Journal of Chemical and Engineering Data, Vol. 23, No. 2, 1978 **103**

Dissociation Constants of Toluic Acids in Aqueous Solution at Different Temperatures and Study of Related Thermodynamic Parameters[†]

M. Sengupta,* K. Pal, A. Chakravarti, and P. Mahapatra

Department of Pure Chemistry, University College of Science, Calcutta 700009, India

Dissociation constants of toluic acids have been determined by the emf method using a buffered cell, without liquid junction, of the type Pt; H_2(1 atm)|HA(m_1), NaA(m_2), NaCl(m_3)|AgCl; Ag. Measurements have been made at seven different temperatures, at 5 °C intervals, over the range 5–35 °C. Two different Ag|AgCl electrodes prepared by the thermoelectrolytic method gave closely agreeing results. At each temperature, measurements were made on several different mixtures of total ionic strengths $\mu \approx 0.01$–0.10. Proper extrapolation of the "apparent" dissociation constant pK_a' ($=2S_f(\mu d_0)^{1/2} - \log [m_{H^+}'(m_2 + m_{H^+}') (m_1 - m_{H^+}')]$) vs. μ plots gave the pK_a value of the acid at the seven different temperatures. Herefrom the thermodynamic parameters $\Delta G°$, $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ of the dissociation equilibrium were calculated.

Introduction

In the determination of dissociation constants of weak acids by the emf method, the electromotive force of the buffered cell without liquid junction using an Ag|AgCl electrode of the type Pt; H_2(1 atm)|HA(m_1), MA(m_2), MCl(m_3)|AgCl; Ag is given by the well-known equation

$$E = E° - RT/F \ln \gamma_{H^+}\gamma_{Cl^-}m_{H^+}m_{Cl^-} \tag{1}$$

The advantages of such a cell for the above mentioned purpose are (i) buffer action permits easy and accurate determination of small hydrogen ion concentrations, (ii) necessary extrapolation is straight forward, and (iii) the concentrations of the weak acid HA and of the two salts MA and MCl (where M = Na or K) may be made approximately equal or different from one another to any convenient extent.

γ_{H^+} and m_{H^+} may be eliminated by incorporating the expression for the thermodynamic dissociation constant of the weak acid HA,

$$K_a = \frac{m_{H^+}m_{A^-}}{m_{HA}} \frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}} \tag{2}$$

into eq 1, resulting in

$$\frac{(E - E°)F}{2.303RT} + \log \frac{m_{Cl^-}m_{HA}}{m_{A^-}} = -\log K_a - \log \frac{\gamma_{Cl^-}\gamma_{HA}}{\gamma_{A^-}} \tag{3}$$

Since $m_{Cl^-} = m_3$, $m_{HA} = m_1 - m_{H^+}$ and $m_{A^-} = m_2 + m_{H^+}$, the left side of eq 3 is known if m_{H^+} is negligible compared to m_1 and m_2. If m_{H^+} is too large to be neglected, then the value of pK_a may be calculated by successive approximations (*21*); otherwise a procedure based upon the calculation of an "apparent" hydrogen ion concentration, m_{H^+}', is convenient. Thus from eq 1 and 2 and also introducing the Debye–Hückel limiting law one obtains

$$-\log m_{H^+}' = \frac{(E - E°)F}{2.303RT} + \log m_{Cl^-} - 2S_f(\mu d_0)^{1/2} \tag{4}$$

The ionic strength is approximately

$$\mu \approx m_2 + m_3 + m_{H^+}' \tag{5}$$

S_f is the limiting slope of the Debye–Hückel log f vs. $\mu^{1/2}$ plot, and d_0 is the density of water. The approximation introduced by the use of limiting law, neglecting medium effects of the un-ionized weak electrolyte, prevents determination of the true m_{H^+} by this method, but the difference between m_{H^+} and m_{H^+}' decreases rapidly with dilution and vanishes in the limit. An apparent value of pK_a' corresponding to m_{H^+}' may be calculated from eq 6, which is obtained by combining eq 1 and the limiting law; thus, pK_a may be obtained by extrapolation of the values of *pK*$_a'$ vs. ionic strength.

