

have a small, but potentially significant, positive effect.

**Registry No.** HY-STOR Alloy 101, 77980-77-9; hydrogen, 1333-74-0; aluminum, 7429-90-5.

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## Vaporization Study of *o*-, *m*-, and *p*-Chloroaniline by Torsion-Weighing Effusion Vapor Pressure Measurements

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A combined torsion-weighing effusion apparatus was used to measure the vapor pressures of *o*-, *m*-, and *p*-chloroaniline; their temperature dependences are given by the equations: *o*-chloroaniline,  $\log P$  (kPa) =  $(8.63 \pm 0.16) - (3006 \pm 56)/T$ ; *m*-chloroaniline,  $\log P$  (kPa) =  $(8.86 \pm 0.10) - (3180 \pm 40)/T$ ; *p*-chloroaniline,  $\log P$  (kPa) =  $(11.20 \pm 0.20) - (4170 \pm 60)/T$ . The standard vaporization enthalpies  $\Delta H^\circ_{298} = 57.5 \pm 5$ ,  $60.9 \pm 5$ , and  $79.0 \pm 5$  kJ mol<sup>-1</sup> for *o*-, *m*-, and *p*-chloroaniline, respectively, were derived. Free energy functions of the gaseous and solid phase for these compounds are also reported.

#### Introduction

Except for the old values selected by Ohe (1) and those referred to *o*- and *m*-chloroaniline published by Walton (2), not accessible to us, apparently no other vapor pressure data for *o*-, *m*-, and *p*-chloroaniline are reported in literature.

In view of filling this lack of experimental data and as a part of our continuing research program on the determination of the thermodynamic properties associated with the vaporization of organic compounds, the vapor pressure of *o*-, *m*-, and *p*-chloroaniline were measured by using a combined torsion-weighing effusion apparatus.

#### Experimental Apparatus

The assembly used to measure the vapor pressure of *o*-, *m*-, and *p*-chloroaniline consists of a conventional torsion-effusion apparatus suspended from one arm of an automatic vacuum electrobalance. Figure 1 shows a schematic representation of the apparatus. The graphite effusion cell was of standard design. Moment arms and thickness of the effusion holes were measured by photographic enlargement. Effective orifice area was obtained by appropriate use of Freeman's (3)

and Clausing's (4) equations in the torsion and Knudsen measurements, respectively. Temperature of the cell, heated by a fluidized sand bath Tecam SLB-1 thermostated within  $\pm 0.1$  °C, was measured by a calibrated iron-copper thermocouple inserted in a second graphite cell placed at the same level of the effusion one and continuously recorded by a Phillips PM 8252 potentiometer. However, the overall accuracy of the reported temperature must be estimated at  $\pm 2$  °C considering the uncertainty in the measurement ( $\pm 1 \times 10^{-3}$  mV) and in the junction potentials. Background pressure of the system during the vaporizations was always less than  $2 \times 10^{-5}$  torr.

The vapor pressures were measured by simultaneous Knudsen and torsion-effusion methods. The pressure values determined from thermogravimetric data were obtained by the following form of the Knudsen equation (5)

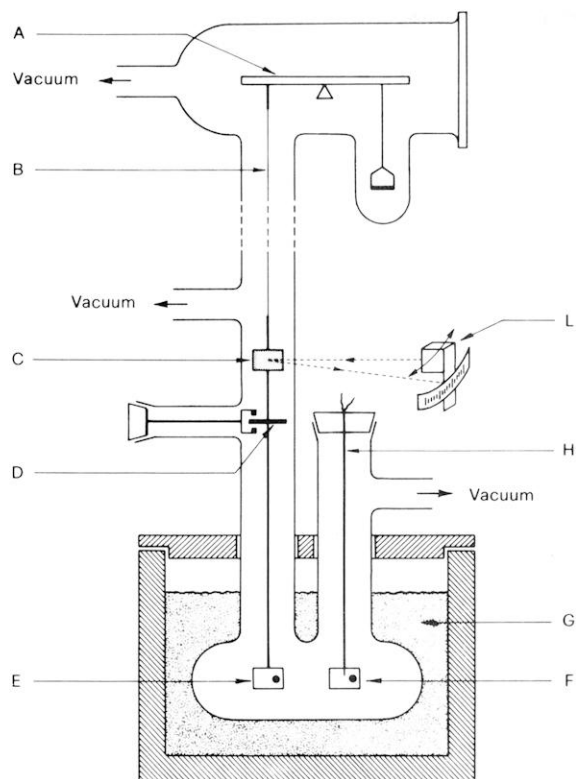
$$P \text{ (kPa)} = \frac{38.2}{A_1 + A_2} (T/M)^{1/2} dg/dt$$

