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Excess enthalpies of 2-alkoxyethanols with trichloroethylene and tetrachloroethylene at 298.15 K

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Abstract

Excess enthalpies H^E for binary mixtures of tricholorethylene and tetrachloroethylene with 2-alkoxyethanols at 298.15 K have been measured over the entire range of composition with Parr's 1451 solution calorimeter. The alkoxyethanols were 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol. The H^E values are positive for the systems tetrachloroethylene + 2-alkoxyethanols, and a change in sign from negative to positive is observed for the systems trichloroethylene + 2-alkoxyethanols. The measured excess enthalpies decrease as the chain length of the alkoxyethanol increases.

Keywords: Alkoxyethanol; Binary system; Calorimeter; Cellosolve; Excess molar enthalpy; Solution calorimetry; Trichloroethylene

1. Introduction

As a continuation of our earlier work [1], we report here the excess enthalpies H^E of trichloroethylene and tetrachloroethylene with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol and 298.15 K. The aim of this paper is to characterize the molecular interactions between chloroethenes and cellosolves. A survey of the literature showed that no literature results are available for these mixtures.

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2. Experiment

A Parr 1451 solution calorimeter was used for the present studies. The calorimeter, shown in Fig. 1, consists of a glass Dewar mixing chamber with a rotating sample cell, a thermister probe and a specially designed temperature measuring bridge, all assembled in a compact cabinet. Temperature changes were plotted directly using a strip chart recorder and were read to an accuracy of 0.001 K.

The two-piece cell which served both as sample holder and agitator consisted of a cell closed with a detachable Teflon disc. Liquid samples were added to the cell from a pipette inserted through the top stem. Excellent thermal insulation was provided by a fully silvered glass Dewar which served as a mixing chamber; from 90 to 120 cm^3 of solvent were used. Temperature measurements in this calorimeter were made with a glass-sheathed thermistor probe, combined with a special bridge, in a system designed for linear response over the range from 293.15 to 303.15 K; within this temperature range each 100 μV change in output from the bridge represented a temperature change of exactly 0.001 K. By connecting the output of the bridge to a strip chart recorder, the temperature change could be measured to 1%. Thus the experimental error in the excess molar enthalpies $H_{\mathrm{M}}^{\mathrm{E}}$ was estimated to be less than 1% over the mole-fraction range studied.

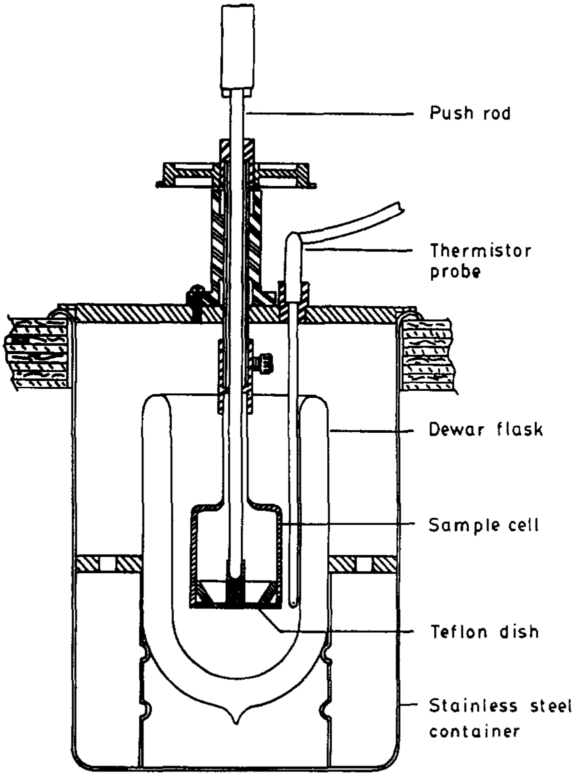

Fig. 1. Parr 1451 solution calorimeter.

