1056 J. Chem. Eng. Data 1995, 40, 1056–1057

Excess Molar Enthalpies of Chloroalkanes or Chloroalkene + 2-Propyn-1-ol at 298.15 K

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Excess molar enthalpies for 2-propyn-1-ol + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, and + trichloroethylene have been measured at 298.15 K with a Parr 1451 solution calorimeter. The excess molar enthalpies are positive over the entire range of composition.

Introduction

A survey of the literature has shown that the enthalpies of binary mixtures of haloalkanes, haloalkenes, and chlorobenzene with 1-propanol has been studied (Chaudari and Katti, 1990; Nagata and Tamura, 1988; Rambabu et al., 1990; Wang et al., 1990). No excess molar enthalpy measurements for 2-propyn-1-ol with chloroalkanes and chloroalkene are reported. We report here excess molar enthalpies for the systems of 2-propyn-1-ol + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, and + trichloroethylene at 298.15 K.

Experimental Section

The chemicals used were purified by the standard methods described by Riddick et al. (1986). 2-Propyn-1-ol (Fluka, >99 mol % pure) was fractionally distilled twice, and the middle fraction of the second distillation was collected. 1,2-Dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and trichloroethylene were purified as described earlier (Vijayakumar et al., 1995). The purity of the chemicals was checked by comparing their measured densities and refractive indices with literature values (Riddick et al., 1986; Vijayakumar et al., 1995). The measured values are in agreement with the literature data within ±0.1% as shown in Table 1.

Table 1. Experimental Densities ϱ and Refractive Indices n_D at 298.15 K Compared with Literature Values

	ϱ/(kg·m^{-3})		n_D	
component	present work	lit.[a]	present work	lit.[a]
2-propyn-1-ol	0.945 2	0.945 0	1.430 1	1.430 0
1,2-dichloroethane	1.246 82	1.246 37	1.442 10	1.442 16
1,1,1-trichloroethane	1.329 50	1.329 90	1.435 90	1.435 88
1,1,2,2-tetrachloroethane	1.586 66	1.586 28	1.491 40	1.491 87
trichloroethylene	1.614 32	1.614 18	1.503 20	1.503 18

[a] Savini et al. (1966).

Excess enthalpies were measured using a Parr 1451 solution calorimeter. The calorimeter consists of a glass Dewar mixing chamber with a rotating sample cell, a thermistor probe, and a specially designed temperature-measuring bridge, all assembled in a compact cabnet. The temperature change can be plotted directly using a strip chart recorder and can be read to an accuracy of ±0.001 K. The two-piece cell serves as both the sampler holder and agitator. It is closed with a detachable Teflon disk. The liquid sample can be added to the cell from a pipet inserted through the top stem. Excellent thermal insulation is provided by the fully silvered glass Dewar mixing chamber. It can contain from 90 to 120 cm^3 of solvent. Temperatures are measured with a glass-sheathed thermister probe, combined with a special bridge designed for a linear response over the range from 298.15 to 303.15 K with the bridge adjusted so that 100 μV represents a temperature change of exactly 0.001 K. The output of the bridge is connected to a strip chart recorder, allowing the temperature change to be measured within an accuracy of ±1%. The experimental error of excess molar enthalpies H_m^E is estimated to be <1% by comparison of our results on (x) benzene + $(1 - x)$ carbon tetrachloride and (x) toluene + $(1 - x)$ chlorobenzene with literature data (Savini et al., 1966; Tanaka and Benson, 1976; Stokes and Marsh, 1972). The compositions reported are accurate to ±0.1%. The components are combined in the Dewar mixing chamber, and the resulting temperature change is measured with the thermister probe. At the start of the experiment, one of the liquids is held in a sealed glass rotating cell in thermal contact with the other component. When the system comes to thermal equilibrium, the contents of the rotating cell are mixed with the surrounding liquid. The temperature changes due to the mixing process are sensed by the thermistor and recorded on the strip chart recorder. The excess molar enthalpy H_m^E is calculated.

Results and Discussion

The experimental results for H_m^E of 2-propyn-1-ol + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, and + trichloroethylene at 298.15 K are given in Table 2 and shown in Figure 1. The results were fitted by the method of least square to the equation

$$H_m^E/(\mathrm{J{\cdot}mol^{-1}}) = (1 - x)x\sum h_j(2x - 1)^j \qquad (1)$$

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0021-9568/95/1740-1056$09.00/0