where  $A_1$  and  $A_2$  are the effective areas of the effusion orifices in cm<sup>2</sup>,  $M$  the molecular weight of the vapor,  $T$  the cell temperature in Kelvin, and  $dg/dt$  the weight loss rate of the sample in milligrams/minute. The weight loss rate was determined under steady-state conditions by a Cahn RH vacuum microbalance coupled with an automatic recording of the mass loss of the sample as a function of time and a time derivative computing. The error in the rate measurement, which is a function of chart speed and balance sensitivity, is less than 1%. The errors due to variations in chart shrinkage or speed and in balance sensitivity were found to be negligible.

Simultaneously, at each experimental temperature, the vapor pressure was determined by the well-known torsion-effusion equation (6)

$$P = \frac{2\alpha K}{A_1^0 I_1 + A_2^0 I_2}$$

where  $K$  is the torsion constant of the torsion tungsten wire,



**Figure 1.** Schematic drawing of torsion-Knudsen assembly: A, electrobalance; B, tungsten torsion wire; C, reflecting mirror; D, braking disk; E, torsion cell; F, twin cell; G, thermostatic sand bath; H, thermocouple; L, zero optical assembly.

$A_1^\circ$ ,  $A_2^\circ$  and  $l_1$ ,  $l_2$  are the effective areas of the orifices and their distances from the rotation axis, respectively.

The torsion constant of the tungsten fiber ( $K = (46.0 \pm 0.5) \times 10^{-3} \text{ N m}$ ) was determined by the usual method (7) of observing the periods of the suspended assembly when cylinders of known but different moments of inertia were added. No change of the torsion constant during the experiments was observed. The torsion angles ( $\alpha$ ) of the cell were measured by a simple zero optical assembly that allows to determine the torsion angle values within an uncertainty of  $\pm 0.2^\circ$ . Vapor pressure determinations of some pure standards (naphthalene and mercury) were made in order to test the apparatus and to obtain a realistic measure of the overall accuracy. The two vapor pressure values obtained simultaneously at each temperature agree within 5–10% between themselves and within about 20% with data from literature (7, 8). This discrepancy could reflect possible systematic errors associated with the effective orifice area, with the torsion constant, and with the temperature measurements. Minor sources of uncertainties are associated with the weight loss and torsion angle measurements.

Some vapor pressure determinations were also carried out by using the same cell in a conventional torsion-effusion apparatus as described in a previous work (9). The results are a further test of the reliability of the data obtained by the previous procedure.

### Thermodynamic Calculations

The average pressure values are presented on a  $\log P$  vs. reciprocal temperature plot; a linear least-squares analysis was performed for each experimental run, resulting in expression of the form

$$\log P = (A \pm \sigma_A) - (B \pm \sigma_B)/T$$

where  $\sigma_A$  and  $\sigma_B$  are the standard deviations of the intercept and slope, respectively. The intercept and slope of the linear

**Table I.** Molecular Parameters and Vibration Frequencies of Gaseous *o*-, *m*-, and *p*-Chloroaniline

bond length, Å		angle, deg	
C-C	1.39	C-N-H	114
C-H	1.08	H-N-H	115
C-Cl	1.70		
C-N	1.40		
N-H	1.02		

Vibration Frequencies, $\text{cm}^{-1}$		
<i>o</i> -chloroaniline	<i>m</i> -chloroaniline	<i>p</i> -chloroaniline
3452	3462	3477
3351	3381	3387
3065 (2)	3059	3059 (2)
3059	3054	3040 (2)
3051	3004 (2)	1622
1615	1617	1602
1589	1592	1596
1492	1480	1496
1480	1473	1420
1455	1447	1380
1312	1314	1292
1262	1298	1180
1155	1260	1118
1145	1166	1092
1083	1078	1089
1052	1076	1054
1047	1040	1004
1024	1000	930
966	996	889
930	962	832
875	925	826
832	863	821
790	832	819
756	800	700
700	774	637
680	694	580
677	690	498
505	520	465
440	500	400
390	445	380
380	408	379
372	380	312
312	312	142

