Table V. Effect of Number of Stages on Resorcinol Recovery

stage	init vol, mL		final vol, mL		[resorcinol], g/mL		resorcinol recovered, wt %	
	aqueous	organic	aqueous	organic	aqueous	organic	per stage	overall
1	150.00	90.00	130.00	106.00	0.0324	0.1094	73.32	73.32
2	128.00	80.00	120.00	84.00	0.0066	0.0401	80.80	94.55
3	119.00	73.00	115.00	75.00	0.007	0.0095	89.86	99.03

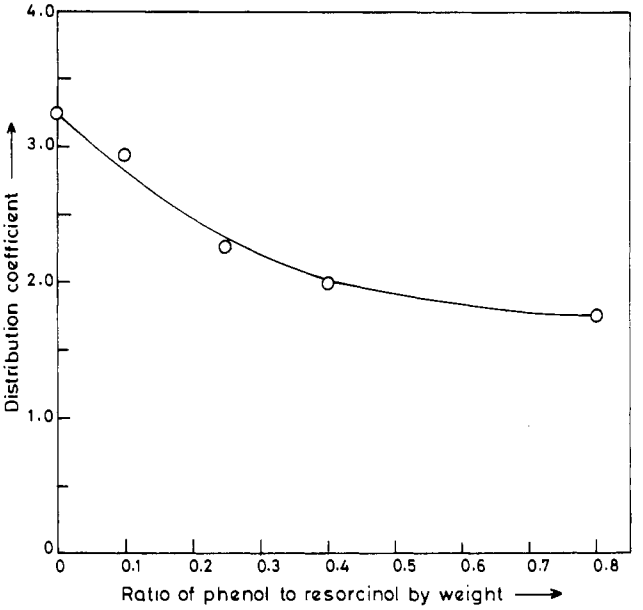

Figure 7. Effect of phenol on distribution coefficient of resorcinol for 10% resorcinol in feed (solvent: butyl acetate).

and can be utilized for the scale-up. These plots have been found to be straight lines for rpm's of 100, 250, and 450 with solvent to feed ratios of 0.38, 0.6, and 0.9. The values of the characteristic constant, K, as presented in Table IV reveal that, for the same solvent to feed ratio, the resorcinol concentration in the aqueous phase reduces with increasing rpm for the same agitation time. It is also observed that the variation of the solvent to feed ratio does not significantly influence the constant K; it instead depends only on the rpm. For a specified feed concentration and the percent recovery with a selected rpm, the extraction time can be estimated from this constant K for a bench-scale unit.

For ascertaining the optimum number of stages required, the composite feed comprising 10% resorcinol, 1.5% phenol, and 5% NaCl was stirred for 1 h with the mixed solvent of 40% butanol and 60% butyl acetate (solvent to feed ratio = 0.6) at 100 rpm in three successive stages. Table V presents the effect of number of stages on resorcinol recovery with concentration in the two layers in successive stages. It can be noted that it is possible to recover 99% of resorcinol from the aqueous phase in three stages and the concentration of resorcinol in the aqueous layer is depleted to 7×10^{-4} g/mL for the selected composite feed composition. However, some butanol is retained in the aqueous phase, which needs to be recovered separately, in addition to the mixed-solvent recovery from the organic phase for recycling. For the solvent recovery from the aqueous phase, vacuum steam stripping is recommended (*8*). Resorcinol (bp 276 °C) is removed by distillation of the organic phase while the mixed solvent is condensed and recovered.

Appendix. Details of Glass Vessel

Type, cylindrical unbaffled glass vessel; vessel diameter (internal), 85 mm; length of vessel, 150 mm; filled height, ~70 mm; thickness of vessel, 5 mm; flange o.d., 135 mm; agitator type, two-blade propeller; agitator sweep, 25 mm; agitator location, 35 mm from bottom; shaft diameter, 6 mm; shaft length, 400 mm.

Registry No. C_6H_5OH, 108-95-2; NaCl, 7647-14-5; Na_2SO_4, 7757-82-6; resorcinol, 108-46-3; butyl acetate, 123-86-4; butanol, 71-36-3; isopropyl ether, 108-20-3; octane, 111-65-9.

