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Excess Enthalpy for the Binary System 1,3-Dioxolane + Halothane

Romolo Francesconi*

Dipartimento di Chimica G. Ciamician, Università degli Studi, via Selmi 2, 40126 Bologna, Italy

Fabio Comelli

Centro di Studio per la Fisica delle Macromolecole del C.N.R., via Selmi 2, 40126 Bologna, Italy

Daria Giacomini

Istituto dei Composti del Carbonio del C.N.R. (ICOCEA), Ozzano Emilia, Bologna, Italy

The excess molar enthalpies H^E of the 1,3-dioxolane + halothane binary system were determined at atmospheric pressure, at 288.15 and 298.15 K by an isothermal flow microcalorimeter. The mixtures studied are highly exothermic, $H^E < 0$, with almost symmetrical H^E vs composition curves and with positive molar excess heat capacity, $C_p^E = dH^E/dT$. This suggests complex formation in the liquid mixture, via hydrogen bonding.

Introduction

In a continuing effort to measure the thermodynamic properties of 1,3-dioxolane + solvent mixtures (*1–3*), we now report the liquid-phase excess enthalpy (enthalpy of mixing) H^E of the 1,3-dioxolane + halothane binary system.

Materials

1,3-Dioxolane (Fluka product; purum, analytical grade 99%) was purified as described previously (*4*) by refluxing for about 10 h on Na wires in an N_2 flow, excluding moisture. It was then fractionated on a Vigreux column.

Halothane, (2-bromo-2-chloro-1,1,1-trifluoroethane) (Aldrich product; analytical grade 99%, stabilized with 0.01% thymol), a particularly nonexplosive useful inhalation anesthetic, was distilled through phosphorus pentoxide and subsequently fractionated through a vacuum-jacketed column. The fraction boiling at 323.35 ± 0.2 K was collected and stored in the dark over type 4A molecular sieves (C. Erba product). For both reagents, gas chromatography analysis failed to show any significant impurities.

Density Measurements

The densities ρ of the pure liquids are necessary to evaluate fluxes in the calorimetric measurements and were determined as a function of temperature with a glass two-capillary pycnometer calibrated with distilled mercury. Temperature stabilization is within 0.05 K. The estimated average uncertainty of ρ is 0.3 kg m^{-3}. The measured density of halothane is shown in Table I, while that of 1,3-dioxolane has been reported in an earlier work (*5*). The density values for halothane were fitted by the straight line

$$\rho/(\text{kg m}^{-3}) = 2685.52 - 2.7856(T/\text{K}) \qquad (1)$$

with correlation coefficient 0.999 776 and standard deviation 0.4 kg m^{-3}. The agreement with literature data (*6*, *7*) is shown in Table I.

Table I. Experimental Density ρ of Pure Halothane as a Function of Temperature T

T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})
291.15	1872.1	303.55	1840.2
292.65	1870.3	304.75	1837.3
293.15	1869.0[a]	306.95	1830.8
293.45	1868.0	309.55	1823.1
294.55	1864.6	310.35	1821.3
296.15	1860.6[b]	311.65	1817.2
298.65	1852.1	312.65	1814.6
299.65	1851.0	313.45	1811.7
300.75	1848.2	314.15	1810.4

[a] At T = 293.15, ρ = 1871 kg m^{-3} (*6*). [b] At T = 295.15, ρ = 1860 kg m^{-3} (*7*).

Table II. Experimental Excess Enthalpies H^E of 1,3-Dioxolane (1) + Halothane (2) as a Function of the Mole Fraction X_1 of 1,3-Dioxolane, at Temperature T, Coefficients a_k, Equation 2, and Standard Deviation σ, Equation 5

T = 288.15 K		T = 298.15 K	
X_1	$-H^E$/(J mol^{-1})	X_1	$-H^E$/(J mol^{-1})
0.0594	438	0.0453	356
0.0769	583	0.0594	463
0.1428	969	0.1122	832
0.2748	1693	0.2022	1364
0.3357	1873	0.2755	1654
0.4312	1980	0.3365	1764
0.5026	1988	0.4320	1889
0.6026	1752	0.5034	1887
0.6948	1436	0.6034	1746
0.7520	1244	0.6697	1527
0.8017	1019	0.7526	1228
0.8584	771	0.8022	1021
0.9010	564	0.8203	944
0.9479	366	0.8589	760
0.9733	213	0.9579	313
$a_1 = -7916$ $a_3 = 2113$ $a_5 = -1387$	$a_2 = 2167$ $a_4 = -1152$ $a_6 = -2768$	$a_1 = -7568$ $a_3 = 1029$ $a_5 = -1675$	$a_2 = 1177$ $a_4 = 3374$ $a_6 = -5337$
σ = 22 J mol^{-1}		σ = 15 J mol^{-1}	

