Dissociation Constants of Acetic, Propionic, and *n*-Butyric Acids in 25 and 50 Mass % 2-Propanol + Water from −10 to 25 °C

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Electromotive-force measurement of cells with hydrogen gas electrodes and silver–silver chloride electrodes have been used to determine the p*K* values of acetic acid, propionic acid, and *n*-butyric acid in 25 and 50 mass % 2-propanol + water at eight temperatures from −10 to 25 °C. Hydrogen gas electrodes and silver chloride electrodes were used, and the cell was free from liquid junctions. The data were used to derive the standard changes of Gibbs energy, enthalpy, and entropy for the dissociation processes. A comparison with data for the water solvent shows that addition of 2-propanol to the solvent medium increases p*K* and the Gibbs energy change for each of the acids, while the entropy of dissociation becomes increasingly negative.

Introduction

During the past two decades, considerable attention has been given to the behavior of acids and bases in mixed media composed of water and an amphiprotic organic solvent such as the alcohols (see, for example, refs 1–4). Nevertheless, very few studies have extended to the subzero temperature range, despite recent successes in the preservation of human tissues and organs in low-temperature media at controlled pH (*5*, *6*). In addition, data on systems of this sort may aid in the elucidation of the complex nature of solute–solvent and solvent–solvent interactions in media containing two types of solvent species.

The electromotive-force (emf) method first used by Harned and co-workers (*7*–*9*) to determine the p*K* of weak monoprotic acids in aqueous solutions over a range of temperatures is readily adaptable to use in many mixed solvents. The highly reliable hydrogen gas and silver–silver chloride electrodes behave reversibly in water-rich media containing ethanol (*10*) and DMSO (*11*) at temperatures below 0 °C, undesirable side reactions not being apparent.

In order to apply the emf method to the determination of p*K* values for acid–base systems, one must know the standard potentials (E°) of the cell over the temperature range involved. We have recently determined E° for 25 and 50 mass % 2-propanol (isopropyl alcohol, IsoPr) + water over the temperature range −10–25 °C (*12*), supplementing and extending earlier data (*13*, *14*) for this solvent system. We have now studied the behavior of three aliphatic monoprotic acids, namely, acetic (HAc), propionic (HPr), and *n*-butyric acid (HBu), in the same two solvent mixtures and over the same range of temperatures. The cell used may be represented schematically as follows:

$$\mathrm{Pt;H_2(g,\ 1\ atm)|HA}\ (m)\mathrm{,NaA}\ (m)\mathrm{,NaCl}\ (m)\ \mathrm{in\ IsoPr} + \mathrm{H_2O|AgCl;Ag}$$

where A represents Ac, Pr, or Bu. From the emf data for this cell, the p*K* values for the three weak acids over the temperature range −10–25 °C have been calculated, as well as the standard changes of Gibbs energy, enthalpy, and entropy for the dissociation processes at 25 °C.

Experimental Section

Hydrochloric acid was diluted to the azeotropic composition and distilled twice, the first and last thirds of the distillate being rejected in each case. A stock solution was standardized both by the gravimetric method of weighing AgCl and by weight titration with a standard solution of NaOH. The latter was prepared by dilution of a 50% carbonate-free solution and standardized vs potassium hydrogen phthalate of primary standard grade.

Glacial acetic acid of reagent grade was distilled four times. The first three distillations were made with the addition of 2% anhydrous chromic trioxide in the manner described by Vogel (*15*). Propionic acid and *n*-butyric acid, with assigned purities of 99% and 99.5%, respectively, were obtained from Sigma Chemical Co. They were used without further purification, following assay by titration with the standard solution of NaOH.

Sodium acetate (assay 100.2%) and sodium propionate were of reagent grade. The latter salt was dried at 105 °C before use. The buffer solutions containing sodium butyrate were prepared from the acid and standard NaOH. Primary standard NaCl (purity 100.05%) was dried for 2 h at 105 °C and kept, along with the sodium acetate and propionate, in a desiccator over anhydrous calcium chloride. A commercial lot of 2-propanol was purified by two distillations.