The operating principle of this calorimeter was very simple. The components were combined in the Dewar mixing chamber and the resulting temperature change was measured with the thermistor probe. At the start of the experiment, one of the liquids was held in a sealed glass rotating cell in thermal contact with the other component. When the system came to thermal equilibrium, the contents of the rotating cell were mixed with surrounding liquid. The temperature change due to the mixing process was sensed by the thermistor and recorded on the strip chart recorder. The excess molar ethalpy H_M^E was then measured, knowing the energy equivalent of the system, via the equation

$$H_M^E = (W_1 C_{p1} + W_2 C_{p2} + E)\Delta T/n \tag{1}$$

where W_i is the weight of liquid i (g), C_{pi} is the heat capacity of liquid i (J g^{-1} K^{-1}), E the energy equivalent of the calorimeter (J K^{-1}), ΔT the temperature change (K), and n the number of moles of mixture. The reliability of the apparatus and the method was established by measuring excess enthalpies of standard systems, i.e. ben-

Table 1
Excess enthalpies of trichloroethylene with 2-alkoxyethanols at 298.15 K

x	H^E/J mol^{-1}	x	H^E/J mol^{-1}
xTrichloroethylene + (1 − x)2-methoxyethanol			
0.0535	−111.7	0.6388	−198.3
0.1487	−266.8	0.7086	−96.1
0.1827	−306.2	0.7442	−21.7
0.2865	−381.8	0.7847	36.2
0.3077	−397.9	0.8335	101.1
0.4202	−380.1	0.8760	147.1
0.4365	−390.0	0.9350	172.8
0.5223	−332.3	0.9695	121.9
0.5854	−267.5		
xTrichloroethylene + (1 − x)2-ethoxyethanol			
0.0508	−159.7	0.7241	−152.7
0.1632	−416.8	0.8069	−8.4
0.2081	−484.8	0.8756	92.2
0.2652	−509.0	0.8815	80.3
0.3457	−520.5	0.9470	133.2
0.4567	−490.4	0.9783	89.6
0.5337	−422.2	0.9803	83.9
0.6255	−300.5	0.9803	82.5
0.6885	−199.5		
xTrichloroethylene + (1 − x)2-butoxyethanol			
0.0639	−197.6	0.5737	−410.4
0.1597	−396.2	0.5906	−415.0
0.2296	−480.6	0.6683	−311.3
0.3307	−544.6	0.7629	−153.7
0.4357	−531.7	0.8584	4.9
0.4958	−509.3	0.9196	104.5
0.5152	−475.6	0.9784	78.5

zene + carbon tetrachloride and chlorobenzene + toluene, throughout the concentration range, at 298.15 K. Results were in good agreement with the reported data in the literature [2, 3].

All chemicals used in this work were purified by the standard methods described by Riddick and Bunger [4]. The purity of the samples was checked by comparing the densities measured with a bicapillary pycnometer [5] and the boiling points of the purified samples were those reported in the literature.

3. Results

The measured excess enthalpies H^E as a function of mole fraction x of trichloroethylene with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol, and of tetrachloroethylene with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol at 298.15 K are given in Tables 1 and 2, and are represented graphically in Figs. 2 and 3, respectively. The results of each mixture were fitted with the smoothing function

$$H^E/\mathrm{J\ mol^{-1}} = x(1-x)\sum_i h_i(2x-1)^i \tag{2}$$

Table 2
Excess enthalpies of tetrachloroethylene with 2-alkoxyethanols at 298.15 K

x	$H^E/\mathrm{J\ mol^{-1}}$	x	$H^E/\mathrm{J\ mol^{-1}}$
xTetrachloroethylene + $(1-x)$2-methoxyethanol			
0.0493	127.1	0.5673	714.6
0.1295	287.2	0.5756	712.7
0.2143	417.5	0.6418	723.1
0.3356	575.2	0.7330	699.3
0.4145	640.1	0.8244	644.1
0.4939	690.0	0.9222	479.5
0.4936	694.9	0.9646	323.5
xTetrachloroethylene + $(1-x)$2-ethoxyethanol			
0.0579	81.8	0.5379	578.2
0.1365	195.0	0.5761	574.8
0.2226	301.9	0.6470	604.8
0.3181	408.1	0.7354	603.1
0.4200	503.8	0.8204	566.7
0.4848	549.8	0.8994	476.0
0.5168	552.5	0.9635	287.7
xTetrachloroethylene + $(1-x)$2-butoxyethanol			
0.0582	45.2	0.5870	478.3
0.1488	127.8	0.6398	493.9
0.2335	204.3	0.7369	516.0
0.3359	293.9	0.8076	506.1
0.4129	355.0	0.9041	418.1
0.5034	426.0	0.9702	229.6
0.5374	442.6		