fit yield respectively the second law  $\Delta S^\circ_T$  and  $\Delta H^\circ_T$  of the vaporization process, where  $T$  is taken as the average temperature of the data set. Since for each compound studied these temperatures are very near 298 K, the found  $\Delta H^\circ_T$  values were considered equal to the standard enthalpy changes,  $\Delta H^\circ_{298}$ , and were used to derive the free energy function changes by a third law treatment of the pressure data. The free energy function values of the gaseous phase of *o*-, *m*-, and *p*-chloroaniline were calculated by using the usual statistical mechanical formulas (10) on the basis of some structural and spectroscopic considerations. The rotation of  $-\text{NH}_2$ , not planar respect to the remanent part of the molecule (11, 12), is not free, and the following torsional barriers (12)  $V_0 = 1299$ , 697, and 512  $\text{cal mol}^{-1}$ , for *o*-, *m*-, and *p*-chloroaniline, respectively, were employed. The necessary molecular parameters and the vibrational frequencies reported in Table I have been determined by using data or suggestions found in literature (10, 13, 14). The free energy function values of the gaseous compounds so calculated are reported in Table II. In the same table are also reported the values for the condensed phases derived from the free energy function changes of the vaporization processes obtained by third law treatment of the experimental results through the equation

$$[(G^\circ_T - H^\circ_{298})/T]_S = [(G^\circ_T - H^\circ_{298})/T]_g + R \ln P + \Delta H^\circ_{298}/T \quad (1)$$

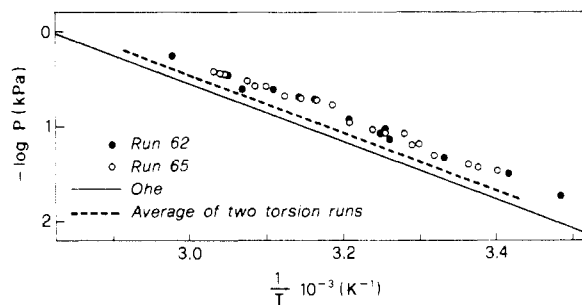
where the  $\Delta H^\circ_{298}$  is the value derived from second law pro-

**Table II. Free Energy Functions ( $\text{J mol}^{-1} \text{K}^{-1}$ ) of Condensed<sup>a</sup> and Gaseous *o*-, *m*-, and *p*-Chloroaniline**

<i>T</i> , K	<i>o</i> -chloroaniline		<i>m</i> -chloroaniline		<i>p</i> -chloroaniline	
	liq	gas	liq	gas	solid	gas
298	225.7	354.6	225.3	351.4	175.6	356.5
300	225.7	354.7	225.3	351.5	175.6	356.6
340	227.0	356.0	226.3	352.8	177.0	358.4
380	229.3	358.3	228.2	355.0	179.1	360.8
420	232.5	361.5	231.0	358.1	181.8	364.0
460	236.0	365.7	234.7	362.0	185.2	367.9
500	241.5	370.6	239.2	366.9	189.3	372.4

<sup>a</sup> Calculated from eq 1.**Table III. Vapor Pressures and Free Energy Function Changes of the *o*-Chloroaniline Vaporization**