The bases for the platinum–hydrogen electrodes were coated with platinum black by electrolysis for 25 min at a current of 30 mA in a solution of chloroplatinic acid. The silver electrodes were formed by thermal decomposition of well-washed silver oxide on platinum helices at 500 °C. They were coated with AgCl by anodizing in 1 M HCl for 45 min at a current of 10 mA. Both types of electrode were soaked for 16 h in the appropriate mixed solvent before use.

The acetate–chloride and propionate–chloride buffer solutions were prepared by adding appropriate amounts of isopropyl alcohol and water to the weighed acid and salts. The butyric acid/sodium butyrate buffers were prepared by adding butyric acid and sodium chloride to the calculated quantity of standard NaOH before adjustment of the solvent composition to the desired 25 or 50 mass % isopropyl alcohol.

Initial emf measurements were made at 25 °C. After an equilibration period of 10 h, the temperature was lowered in intervals of 5 deg to −10 °C. Equilibrium required 2 h at the higher temperatures after a change of 5 deg but somewhat longer at 0 °C and below. Final measurements at 25 °C differed from the initial values by less than ±0.3 mV. Other details of the experimental procedures will be found elsewhere (*12*–*15*).

Results and Calculations

In our earlier paper (*12*), we have listed the properties of the two solvents, 25 and 50 mass % isopropyl alcohol + water, over the temperature range studied. These include the solvent vapor pressure, density, and dielectric constant, as well as the values of the Debye–Hückel constants *A* and *B* derived from

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Table I. Corrected emf (in Volts) for the Cell Pt;H_2(g, 1 atm)|HA (m),NaA (m),NaCl (m) in 25 Mass % 2-Propanol + H_2O|AgCl;Ag from −10 to 25 °C

	emf at various temperatures (°C)							
m/(mol kg^{-1})	−10	−5	0	5	10	15	20	25
HA = Acetic Acid								
0.00742	0.60464	0.60927	0.61437	0.61913	0.62376	0.62848		0.63710
0.00989	0.59801	0.60256	0.60662	0.61144	0.61605	0.62183		0.62989
0.02983	0.57326	0.57787	0.58248	0.58685	0.59113	0.59528	0.59931	0.60308
0.03345	0.57200	0.57618	0.58046	0.58463	0.58871	0.59277	0.59654	0.60034
0.04383		0.56970	0.57412	0.57827	0.58222	0.58607	0.58967	0.59344
0.05616	0.55938	0.56365	0.56799	0.57207	0.57620	0.58012	0.58386	0.58728
0.06143	0.55776	0.56196	0.55606	0.57013	0.57362	0.57737	0.58103	0.58430
0.07517	0.55453	0.55823	0.56238	0.56603	0.56966	0.57320	0.57661	0.57983
0.11645	0.55439	0.54804	0.55179	0.55534	0.55889	0.56223	0.56562	0.56874
HA = Propionic Acid								
0.00530	0.62479	0.63036	0.63591	0.64127	0.64461	0.65170	0.65653	0.66173
0.01036	0.61015	0.61524	0.61989	0.62523	0.63003	0.63479	0.63959	0.64364
0.02038	0.59329	0.59822	0.60362	0.60846	0.61314	0.61773	0.62224	
0.03041	0.58509	0.58990	0.59470	0.59956	0.60412	0.60850	0.61266	0.61666
0.04000	0.58063	0.58510	0.58910	0.59343	0.59771	0.60198	0.60604	0.60951
0.05116	0.57443	0.57884	0.58344	0.58746	0.59157	0.59589	0.59980	0.60318
0.05818			0.58148		0.58980	0.59344	0.59697	0.60056
0.06983	0.56913	0.57323	0.57760	0.58135	0.58510	0.58879	0.59244	0.59580
0.08300	0.56546	0.56930	0.57319	0.57729	0.58097	0.58467	0.58812	0.59159
0.10199	0.55933	0.56328	0.56737	0.57107	0.57460	0.57818	0.58160	0.58479
HA = *n*-Butyric Acid								
0.00537	0.62367	0.62947	0.63588	0.64190	0.64778		0.65866	0.66340
0.00767	0.61573	0.62183	0.62792	0.63366	0.63915	0.64467	0.64994	
0.01006	0.61085	0.61670	0.62239	0.62799	0.63340	0.63905	0.64415	
0.03016	0.58592	0.59135	0.59676	0.60197	0.60729	0.61220		
0.03894		0.58486	0.59005	0.59609	0.60081	0.60522	0.60946	0.61338
0.05103	0.57455	0.58000	0.58514	0.58997	0.59476	0.59913	0.60327	0.60715
0.05900		0.57709	0.58167	0.58620	0.59054		0.59903	0.60290
0.07610	0.56567	0.57063	0.57565	0.58030	0.58505	0.58931	0.59333	0.59706
0.08510	0.56410	0.56912	0.57383	0.57836	0.58262	0.58678	0.59065	0.59428
0.09188	0.56182	0.56666	0.57130	0.57586	0.58020		0.58884	0.59247
0.10113	0.56068	0.56544	0.57006	0.57455	0.57889	0.58299	0.58681	0.59037