by the method of least squares, with each point weighted equally. Values of the coefficients h_i and the percentage of standard deviation % $\sigma(H^E)$ for the fit of each set of results are given in Table 3.

4. Discussion

The study of cellosolves is of interest because of the effect of the simultaneous presence of etheric and alcoholic oxygen atoms on the molecular interactions. The presence of the etheric oxygen enhances the ability of the –OH group to form hydrogen bonds.

The excess enthalpies are positive for the systems tetrachloroethylene + 2-alkoxyethanols over the whole range of composition. For the systems trichloroethylene + 2-alkoxyethanols, a change in sign from negative to positive is observed. The positive excess enthalpies can be ascribed to breaking of the

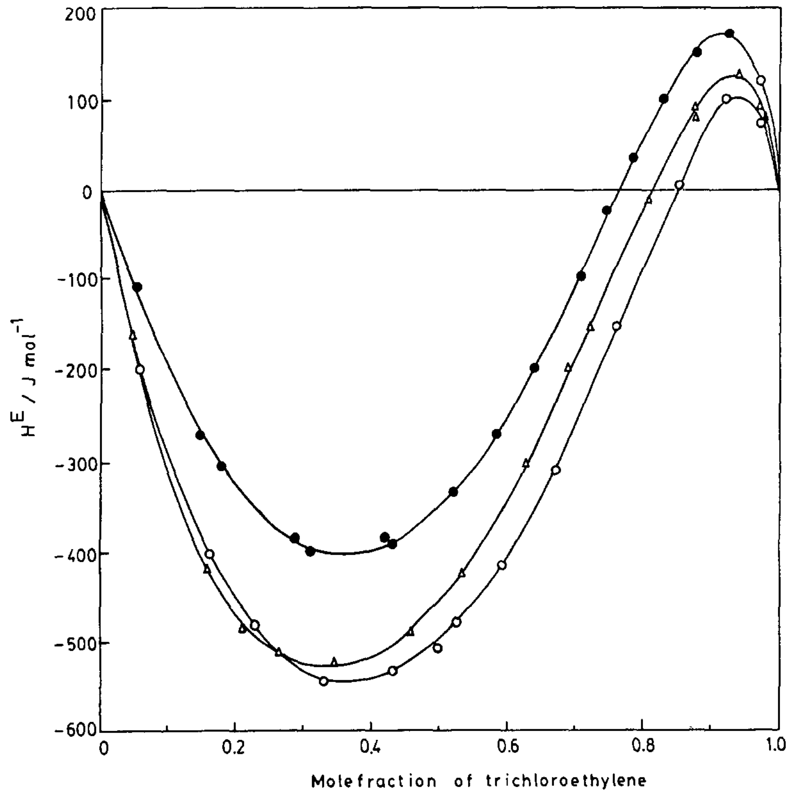

Fig. 2. Excess enthalpies H^E of $x$trichloroethylene + $(1-x)$2-methoxyethanol (●), +$(1-x)$2-ethoxyethanol (△), +$(1-x)$2-butoxy-ethanol (○) at 298.15 K.

