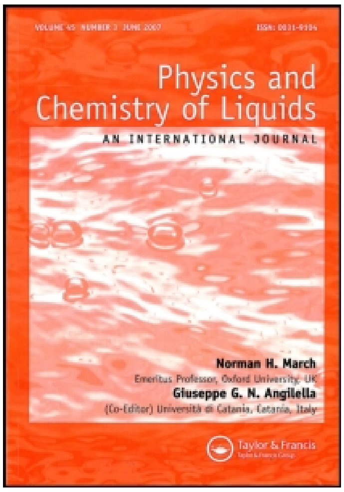

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Enthalpies of Mixing for the Binary Mixtures of Tetrachloroethylene with Some Alkan-1-OLS (C_3-C_8) at 298.15 K

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ENTHALPIES OF MIXING FOR THE BINARY MIXTURES OF TETRACHLOROETHYLENE WITH SOME ALKAN-1-OLS (C_3-C_8) AT 298.15 K

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Enthalpies of mixing H_m^E have measured for binary mixtures of tetrachloroethylene with six alkan-1-ols (propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol and octan-1-ol) at 298.15 K using a Parr 1451 solution calorimeter. All the studied mixtures present exothermic event and showed minimum negative H_m^E values in mixtures from propan-1-ol to octan-1-ol in mixtures rich in tetrachloroethylene region around 0.65-0.70 mole fraction. The mixing $-H_m^E$ values increases with the chain length of alkan-1-ols. The experimental data explained in term of dissociation of self-associated alkan-1-ols and tetrachloroethylene.

Keywords: Enthalpies of mixing; tetrachloroethylene; alkan-1-ol; dissociation

1. INTRODUCTION

Thermodynamic properties of mixing such as enthalpies of mixing H_m^E for nonelectrolyte solution can be quite significant and give a measure of molecular interactions and hence, mixing H_m^E can provide information needed to test existing theories of solution. This paper forms continuous work on regard the measurement of thermodynamic properties of nonelectrolyte solutions for binary mixtures with tetrachloroethylene as a component in which specific interactions between unlike molecules can occur [1 - 4]. An attempt has been made to measure enthalpies of mixing H_m^E for tetrachloroethylene + propan-1-ol, butan-1-ol, + pentan-1-ol, + hexan-1-ol, + heptan-1-ol and + octan-1-ol at

298.15 K. The purpose of this investigation is to study the influence of associated species of alkan-1-ols by dilution with tetrachloroethylene.

2. EXPERIMENTAL SECTION

Materials

The chemicals used in this study, their suppliers, and their purities are listed in Table I. Analytical reagent grade tetrachloroethylene was dried over sodium carbonate and fractionally distilled. All alkan-1-ols were purified by the method described by Perrin and Armarego [5].

The purity of the components were checked by measuring their densities and boiling points. The densities were measured at 303.15 K using a bi-capillary pycnometer with an accuracy of 5 parts in 10^5. The boiling points at 101.325 kPa were measured using a Swietoslawski-type ebulliometer which gave an accuracy of ±0.2 K. Table I also gives the density and boiling point measurements for these components together with values obtained from the literature [6–9].

3. SOLUTION CALORIMETER

A Parr 1451 solution calorimeter was used. The calorimeter consists of a dewar glass mixing chamber with a rotating sample cell, a thermistor probe and a specially designed temperature measuring bridge, all

TABLE I Source, Purity Grades, Densities ρ and Boiling points T_b of the Pure components at 303.15 K

Component	*Source*	*Purity/ (mass%)*	*ρ(g.cm^{-3})*		*T_b(K)*	
			exptl	*lit.*[a]	*exptl*	*lit.*[c]
Tetrachloroethylene	Merk	99.5%	1.60632	1.60640	394.2	394.4
Propan-1-ol	Fluka	99%	0.79590	0.79600	370.2	370.3
Butan-1-ol	Merk	99%	0.80202	0.80206	390.7	390.9
Pentan-1-ol	Merk	99%	0.80757	0.80764	411.0	411.2
Hexan-1-ol	Fluka	≥99.5%	0.81192	0.81201	430.9	431.0
Heptan-1-ol	Fluka	≥99.%	0.82181	0.8219[b]	448.9	449.1
Octan-1-ol	Fluka	≥99.5%	0.82183	0.82192	467.4	467.6