Table II. Corrected emf (in Volts) for the Cell Pt;H_2(g, 1 atm)|HA (m),NaA (m),NaCl (m) in 50 Mass % 2-Propanol + H_2O|AgCl;Ag from −10 to 25 °C

	emf at various temperatures (°C)							
m/(mol kg^{-1})	−10	−5	0	5	10	15	20	25
HA = Acetic Acid								
0.00537	0.63238	0.63584	0.63992	0.64337				
0.03423				0.59893	0.60309	0.60628	0.60940	0.61229
0.04811	0.58253	0.58625	0.58850	0.59161				
0.04820	0.58294	0.58579	0.58885	0.59164	0.59470	0.59755	0.60073	0.60355
0.07146		0.57593	0.57867		0.58509			
0.07864	0.57274	0.57564			0.58381	0.58636	0.58885	0.59121
0.07902					0.58387	0.58638	0.58889	0.59126
0.08622	0.57030	0.57295	0.57590	0.57839				
0.09351		0.57050	0.57333	0.57651		0.58204	0.58457	0.58690
0.10621	0.56547	0.56858	0.57087	0.57354	0.57609	0.57864	0.58091	0.58333
HA = Propionic Acid								
0.00573	0.65160	0.65546	0.65925	0.66361	0.66721	0.67119	0.67483	0.67824
0.02748	0.61397	0.61747	0.62097	0.62457	0.62750	0.63063	0.63395	0.63675
0.03828	0.60769	0.61060	0.61354	0.61638	0.61950	0.62245	0.62531	0.62815
0.05700				0.60678	0.60977	0.61289	0.61576	0.61842
0.07374	0.59348	0.59676	0.59896	0.60164	0.60426	0.60669	0.60923	0.61174
0.07653	0.59305	0.59571	0.59832	0.60117	0.60422	0.60636	0.60881	0.61116
0.08671	0.58980	0.59238	0.59507	0.59761	0.60030	0.60286	0.60536	0.60774
HA = *n*-Butyric Acid								
0.00666	0.65499	0.65853		0.66580	0.66979	0.67350	0.67694	0.68005
0.00933	0.64797	0.65157	0.65516	0.65908	0.66236	0.66591	0.66950	0.67274
0.01957	0.63140	0.63465	0.63784	0.64150	0.64441	0.64761	0.65079	0.65360
0.03532	0.61707	0.62002	0.62205	0.62636	0.62905	0.63205	0.63426	0.63777
0.07530	0.60204	0.60403	0.60540	0.60891	0.61134	0.61379	0.61614	0.61775
0.08660	0.59750	0.59983	0.60123	0.60495	0.60749	0.61006	0.61249	0.61474
0.09577	0.59433	0.59704	0.59946	0.60222	0.60447	0.60729	0.60982	0.61218

them. The emf values given in Tables I and II have been corrected in the usual way from the ambient partial pressure of hydrogen (barometric pressure less the solvent vapor pressure) to a partial pressure of 1 atm (760 Torr).