$$\text{p}K_a' = 2S_f(\mu d_0)^{1/2} - \log \frac{m_{H^+}'(m_2 + m_{H^+}')}{(m_1 - m_{H^+}')} \tag{6}$$

The observed values of pK_a for the three isomeric toluic acids at the seven different temperatures could be expressed as a function of the absolute temperature T($=t$ °C + 273.15) by an equation of the form suggested by Harned and Robinson (*22*), namely

$$\text{p}K_a = \alpha/T - \beta + \gamma T \tag{7}$$

The choice of the above form has also been preferred in a very recent paper by Bates, Roy, and Robinson (*2*). The standard thermodynamic quantities $\Delta G°$, $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ for the dissociation process are related in simple fashion to the constants of eq 7. Thus,

$$\Delta G° = (R \ln 10)(\alpha - \beta T + \gamma T^2) \tag{8}$$

$$\Delta H° = (R \ln 10)(\alpha - \gamma T^2) \tag{9}$$

$$\Delta S° = (R \ln 10)(\beta - 2\gamma T) \tag{10}$$

and

$$\Delta C_p° = (R \ln 10)(-2\gamma T) \tag{11}$$

The value of R ln 10 is 4.57493 cal K^{-1} mol^{-1}.

The dissociation constants of a large number of substituted benzoic acids have been reported in the literature (*27*), mostly at one temperature (25 °C), and also for some at different temperatures. Such dissociation constant values are determined by the electrometric and also conductometric, spectrophotometric, etc., methods. The *o*-, *m*-, and *p*-toluic acids have been studied only at 25 °C; the first one (ortho) by Dippy and Lewis (*7, 8*) and also by Halban and Brüll (*14*) using the indicator method, and the other two (meta and para) by Dippy and Lewis (*7, 8*) by the same method. A reevaluation of the dissociation data for all these three acids using an emf method at a number of different temperatures has been taken up and the results are presented.

[†] A part of this paper was presented at the Convention of Chemists (1976) held at Bangalore, India.

0021-9568/78/1723-0103$01.00/0

Table I. E° Values

	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C
o-Toluic acid	0.23390	0.23125	0.22840	0.22524	0.22202	0.21869	0.21496
m-Toluic acid	0.23406	0.23111	0.22844	0.22537	0.22200	0.21841	0.21465
p-Toluic acid	0.23411	0.23144	0.22862	0.22556	0.22231	0.21900	0.21523
				Standard (lit.) values			
	0.23400	0.23134	0.22855	0.22558	0.22246	0.21919	0.21570

Table II. Electromotive Force (E, in Volts) of the Cell Pt; H_2(1 atm)|*o*-Toluic Acid(m_1), Na Salt of *o*-Toluic Acid(m_2), NaCl(m_3)|AgCl; Ag from 5 to 35 °C (m_1 = 0.006 378 mol kg^{-1} ; m_2 = 0.006 480 mol kg^{-1})

	E, V						
m_3, mol kg^{-1}	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C
0.005 599		0.584 31	0.584 24	0.585 39	0.587 02	0.590 28	0.595 11
0.016 04	0.558 52						0.567 62
0.031 92	0.542 19	0.542 41		0.541 98	0.543 55	0.546 19	
0.045 35	0.534 05		0.533 07	0.533 35			0.540 95
0.062 67					0.527 52		
0.062 64	0.526 48	0.526 41	0.525 36			0.530 02	
0.067 23		0.524 81	0.523 63		0.525 91	0.528 37	0.531 30
0.081 45	0.520 37	0.520 36	0.519 05	0.519 21			
0.106 3	0.514 29	0.514 26	0.512 91	0.512 96	0.515 70	0.518 15	0.520 35

Experimental Procedure

o-Toluic acid (99%, Fluka) and *m*- and *p*-toluic acids (99%, B.D.H.) were purified by recrystallization from 50% aqueous ethanol and dried in a vacuum desiccator. The sodium salt of the acids was prepared by neutralizing weighed amounts of dry acid with a requisite quantity of NaOH solution (the fresh beads were washed with double distilled water several times to free them from any surface-carbonate layer, and the prepared NaOH solution was stored in an air tight jena-glass bottle). Sodium chloride (G. R., E. Merck) was recrystallized twice from double distilled water, dried in an air-oven, and preserved in a vacuum desiccator. All aqueous solutions were prepared using water of conductivity 2 × 10^{-6} mho cm^{-1}, and stored in jena-glass containers. Solutions of different ionic strenghts were prepared by mixing requisite weighed quantities of sodium chloride solution (of known molality) with a definite weighed quantity of acid–salt mixture of constant molality ratio.