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Influence of the Ionic Strength on the Ionization of Amino Acids

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The ionization equilibria of the amino acids glycine, L-leucine, L-serine, L-threonine, L-lysine, and L-glutamic acid have been studied at 298 K and I = 0.5, 0.3, 0.2, 0.1, 0.05, and 0.025 M. Thermodynamic parameters and the dependence of each protonation constant on ionic strength have been calculated from the experimental data. The effect of the structure of the amino acids is also discussed.

Introduction

The study of the ionization equilibria of α-amino acids, and of the effect of the medium in those equilibria, is of interest for studying the complexes formed by these compounds and hence for establishing the species present in media containing them. Previous work in this area (*1-11*) has been unsystematic and carried out under quite widely varying conditions, so that comparison of the results and analysis of the influence of the factors

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Table I. Protonation Constants of the Amino Acids Studied at 298 K

I	glycine	L-leucine	L-serine	L-threonine	L-lysine	L-glutamic acid
			log K at $p:q \equiv 1:1$[a]			
0.5	9.751 ± 0.006	9.909 ± 0.006	9.252 ± 0.008	9.133 ± 0.003	11.21 ± 0.02	9.84 ± 0.02
0.3	9.715 ± 0.005	9.887 ± 0.006	9.242 ± 0.005	9.106 ± 0.002	10.89 ± 0.01	9.64 ± 0.02
0.2	9.680 ± 0.005	9.887 ± 0.006	9.243 ± 0.004	9.082 ± 0.005	10.72 ± 0.02	9.51 ± 0.02
0.1	9.700 ± 0.005	9.893 ± 0.005	9.249 ± 0.003	9.085 ± 0.004	10.75 ± 0.02	9.49 ± 0.02
0.05	9.721 ± 0.006	9.903 ± 0.004	9.256 ± 0.003	9.119 ± 0.005	10.77 ± 0.02	9.51 ± 0.02
0.025	9.756 ± 0.006	9.910 ± 0.004	9.260 ± 0.004	9.146 ± 0.005	10.80 ± 0.01	9.53 ± 0.02
			log K at $p:q \equiv 1:2$			
0.5	2.484 ± 0.009	2.437 ± 0.009	2.197 ± 0.003	2.312 ± 0.005	9.49 ± 0.03	4.34 ± 0.01
0.3	2.360 ± 0.008	2.257 ± 0.008	1.960 ± 0.009	2.230 ± 0.005	9.43 ± 0.03	4.22 ± 0.03
0.2	2.301 ± 0.003	2.215 ± 0.005	1.890 ± 0.003	2.190 ± 0.009	9.40 ± 0.03	4.12 ± 0.01
0.1	2.285 ± 0.007	2.223 ± 0.009	1.893 ± 0.003	2.182 ± 0.008	9.39 ± 0.03	4.08 ± 0.01
0.05	2.302 ± 0.003	2.234 ± 0.008	1.922 ± 0.009	2.195 ± 0.009	9.39 ± 0.03	4.09 ± 0.03
0.025	2.330 ± 0.009	2.267 ± 0.009	1.944 ± 0.008	2.218 ± 0.006	9.41 ± 0.02	4.11 ± 0.01
			log K at $p:q \equiv 1:3$			
0.5					2.53 ± 0.04	2.33 ± 0.02
0.3					2.31 ± 0.03	2.22 ± 0.01
0.2					2.20 ± 0.02	2.15 ± 0.02
0.1					2.17 ± 0.03	2.16 ± 0.02
0.05					2.17 ± 0.02	2.18 ± 0.01
0.025					2.17 ± 0.02	2.20 ± 0.02

[a] p and q refer to L_pH_q systems; L = ligand, H = H^+.

varied are difficult. Therefore, in the present paper we make a systematic study of the effect of the ionic strength on the acid–base behavior of amino acids glycine, L-leucine, L-serine, L-threonine, L-lysine, and L-glutamic acid.

Experimental Section

All reagents were Merck p.a. Amino acids were purified by recrystallization three times from ethanol/water mixtures and dried at 80–100 °C in an electric oven. Their final purity was checked by gas chromatography (*12*).

