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Studies on Solvent Extraction of Resorcinol

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Liquid-liquid equilibrium data and distribution coefficients have been generated to ascertain the effect of associated constituents on the recovery of resorcinol from the neutralized fusion mass. Butyl acetate has been found to be a better solvent than butanol, and the distribution coefficient of resorcinol has been found to be 50% greater in a mixed solvent comprising 40% butanol and 60% butyl acetate by weight than in butyl acetate alone. The presence of salt increases the distribution coefficient whereas that of phenol decreases its value. The combined presence of the associated constituents, such as phenol and salt, in the composite feed favors the distribution coefficient of resorcinol in the mixed solvent. The effects of revolutions per minute, solvent to feed ratio, and number of stages on the solvent recovery and extraction time have been analyzed, and a correlation constant, *K*, has been determined for scale-up. It is observed that 99% recovery of resorcinol can be achieved in three stages with the mixed solvent for the selected feed composition.

Introduction

Solvent extraction is a key step in the manufacturing process of resorcinol as it controls the overall economics not only by its maximum recovery but also by minimizing the amount of pollutants released. In view of the expanding demand for resorcinol, a systematic study has been carried out for the selection of a better solvent and the generation of some process parameters for extraction of resorcinol from the neutralized fusion mass, a typical composition of which is given in Table I. LLE data have been generated for various systems with a view to ascertaining the individual effects of various associated constituents on the distribution coefficient of resorcinol prior to studying their combined effect. An attempt has also been made to study the performance of the extractor to analyze the effects of certain parameters needed for the process design.

Solvent Selection

The selection of solvent for extraction is based on several criteria, such as selectivity, distribution coefficient, capacity, solubility, and physical and chemical properties, besides its cost. The distribution coefficient at infinite dilution is often used as the basis for preliminary screening of the solvent, as has been considered by Won and Prausnitz (*1*). For the extraction of both phenol and resorcinol, ketones and esters are considered better solvents than alcohols and ethers. Polar solvents are better than nonpolar solvents, but then they have the problem of miscibility with water, which increases the cost of solvent recovery. An interesting possibility is the use of mixed solvents (*2*), when one of them is hydrogen-bonding acceptor, e.g., ketones, esters, or ethers, and another is a donor, e.g., alcohols, with the result that the solubility of solute in the organic phase increases. Medir and McCay (*3*) observed that the mixed solvent comprising octanol and butyl acetate gave the highest distribution coefficient of phenol. A preliminary investigation reveals that butyl acetate is better than butanol as a single solvent for the extraction of resorcinol. Binary combinations of mixed solvents comprising butyl acetate, 1-butanol, Diisopropyl ether (DIPE), and *n*-octane have been selected for the present investigation. The physical properties of these solvents are presented in Table II.

Table I. Composition of Neutralized Fusion Mass

component	composn (w/v), g/100 cm^3
Na_2SO_4	15
resorcinol	8
phenol	0.4
tarry mass	1.0
water	75.6

Experimental Section

With a view to ascertaining the domain of immiscibility and LLE behavior, the binodal curve was determined by the turbidity method, as described in the textbook by Alders (*4*), while maintaining a constant temperature at 35 °C. The binodal compositions were plotted against density for the calibration of the tie-line compositions. For generation of the tie-line data, several heterogeneous mixtures of known composition were prepared and shaken for about 4 h and later settled for the same amount of time at 35 °C. After careful separation of the clear phases, volumes and densities of these phases were measured. The tie-line compositions were determined from the knowledge of their densities and the binodal composition vs density calibration. The reliability of the tie-line compositions was verified by checking the validity of the material balance. However, for concentrations of less than 10% resorcinol in the aqueous phase, the tie-line compositions were determined iodimetrically by the chemical analysis method of Willard (*5*), in which the sample containing about 0.05 mg of resorcinol was mixed with 50 mL of acetate buffer (acetic acid-sodium acetate) solution and 50 mL of 0.1 N iodine solution in potassium iodide. After 1 min, excess iodine was titrated with the standard 0.1 N sodium thiosulfate solution using starch as the indicator. The percentage of resorcinol in the sample was calculated according to the stoichiometry of the prevailing chemical reaction. The amount of resorcinol in the extract phase was

