J. Chem. Eng. Data **1997,** *42,* 802−804

Excess Molar Enthalpies for Binary Mixtures with Trichloroethylene + Alkan-1-ols (C_3−C_8) at 298.15 K

H. Iloukhani

Department of Chemistry, Faculty of Science, Bu-Ali-Sina University, Hamadan, Iran

Excess molar enthalpies H_m^E for trichloroethylene + propan-1-ol, + butan-1-ol, + pentan-1-ol, + hexan-1-ol, + heptan-1-ol, and + octan-1-ol have been measured at 298.15 K with a Parr 1451 solution calorimeter. The H_m^E values are found to be endothermic for all the mixtures rich in alkan-1-ols and become exothermic around 0.15 mole fraction of trichloroethylene. For all the systems, the value of $-H_m^E$ at the minimum increases from propan-1-ol to octan-1-ol. The results are explained in terms of dissociation of the self-associated alkan-1-ol molecules and the formation of aggregates between unlike molecules through Cl···H···O bonding.

Introduction

The magnitude of excess thermodynamic properties such as excess molar enthalpies H_m^E for nonelectrolyte solutions can give a measure of molecular interactions and, hence, can provide information needed to test existing theories of solutions.

This paper forms part of a series on the measurement of thermodynamic properties of nonelectrolyte solutions for binary mixtures with trichloroethylene and tetrachloroethylene as a component in which specific interactions between unlike molecules can occur (Iloukhani et al., 1985a,b; Iloukhani and Rao, 1985). Excess molar enthalpies H_m^E for trichloroethylene + propan-1-ol, + butan-1-ol, + pentan-1-ol, + hexan-1-ol, + heptan-1-ol, and + octan-1-ol at 298.15 K are reported. An inversion of the sign of H_m^E was observed at some mole fraction of trichloroethylene for all binary mixtures. Excess volumes V_m^E for these binary mixtures also showed a similar inversion of sign (Iloukhani et al., 1984).

Experimental Section

Materials. The materials used in this study, their suppliers, and their purities are listed in Table 1. Trichloroethylene was purified by the standard method described by Riddick and Bunger (1970). All alkan-1-ols were purified by the standard method described by Perrin and Armarego (1989).

The purities of the components were checked by measuring their densities and boiling points. The densities were measured at 303.15 K using a bicapillary 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 1 also gives the density and boiling point measurements for these components together with values obtained from the literature (Riddick and Bunger, 1970; Timmermans, 1962).

Solution Calorimetry. A Parr 1451 solution calorimeter was used. 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 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 cell from a pipet inserted through the top stem. Excellent thermal insulation is provided by the fully silvered glass Dewar which serves as a mixing chamber. Other information regarding the Parr 1451 solution calorimeter has been reported previously (Kumar et al., 1995).