[a] Ref. 6,7. [b] Ref. 9. [c] Ref. 6–8.

assembled in a compact cabinet. Temperature changes 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 sample 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 dewar glass which serves as a mixing chamber. Other information regarding Parr 1451 solution calorimeter has been reported previously [10]. The enthalpy of mixing experiments were conducted in the calorimeter by considering 100 cm^3 of one component as solvent and a maximum of 25 cm^3 of other component as solute. In the subsequent runs 100 cm^3 of the previous solution was taken as the solvent and the pure solute was added to it. These experiments were continued till the concentration reaches 50 – 60 volume percent. This procedure was repeated by interchanging the components. By this method small errors in the earlier additional lead to a large error in latter experiments. Because of the limitations of the calorimeter, one is forced to adopt this method to cover the entire concentration range.

Initially, in order to determine the calorimeter equivalent, it was calibrated with 0.5 g of hydroxy methylaminomethane dissolved in 0.1 $mol.dm^{-3}$ hydrochloric acid solution which releases 245.52 $J.g^{-1}$ at 298.15 K. The performance and reliability the solution calorimeter was checked by making measurements on both exothermic and endothermic systems: $C_6H_6 + CCl_4$ and $C_6H_5Cl + C_6H_5CH_3$. The excess enthalpies H_m^E agreed within 2% with the reported values [11,12].

4. RESULT AND DISCUSSION

The experimental results for the enthalpies of mixing for the binary mixtures of tetrachloroethylene + propan-1-ol, + butan-1-ol, + pentan-1-ol, + hexan-1-ol, + heptan-1-ol and + octan-1-ol at 298.15 K are listed in Table II, together with the deviations $\delta(H_m^E)$ and shown graphically in Figure 1. To each set of H_m^E values, a Redlich-Kister function:

$$H_m^E = x(1-x)\sum A_r(1-2x)^{r-1} \qquad (1)$$

TABLE II Excess molar enthalpies H_m^E and deviations $\delta(H_m^E)$ for the binary mixture of tetrachloroethylene + alkan-1-ols at 298.15 K