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Table II. Properties of Solvents[a]

solvent	sp gr	viscosity, cP	bp, °C	latent heat, cal/(g mol)	solubility in H_2O, wt %	solubility of H_2O, wt %
n-butyl acetate	0.930	0.650	126.11	7268	0.43	1.86
1-butanol	0.810	2.271	117.66	10310	7.80	20.00
diisopropyl ether	0.720	0.379	89.65	7010	1.20	0.57
n-octane	0.702	0.500	125.70	8350		
butanol + butyl acetate (40% butanol by wt)	0.876		103.60			

[a] From ref *9* and *10*.

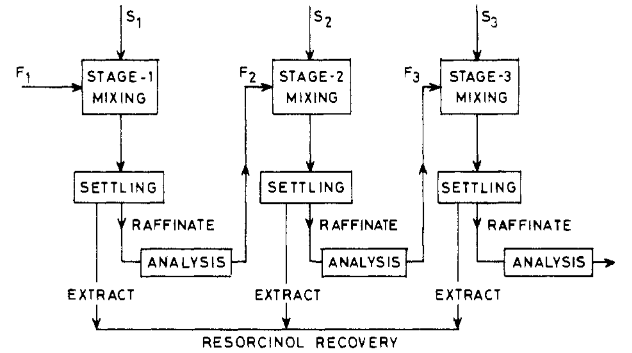

Figure 1. Block diagram to study the effect of number of stages on resorcinol recovery.

determined from the amount present in the aqueous phase, as calculated above, and the resorcinol material balance.

The experimental procedure for the generation of LLE data in the presence of salts is similar except that, instead of pure water, aqueous salt solution was used for determining the binodal curve and tie-line data. Both the chemical analysis and the density-calibration methods were adopted for the generation of tie-line data for 5% NaCl in water for comparing the validity and accuracy of the methods. Then the chemical analysis method was selected for the study of the effect of NaCl and Na_2SO_4 of varying concentrations in aqueous solutions of 10% resorcinol by weight.

Tie-line compositions were determined for various mixed solvents of different compositions according to the chemical analysis method. To study the effect of phenol, LLE data were similarly generated for various phenol to resorcinol ratios for a constant resorcinol concentration of 10% in the feed mixture (i.e., phenol + water + resorcinol). Care was taken at each step of the experiments for the reproducibility and accuracy of the data, and only the best data sets were reported and considered for the analysis.

The performance study was carried out in a thermostated and agitated cylindrical glass vessel (details of the vessel are given in the Appendix) provided with a glass cover with nozzles and a condenser attached through one of them. A fixed volume of solution of 10% resorcinol by weight in water was added, and then a fixed amount of solvent was charged with the stopwatch and agitator on. After regular time intervals the agitator was stopped, and the solution was allowed to settle for a few seconds to obtain two clear layers. About 1 mL of sample was then withdrawn from the aqueous layer for determination of the resorcinol concentration by the chemical analysis method, and the agitator was again started. This procedure was repeated until the titration reading in the chemical analysis method remained constant, indicating equilibrium. This procedure was repeated for various rpm's and solvent to feed ratios. The effect of number of stages on resorcinol recovery was studied for composite system with the mixed solvent up to three stages in accordance with the schematic diagram in Figure 1. A cross-current scheme was chosen for the study as the commercial resorcinol extraction is often carried out in the batch process and this scheme yields maximum recovery. Throughout this experiment, the rpm, solvent to feed volumetric ratio, and temperature of 35 °C were maintained constant. The aqueous phase from each stage was subjected to chemical analysis and the organic phase to solvent recovery. At each stage a fixed amount of mixed solvent was added.