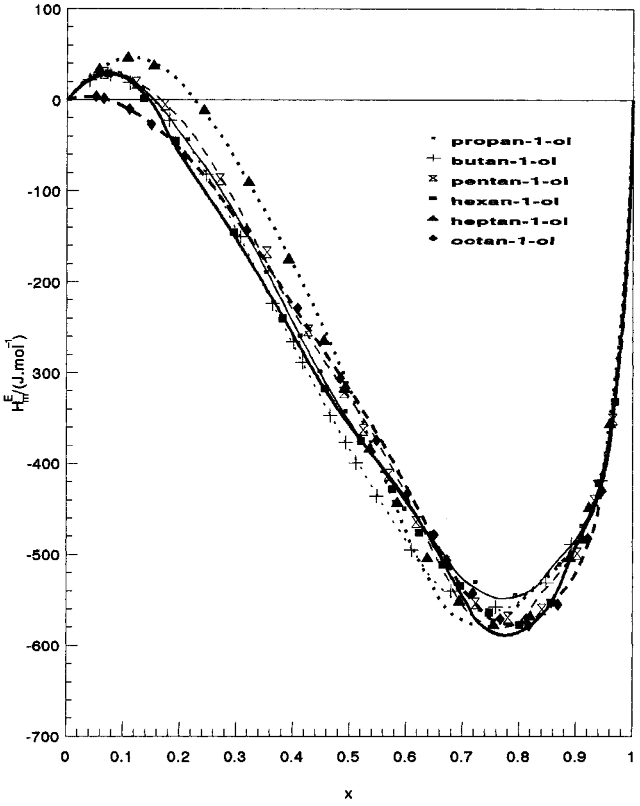

Figure 1. Excess enthalpies for binary mixtures of (x) trichloroethylene + (1 − x)alkan-1-ols at 298.15 K. Continuous curves, (—) propan-1-ol, (···) butan-1-ol, (- - -) pentan-1-ol, (—) hexan-1-ol, (···) heptan-1-ol, and (- - -) octan-1-ol, were calculated from coefficients of eq 1 given in Table 3.

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 the other component as solute. In the subsequent runs, 100 cm^3 of the previous solution was taken as the solvent and to this pure solute was added. These experiments were continued untill the concentration reached 50−60 vol %. This procedure was repeated by interchanging the components. By this method small errors in the earlier part leads to large

S0021-9568(97)00024-1 CCC: $14.00

Table 1. 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.[a]
trichloroethylene	Merk	99.5%	1.451 31	1.451 4	360.2	360.3
propan-1-ol	Fluka	99%	0.795 91	0.796 00	370.2	370.3
butan-1-ol	Merk	99%	0.802 01	0.802 06	390.7	390.9
pentan-1-ol	Merk	99%	0.807 57	0.807 64	411.0	411.2
hexan-1-ol	Fluka	≥99.5%	0.811 93	0.812 01	430.9	431.0
heptan-1-ol	Fluka	≥99%	0.821 84[b]		448.9	449.1
octan-1-ol	Fluka	≥99.5%	0.821 87	0.821 92	467.4	467.6

[a] Riddick and Bunger 1970; Timmermans, 1962. [b] At 293.15 K.