Ag|AgCl electrodes prepared by the thermoelectrolytic method (*23*) were used. Four different hydrochloric acid solutions of molalities, 0.01, 0.02, 0.03, and 0.04, prepared from the middle fraction distillate of an azeotropic mixture of A.R. hydrochloric acid and water, were used in the determination of $E°$ values of the electrodes. A pair of two different electrodes, for duplicate emf measurements of each set, was used, and the emf values for the two electrodes were found to agree closely. An LN type K2 potentiometer in conjunction with a sensitive LN moving coil galvanometer of sensitivity 1 mm/m at 10^{-5} V was used. A thermostatic bath with a temperature regulation of ±0.1 °C was used to obtain measurements at seven different temperatures: 5, 10, 15, 20, 25, 30, and 35 °C. Electrolytic hydrogen gas was freed of any oxygen and then washed by bubbling through distilled water; the gas stream was divided into four parts to feed each of the four electrode vessels in any particular run; the flow in each could be conveniently controlled. The barometric pressure was never very different from the standard value during the experiments and the depth of hydrogen gas inlet below the level of the solution in the vessel was very small (only a few millimeters). Therefore neither the "barometric pressure correction" nor the "depth correction" was deemed significant and hence was neglected.

Calculations and Results

Equations 4, 5, and 6 were used to calculate the "apparent" value of pK_a'. To begin with, the ionic strength was taken to be given by $\mu = m_2 + m_3$, and an approximate value of m_{H^+}' was obtained therefrom by using eq 4. The E^0 values (in volts) of the Ag|AgCl electrodes used in the eq 4, for the three acids, at the seven different temperatures, were obtained previously by the usual extrapolation procedure for emf values in pure hydrochloric acid solutions of different molalities and are given in Table I. Also given, for comparison, are the literature values of E^0 of the Ag|AgCl electrode in pure HCl at the same seven temperatures. The improved estimate of the ionic strength, obtained by using this value of m_{H^+}' in eq 5 was then put into eq 6 to obtain the apparent value of pK_a'. As the difference between m_{H^+} and m_{H^+}' decreases rapidly with dilution, the true value of pK_a may be obtained from a plot of the pK_a' values vs. ionic strengths of the solutions using eq 5 and by making necessary extrapolation against μ.

The following expressions for *o*-, *m*-, and *p*-toluic acids were obtained by the method of least squares:

$$\mathrm{p}K_a(o\text{-toluic acid}) = 10361.0/T - 65.4492 + 0.1160T \quad (12)$$

$$\mathrm{p}K_a(m\text{-toluic acid}) = 4582.0/T - 26.6484 + 0.05205T \quad (13)$$

$$\mathrm{p}K_a(p\text{-toluic acid}) = 12086.0/T - 74.9297 + 0.13000T \quad (14)$$

All calculations were performed with the aid of an IBM 1130 computer at the University of Calcutta Computing Center. The emf data for the cells are summarized in Tables II–IV.

The pK_a values obtained at different temperatures are listed in second, fifth, and eighth columns of the Table V. The same calculated by using eq 12, 13, and 14 and the corresponding standard deviations are respectively shown in columns 4, 7, and 10, 3, 6, and 9 in the same table. The standard deviations recorded are well within the limits of precision measurements.

The values of the standard thermodynamic quantities $\Delta G°$, $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ evaluated by using eq 8, 9, 10, and 11 are listed in Table VI.