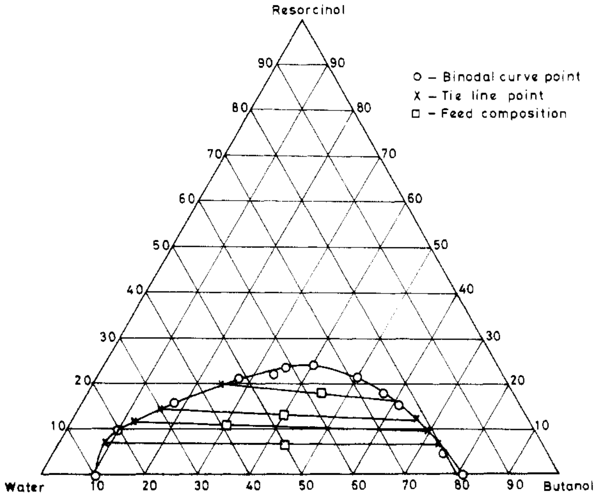

Figure 2. Ternary diagram: resorcinol–water–butanol.

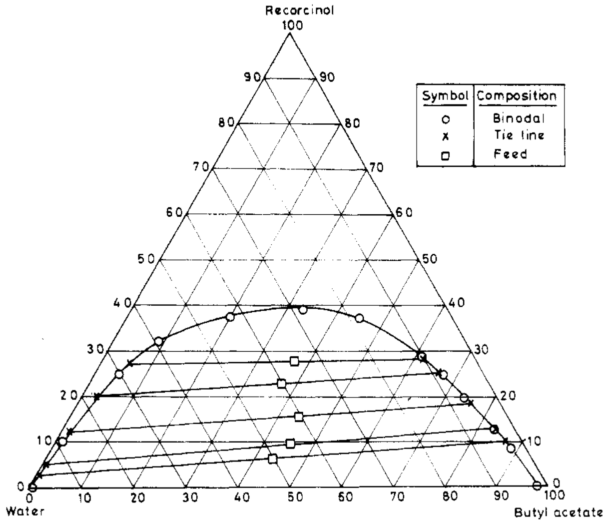

Figure 3. Ternary diagram: resorcinol–water–butyl acetate.

Results and Discussions

Both binodal curve and tie-line data have been first generated for the systems (1) resorcinol–water–butanol, (2) resorcinol–water–*n*-butyl acetate, and (3) resorcinol–5% NaCl in water–butyl acetate. Tie-line compositions have been determined by both chemical analysis and density calibration for systems 1 and 3. The former method has been observed to be more accurate and less time-consuming for dilute resorcinol concentrations less than 10%, with a maximum error of 2%. Accordingly, the chemical analysis method has been chosen for the remaining systems. The tie-line and feed compositions have been plotted on a ternary diagram along with the binodal curve in Figure 2

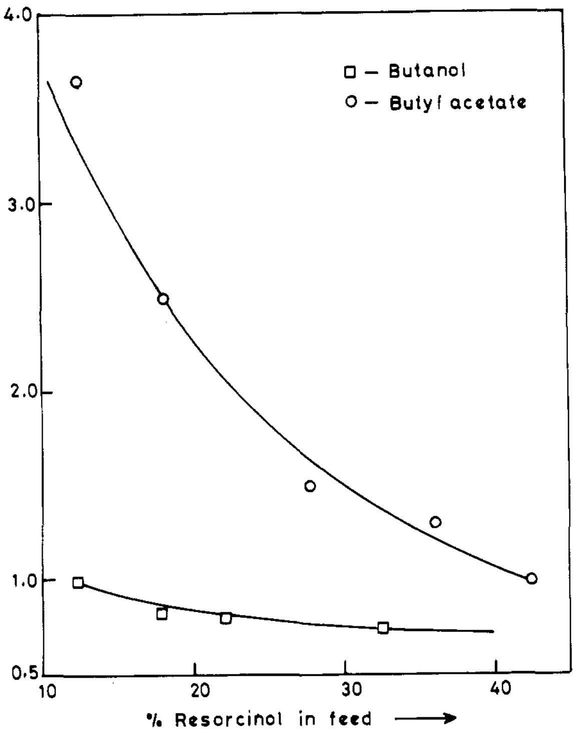

Figure 4. Distribution coefficient of resorcinol in pure solvents (density method).

and 3, respectively, for systems 1 and 2. The distribution coefficients of resorcinol in the organic to the aqueous phases have been plotted in Figure 4 against the feed concentration of resorcinol. It can be seen that the distribution coefficient is higher with *n*-butyl acetate than with 1-butanol. The distribution coefficient also increases with the decrease in resorcinol concentration in the feed, as can be seen in Figure 4. Besides this, butanol has a higher solubility, in water than butyl acetate; hence butyl acetate is considered to be better than butanol as a single solvent for extraction of resorcinol.