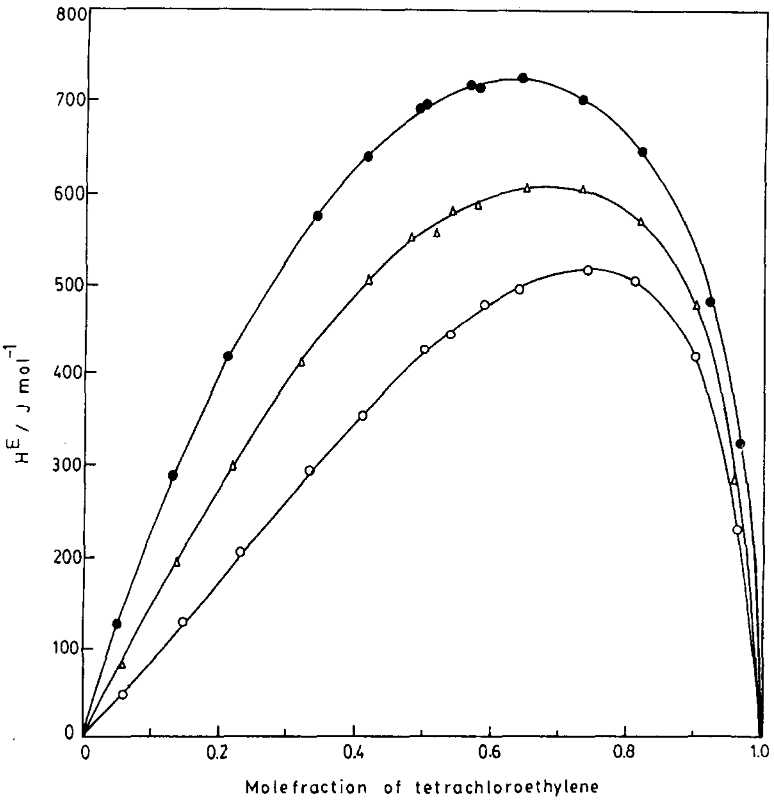

Fig. 3. Excess enthalpies H^E of $x$tetrachloroethylene + $(1-x)$2-methoxyethanol (●), $+(1-x)$2-ethoxyethanol (△), $+(1-x)$2-butoxy-ethanol (○) at 298.15 K.

Table 3
Coefficients h_i in J mol^{-1} and percentage standard deviation $\sigma(H^E)$ in % for representation of excess enthalpies at 298.15 K by Eq. (2)

System	h_0	h_1	h_2	h_3	h_4	h_5	h_6	$\sigma(H^E)$
Trichloroethylene								
+2-methoxyethanol	−1397.6	1561.8	1378.4	281.2	−614.4	1978.8	2372.9	2.6
+2-ethoxyethanol	−1824.3	1948.4	1427.9	−168.4	−4485.6	2400.8	6315.6	1.5
+2-butoxyethanol	−1986.6	1607.4	807.1	−384.5	−1192.4	2924.7	3139.8	2.8
Tetrachloroethylene								
+2-methoxyethanol	2731.5	1206.4	2561.1	−1767.5	−5987.5	5125.1	8793.1	2.9
+2-ethoxyethanol	2195.1	1357.6	1608.5	−1174.8	−2930.4	4352.5	5424.7	2.4
+2-butoxyethanol	1650.0	1611.7	2059.8	−1429.0	−4601.3	4284.2	6588.8	3.4

hydrogen bonds in 2-alkoxyethanol by the addition of chloroethenes, and negative values can be ascribed to complex formation between the π-electrons of the chloroethenes and the oxygen (–O–) in 2-alkoxyethanols. Kimura et al. [6] suggested that the contribution due to formation of the intramolecular hydrogen bond between the hydroxyl hydrogen and the etheric oxygen on the same molecule must also be considered [7–12]. The result is an endothermic effect which decreases as the aliphatic chain length of the cellosolve in each homologous series increases. The observed excess enthalpies result from the above major effects. This behaviour is consistent with that of the excess volumes for the same systems [1], which also decrease with increase in chain length of the cellosolve.

The algebraic values of H^E of all the binary systems with trichloroethylene and tetrachloroethylene fall in the order 2-methoxyethanol > 2-ethoxyethanol > 2-butoxyethanol.

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