Discussion

It has already been mentioned that earlier workers (*7*, *8*, *14*) determined the ionization constant values of isomeric toluic acids by the colorimetric method. Modified photoelectric colorimetry (*15*, *20*, *25*) and conductometry (*21*) have also been applied

Table III. Electromotive Force (E, in Volts) of the Cell Pt; H_2(1 atm)| m-Toluic Acid(m_1), Na Salt of m-Toluic Acid(m_2), NaCl(m_3)|AgCl; Ag from 5 to 35 °C (m_1 = 0.005 303 mol kg^{-1}; m_2 = 0.005 014 mol kg^{-1})

	E, V						
m_3, mol kg^{-1}	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C
0.024 91	0.559 41	0.561 46					0.573 36
0.036 27	0.550 53	0.552 60	0.554 80	0.556 78	0.558 87	0.561 10	0.563 62
0.040 84		0.549 81	0.552 00	0.553 98	0.556 04		
0.055 15	0.540 78	0.542 85	0.545 03				
0.063 69	0.537 40	0.539 52	0.541 66	0.543 65	0.545 65	0.547 54	0.549 24
0.074 98	0.533 67		0.537 92	0.539 96	0.542 00	0.543 70	0.545 17
0.075 58				0.539 78	0.541 80	0.543 52	
0.100 73		0.529 23		0.533 54	0.535 62	0.537 05	0.539 10

Table IV. Electromotive Force (E, in Volts) of the Cell Pt; H_2(1 atm)|p-Toluic Acid(m_1), Na Salt of p-Toluic Acid(m_2), NaCl(m_3)|AgCl; Ag from 5 to 35 °C (m_1 = 0.002 312 mol kg^{-1}; m_2 = 0.002 333 mol kg^{-1})

	E, V						
m_3, mol kg^{-1}	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C
0.007 774	0.609 57	0.608 62	0.607 78				
0.017 52	0.590 25	0.589 07	0.587 81	0.587 04			
0.029 81					0.575 04	0.576 51	0.578 66
0.040 32	0.570 78	0.569 39	0.567 91	0.566 95	0.568 40	0.569 26	0.571 21
0.045 50				0.564 26	0.565 76	0.566 80	0.568 20
0.057 99	0.562 35	0.560 98	0.559 25	0.558 65	0.560 86	0.561 45	0.562 37
0.068 10	0.558 81	0.557 49	0.555 69	0.555 00			
0.076 44	0.556 17	0.554 85	0.553 12	0.554 40	0.555 75	0.555 89	
0.087 36							0.552 67

Table V. Acidic Dissociation Constants of o-, m-, and p-Toluic Acids in Water from 5 to 35 °C

	o-Toluic acid			m-Toluic acid			p-Toluic acid		
t, °C	pK_a(obsd)	Sd[a]	pK_a(calcd)[b]	pK_a(obsd)	Sd[a]	pK_a(calcd)[b]	pK_a(obsd)	Sd[a]	pK_a(calcd)[b]
5	4.063	0.0006	4.067	4.299	0.0003	4.302	4.678	0.0007	4.683
10	4.009	0.0004	3.989	4.278	0.0002	4.271	4.585	0.0008	4.565
15	3.946	0.0006	3.935	4.260	0.0005	4.251	4.500	0.0012	4.475
20	3.912	0.0003	3.901	4.242	0.0002	4.240	4.424	0.0008	4.409
25	3.885	0.0004	3.889	4.234	0.0003	4.238	4.357	0.0006	4.368
30	3.892	0.0004	3.895	4.242	0.0002	4.244	4.347	0.0017	4.349
35	3.937	0.0006	3.921	4.267	0.0002	4.259	4.375	0.0007	4.352

[a] Standard deviation of the intercept. [b] Calculated by eq 12 for o-, eq 13 for m-, and eq 14 for p-toluic acids.

Table VI. Thermodynamic Functions for the Dissociation of o-, m- and p-Toluic Acids in Water from 5 to 35 °C