In order to study the effect of salt on the LLE behavior, the tie line and feed compositions have been plotted on a triangular diagram in Figure 5 along with the binodal curve for system 3. It can be noted that the binodal curve gets wider in the presence of a salt, indicating a broader region of heterogeneity and higher distribution coefficient than in pure solvent for the same resorcinol concentration in the feed. This can be attributed to the fact that more resorcinol is released to the organic phase in the presence of salt, resulting in a higher distribution coefficient.

On analysis of the variations of the distribution coefficients of resorcinol in butyl acetate with various salt concentrations of NaCl and Na_2SO_4, it has been observed that the distribution coefficient is slightly higher with Na_2SO_4 for the same salt concentration in the feed. The distribution coefficients with and without the presence of salt can be correlated by Stratula's equation (*6*) as

$$\log (K_s/K_0) = H_0C_s \quad (1)$$

The values of H_0 have been found to be 2.86 and 2.94 for NaCl and Na_2SO_4, respectively. This justifies the use of dilute sulfuric acid rather than dilute hydrochloric acid in the neutralization step of the resorcinol manufacture apart from the fact that dilute hydrochloric acid is more corrosive.

The distribution coefficients of resorcinol have been analyzed for 10% resorcinol in the feed using the following mixed solvents with 1:1 solvent to feed ratio by volume: (1) butyl acetate–butanol; (2) butyl acetate–DIPE; (3) butyl acetate–*n*-octane; (4) *n*-octane–DIPE; (5) butanol–DIPE. The values have been plotted in Figure 6 against the solvent concentration. It can be seen that a positive deviation from linearity is observed for the mixed solvents, butanol–butyl acetate and butanol–DIPE, a nearly linear variation is observed for the system butyl acetate–DIPE, and a negative deviation from linearity is observed for *n*-octane–butyl acetate and *n*-octane–DIPE. This can be explained by the fact that more –OH groups from alcohol and more >C=O groups from acetate preferentially bond with resorcinol than from only butanol or from only butyl acetate, thus yielding higher distribution coefficients. The same explanation is true for the mixed solvent *n*-butanol–DIPE as well. For the mixed solvent butyl acetate–DIPE, there is no change in the mode of hydrogen bonding with the change in solvent mixture composition, and hence linear variation is observed. On the other hand, with *n*-octane added to butyl acetate or DIPE, the total number of groups for hydrogen bonding with resorcinol is diluted, and hence there is the negative deviation from linearity. The distribution coefficient in the mixed solvent containing 40% 1-butanol and 60% butyl acetate by weight is 50% more than in butyl acetate alone.

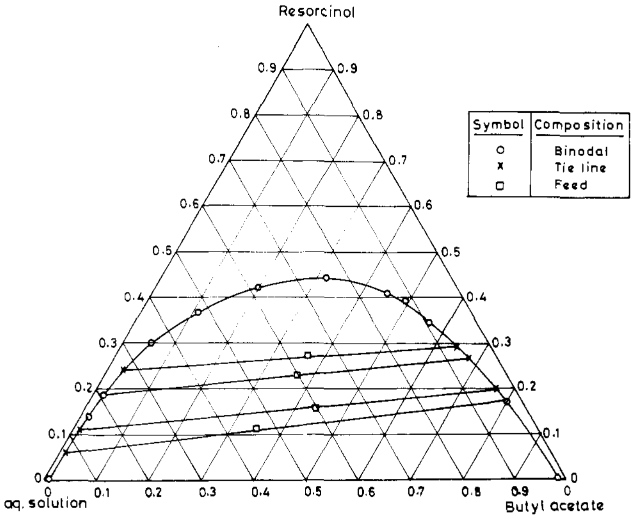

Figure 5. Ternary diagram: resorcinol–5% NaCl in water–butyl acetate.

The distribution coefficients in butyl acetate have been plotted in Figure 7 for 10% resorcinol in the feed. It can be noted that the distribution coefficient of resorcinol decreases with the increase of the phenol to resorcinol ratio and tends to be constant beyond the ratio of 0.8. The maximum reduction in the distribution coefficient is about 45%, whereas for a phenol to resorcinol ratio of 0.05, as per Table I, the reduction is only 10%. Due to the competition between phenol and resorcinol for retention in the organic phase, the distribution coefficient of resorcinol decreases.