x	H_m^E/ ($J.mol^{-1}$)	δH_m^E/ ($J.mol^{-1}$)	x	H_m^E/ ($J.mol^{-1}$)	$\delta(H_m^E)$/ ($J.mol^{-1}$)	x	H_m^E/ ($J.mol^{-1}$)	$\delta(H_m^E)$/ ($J.mol^{-1}$)
			$xC_2Cl_4 + (1-x)C_3H_7OH$					
0.0766	−69.1	−1.3	0.4019	−392.5	−0.7	0.7891	−464.2	−2.2
0.0978	−85.7	−0.1	0.4414	−433.5	−1.6	0.8350	−393.9	1.2
0.1611	−143.6	−0.1	0.5013	−486.6	−1.1	0.8826	−302.3	2.8
0.2281	−205.4	−0.2	0.5961	−542.3	−2.1	0.9103	−241.8	1.5
0.2943	−277.3	−0.1	0.6616	−547.6	−0.7	0.9452	−157.9	−1.9
0.3584	−341.9	3.4	0.7219	−525.8	−1.4			
			$xC_2Cl_4 + (1-x)C_4H_9OH$					
0.0962	−94.3	0.6	0.4789	−485.3	−2.5	0.7314	−553.6	0.2
0.1377	−135.7	−1.1	0.5083	−508.2	−0.4	0.8003	−491.2	−1.1
0.2205	−217.7	−1.7	0.5284	−523.5	−0.5	0.8555	−403.4	−0.4
0.2949	−294.6	−0.4	0.5570	−541.6	0.5	0.8765	−362.1	−1.5
0.3627	−365.1	1.7	0.6102	−565.6	1.2	0.9033	−297.8	1.1
0.4237	−430.1	0.3	0.6683	−574.6	−0.3	0.9388	−203.3	−0.1
			$xC_2Cl_4 + (1-x)C_5H_{11}OH$					
0.0882	−89.2	0.5	0.5148	−524.6	−2.4	0.8224	−487.6	−2.3
0.1559	−157.5	−1.2	0.5643	−558.4	−0.3	0.8585	−426.5	−3.6
0.2463	−251.5	−3.0	0.6032	−577.6	0.6	0.8914	−350.6	0.6
0.3261	−341.3	9.9	0.6671	−591.3	1.2	0.9481	−190.3	−0.5
0.3968	−416.4	−6.9	0.7160	−581.1	2.2			
0.4591	−474.7	−1.9	0.7581	−556.8	1.7			
			$xC_2Cl_4 + (1-x)C_6H_{13}OH$					
0.0771	−88.8	1.8	0.4743	−500.3	3.8	0.7969	−553.5	2.2
0.1332	−151.7	2.5	0.5696	−579.2	−4.4	0.8529	−475.5	−1.1
0.1874	−216.6	−2.4	0.5966	−593.6	−4.0	0.9111	−340.5	−1.9
0.2898	−326.3	−2.2	0.6432	−611.9	−4.9	0.9380	−255.7	−1.1
0.3763	−408.2	4.3	0.6920	−610.8	1.1	0.9511	−206.8	1.4
0.4506	−478.6	4.8	0.7432	−595.3	2.4			
			$xC_2Cl_4 + (1-x)C_7H_{15}OH$					
0.0886	−105.3	−3.0	0.4873	−548.5	−2.7	0.8390	−524.2	−4.2
0.1214	−138.9	3.0	0.5430	−590.3	−2.0	0.9020	−375.1	4.3
0.1716	−200.6	2.6	0.6113	−629.4	−4.1	0.9325	−286.9	−1.8
0.2682	−320.4	−1.3	0.6697	−639.4	−0.6	0.9498	−223.3	−0.6
0.3513	−411.3	1.8	0.7227	−629.1	2.3			
0.4240	−489.5	−1.3	0.7919	−578.6	5.2			
			$xC_2Cl_4 + (1-x)C_8H_{17}OH$					
0.0612	−84.3	−1.1	0.4516	−538.5	−2.4	0.7854	−610.6	−10.8
0.1025	−132.6	3.2	0.5066	−589.9	−2.3	0.8155	−571.3	3.3
0.1717	−223.5	−3.4	0.5716	−634.6	1.8	0.8818	−441.7	−0.7
0.2415	−301.6	0.8	0.6126	−657.1	0.7	0.9211	−326.2	0.4
0.3010	−372.2	−0.7	0.6801	−666.3	4.8			
0.3995	−480.8	0.9	0.7204	−659.6	2.8			