Potentiometric titrations were performed in a 250-mL cell mantained at 298.0 ± 0.1 K by a Haake D3 thermostat. The cell solution was stirred and the atmosphere kept inert by bubbling nitrogen purified by Fieser solutions. The emf was measured by use of a Crison Digilab 517 pH meter accurate to ±0.1 mV equipped with an Ingold electrode. The electrode was calibrated as per Williams (*13*); that is, for each of the ionic strengths, HCl solutions of previously known concentrations of H^+ ion ranging from 5×10^{-3} to 1.5×10^{-3} M were prepared, the potential was measured, and the parameters of the Nernst type equation were calculated.

Aqueous solutions with total amino acid concentration ranging from 0.5×10^{-3} to 1.1×10^{-3} M and with different ionic strengths (0.5, 0.3, 0.2, 0.1, 0.05, and 0.025) controlled with KNO_3 were titrated against HCl or NaOH solutions of the same ionic strength using a Crison 738 automatic burette. All titrations were performed at least twice, and replicate values were always within ±0.1 mV of each other.

Potentiometric constants were calculated on a Univac 1100 computer using the program MINIQUAD 75.

Results

Table I lists the logarithms of the protonation constants determined for the amino acids studied at the six ionic strengths considered. The corresponding thermodynamic protonation constants K_0 were estimated by fitting the equation

$$\log K = \log K_0 - AI^{1/2} + BI \qquad (1)$$

to these data. The results (log K_0, A, and B) are listed in Table II. The standard deviation of the fitted line was in all cases less than 0.01.

According to the theory of electrolytic solutions (*14*) the $AI^{1/2}$ term in eq 1 accounts for ion–ion interaction, while the BI term accounts for disturbances in ion–solvent interactions. Consideration of the constants A and B should therefore yield information about these interactions in the systems studied. At low ionic strength, as the solvent ions become separated, the solvent shell of each ion is freed of disturbances and the term BI becomes negligible, making log K a linear function of $AI^{1/2}$. At high ionic strength, on the other hand, the term due to solvent interaction dominates the $AI^{1/2}$ term and log K is a linear function of ionic strength (Figure 1).

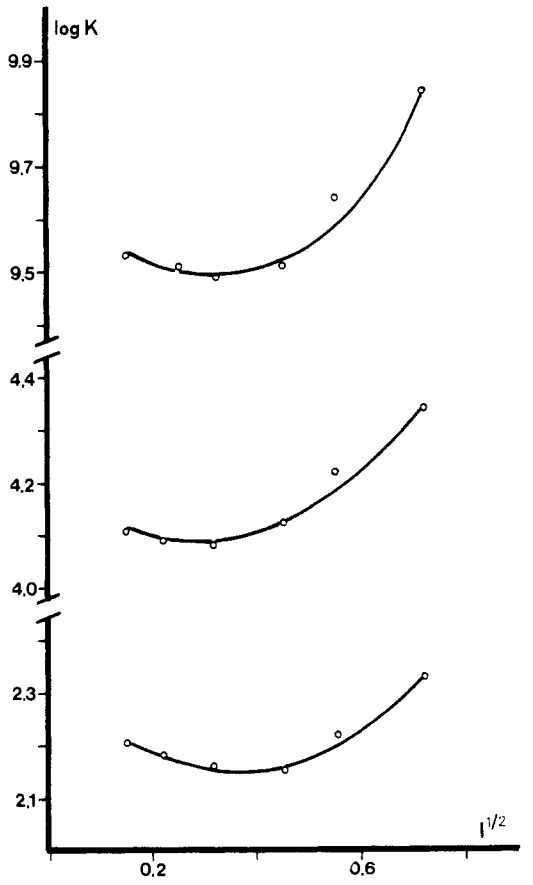

Figure 1. Plot of log K versus $I^{1/2}$ for L-glutamic acid/H^+ system.