	o-Toluic acid				m-Toluic acid				p-Toluic acid			
t, °C	$\Delta G°$, cal mol^{-1}	$\Delta H°$, cal mol^{-1}	$\Delta S°$, cal K^{-1} mol^{-1}	$\Delta C_p°$, cal K^{-1} mol^{-1}	$\Delta G°$, cal mol^{-1}	$\Delta H°$, cal mol^{-1}	$\Delta S°$, cal K^{-1} mol^{-1}	$\Delta C_p°$, cal K^{-1} mol^{-1}	$\Delta G°$, cal mol^{-1}	$\Delta H°$, cal mol^{-1}	$\Delta S°$, cal K^{-1} mol^{-1}	$\Delta C_p°$, cal K^{-1} mol^{-1}
5	5175	6340	4.2	−295	5474	2540	−10.5	−132	5958	9277	11.9	−330
10	5167	4851	−1.1	−300	5532	1871	−12.9	−134	5913	7608	6.0	−336
15	5186	3335	−6.4	−305	5603	1191	−15.3	−137	5898	5909	0.0	−342
20	5232	1792	−11.7	−311	5685	499	−17.7	−139	5913	4180	−5.9	−348
25	5304	223	−17.0	−316	5780	−204	−20.1	−142	5957	2422	−11.8	−354
30	5402	−1371	−22.3	−321	5886	−920	−22.4	−144	6032	633	−17.8	−360
35	5527	−2993	−27.6	−327	6004	−1648	−24.8	−146	6136	−1184	−23.7	−366

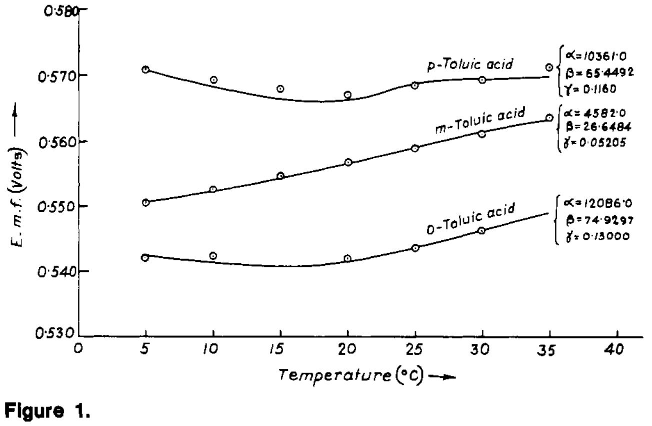

Figure 1.

for determining ionization constants of a good number of weak electrolytes in aqueous solutions. The colorimetric method is often applicable at concentrations outside the range which can be investigated by the emf method, and the conductometric method in many cases gives accurate values of the ionization constant and also provides insight into the medium effect upon the latter. Both of these methods, as generally used so far, are limited to a particular temperature, and therefore yield no knowledge regarding heats of ionization and other thermochemical quantities associated with the ionization reactions. The electromotive force method, however, may be applied for computing the variation of ionization constants with temperature and also the thermochemical quantities related to the process. Moreover, the method may be applied to gather information concerning medium effects also. In several of these respects the emf method is superior to either the colorimetric or the conductometric method.

Electrometrically determined pK_a values for the three isomeric toluic acids, as obtained by us, are slightly different (0.12 and 0.15% lower for the ortho and meta isomers, respectively, and 0.35% higher for the para isomer) from the literature values (*3*, *11*, *26*), at 25 °C. An idea about the scatter of our experimental emf data, in its temperature dependence at any particular composition, for example, can be seen from Figure 1 (the data plotted are for m_3 = 0.040 32, 0.036 27, and 0.031 92 M for the para, meta, and ortho isomers, respectively). The pK_a values of these three acids at all the seven different working temperatures can be calculated by the respective equations 12–14; the corresponding pK_a' values for the compositions mentioned can be calculated herefrom by correcting for the ionic strength effect, using the values of the extrapolation parameters as obtained earlier while extrapolating the pK_a' values of any acid at any particular temperature so as to give the pK_a value at that temperature. The emf values can now be back-calculated using eq 4–6; these are shown plotted as continuous curves in Figure 1, to be compared with the experimental emf values at the different temperatures. It is seen that the scatter of the experimental value from the calculated one at any temperature is generally no more than 1–1.5 mV, usually much smaller, for all three acids.

Based upon our meticulous adaptation of experimental precautions, accurate emf recording, and proper data processing, we can expect our results to be accurate at least up to the second decimal place for all seven temperatures.