In order to study the effect of solvent to feed ratio on the composite system comprising water, resorcinol, phenol, salt, and mixed solvent, the distribution coefficients have been calculated for three solvent to feed ratios, as presented in Table III. It can be noted that the distribution coefficient increases with increasing solvent to feed ratios and the distribution coefficients for the composite systems are higher than for any other systems mentioned earlier. This is attributed to the fact that the presence of phenol reduces the distribution coefficient of resorcinol to a lesser extent than its increase facilitated by the presence of salt and mixed solvent. However, an increase in solvent to feed ratio amounts to higher solvent cost, and hence it is preferable to use a lower solvent to feed ratio and 2–3 stages where solvent recovered from earlier stages can be utilized.

The performance study of the system resorcinol–water–butyl acetate has been aimed at analyzing the effect of process

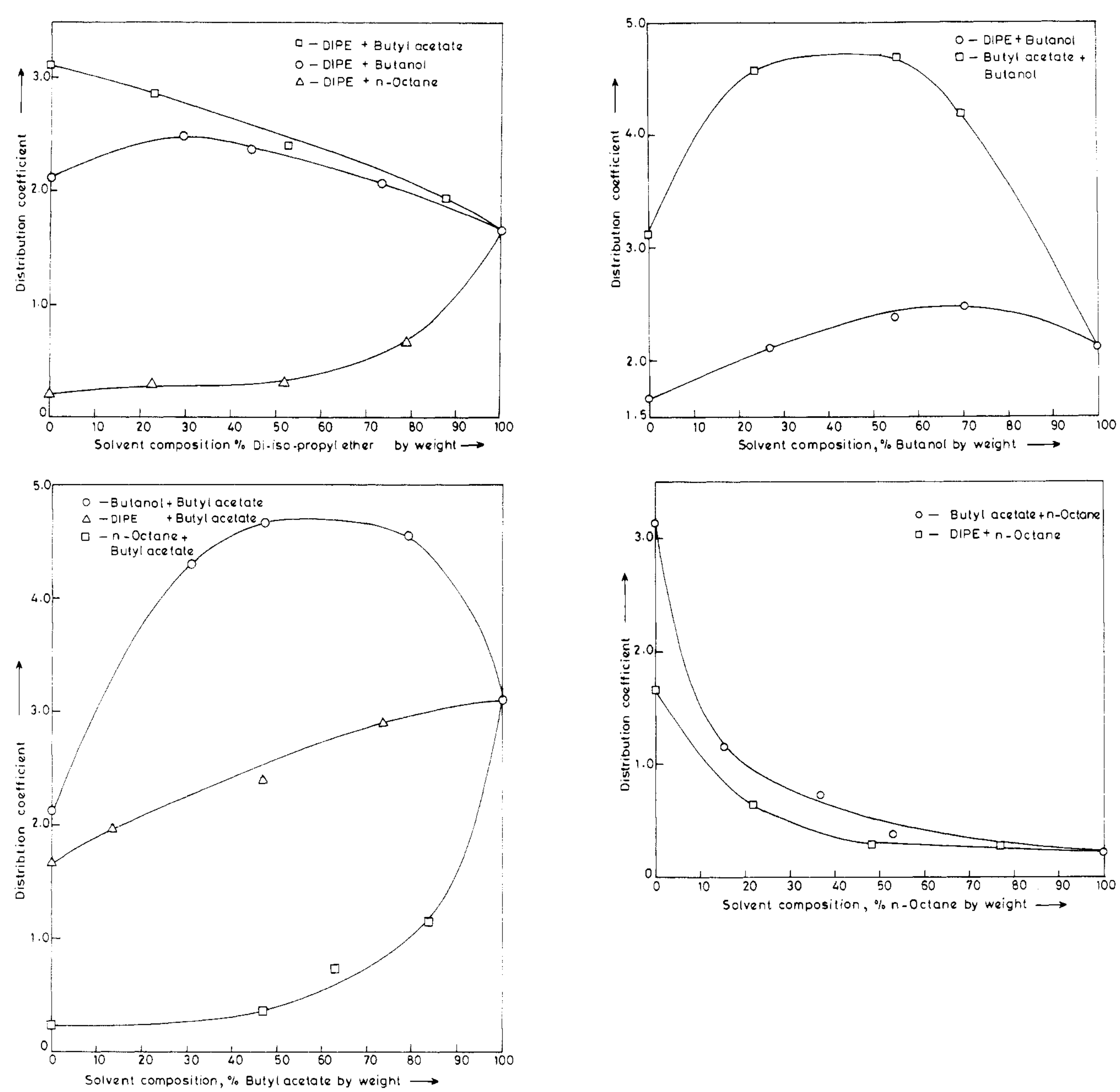

Figure 6. Distribution coefficient in mixed solvents for 10% resorcinol in feed.

Table III. Distribution Coefficient of Resorcinol for Composite Systems with Mixed Solvent

composite system	S:F[a] (by vol)	init vol, mL		final vol, mL		[resorcinol], g/mL		distribn coeff
		aqueous	organic	aqueous	organic	aqueous	organic	
I[b]	0.5	30.00	15.00	27.00	15.50	0.0279	0.1554	5.57
