

of formation of HCl solutions (4) with a standard deviation of 3 cal/mol is -61 cal/mol of H_2O .

Substitution in eq 12 of the enthalpies of solution for the stoichiometric amounts of the compounds gives $-19\,985$ cal for ΔH_2 .

The standard enthalpy of formation of $KCl(c)$ (3) is -104.175 kcal/mol. The standard enthalpy of formation of $HCl \cdot 13.88H_2O$ calculated from the same data used in solving eq 13 is -13.899 kcal/mol. The standard enthalpy of formation of $H_3PO_4 \cdot 100H_2O$ (5) was combined with the enthalpies of solution of H_3PO_4 solutions (1) to calculate the standard enthalpies of formation of $H_3PO_4 \cdot 1.51H_2O$ and $H_3PO_4 \cdot 13.88H_2O$ as -306.8 and -309.2 kcal/mol, respectively. Substituting these enthalpies of formation and the enthalpies of reactions 1 and 2 in the equations

$$\begin{aligned} \Delta H_f^\circ(KH_2PO_4) &= \Delta H_1 + \Delta H_f^\circ(KCl) \\ &+ \Delta H_f^\circ(H_3PO_4 \cdot 13.88H_2O) - \Delta H_f^\circ(HCl \cdot 13.88H_2O) \quad (14) \end{aligned}$$

and

$$\begin{aligned} \Delta H_f^\circ(K_2HPO_4) &= 2(\Delta H_f^\circ(KH_2PO_4)) \\ &- \Delta H_f^\circ(H_3PO_4 \cdot 1.51H_2O) - \Delta H_2 \quad (15) \end{aligned}$$

gives -376.1 kcal/mol as the standard enthalpy of formation of KH_2PO_4 and -425.4 kcal/mol as the standard enthalpy of formation of K_2HPO_4 .

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Thermodynamic Properties of Toluene-1,1,2,2-Tetrachloroethane

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Data on heats of mixing at 298.15 and 308.15 K, vapor-liquid equilibria, latent heats of vaporization at 686 mmHg, and vapor pressures for the system toluene-1,1,2,2-tetrachloroethane are presented. The effect of alkyl substitution on heats of mixing is discussed.

Thermodynamic properties of liquid mixtures have an important place in industrial and academic work. Aromatic hydrocarbons and chlorinated hydrocarbons are one such class of important substances. This laboratory has embarked on a program of collecting experimental data on vapor pressure, vapor-liquid equilibria, heats of mixing, and latent heats of vaporization of aromatic hydrocarbon-chloroethane mixtures. The data for toluene-1,2-dichloroethane have been reported (12). This paper presents the data for toluene-1,1,2,2-tetrachloroethane.

Materials Used and Purification

Analar toluene supplied by British Drug House, Bombay, and laboratory grade 1,1,2,2-tetrachloroethane supplied by BDH Chemicals, England, were purified by the methods described by Weissburger (14) and Riddick and Bunger (10). The refractive index and density of the chemicals used along with literature values (4) are reported in Table I. Vapor-phase chromatographs were obtained for the liquid using the AIMIL-NCL dual column gas chromatograph using silicone gum rubber S.E. 30 as column material. A single peak was obtained for both the liquids. Because of the excellent agreement of refractive index and density and the vapor phase chromatograph, the purity of the substances can be taken as 99.9 mol %.

Vapor Pressure Data

The present data for 1,1,2,2-tetrachloroethane reported in Table II fitted the equation

$$\log P_2 = 7.88347 - (2096.8606/T) \quad (0.25, 0.8) \quad (1)$$

The values in parentheses denote the percent average absolute deviation and maximum deviation, respectively. The vapor pressure at the normal boiling point calculated from eq 1 deviated from the data reported by Driesbach (4) by 0.6%. The present data compare with the data of Nelson (8) and Matthews (7) with average absolute deviations of 2.5 and 3%, respectively. The rather large deviations may be due to the purity of the chemicals.