The acidic character of the substituted aromatic acids is to be considered from the point of view of the inductive effect of the substituent and the resonance of the carboxylate ion as also the substituted aromatic nucleus. The acid weakening groups are the ones that activate the ring toward electrophilic substitution, and the acid strengthening groups are the ones that deactivate it toward electrophilic substitution. Alkyl groups when present in the aromatic ring behave either as activating (weakly) in ortho or para positions or deactivating in meta position with respect to the COOH group. The *o*- and *p*-toluic acids from this point of view should be less acidic than benzoic acid and the *m*-toluic acid should be stronger than either the ortho or the para acid. We have recognized from our experiment that the para acid ($K_a = 4.395 \times 10^{-5}$ at 25 °C) is less strong than benzoic acid ($K_a = 6.30 \times 10^{-5}$ at 25 °C), and the meta acid is stronger ($K_a = 5.97 \times 10^{-5}$ at 25 °C) than the para acid. The ortho acid is, however, stronger than either the meta or the para acid.

Ortho-substituted aromatic acids do not fit into the pattern set by their meta and para isomers. Nearly all ortho substituents exert an effect of the same kind, acid strengthening, whether they are electron withdrawing or electron releasing, and the effect is unusually large (*26*). This "ortho effect" undoubtedly has to do with the nearness of the groups involved, but it is more than just steric hinderance arising from their bulk. The relatively higher value of K_a for *o*-hydroxybenzoic acid, for example, as compared to its other isomers is explained on the basis of the existence of hydrogen bonding between the hydrogen atom of the hydroxyl group and one of the oxygen atoms of the carboxyl group. This is also supported by the comparatively lower solubility in water of salicylic acid than that of the other isomers (*26*). In the present case, however, the possibility of intramolecular hydrogen bonding as being responsible for the decreasing order of the dissociation constant values (as also, of the solubilities in water) from ortho to para can be discounted.

The order of relative acidic behavior of the three isomeric toluic acids has been found to be maintained throughout the temperature range we studied. A closer examination of the variation of the dissociation constant values with temperature for the isomeric toluic acids reveals the fact that in each case the dissociation constant at first increases and then decreases as the temperature is raised. This type of behavior has been found to be quite general with weak acids. The actual temperature at which the maximum value of the dissociation constant is attained depends on the nature of the acid; for formic and acetic acids, for example, it is between 20 and 25 °C, but higher and lower values have also been found for other acids (*12*). For the isomeric toluic acids, the corresponding temperatures of maximum dissociation constant values as found here are the following: (a) *o*-toluic acid, 25.7 °C; (b) *m*-toluic acid, 23.5 °C; (c) *p*-toluic acid, 31.7 °C.

The attainment of a maximum dissociation constant value of carboxylic acids at a particular temperature may be attributed to the relative effectiveness of two opposite phenomena occurring simultaneously (*13*). The first one arises from the nature of the medium (water here), the reciprocal of the dielectric constant (D) of which is linearly related to $-\log K_a$ (provided $D > 25$); an increase in ($1/D$) with temperature would thus result in an increase in pK_a value. Contrary to this is the second one, which is but a normal tendency for the dissociation constant (regarded as an equilibrium constant) of an endothermic reaction to increase with increasing temperature.

The gradual increase in the free energy change with increasing temperature for the dissociation process of the three isomeric toluic acids, as we have observed, may be accounted for, according to Born (*6*), by the gradual increase in the electrostatic free energy of the system which accompanies an enhancement of the work of charging of the anion in the acid and simultaneous transfer of the corresponding hydrogen ion in aqueous medium.

It is seen from Table VI that the entropy and heat capacity values for the ionic dissociation process of each of the three isomeric toluic acids decrease with gradual increase in temperature (5–35 °C). Such a gradual decrease in the two thermodynamic quantities may be explained in light of the Bernal–Fowler theory of the quasi-crystalline structure (*1*, *4*, *5*) of liquid water, and the orientation of the water molecules around ions, which has been applied for the computation of ionic heat capacities by Everett and Coulson (*10*) and of the entropy of ions by Eley and Evans (*9*) and Latimer (*24*). The entropy characterizes the degree of disorder in a system. Dissociation of electrolytes into ions increases the degree of ordering of the solvent molecules. The entropy of solvation of the ions of the electrolyte is therefore always negative. The process $HA + H_2O = A^- + H_3O^+$ thus reflects a net loss of freedom of the solvent molecules resulting from the interaction of the solvent with the ions produced. With increase in temperature the orientation of solvent molecules around the ions and hence the orderliness of the arrangement of solvent molecules would be decreased, which would not happen in the case of the undissociated acid.