The equilibrium constant K for the dissociation of each of the weak acids can be represented simply by

$$K = a_H a_A / a_{HA} \quad (1)$$

Table III. Summary of p*K* Values for Weak Acids in 25 and 30 Mass % 2-Propanol + Water from 263.15 to 298.15 K and constants for Equation 7

	T/K	p*K* acetic acid	p*K* propionic acid	p*K* *n*-butyric acid
		25 Mass %		
	263.15	5.327 ± 0.011[a]	5.564 ± 0.018[a]	5.560 ± 0.009[a]
	268.15	5.285 ± 0.009	5.527 ± 0.016	5.533 ± 0.011
	273.15	5.253 ± 0.012	5.499 ± 0.013	5.519 ± 0.009
	278.15	5.231 ± 0.012	5.481 ± 0.011	5.511 ± 0.007
	283.15	5.215 ± 0.012	5.469 ± 0.012	5.506 ± 0.008
	288.15	5.214 ± 0.008	5.462 ± 0.010	5.511 ± 0.007
	293.15	5.222 ± 0.004	5.461 ± 0.009	5.508 ± 0.007
	298.15	5.209 ± 0.010	5.465 ± 0.009	5.503 ± 0.004
A		6401.04	5649.04	3184.07
B		−141.6124	−124.0314	−67.8360
C		22.002 27	19.402 95	10.998 51
sd[b]		0.007	0.001	0.005
		50 Mass %		
	263.15	5.933 ± 0.007	6.313 ± 0.016	6.471 ± 0.016
	268.15	5.902 ± 0.012	6.281 ± 0.014	6.432 ± 0.012
	273.15	5.881 ± 0.010	6.255 ± 0.011	6.403 ± 0.014
	278.15	5.858 ± 0.004	6.240 ± 0.014	6.379 ± 0.011
	283.15	5.862 ± 0.009	6.220 ± 0.013	6.357 ± 0.009
	288.15	5.860 ± 0.006	6.211 ± 0.011	6.342 ± 0.007
	293.15	5.866 ± 0.005	6.205 ± 0.009	6.328 ± 0.011
	298.15	5.868 ± 0.003	6.197 ± 0.008	6.318 ± 0.009
A		5696.71	3517.95	3536.29
B		−126.47367	−72.04829	−70.64374
C		19.874 87	11.662 42	11.426 18
sd		0.005	0.002	0.001

[a] Standard deviation for regression. [b] Standard error of fit.

which when combined with the Nernst equation for the cell, yields

$$\mathrm{p}K \equiv -\log K = \frac{E - E^\circ}{k} + \log \frac{m_{\mathrm{Cl}} m_{\mathrm{HA}}}{m_{\mathrm{A}}} + \log \frac{\gamma_{\mathrm{Cl}} \gamma_{\mathrm{HA}}}{\gamma_{\mathrm{A}}} \qquad (2)$$

where k is written for $(RT \ln 10)/F$, the Nernst slope. Inasmuch as Cl^- and A^- bear the same charge, it is expected (and usually found) that the last (activity-coefficient) term of eq 2 is a linear function of the ionic strength I. It is, of course, zero in the limit $I = 0$. If the slope is designated b and the slight dissociation of HA is taken into account, one can write

$$\mathrm{p}K' \equiv \mathrm{p}K - bI = \frac{E - E^\circ}{k} + \log \frac{m(m - m_{\mathrm{H}})}{m + m_{\mathrm{H}}} \qquad (3)$$

where m_{H} is the molality of free hydrogen ion. Values of E°, the standard emf, were determined in our earlier study (*12*). They are given as a function of the thermodynamic temperature T by the quadratic equations

for 25% isopropyl alcohol

$$E^\circ/\mathrm{V} = 4.8263 \times 10^{-3} T - 9.19048 \times 10^{-6} T^2 - 0.41846 \qquad (4)$$

for 50% isopropyl alcohol

$$E^\circ/\mathrm{V} = 2.2879 \times 10^{-3} T - 5.37619 \times 10^{-6} T^2 - 0.02589 \qquad (5)$$

