 297.45 K).

The following empirical straight lines fit the experimental data for 1,3-dioxolane and chlorobenzene in the temperature range 288.15–313.15 K

$$\rho_1\ (\text{kg m}^{-3}) = 1089.83 - 1.23358T\ (\text{K}) \qquad (8)$$

$$\rho_2\ (\text{kg m}^{-3}) = 1126.64 - 1.06560T\ (\text{K}) \qquad (9)$$

with correlation coefficients −0.99971 and −0.99996 and a maximum deviation between calculated and experimental values of density given by 0.43 and 0.12, respectively.

Correlation of Molar Heat of Mixing Data. The data of Table I were correlated by means of the Redlich–Kister empirical expression

$$\Delta H_m = x_1x_2\sum_{k=1}^{\infty} c_k(x_1 - x_2)^k \qquad (10)$$

where the c_k's are the adjustable parameters given in Table I, together with their estimated errors, and obtained by a least-squares analysis. The objective function, which is minimized for each set of isothermal data, is chosen as

$$\Phi = \sum_{K=1}^{n} W\left(\frac{\Delta H_{m,\text{calcd}}}{x_1x_2} - \frac{\Delta H_{m,\text{exptl}}}{x_1x_2}\right)^2 \qquad (11)$$

The root-mean-square deviation σ, reported in Table I, is defined as $(\Phi_{\min}/(n - n_c))^{0.5}$, with n_c the number of adjustable parameters and $\Phi_{\min}$ the value of Φ at its minimum. W is the weight of each experimental $\Delta H_m/(x_1x_2)$ calculated from the sample variance $s^2(\Delta H)$ of eq 3.

The use of unit weight in eq 11, however, leads only to small variations in σ and slight differences in the parameters and in the calcualted values of the heat of mixing respect to the case of $W \neq 1$ (*1*).

Four parameters afforded the best correlation of the data at T = 288.35 and 313.15 K, whereas three parameters were sufficient at T = 298.15 K and the same number of parameters was chosen for the mixture at T = 298.65 K for which only four experimental data were available.

Conclusions

From Table I and Figure 1 we note the following:

The sign of ΔH_m is changed as a function of the temperature, the mixture being athermic near T = 298 K, whereas exothermal and endothermal effects are measured below and above this temperature.

The molar enthalpies of mixing ΔH_m of the system 1,3-dioxolane-chlorobenzene are small, with a maximum value of about 40 J mol^{-1} in the temperature range 288.15-313.15 K. For comparison, the corresponding maximun value of ΔH_m for the system 1,3-dioxolane-water at T = 318 K is about 900 J mol^{-1}. However, these low values of ΔH_m are coupled with liquid-phase activity coefficients up to 1.9 and 1.5 for 1,3-dioxolane and chlorobenzene, as evaluated by VLE measurements in the previous work (*1*).

Thus, we must think in terms of a balance between interaction and free volume contribution to ΔH_m rather than feeble interactions between molecules in a nearly ideal solution.

Registry No. PhCl, 108-90-7; 1,3-dioxolane, 646-06-0.

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Received for review June 3, 1965. Revised manuscript received October 1, 1985. Accepted October 23, 1985. This work was funded by Consiglio Nazionale delle Ricerche, Roma, Italy, "Progetto Finalizzato Chimica Fine e Secondaria", Grant No. 82.00596/95.

NEW COMPOUNDS

Organic Disulfides and Related Substances. 45. Synthesis and Properties of Some Disulfide Sulfinate Salts Containing No Nitrogen

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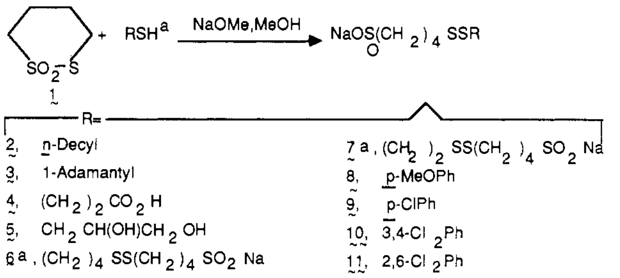
Disulfide sulfinates of the structure $RSS(CH_2)_4SO_2Na$ were synthesized by reaction of 1,2-dithiane 1,1-dioxide (1), thiols, and sodium methoxide in methanol. Disproportionation was minimized by precipitating and reprecipitating the products with ether as quickly as possible; where R = aryl, protection from light is advisable. The groups R typify large lipophilic ones (*n*-decyl, 1-adamantyl), small hydrophilic ones (2-carboxyethyl, 2,3-dihydroxypropyl), disulfide sulfinates [$(CH_2)_nSS(CH_2)_4SO_2Na$], and aryl groups substituted by electron-donating or electron-withdrawing groups. The products usually were quite hygroscopic and were isolated as hydrates. They disproportionated with varying ease in aqueous solution either to 1 or to the two symmetrical disulfides, RSSR and $NaO_2S(CH_2)_4SS(CH_2)_4SO_2Na$.

Introduction

Several disulfide sulfinate salts of the general structure $RSS(CH_2)_4SO_2Na$ afford promising mammalian protection against ionizing radiation (*1-6*). This paper reports new types of disulfide sulfinates obtained by reaction of 1,2-dithiane 1,1-dioxide (**1**) with heretofore unexplored types of thiols, in a search for radioprotective agents that lack the nitrogen functions believed to cause adverse effects (Scheme I); once optimum thiols are known, the model dioxide **1** can be replaced by other dioxides. Stability of **2-11** in solution was examined, since this property is clearly important in biological administration, is probably so in biological activity (cf. ref *6*), and is chemically significant for clarification of factors involved in disproportionation to symmetrical disulfides.

Scheme I



[a] For 6, R of $RSH = HS(CH_2)_4$. For 7, R of $RSH = HS(CH_2)_2$. For other thiols, R of RSH has the same structure R shown for the product.

Results and Discussion

Apparent advantages of high lipophilicity for antiradiation activity (*7*) made the *n*-decyl and 1-adamantyl groups attractive (Scheme I, **2** and **3**). To assess the effect of small hydrophilic groups, **4** and **5** were synthesized; only 1 equiv of base was used for **4** (cf. ref *4*), since the carboxylate ion first engenders

0021-9568/86/1731-0252$01.50/0