Acknowledgment

The award of a Senior Research Fellowship to one of the authors (P.M.) by the C.S.I.R., Government of India, is gratefully acknowledged.

Literature Cited

(1) Anthropov, L., "Theoretical Electrochemistry", Mir Publishers, Moscow, 1972, p 88.
(2) Bates, R. G., Roy, R. N., Robinson, R. A., *J. Solution Chem.*, **3**, 905 (1974).
(3) Bell, R. P., "Acids and Bases. Their Quantitative Behavior", 2nd ed, Methuen and Co. Ltd., London, 1969, p 54.
(4) Bernal, J. D., Fowler, R. H., *J. Chem. Phys.*, **1**, 515 (1933).
(5) Bockris, J. O'M., Reddy, A. K. N., "Modern Electrochemistry", Vol. I, Plenum, New York, N.Y., 1970, Chapter 2.
(6) Born, M., *Z. Phys.*, **1**, 45 (1920).
(7) Dippy, J. F. J., Lewis, R. H., *J. Chem. Soc.*, 1426 (1937).
(8) Dippy, J. F. J., Lewis, R. H., *J. Chem. Soc.*, 644 (1936).
(9) Eley, D. D., Evans, M. G., *Trans. Faraday Soc.*, **34**, 1093 (1938).
(10) Everett, D. H., Coulson, C. A., *Trans. Faraday Soc.*, **36**, 633 (1940).
(11) Finar, I. L., "Organic Chemistry", 6th ed, Vol. I, Longmans, Green and Co., New York, N.Y., 1973, p 771.

(12) Glasstone, S., "An Introduction to Electrochemistry", 9th Printing, D. Van Nostrand, New York, N.Y., 1960, p 336.
(13) Gurney, R. W., *J. Chem. Phys.*, **6**, 499 (1938).
(14) Halban, H. v., Brüll, J., *Helv. Chim. Acta*, **27**, 1719 (1944).
(15) Halban, H. v., Ebert, L., *Z. Phys. Chem., Abt. A*, **112**, 321 (1924).
(16) Halban, H. v., Ebert, L., *Z. Phys. Chem., Abt. A*, **112**, 359 (1924).
(17) Halban, H. v., Eisenbrand, J., *Z. Phys. Chem., Abt. A*, **122**, 337 (1926).
(18) Halban, H. v., Eisenbrand, J., *Z. Phys. Chem., Abt. A*, **146**, 294 (1930).
(19) Halban, H. v., Siedentopf, K., *Z. Phys. Chem., Abt. A*, **100**, 208 (1922).
(20) Halban, H. v., Siedentopf, K., *Z. Phys. Chem., Abt. A*, **103**, 71 (1922).
(21) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolytic Solutions", 3rd ed, Reinhold, New York, N.Y., 1958, pp. 651 and 456.
(22) Harned, H. S., Robinson, R. A., *Trans. Faraday Soc.*, **36**, 973 (1940).
(23) Ives, D. G. J., Janz, G. J., "Reference Electrodes", Academic Press, New York, N.Y., 1961, p 209.
(24) Latimer, W. M., Pitzer, K. S., Shansky, C. M., *J. Chem. Phys.*, **7**, 108 (1939).
(25) Meyer, E., Rosenberg, H., *Vierteljahresschr. Astron. Ges.*, **48**, 3 (1913).
(26) Morrision, R. T., Boyd, R. N., "Organic Chemistry", 2nd ed., Prentice-Hall of India, 1966, pp 600 and 579.
(27) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions", 2nd ed, Butterworths, London, 1959, p 526.

Received for review July 5, 1977. Accepted December 20, 1977.