Although very little hydrogen ion was formed by hydrolysis compared with the molalities of the buffer components, corrections were made for its presence. Estimates of m_{H} were obtained from the emf values with the aid of activity coefficients derived from the Debye–Hückel equation with a reasonable ion size of 4 Å

$$-\log m_{\mathrm{H}} = \frac{E - E^\circ}{k} + \log m - \frac{2A(I)^{1/2}}{1 + 4B(m)^{1/2}} \qquad (6)$$

Table IV. Standard Thermodynamic Quantities for the Dissociation of Weak Acids in Water and in 25 and 50 Mass % 2-Propanol + Water at 298.15 K

	acetic acid	propionic acid	*n*-butyric acid
	Water[a]		
ΔG°, J mol^{-1}	27 146	27 819	27 512
ΔH°, J mol^{-1}	−394	−692	−2908
ΔS°, J K^{-1} mol^{-1}	−92	−96	−102
	25 Mass % 2-Propanol		
ΔG°, J mol^{-1}	29 778	31 198	31 442
ΔH°, J mol^{-1}	−3043	−2603	−1821
ΔS°, J K^{-1} mol^{-1}	−110	−113	−112
	50 Mass % 2-Propanol		
ΔG°, J mol^{-1}	33 518	35 382	36 067
ΔH°, J mol^{-1}	−4384	781	2481
ΔS°, J K^{-1} mol^{-1}	−127	−116	−113

[a] Calculated from the p*K* vs *T* equations given by Robinson and Stokes (*19*).

where A and B are the Debye–Hückel constants and the ionic strength is $2m + m_{\mathrm{H}}$. Only one iteration was made, as the contribution of m_{H} to the ionic strength was negligible.

Values of the "apparent" pK, namely, pK', were calculated by eq 3, and the intercept pK at $I = 0$ was determined by linear regression. The results are summarized in Table III, together with the standard deviations for regression from linearity.

Discussion

Included in Table III are the constants of the equation relating pK to thermodynamic temperature T

$$\mathrm{p}K = A/T + B + C \ln T \qquad (7)$$

and the standard deviation of fit. The best least-squares fit was determined by a modified Marquardt procedure described by Nash (*16*). The Ives–Moseley method (*17*), which smoothes first-order differences, is suitable when the data are obtained at equal temperature intervals. In addition, the equation

$$\mathrm{p}K = A'/T + B' + C'T \qquad (8)$$

suggested by Harned and Robinson (*18*) was also tried. All three procedures fitted the pK values within experimental error, but the thermodynamic functions derived from the constants obtained in the Ives–Moseley treatment differed significantly from those yielded by the other two procedures.

The standard changes in Gibbs energy, enthalpy, and entropy for the dissociation of the weak acids in the two isopropanol + water solvents were obtained by the usual thermodynamic relationships, utilizing the constants of eq 7:

$$\Delta G^\circ = R(\ln 10)(A + BT + CT \ln T) \qquad (9)$$

$$\Delta H^\circ = R(\ln 10)(A - CT) \qquad (10)$$

$$\Delta S^\circ = R(\ln 10)[-B - C(1 + \ln T)] \qquad (11)$$

The values at 25 °C (298.15 K) are given in Table IV. For comparison, the corresponding functions for the dissociation in water are included.

The following are estimates of the uncertainties of the thermodynamic functions: ΔG°, 10 J mol^{-1}; ΔH°, 220 J mol^{-1}; ΔS°, 1 J K^{-1} mol^{-1}. It must be recognized, however, that these statistical estimates do not include other sources of error in procedures, in the standard potentials, and the like.

It is evident that replacement of a portion of the water solvent by isopropyl alcohol has a destabilizing effect on the solvated hydrogen ion, increasing pK and ΔG°. There is a concomitant decrease in the entropy of dissociation for the three acids, as found for formic acid and acetic acid in methanol–water and dioxane–water (*20*). The enthalpy change, however, does not display this regularity, decreasing for acetic acid and increasing for butyric acid. The apparent reversal with propionic acid caused by addition of isopropyl alcohol is beyond the limits of experimental uncertainty and seems especially anomalous. These observations serve to illustrate the complexity of ion–solvent interactions in multicomponent systems.