Table 2. Excess Molar Enthalpies, H_m^E, for Binary Mixtures of Trichloroethylene + 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})	δH_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})	δH_m^E/(J·mol^{-1})
				$xC_2Cl_3H + (1 - x) C_3H_7OH$				
0.0486	26.1	0.1	0.4128	−259.1	1.0	0.7224	−530.1	6.6
0.0926	28.6	0.4	0.4471	−298.3	1.4	0.7938	−544.4	1.2
0.1328	11.9	−0.2	0.4927	−342.5	4.6	0.8719	−510.7	−6.7
0.2130	−43.6	3.8	0.5184	−369.5	1.8	0.9108	−468.1	4.4
0.2861	−117.9	−4.5	0.5972	−449.1	−9.2	0.9533	−388.9	−0.6
0.3526	−189.2	−1.9	0.6573	−493.3	−1.9			
				$xC_2Cl_3H + (1 - x)C_4H_9OH$				
0.0400	21.5	−0.1	0.4004	−266.1	3.1	0.6797	−540.2	4.9
0.0764	27.3	0.7	0.4168	−288.8	0.4	0.7583	−557.8	4.0
0.1111	18.5	−0.6	0.4658	−347.1	−0.9	0.8474	−531.1	−8.2
0.1809	−22.3	−0.9	0.4933	−376.9	−0.5	0.8928	−488.9	4.6
0.2461	−81.7	−0.1	0.5113	−399.3	−3.8	0.9434	−418.5	−0.6
0.3071	−150.3	1.8	0.5484	−435.7	−2.0			
0.3639	−223.9	−0.4	0.6102	−495.1	−2.0			
				$xC_2Cl_3H + (1 - x)C_5H_{11}OH$				
0.0652	29.1	0.2	0.4903	−321.6	−2.8	0.7805	−569.5	10.1
0.1224	18.3	−0.3	0.5246	−363.1	−12.3	0.8403	−560.2	−18.0
0.1731	−5.3	1.1	0.5697	−412.1	−14.3	0.9209	−499.0	−9.1
0.2704	−87.2	3.3	0.6183	−464.1	−7.7	0.9331	−440.4	13.1
0.3538	−167.3	−12.6	0.6694	−508.4	11.7	0.9654	−351.2	−2.6
0.4268	−253.2	− 6.3	0.7233	−553.4	16.6			
				$xC_2Cl_3H + (1 - x)C_6H_{13}OH$				
0.0730	28.6	0.6	0.5203	−375.3	−0.6	0.8004	−577.1	8.1
0.1361	1.4	−4.5	0.5757	−428.2	−9.9	0.8558	−552.6	−15.0
0.1911	−45.2	6.4	0.6236	−476.1	−13.6	0.9130	−483.5	−9.1
0.2947	−145.3	3.0	0.6653	−511.1	−3.7	0.9403	−421.3	12.7
0.3818	−240.1	−2.3	0.6959	−534.2	7.0	0.9692	−332.2	−2.6
0.4563	−317.2	1.2	0.7471	−563.9	19.6			
				$xC_2Cl_3H + (1 - x)C_7H_{15}OH$				
0.0569	34.5	1.1	0.4551	−263.6	−11.8	0.7546	−576.3	−1.4
0.1076	47.4	1.9	0.4913	−316.6	−12.6	0.8197	−566.8	−25.5
0.1532	38.5	−1.6	0.5364	−382.3	−8.1	0.8894	−502.0	−4.2
0.2425	−10.1	4.0	0.5850	−441.9	9.0	0.9234	−447.3	14.2
0.3213	−89.2	2.2	0.6375	−503.0	19.8	0.9602	−354.8	−3.3
0.3922	−173.7	−2.5	0.6940	−550.2	20.0			
				$xC_2Cl_3H + (1 - x) C_8H_{17}OH$				
0.0513	3.7	0.1	0.4080	−229.1	4.2	0.7186	−542.3	8.7
0.0652	1.3	−0.2	0.4839	−306.0	−2.7	0.7670	−570.0	4.2
0.1104	−10.3	0.6	0.5479	−374.4	−8.4	0.8171	−578.2	−5.3
0.1492	−27.3	−0.4	0.6025	−433.3	−6.2	0.8685	−554.9	−7.3
0.2082	−61.9	−1.5	0.6494	−478.1	4.2	0.9212	−482.6	7.3
0.3176	−143.5	4.2	0.6719	−506.3	1.2	0.9460	−429.8	−2.8

Table 3. Values of the Adjustable Coefficients, A_i, in Eq 1 and the Standard Deviation, $\sigma(H_m^E)$, in Eq 2 for Trichloroethylene+ Alkan-1-ols at 298.15 K

	$C_2Cl_3H +$					
A_i, σ	C_3H_7OH	C_4H_9OH	$C_5H_{11}OH$	$C_6H_{13}OH$	$C_7H_{15}OH$	$C_8H_{17}OH$
A_1	−1416.8	−1534.4	−1311.0	−1432.9	−1268.8	−1273.6
A_2	1907.9	2133.3	1839.2	1674.0	3054.3	1899.4
A_3	−121.1	−840.3	−1899.7		−2643.4	−2024.3
A_4	4120.3	2965.8	7261.8	5836.1		4528.4
A_5	−6886.2			−14532.5	8105.0	
A_6	−10105.7	−7936.9	−18921.5	−12718.6	−3427.1	−10388.7
A_7	17582.9	2810.5	7307.9	39810.6	−10792.7	3572.6
A_8	11984.3	10542.3	18528.1	12963.4	7858.5	11512.4
A_9	−16813.5	−7438.6	−11836.7	−33395.8		−7280.3
σ	5.7	3.9	13.1	12.3	14.7	6.4

errors in later experiments. Because of the limitations of the calorimeter, one is forced to adopt this method to cover the entire concentration range.