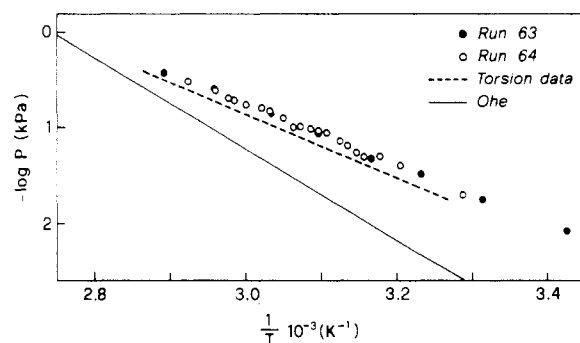
run	<i>T</i> , K	torsion		weighing		av 10 <sup>5</sup> <i>P</i> , Pa	$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ , J mol <sup>-1</sup> K <sup>-1</sup>	
		$\alpha$ , deg	10 <sup>5</sup> <i>P</i> , Pa	<i>dg/dt</i> , mg/min	10 <sup>5</sup> <i>P</i> , Pa			
62	287	4.5	1.7	0.184	2.3	1.8	128.6	
	293	8	3.1	0.331	4.1	3.2	129.3	
	300	10	3.9	0.652	8.4	4.5	127.6	
	305	18	7.0	0.612	7.8	7.2	128.5	
	307	22	8.7	0.779	10.0	9.6	129.6	
	307.5	23	8.9	0.652	8.4	8.6	128.4	
	311	30	11.7			11.7	128.9	
	316	55	21.4	1.399	18.2	20.0	130.4	
	318	57	22.2	1.417	18.5	20.3	129.3	
	321.5	73	28.4	1.769	23.2	25.1	129.2	
	325.5	94	36.6	2.381	31.5	34.7	129.6	
	327	99	38.6	2.570	34.0	36.2	129.2	
	336	120	46.7	4.082	54.2	50.5	127.9	
	65	294	9	3.5	0.276	3.5	3.5	129.4
		296	10	3.7	0.293	3.6	3.6	128.5
		297	11	4.1			4.1	128.8
		301	13	5.1	0.378	4.8	5.0	128.0
		303	17.5	6.8	0.482	6.1	6.6	129.0
		304	16	6.2			6.2	127.9
305		21.5	8.3			8.3	129.7	
307		26	10.1	0.586	7.5	8.7	128.8	
308		27	10.5	0.624	8.0	9.0	128.6	
311		32	12.4	0.737	9.5	11.2	128.5	
314		43	16.7			16.7	130.1	
316		50	19.4	1.247	16.2	19.0	130.0	
318		61	23.7	1.323	17.3	20.0	129.2	
320		56	21.8			21.8	128.8	
322	77	30.0	1.814	23.9	26.9	129.5		
324	70	27.2	2.098	27.7	27.5	128.6		
325	87	33.9	2.079	27.4	30.9	129.0		
328	88	34.3			34.3	128.2		
329	91	35.4			35.4	127.9		
330	99	37.0	3.175	42.7	39.8	128.4		

**Figure 2.** Vapor pressure of *o*-chloroaniline.

cedure and *P* the vapor pressure at the experimental temperature *T*.

### Results and Conclusions

The employed *o*-, *m*-, and *p*-chloroaniline samples were supplied by Koch-Light Laboratories Ltd., England (99.8% pure). In order to avoid the wettability, Teflon liners were fitted in the effusion cells used. The vapor pressures of *o*-, *m*-, and *p*-chloroaniline, measured simultaneously by torsion and Knudsen

**Figure 3.** Vapor pressure of *m*-chloroaniline.

effusion methods, are summarized in Table III, IV, and V, and their average values are reported in Figures 2, 3, and 4. The Knudsen data were calculated by assuming that the compounds vaporize congruently to monomeric gas. The agreement of the Knudsen values with those obtained by the torsion method, which do not depend on the molecular weight of the effusing gas, can be taken as support for this assumption.

In Table VI are summarized the pressure-temperature equations for each vaporization run following the procedure

Table IV. Vapor Pressures and Free Energy Function Changes of the *m*-Chloroaniline Vaporization

run	<i>T</i> , K	torsion		weighing			$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ , J mol <sup>-1</sup> K <sup>-1</sup>			
		$\alpha$ , deg	10 <sup>5</sup> <i>P</i> , Pa	dg/dt, mg/min	10 <sup>5</sup> <i>P</i> , Pa	av 10 <sup>5</sup> <i>P</i> , Pa				
63	292	3	0.7	0.078	1.0	0.8	126.8			
	302			0.136	1.7	1.7	125.9			
	309.5			0.255	3.3	3.3	126.3			
	316	25	9.7	0.378	4.9	4.9	125.6			
	323			0.624	8.2	8.9	126.5			
	330.5			1.021	13.6	14.5	126.3			
	338			1.682	22.6	25.0	126.9			
	346			2.722	37.1	37.6	126.6			
	64			304	5	1.9			1.9	125.4
				312	10.5	4.1			4.1	126.5
315		14	5.4			5.4	127.1			
317		12.5	4.9	0.397	5.2	5.0	125.2			
318		15	5.8	0.397	5.2	5.6	125.6			
319		17	6.7	0.454	6.9	6.6	126.3			
320		18	7.0			7.0	126.2			
322		23	8.9			8.9	127.1			
323		22	8.5			8.5	126.1			
324		25	9.7	0.680	9.0	9.5	126.5			
325	27	11.3	0.737	9.7	10.5	126.7				
326	26	10.3			10.2	125.9				
328	37.5	14.6	0.850	11.3	12.6	126.5				
330	41	16.1	1.021	13.6	14.6	126.6				
331	43	17.0	1.026	13.6	15.1	126.4				
333.5	47	18.3	1.191	15.9	17.0	127.0				
335	50	19.4	1.361	18.2	19.0	126.2				
336	53	20.4			20.4	126.3				
338	71	27.6	1.531	20.6	24.0	126.5				
342	82	31.9	1.028	26.1	29.6	126.2				