	1.0	30.00	39.00	24.00	33.00	0.0120	0.0872	7.24
	1.5	30.00	45.00	25.00	46.50	0.0067	0.0681	10.16
II[c]	0.64	25.00	16.00	25.00	15.00	0.0155	0.1076	6.93
	1.0	25.00	25.00	24.00	23.00	0.0088	0.0778	8.86

[a] S:F, solvent to feed ratio. [b] Composition: resorcinol, 10%; NaCl, 5%; phenol, 1.5% by wt. Mixed-solvent to feed ratio 1:1 (by vol). [c] Composition as given in Table I.

parameters, such as rpm, solvent to feed ratio, and number of stages, on the effectiveness factor E, which is defined as

$$E = \frac{C_0 - C_t}{C_0 - C_e} \tag{2}$$

where, C_0, C_t, and C_e are concentrations in the aqueous phase initially, at time t, and at equilibrium, respectively. The extraction time, t, and the effectiveness factor, E, can be correlated by the expression (7)

$$\ln (1 - E) = -Kt \tag{3}$$

Table IV. Effect of rpm and S:F Ratio on Characteristic Constant K

S:F (v/v)	rpm	K	S:F (v/v)	rpm	K
0.9	450	0.103		100	0.052
	250	0.065	0.38	450	0.098
	100	0.055		250	0.060
0.6	450	0.087		100	0.055
	250	0.060			

From the plot of ln (1 − E) vs t, which is normally a straight line, the characteristic constant K, has been evaluated from its slope

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

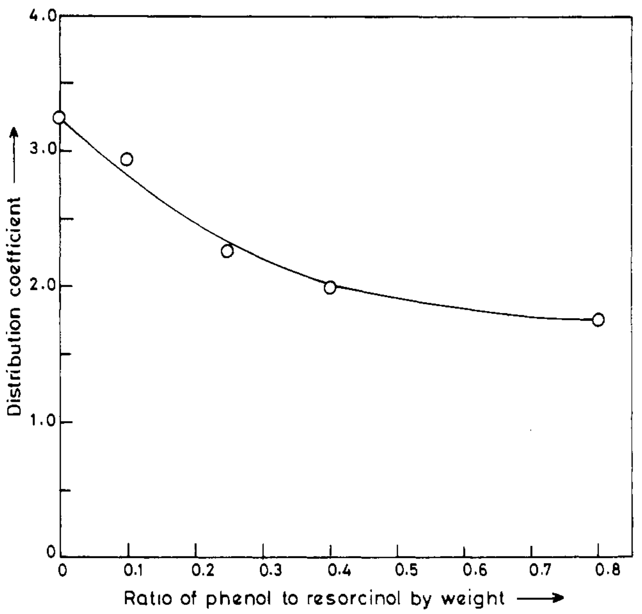

Figure 7. Effect of phenol on distribution coefficient of resorcinol for 10% resorcinol in feed (solvent: butyl acetate).

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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