Calorimetric Measurements

The enthalpy of mixing was measured at T = 288.15 and 298.15 K by a flow microcalorimeter Model 2107, LKB Produkter AB (Sweden). The microcalorimeter was electrically calibrated (*5*) before use and the calibration subsequently checked by using the standard cyclohexane + hexane mixture (*8*). The discrepancy between the measured and published values was less than 0.5% over the central range of concentration. The estimated accuracy of the calorimetric data is about 1% (never exceeding 2% for dilute samples of both components).

The experimental H^E values are given in Table II. Measurements were also performed at 318.15 K but were rejected because some degradation of halothane (development of bromine) was observed. This phenomenon did not occur during the density measurements since in this case a good light protection of the product was possible.

The Redlich-Kister smoothing function

$$H^E/(\mathrm{J\ mol^{-1}}) = X_1X_2\sum_{k=1}^{n} a_k(X_1 - X_2)^{k-1} \tag{2}$$

where n is the number of coefficients a_k, was fitted to both sets of results by the least squares method. The objective function used was

$$\phi = \sum_{j=1}^{N} W_j\eta_j^2 \tag{3}$$

where N is the number of calorimetric experimental points and

$$\eta_j = \frac{H^E}{X_1X_2} - \sum_{k=1}^{n} a_k(X_1 - X_2)^{k-1} \tag{4}$$

The a_k values and the standard deviation σ, defined as

$$\sigma = [\phi/(N - n)]^{0.5} \tag{5}$$

are listed in Table II. The data were correlated via a six-parameter Redlich-Kister equation, ensuring a value of σ close to the experimental uncertainty of H^E, calculated through the formula given in ref 6. The calculation procedure is the same as that reported in ref 5, giving also details on the estimation of weights W_j.

Conclusions

As shown in Table II and Figure 1, the 1,3-dioxolane + halothane system is strongly exothermal. At both temperatures, the H^E vs X_1 curves are almost symmetrical, with minima at values of X_1 slightly below 0.5, increasing slowly with the rise in temperature (that is, $C_p{}^E = dH^E/dT > 0$).

This suggests complex formation, most probably of a hydrogen bond type, between the H atom of halothane (owing to the presence of the strong electronegative three F atoms) and the O atoms of 1,3-dioxolane.

In a future work, spectroscopic measurements will be performed to confirm these qualitative considerations with the intent of better defining the association pattern of the system.

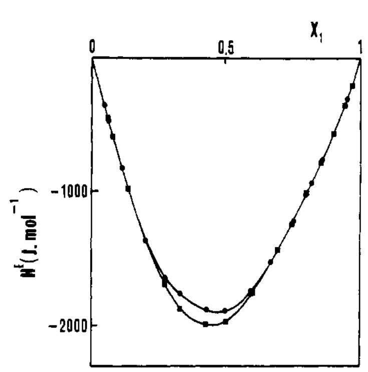

Figure 1. Molar excess enthalpies H^E of the 1,3-dioxolane (1) + halothane (2) system as a function of the mole fraction X_1 of 1,3-dioxolane. Key: experimental values, (■) at 288.15 K, (●) at 298.15 K; (—) calculated by eq 2 with the parameters a_k of Table II.

Glossary

a_k	parameters in eq 2
H^E	molar excess enthalpy of mixing, J mol^{-1}
N	number of calorimetric experimental data
n	number of parameters a_k
T	absolute temperature, K
W_j	weight of residual η_j, eq 3
X_1	mole fraction of 1,3-dioxolane
X_2	mole fraction of halothane

Greek Letters

ρ	density, kg m^{-3}
ϕ	objective function, eq 3
σ	standard deviation, eq 5
η	residual, eq 4

Registry No. 1,3-Dioxolane, 646-06-0; halothane, 151-67-7.

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