The experimental vapor pressures of toluene agreed with those calculated from the Antoine equation reported in the A.P.I. Tables (11) with an average absolute deviation of 0.1% and a maximum deviation of 0.3%.

Heats of Mixing

A new calorimeter with negligible vapor space described elsewhere (13) was used in the present work. The data on heats of mixing at 298.15 and 308.15 K given in Table III were fitted to eq 2 and 3, respectively.

$$\begin{aligned} H^E/x_1x_2 &= -6680.2 + 5115.5(2x_1 - 1) \\ &- 2155.8(2x_1 - 1)^2 - 2555.2(2x_1 - 1)^3 \\ &+ 3917.7(2x_1 - 1)^4 \quad (0.8, 2.2) \quad (2) \end{aligned}$$

$$\begin{aligned} H^E/x_1x_2 &= -6194.5 + 6142.3(2x_1 - 1) \\ &- 2347.2(2x_1 - 1)^2 - 5349.9(2x_1 - 1)^3 \\ &- 5744.4(2x_1 - 1)^4 + 43.3(2x_1 - 1)^5 \quad (1.0, 3.0) \quad (3) \end{aligned}$$

Effect of Alkyl Substitution on Heats of Mixing

The heat of mixing of benzene-1,1,2,2-tetrachloroethane at 308.15 K and 0.5 mole fraction has been reported (9) as -570 J mol⁻¹. The value under similar conditions for toluene-1,1,2,2-tetrachloroethane is -1550 J mol⁻¹. These systems are similar to benzene and toluene with carbon tetrachloride. Here, alkyl substitution to benzene increases exothermicity, with the aromatic group acting as an electron donor. It is known that on

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Table I. Properties of Toluene and 1,1,2,2-Tetrachloroethane at 303.15 K

Material	Refractive index using sodium D line		Density/g cm ⁻³	
	Present work	Lit. (4)	Present work	Lit. (4)
Toluene	1.49142	1.49129	0.8578	0.8576
1,1,2,2-Tetrachloroethane	1.4887	1.4884	1.5784	1.5786

Table II. Vapor Pressure Data for 1,1,2,2-Tetrachloroethane

T/K	P ₂ /mm (exptl)	% devn ^a (eq 1)
377.35	212.0	0.28
382.25	250.0	0.19
384.95	272.5	0.26
389.05	313.0	-0.44
392.75	350.8	-0.10
399.25	430.3	-0.50
404.45	501.5	-0.12
408.65	566.5	-0.04
411.05	605.5	0.06
413.35	646.5	0.04
415.25	681.0	0.32
415.45	685.0	0.16
419.05	753.0	0.80
		% av abs devn 0.25

^a (P₂(calcd) - P₂(exptl))/P₂(calcd) × 100.

Table III. Heats of Mixing Data of Toluene-1,1,2,2-Tetrachloroethane

T/K = 298.15		T/K = 308.15	
x ₁	H ^E /J mol ⁻¹	x ₁	H ^E /J mol ⁻¹
0.050	-410.0	0.080	-518.0
0.136	-1065.0	0.143	-950.0
0.182	-1409.0	0.185	-1310.0
0.242	-1701.0	0.262	-1712.0
0.301	-1849.0	0.320	-1823.0
0.360	-1920.0	0.367	-1846.0
0.378	-1922.0	0.385	-1812.0
0.459	-1742.0	0.433	-1694.0
0.544	-1543.0	0.485	-1566.0
0.595	-1377.0	0.546	-1406.0
0.664	-1182.0	0.610	-1228.0
0.735	-936.0	0.690	-918.0
0.817	-658.0	0.790	-630.0
0.897	-336.0	0.898	-291.0