Table V. Vapor Pressure and Free Energy Function Changes of the *p*-Chloroaniline Vaporization

run	<i>T</i> , K	torsion		weighing			$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ , J mol <sup>-1</sup> K <sup>-1</sup>
		$\alpha$ , deg	10 <sup>5</sup> <i>P</i> , Pa	dg/dt, mg/min	10 <sup>5</sup> <i>P</i> , Pa	av 10 <sup>5</sup> <i>P</i> , Pa	
58	299			0.024	0.3	0.3	179.7
	304			0.033	0.6	0.6	181.0
	307			0.066	0.8	0.9	181.0
	311.5	5.5	2.1	0.104	1.3	1.3	181.0
	313			0.113	1.5	1.7	181.9
	316			0.151	2.0	2.0	180.6
	321			0.236	3.1	3.1	180.4
	322.5	8	3.1	0.269	3.5	3.5	180.4
	326			0.373	4.9	4.8	180.2
	332			0.624	8.3	8.7	180.8
	333.5			0.709	9.4	10.0	180.9
	336.5			0.893	12.0	12.7	180.9
	340			1.113	15.0	17.0	181.1
	342.5			1.380	18.7	22.4	181.3
	355.5	135	54.9	54.9	54.9	180.3	
	361.5	135.5	83.2		83.2	180.0	
	66	325			0.397	5.2	5.6
329.5				0.567	7.5	7.5	181.4
334				0.964	12.8	12.8	182.6
336				1.021	13.6	13.6	181.7
338				1.130	15.2	15.2	181.2
341				1.758	23.8	23.8	182.8
344		70	28.8	1.984	26.9	27.5	182.0
345		79	32.8	2.192	29.8	31.6	182.5

Table VI. Summary of the Vapor Pressure and the Vaporization Enthalpy and Entropy Changes of *o*-, *m*-, and *p*-Chloroaniline<sup>a</sup>

compd	method	run	no. of points	<i>T</i> , K	log <i>P</i> (kPa) = <i>A</i> - <i>B</i> / <i>T</i>		$\Delta H^\circ_T \approx \Delta H^\circ_{298}$ , kJ mol <sup>-1</sup>	$\Delta S_T$ , J mol <sup>-1</sup> K <sup>-1</sup>
					<i>A</i>	<i>B</i>		
<i>o</i> -chloroaniline	tors-weigh	62	13	287-336	8.85 ± 0.18	3041 ± 73	58.2 ± 1.4	131 ± 3
		65	20	294-330	8.65 ± 0.15	2983 ± 47	57.1 ± 1.0	127 ± 3
	torsion		16	292-342	8.49 ± 0.20	3003 ± 52	57.5 ± 1.0	124 ± 4
			20	291-338	8.59 ± 0.13	3009 ± 58	57.6 ± 1.0	126 ± 3
<i>m</i> -chloroaniline	tors-weigh	63	8	292-346	8.70 ± 0.10	3151 ± 32	60.3 ± 0.6	128 ± 2
		64	20	304-342	8.81 ± 0.13	3188 ± 43	61.0 ± 0.8	130 ± 3
	torsion		35	307-349	9.06 ± 0.10	3204 ± 34	61.4 ± 0.6	135 ± 2
<i>p</i> -chloroaniline	tors-weigh	58	16	299-316	11.40 ± 0.10	4139 ± 88	79.3 ± 1.7	179 ± 2
		66	8	325-345	11.60 ± 0.40	4185 ± 14	80.1 ± 0.3	184 ± 8
	torsion		27	315-346	10.33 ± 0.30	4097 ± 77	78.5 ± 1.8	159 ± 6

<sup>a</sup>The errors are standard deviations.