Enthalpies of Fusion, Freezing Points, Heat Capacities, Densities, and Shear Viscosities of Hydrogenated Dimers of Norbornadiene and Cyclopentadiene

Cornelius T. Moynihan,* Hiroyuki Sasabe, David S. Czaplak, and Urban E. Schnaus

Vitreous State Laboratory, Chemical Engineering and Materials Science Department, Catholic University of America, Washington, D.C. 20064

Enthalpies of fusion, freezing points, crystal and liquid heat capacities, liquid densities, and shear viscosities have been determined for four isomeric hydrogenated dimers of norbornadiene (NBD) and one hydrogenated cyclopentadiene dimer. The hydrogenated NBD dimers exhibit a large spread in their enthalpy of fusion values. The viscosities of the hydrogenated NBD dimers are all of comparable magnitude and considerably larger than the viscosity of the hydrogenated cyclopentadiene dimer. Relative magnitudes of the viscosities appear to be governed primarily by the T_2 parameter in the VTF equation.

Introduction

In this paper we report determinations of the freezing points, enthalpies of fusion, heat capacities, densities, and shear viscosities of high-purity specimens of four isomers of the hydrogenated dimers of norbornadiene (NBD) and of one lower molecular weight polycyclic alkane (*exo*-tetrahydrodicyclopentadiene). The structures of these compounds in terms of their carbon atom skeletons are shown in Figure 1, along with the abbreviations (HXX, etc.) by which they will be designated in the remainder of this paper.

Experimental Section

Samples of the five compounds of Figure 1 were obtained from Dr. A. Schneider of Suntech, Inc. Their purities, as determined by him using vapor-phase chromatography (VPC), are given in Table I. In all cases the impurities were other isomers of the same compound.

The heat capacity and melting behavior of these compounds were characterized using a Perkin-Elmer DSC-2 differential scanning calorimeter linked to a digital data acquisition system and cooled by a two-stage refrigerator when measurements were in the range −70 °C and above or by liquid N_2 when measurements at lower temperatures were required. The DSC temperature scale at each heating rate was calibrated using the melting points of Hg and H_2O. Samples were contained in sealed Al volatile sample pans. Sample masses ranged from 0.7 to 15.7 mg, smaller samples being used for enthalpy of fusion determinations and larger samples for crystal and liquid heat capacity determinations. Each sample was slowly cooled or held at a low temperature on the DSC until freezing occurred, as manifested by an exothermic signal on the DSC output. For enthalpy of fusion determinations the heat capacity C_p was then measured over the melting region while heating at a rate of 0.62 K/min. For crystal and liquid heat capacity determinations C_p was measured over a larger temperature interval at a heating rate of 5 or 10 K/min. Single-crystal Al_2O_3 and benzoic acid were used as heat capacity calibration standards. Temperature corrections during the fusion process necessitated by the thermal resistance between the sample pan and sample holder were made according to a previously described procedure (*11*).

Liquid kinematic viscosities ν were measured with factory calibrated Ubbelohde semimicrocapillary viscometers from the Cannon Instrument Co. Liquid densities ρ were measured with a dilatometer constructed by sealing off one end of a 1-mL pipet graduated in 0.01-mL divisions and calibrated by determining the mass of water needed to fill it to a reference mark. The shear viscosity η was obtained by taking the kinematic viscosity–density product $\nu\rho$. The viscometers and dilatometer were thermostated in a water bath (above 0 °C) or methanol bath (below 0 °C) contained in an unsilvered 4-qt Dewar flask. Bath temperatures were measured with a calibrated copper–constantan thermocouple. Viscosities and densities were measured from 70 or 75 °C down to either −69 °C or the temperature at which the sample froze; in the latter case this temperature was generally somewhat below the equilibrium freezing point due to supercooling of the sample. Shear viscosities are estimated to be accurate to about 1% above 0 °C and about 2% below 0 °C; the accuracy of the densities is estimated to be about 0.3%.

Results and Data Analysis

Equilibrium Freezing Point and Enthalpy of Fusion. In Figure 2 is shown a typical plot of heat capacity C_p vs. temperature T in the melting region. Integration of the excess heat capacity, $C_p^{\,x}$, above the baseline shown in Figure 2 gives the apparent specific enthalpy increase due to fusion as a function of the temperature:

$$\Delta h(T) = \int_{T' << T_0}^{T} C_p^{\,x}\, dT' \qquad (1)$$

0021-9568/78/1723-0107$01.00/0