Table IV. T-x-y Data at 686 mmHg for Toluene-1,1,2,2-Tetrachloroethane

T/K	x ₁	y ₁
412.65	0.066	0.132
411.75	0.084	0.167
410.35	0.122	0.235
408.35	0.173	0.319
404.85	0.273	0.463
402.35	0.336	0.544
401.45	0.359	0.570
399.35	0.412	0.631
396.05	0.495	0.716
392.65	0.592	0.799
388.95	0.694	0.868
386.25	0.775	0.914
384.25	0.838	0.944
381.85	0.931	0.979

Table V. Experimental and Calculated Heats of Vaporization

x ₁	L _{exp} /kJ mol ⁻¹	L _{cal} /kJ mol ⁻¹	% devn
0.000	38.69	38.34	-0.9
0.125	37.68	37.51	-0.5
0.210	36.77	36.65	-0.3
0.350	35.83	35.73	-0.3
0.470	35.55	35.50	-0.1
0.580	35.38	35.30	-0.2
0.690	35.26	35.10	-0.5
0.795	34.81	34.76	-0.1
0.850	34.64	34.50	-0.4
0.925	34.12	34.06	-0.2
1.00	33.38	33.50	0.4
			% av abs devn 0.35

alkyl substitution the electron density of the aromatic ring increases and this accounts for the increase in exothermicity. It can therefore be concluded that the present system behaves as a donor-acceptor system. Bittrich (2) has also reviewed the various donor-acceptor systems and the effect of alkyl substitution. It should be further noted that both carbon tetrachloride and 1,1,2,2-tetrachloroethane are symmetric molecules. One more important feature is that an increase in temperature decreases exothermicity for both the systems.

The rather large exothermic heats of mixing of the present system compared to the carbon tetrachloride system may be partly due to hydrogen bonding between toluene and tetrachloroethane. To assess exactly which of the mechanisms, donor-acceptor, hydrogen bonding, or both, contributes to the behavior of this system a knowledge of spectroscopic evidence seems to be necessary.

Vapor-Liquid Equilibria

The isobaric vapor-liquid equilibrium data at 686 mmHg, the prevailing laboratory pressure, were taken in a Brown still (3) and are given in Table IV.

Density measurements were used to analyze the mixtures and the density-mole fraction of toluene calibration was fitted to eq 4

$$\rho = 1.57987 - 0.725124x_1 \quad (0.1, 0.2) \quad (4)$$

To check the consistency of the data the rigorous equation

$$\int_0^{1.0} \log \frac{\gamma_1}{\gamma_2} dx_1 + \int_0^{1.0} \frac{-H^E}{RT^2} \frac{dT}{dx_1} dx_1 = 0 \quad (5)$$

was used along with (i) heats of mixing at 308.15 K given by eq 3, (ii) bubble point-liquid composition relation given by eq 6

$$T = 142.24 - 41.16x_1 + 5.01x_1^2 \quad (0.2, 0.4) \quad (6)$$

(iii) second virial coefficient of toluene (1) and the second virial coefficients of 1,1,2,2-tetrachloroethane evaluated by the method reported earlier (9), and (iv) liquid molal volumes taken from Francis (5) and Gallant (6).

The data satisfied eq 5 for consistency with the sum of the two integrals being equal to -0.1. Herington's criteria was also satisfied with $D < J$, D being equal to 4.5 and J equal to 13.9.

Heats of Vaporization

The heats of vaporization were determined using a modified Dana apparatus (12) and are given in Table V. Calculated values of heats of vaporization (12) also shown in Table V reveal very good agreement with experimental values.

Glossary

H^E excess enthalpy, J mol⁻¹

- L* latent heat of vaporization, k J mol⁻¹
P vapor pressure, mmHg
T temperature, K
x mole fraction in liquid phase

Greek letters

- γ activity coefficient
 ρ liquid density, g cm⁻³

Subscripts

- 1 toluene
 2 1,1,2,2-tetrachloroethane

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Acidities of Some *N*-Haloamides (ZCONHX) in Water and Ethanol-Water Mixtures at 25 °C

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The acidities of ten *N*-haloacetamides and of *N*-chlorourethane and *N*-fluorourethane in water and ethanol-water mixtures (25, 50, and 75% by weight) were determined by potentiometric titration at 25 °C. The pK_a s of *N*-chloroacetamide and *N*-chloro- α -haloacetamides in water are compared with those of the corresponding acetic acids.