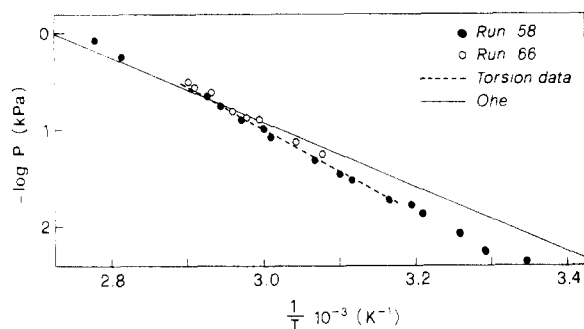


Figure 4. Vapor pressure of *p*-chloroaniline.

discussed in previous section. In the same table the results obtained by the conventional torsion apparatus and the derived enthalpy and entropy changes associated to the vaporization process are also reported. The associated errors are only standard deviations.

From the results, the following pooled equations were selected

*o*-chloroaniline

$$\log P \text{ (kPa)} = (8.63 \pm 0.16) - (3006 \pm 56)/T$$

*m*-chloroaniline

$$\log P \text{ (kPa)} = (8.86 \pm 0.10) - (3180 \pm 40)/T$$

*p*-chloroaniline

$$\log P \text{ (kPa)} = (11.20 \pm 0.20) - (4170 \pm 60)/T$$

where the values reported for each compound are the weighed ( $1/\sigma$ ) averages of the data for each individual experimental run. The overall errors are estimated.

A comparison of our results with those reported in literature (see Figures 2, 3, and 4) shows a substantial agreement among the absolute vapor pressures in the covered temperature range but a disagreement as concerns the vaporization enthalpy values of *m*- and *p*-chloroaniline. In particular, our enthalpy value of *m*-chloroaniline is lower by about 30 kJ mol<sup>-1</sup> than that selected by Ohe, while the value obtained for the *p*-chloroaniline is higher by about 20 kJ mol<sup>-1</sup>. The agreement between the

results obtained by two different methods leads to the conclusion that our vapor pressure values are more reliable than the very few data found in literature, and, therefore, we believe that the vaporization enthalpies of *o*-, *m*-, and *p*-chloroaniline,  $\Delta H^\circ_{298} = 57.5, 60.9, \text{ and } 79.0 \text{ kJ mol}^{-1}$ , respectively, are most reliable and that the associated overall uncertainties in all cases should not exceed 5 kJ mol<sup>-1</sup>. It is surprising that *p*-chloroaniline shows a vaporization enthalpy value higher than those of *m*- and *o*-chloroaniline while the corresponding  $\Delta H$  values (in kJ mol<sup>-1</sup>, referred to *o*-, *m*-, *p*- structures respectively) of similar chloro compounds reported in literature, as chlorophenol (46, 53, 57) (1), chlorotoluene (38, 46, 44) (1), chlorobenzoyl chloride (53, 50, 52) (15), and chloroethylbenzene (46, 45, 44) (15) resemble very closely.

**Registry No.** *o*-Chloroaniline, 95-51-2; *m*-chloroaniline, 108-42-9; *p*-chloroaniline, 106-47-8.

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## Thermodynamics of the Dissociation of Protonated Tris(hydroxymethyl)aminomethane in 25 and 50 wt % 2-Propanol from 5 to 45 °C

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The dissociation constants of the isoelectric dissociation of the protonated base tris(hydroxymethyl)aminomethane ( $\text{TrisH}^+$ ) has been measured in 25 and 50 wt % 2-propanol as a function of temperature. The usual associated thermodynamic functions are calculated from the results. The effect of the added solvent (2-propanol) on the thermodynamics of this dissociation is compared to that of other alcohols for which comparable data is available. In this work the  $pK_a$  of  $\text{TrisH}^+$  in the two solvent systems studied could be fitted to the following equations: 25 wt % (2-propanol),  $pK_a = 2546.3/T - 0.16244 - 0.00195787$ ; 50 wt % (2-propanol),  $pK_a = 3346.0/T - 6.7042 + 0.0106407$  with a standard deviation of fit to the line of 0.002 at the temperatures used.

#### Introduction

Studies of acid-base behavior in mixed solvents generally include several acids which are easy to purify and work with and which represent fundamental acid or base "types". One of these is the protonated form of tris(hydroxymethyl)aminomethane which is readily available in a highly pure crystalline form and whose  $pK_a$  (near 8 at 25 °C) makes it a useful buffer for medical and marine chemical studies.

The effects of water and organic solvent mixtures on the dissociation of  $\text{TrisH}^+$  are of even greater interest because of the presence of three hydroxyl groups, which give the base a potentially high degree of hydrogen bonding.

The dissociation of  $\text{TrisH}^+$  has been studied in a number of solvent/water mixtures (1-8). The  $pK_a$  of  $\text{TrisH}^+$  is always