Registry No. Acetic acid, 64-19-7; propionic acid, 79-09-4; butyric acid, 107-92-6.

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Solubility of CO_2 in an AMP Solution

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The solubility of CO_2 in a 2.00 mol/L solution of 2-amino-2-methyl-1-propanol (AMP) has been determined at 40 and 70 °C at partial pressures between 0.2 and 5279 kPa.

Introduction

Aqueous alkanolamine solutions are widely used for the removal of the acid gases H_2S and CO_2 from natural gases. Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyldiethanolamine (MDEA) are those most commonly used (*1*, *2*). Except for MDEA at high pressures, these alkanolamines have a relatively low maximum capacity for the acid gases. Sartori and Savage (*3*) discovered a new class of amines, sterically hindered amines. They are capable of high loadings of the acid gases because their carbamates are relatively unstable. AMP (2-amino-2-methyl-1-propanol) is a hindered primary alkanolamine that forms a carbamate with a much lower stability than the carbamates of MEA and DEA (*4*). The formation of bicarbonate becomes the only important reaction, and loadings approaching 1 mol of CO_2/mol of AMP are possible at moderate partial pressures.

The present work reports the solubility of CO_2 in a 2.00 M aqueous AMP solution at 40 and 70 °C over a wide range of pressures.

Table I. Solubility of CO_2 in 2.00 mol/L AMP[a]

at 40 °C			at 70 °C		
P/kPa	p/kPa	α	P/kPa	p/kPa	α
434.8	0.162	0.035	444.9	0.586	0.033
398.3	0.189	0.068	420.6	0.878	0.054
383.1	0.373	0.294	380.3	2.43	0.197
425.1	1.283	0.466	448.7	6.95	0.336
434.3	6.01	0.693	447.9	10.92	0.436
466.7	142.7	0.982	432.3	26.6	0.597
565.4	283.7	1.001	445.0	50.9	0.725
			463.3	87.6	0.817
			501.4	148.5	0.851
			566.0	224.4	0.883
			813.9	434.6	0.927
			669.7	641.0	0.971*
			1126.9	791.5	1.026
			1492.1	1461.6	1.099*
			2645.9	2615.0	1.176*
			3489.7	3458.0	1.205*
			5306.9	5279.0	1.265*

[a] Abbreviations: P = total pressure; p = partial pressure, yP; y = mole fraction of CO_2 in the vapor phase; α = mole ratio in the liquid phase, CO_2/AMP. Values marked with an asterisk, no addition of N_2.

Experimental Details

An aqueous solution of AMP was prepared from distilled water and AMP, which was obtained from Matheson, Coleman, and Bell. The AMP had a purity of 98% and was used without further purification. The concentration in the resulting solution was determined by titration with standardized 1 N H_2SO_4 solution, using methyl red indicator. The carbon dioxide and nitrogen were obtained from Matheson and had purities greater than 99%. The equipment used for the solubility measurements was essentially the same as that used previously in this laboratory (*5*). It consists of a windowed equilibrium cell into which the AMP solution and the CO_2 were introduced and brought to equilibrium. The cell had an internal volume of about 75 mL with a 250-mL cylindrical reservoir mounted on the top of the cell to increase the amount of vapor in equilibrium with the solvent. The vapor in the reservoir was recirculated through the solvent by means of a magnetically driven piston pump similar to that devised by Ruska et al. (*6*). The pump and cell were enclosed in an air bath, the temperature of which was controlled to within ±0.5 °C. A Leeds and Northrup potentiometer was used to measure the output of an iron–constantan thermocouple, which extended through the wall of the cell into the fluid. The fluid pressure in the cell was measured by a calibrated Heise bourdon gauge. The gas was recirculated and bubbled through the solution for at least 8 h to allow the system

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