Our studies on radical reactions of *N*-haloamides (ZCONHX) (3, 4, 8) and their electrochemical behavior (2) required a knowledge of their acidities. The pK_a values of various *N*-haloamides in water and ethanol-water mixtures at 25 °C are recorded in Table I; they increase as the polarity of the medium decreases as expected. Literature values of the pK_a s of some carboxylic acids in water at 25 °C (6) are included for comparison purposes.

The *N*-chloroacetamides are less acidic than the corresponding acetic acids by about 2.5–3 pK_a units. If the substituent effects on the acidity of the *N*-chloroacetamides and on the acidity of the corresponding acetic acids were exactly the same, we would expect a straight line of slope unity by plotting the pK_a of ZCONHCl against the pK_a of ZCOOH. As shown in Figure 1, this is nearly the case except for *N*-chlorofluoroacetamide. Repeated pK_a determinations on different samples gave consistently a pK_a value of 5.74 ± 0.02 . *N*-Chlorofluoroacetamide appears to be less acidic than *N*-chloroiodoacetamide (except in 50 and 75% ethanol-water where the acidities are similar), which is quite unexpected considering the much higher electronegativity of the fluorine atom. Assuming that the correlation shown in Figure 1 would hold for Z = C₂H₅O, the pK_a of C₂H₅OCO₂H would be of the order of 5.5 (as compared with 6.35 for the pK_a of aqueous carbon dioxide); it cannot be measured directly because of spontaneous decarboxylation.

Table I. pK_a Values of *N*-Haloamides (ZCONHX) in Water and Ethanol-Water Mixtures at 25 °C^a

ZCONHX	% ethanol-water by weight				ZCOOH	pK_a (water) ^b
	0%	25%	50%	75%		
CH ₃ CONHCl	7.22	7.72	8.11	8.89	CH ₃ COOH	4.756
ICH ₂ CONHCl	5.51	6.02	6.50	7.11	ICH ₂ COOH	3.175
BrCH ₂ CONHCl	5.36	5.78	6.24	6.90	BrCH ₂ COOH	2.90
ClCH ₂ CONHCl	5.42	5.80	6.21	6.84	ClCH ₂ COOH	2.829
FCH ₂ CONHCl	5.74	6.13	6.45	7.09	FCH ₂ COOH	2.585
Cl ₂ CHCONHCl	3.71	4.16	4.58	5.12	Cl ₂ CHCOOH	1.366
CCl ₃ CONHCl	2.91	3.37	3.70	4.22	CCl ₃ COOH	0.63
CF ₃ CONHCl	2.85	3.18	3.39	3.61	CF ₃ COOH	0.230
CH ₃ CONHBr	7.89	8.30	8.88	9.59		
ClCH ₂ CONHBr	6.20					
C ₂ H ₅ OCONHCl	8.02	8.55	9.18	10.21		
C ₂ H ₅ OCONHF	5.69	6.33	7.06	8.10		

^a Three determinations were made for each pK_a value, the standard deviation being ± 0.02 pK_a unit. ^b Taken from ref 6.

The lower acidity of *N*-chlorourethane as compared with *N*-chloroacetamide can be accounted for by the fact that the carboxy group is resonance stabilized to a greater extent than the acetyl group; acetates ($pK_a \approx 25$) are less acidic than acetone ($pK_a \approx 20$) for the same reason.

An *N*-chloroamide is about four to five times more acidic than the corresponding *N*-bromoamide and *N*-fluorourethane is much more acidic than *N*-chlorourethane in agreement with the electronegativities of the bromine, chlorine, and fluorine atoms. In basic medium, decomposition of *N*-fluorourethane occurs slowly but we believe the pK_a values obtained are reliable.