Comparison of the ionization constants of glycine and serine with those of leucine and threonine, respectively, shows that the carbon chain has only a very slight influence on the acid–

Table II. Thermodynamic Protonation Constants of Glycine, L-Leucine, L-Serine, L-Threonine, L-Lysine, and L-Glutamic Acid, Together with Parameters A and B of Eq 1

amino acid	$p:q^a$	log K_0	A	B
glycine	1:1	9.85 ± 0.02	0.73	0.85
	1:2	2.54 ± 0.02	0.83	1.41
L-leucine	1:1	9.95 ± 0.03	0.26	0.31
	1:2	2.44 ± 0.03	1.31	1.84
L-serine	1:1	9.28 ± 0.01	0.17	0.17
	1:2	2.18 ± 0.03	1.74	2.49
L-threonine	1:1	9.23 ± 0.02	0.65	0.74
	1:2	2.28 ± 0.03	0.61	0.82
L-lysine	1:1	11.10 ± 0.04	2.30	3.47
	1:2	9.47 ± 0.02	0.48	0.63
	1:3	2.27 ± 0.03	0.88	1.92
L-glutamic acid	1:1	9.69 ± 0.04	1.13	2.19
	1:2	4.18 ± 0.04	0.71	1.34
	1:3	2.32 ± 0.03	0.97	1.40

[a] $p:q$ refers to L_pH_q systems; L = amino acid, H = H^+.

base behavior of amino acids. Comparison of the constants of glycine and leucine with those of serine and threonine shows that the presence of the electrophilic OH group close to the α-carbon of the amino acid reduces the basicity for the amino group and increases the acidity of the carboxyl group. A similar effect is produced in glutamic acid by the presence of a second acid group, and in L-lysine by a second amine group, although in both these cases the effect is softened by the length of the interposed carbon chain.

Registry No. L-Leucine, 61-90-5; L-serine, 56-45-1; L-threonine, 72-19-5; L-lysine, 56-87-1; L-glutamic acid, 56-86-0.

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Viscosity of Pure Hydrocarbons

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Accurate viscosity measurements have been performed on eight pure hydrocarbons at atmospheric pressure in the temperature range 20–150 °C, or up to approximately 20 °C below the boiling point of the hydrocarbon, by use of an absolute oscillating viscometer. The hydrocarbons are cyclohexane and benzene and the *n*-alkanes of hexane, heptane, octane, decane, dodecane, and tetradecane. The viscosities are described with a modified Arrhenius equation, and the deviation in fit is 0.12% or less. The accuracy is estimated to be 0.33–0.56%. The lowest viscosities are assumed to have the highest deviation. Literature data reported by Dymond and Young normally fit our viscosities within our estimated accuracy. Other literature viscosities tend to be higher than our results, especially for the *n*-alkanes.

1. Introduction

A high-precision viscometer for studies of low-viscous liquids up to 1100 °C has been developed at the Institute of Inorganic Chemistry. The viscometer is absolute and no calibration is needed. Our determination of the viscosity of molten NaCl has been recommended as a standard to the U.S. National Bureau of Standards by Janz (*1*). The viscosity measurements of pure hydrocarbons at atmospheric pressure are part of a program on viscosity measurements of oil-related fluids pressurized up to 400 bar. The aim of the present study is to produce accurate data over a wide temperature range for computer modelling of viscosity and to check or eventually establish new reference values.

2. Experimental Section

2.1. Apparatus. A thorough description of the oscillation viscometer is given by Tørklep and Øye (*2*). The viscometer measures the damping of a right circular cylinder oscillating in contact with the liquid under consideration. The cylinder may be a solid cylinder immersed in the liquid, or it may be a cylindrical hollow cup containing the liquid. Absolute viscosities are calculated from the damping by using the working equations of the solid cylinder, Tørklep and Øye (*2*), or the hollow cup, Brockner, Tørklep, and Øye (*3*).

A completely filled hollow cup is used in this study (Figure 1). To maintain a filled cup, a capillary tube, F, fixed to the bottom lid of the cup, is inserted into a sample reservoir, G, situated at room temperature. The sample reservoir is open at the top, and the capillary tube fixed to the cup can oscillate freely during the measurements. This system allows us to change the temperature set point, both up and down, and still maintain a completely filled cup. Figure 1 also shows a syringe, I, with a 50-cm-long needle. The needle is inserted through a bottom septum of the reservoir, G, and can go through the capillary

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