Table 2. Excess Molar Enthalpies H_m^E for Chloroalkanes or Chloroalkene + 2-Propyn-1-ol at 298.15 K

x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})
			(1 − x)1,2-Dichloroethane + (x)2-Propyn-1-ol						
0.0760	582.0	0.2811	1068.7	0.4904	1118.4	0.7180	836.2	0.9107	330.4
0.1432	835.7	0.3477	1101.1	0.5654	1051.3	0.7802	699.3	0.9793	58.0
0.2139	984.0	0.4186	1086.1	0.6308	966.4	0.8432	522.4		
			(1 − x)1,1,1-Trichloroethane + (x)2-Propyn-1-ol						
0.0447	493.1	0.2904	1008.8	0.4782	1031.6	0.6281	895.6	0.8313	559.8
0.1471	831.7	0.3490	1042.9	0.4966	1007.0	0.6962	811.3	0.9161	309.0
0.2182	939.4	0.4121	1046.9	0.5635	963.0	0.7713	717.2	0.9814	69.1
			(1 − x)1,1,2,2-Tetrachloroethane + (x)2-Propyn-1-ol						
0.0382	402.1	0.2081	800.9	0.4212	673.2	0.6188	463.1	0.8383	148.5
0.1004	657.5	0.2655	796.7	0.4849	632.4	0.7017	338.8	0.9099	64.8
0.1358	745.8	0.3436	747.7	0.5437	563.2	0.7732	233.3	0.9802	6.6
			(1 − x)Trichloroethylene + (x)2-Propyn-1-ol						
0.0756	552.4	0.2724	875.2	0.4871	930.7	0.6357	871.6	0.8452	506.5
0.1480	723.2	0.3371	913.0	0.4971	949.5	0.6989	786.6	0.9013	348.5
0.2076	816.8	0.4201	938.1	0.5596	924.1	0.7743	663.4	0.9670	131.6

Table 3. Parameters h_j and Standard Deviation [$\sigma(H_m^E)$] from Eq 1 (T = 298.15 K)

system	h_0	h_1	h_2	h_3	h_4	h_5	$100\sigma(H_m^E)$
(x)2-propyn-1-ol + (1 − x)1,2-dichloroethane	4340.58	−1376.91	1676.89	1042.52	882.89	−4049.05	4.09
(x)2-propyn-1-ol + (1 − x)1,1,1-trichloroethane	4111.23	−1559.09	187.38	2259.40	5039.05	−6757.54	2.39
(x)2-propyn-1-ol + (1 − x)1,1,2,2-tetrachloroethane	2504.07	−2561.97	−133.70	481.84	4477.63	−4717.43	5.88
(x)2-propyn-1-ol + (1 − x)trichloroethylene	3782.66	57.97	690.75	−3204.47	3082.98	−	2.03

[a] $\sigma(H_m^E) = [[\Sigma\{(H_m^E(\text{exp}) - H_m^E(\text{calcd}))/H_m^E(\text{exp})\}]/(n-p)]^{1/2}$.

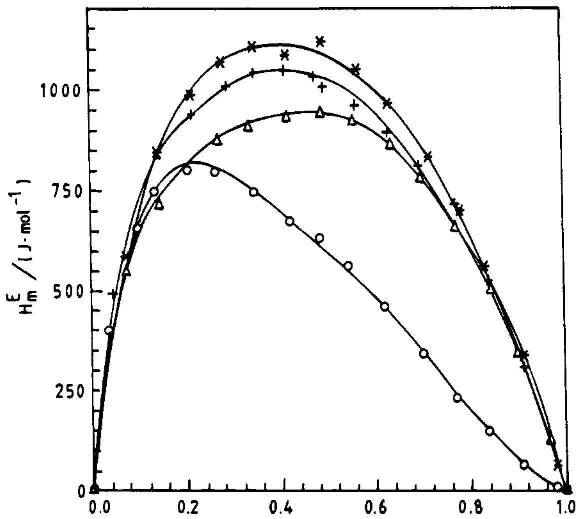

Figure 1. H_m^E versus x for the following systems at 298.15 K (*) $HC{\equiv}CCH_2OH$ (x) + ClH_2CCH_2Cl (1 − x), (+) $HC{\equiv}CCH_2OH$ (x) + Cl_3CCH_3 (1 − x), (○) $HC{\equiv}CCH_2OH$ (x) + $Cl_2HCCHCl_2$ (1 − x), (△) $HC{\equiv}CCH_2OH$ (x) + $Cl_2C{=}CHCl$ (1 − x).

Where x is the mole fraction of 2-propyn-1-ol. The coefficients h_j along with the standard deviation $\sigma(H_m^E)$ are included in Table 2. For the systems studied, the excess enthalpies at 298.15 K are endothermic. According to our results for the systems studied, the excess enthalpies may be influenced by the dissociation of self-associated alcohols by chloroalkanes and chloroalkene and reduction in dipole−dipole interaction between like molecules. The excess enthalpies for 2-propyn-1-ol with chloroalkane and chloroalkene are in the following order: 1,2-dichloroethane (1118.4) > 1,1,1-trichloroethane (1046.0) > trichloroethylene (949.5) > 1,1,2,2-tetrachloroethane (800.9). The maximum H_m^E values are observed at 0.5 mole fraction of 2-propyn-1-ol.

Acknowledgment

The authors gratefully acknowledge Dr. A. Rajiah, Scientist, IICT, for his helpful suggestion.

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Received for review December 28, 1994. Accepted April 4, 1995.[⊗]

JE9402839

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.