Initially, the calorimeter was caliberated with 0.5 g of (hydroxymethyl)aminomethane dissolved in 0.1 mol·dm^{-3} hydrochloric acid solution to evolve 245.52 J·g^{-1} at 298.15 K to determine the calorimeter equivalent. The performance and reliability of the solution calorimeter were checked by making measurements on both endothermic and exothermic systems: $C_6H_6 + CCl_4$ and $C_6H_5Cl + C_6H_5$-CH_3. The excess enthalpies H_m^E agreed with the literature values to within 2% (Nicolaides and Eckert, 1978; Tanaka and Benson, 1976).

Results and Discussion

The measured molar excess enthalpies H_m^E of trichloroethylene + 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 2, together with the deviations $\delta(H_m^E)$ and shown graphically in Figure 1. The results were fitted to the Redlich−Kister (R−K) polynominal

$$H_m^E/(\mathrm{J\cdot mol^{-1}}) = x(1-x)\sum A_i(1-2x)^{i-1} \quad (1)$$

where A_i are the coefficients for the binary systems. They are presented in Table 3 together with the standard deviation $\sigma(H_m^E)$ which is evaluated from the equation

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

where n is the number of the experimental points and p the number of adjustable parameters A_i. ϕ is the objective function defined as

$$\phi = \sum \delta^2(H_m^E) \quad (3)$$

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

The excess enthalpies varies very little with the chain length of the alkan-1-ols, and the minimum value of H_m^E decreases from octan-1-ol to propan-1-ol.

Acknowledgment

The author is thankful to the university authorities for providing the necessary facilities to carry out the work.

Literature Cited

Iloukhani, H.; Rao, M. V. P. R. Ultrasonic Studies of Binary Mixtures of Trichloroethylene and Tetrachloroethylene with Some Aliphatic and Alicyclic Ketones at 303.15 K. *J. Phys. Chem. Liq.* **1985**, *15* (1), 11−18.

Iloukhani, H.; Reddy, K. D.; Rao, M. V. P. R. Excess Volumes of the Binary Mixtures of Trichloroethylene with N-Alcohols at 30 and 40 °C. *J. Solution Chem.* **1984**, *13* (3), 203−208.

Iloukhani, H.; Reddy, K. D.; Rao, M. V. P. R. Excess Volumes of Trichloroethylene with Some Aliphatic and Alicyclic Ketones at 303.15 K and 313.15 K. *J. Phys. Chem. Liq.* **1985a**, *14* (3), 181−188.

Iloukhani, H.; Reddy, K. D.; Rao, M. V. P. R. Excess Volumes of Trichloroethylene with Some Aliphatic and Alicyclic Ketones at 303.15 K and 313.15 K. *J. Chem. Eng. Data* **1985b**, *30*, 306−308.

Kumar, R. V.; Rao, M. A.; Rajiah, A.; Rao, M. V. Excess Molar Enthalpies of Chloroalkanes or Chloroalkenes + Benzyl Alcohol at 298.15 K. *J. Chem. Eng. Data* **1995**, 40, 99−101.

Nicolaides, G. L.; Eckert, C. A. Experimental Heats of Mixing of Some Miscible and Partially Miscible Nonelectrolyte Systems. *J. Chem. Eng. Data* **1978**, *23* (2), 152−156.

Perrin, D. D.; Armarego, W. L. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1989.

Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1970.

Tanaka, R.; Benson, G. C. Excess Enthalpies and Volumes for Mixtures of Chlorobenzene with Some Aromatic Hydrocarbons at 298.15 K. *J. Chem. Eng. Data* **1976**, *21* (3), 320−324.

Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1962.

Received for review January 21, 1997. Accepted May 1, 1997.⊗

JE970024U

⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.