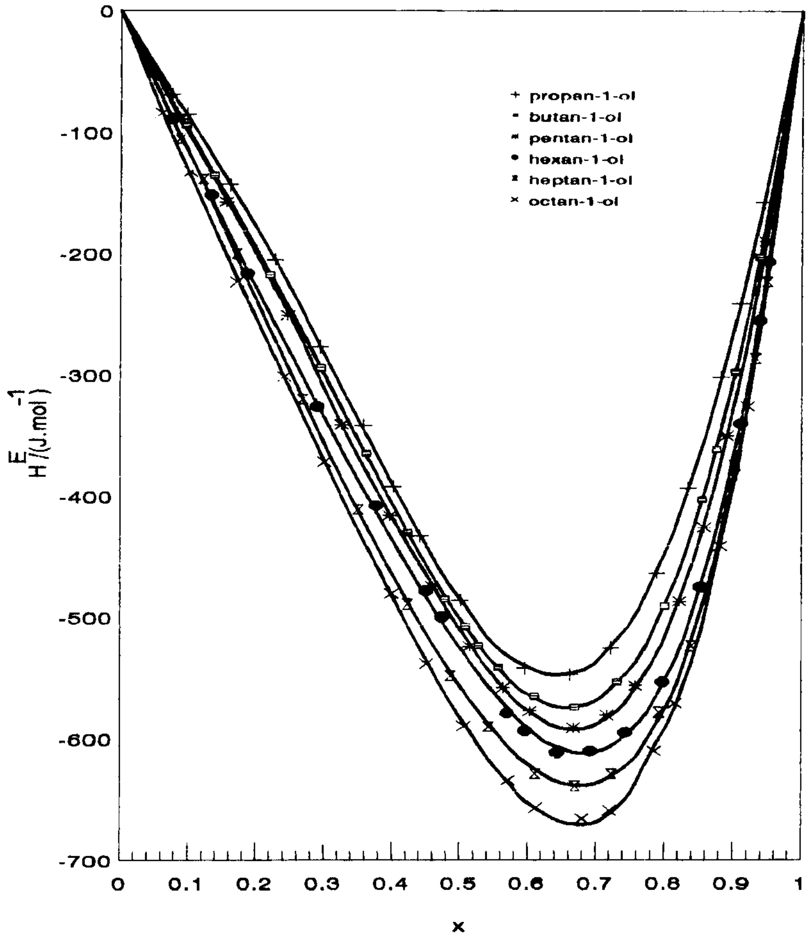

FIGURE 1 Enthalpies of mixing for the binary mixtures of (x) tetrachloroethylene + (1-x) alkan-1-ols. Continuous curves were calculated from coefficients of Eq. (1) given in Table III.

was fitted, where x is the mole fraction of tetrachloroethylene. The coefficients A_r were calculated by a least-square analysis. They are presented in Table III together with the standard deviation $\sigma(H_m^E)$ which is evaluated from the equation:

$$\sigma(H_m^E) = |\zeta/(n-p)|^{0.5} \tag{2}$$

TABLE III Values of adjustable coefficients A_r in Eq. (1) and standard deviation, $\sigma(H_m^E)$ in Eq. (2) for Tetrachloroethylene + alkan-1-ols at 298.15 K

System	A_1	A_2	A_3	A_4	$\sigma(H_m^E)/(J.mol^{-1})$
$xC_2Cl_4 + (1\text{-}x)C_3H_7OH$	−1938.8	1602.6	−57.9	−565.1	1.8
$x\ C_2Cl_4 + (1\text{-}x)C_4H_9OH$	−2004.5	1648.4	−389.4	−314.0	1.2
$x\ C_2Cl_4 + (1\text{-}x)C_5H_{11}OH$	−2040.7	1715.9	−555.2	−201.6	4.0
$x\ C_2Cl_4 + (1\text{-}x)C_6H_{13}OH$	−2103.0	1608.8	−933.2	223.6	3.4
$x\ C_2Cl_4 + (1\text{-}x)C_7H_{15}OH$	−2225.8	1611.7	−871.9	400.1	3.4
$x\ C_2Cl_4 + (1\text{-}x)C_8H_{17}OH$	−2327.6	1768.0	−915.9	47.4	4.0

where n is the number of the experimental points and p the number of adjustable parameters $A_r \cdot \zeta$ is the objective function defined as:

$$\zeta = \sum \delta^2(H_m^E) \tag{3}$$

where $\delta(H_m^E) = H_{m,expt}^E - H_{m,calcd}^E$

All the binary mixtures showed minimum negative H_m^E values in mixtures rich in tetrachloroethylene region around 0.65–0.70 mole fraction. Excess enthalpies vary little with the chain length of the alkan-1-ols and negative values of enthalpies increase from propan-1-ol to octan-1-ol. Since alkan-1-ols are strongly associated through hydrogen bonding, dilution with a non polar solvent like tetrachloroethylene, results changes in thermodynamic function which may be due to: (i) the break-up of hydrogen bonds with diluent; and (ii) the formation of new species acting as an adduct between the alkan-1-ols and tetrachloroethylene. The observed negative excess enthalpies of mixing indicates that the dissociation of the associated species of the alkan-1-ols on dilution with tetrachloroethylene is the dominating force.

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