Vapor-Liquid and Liquid-Liquid Vapor Phase Behavior of the Carbon Monoxide-Propane and the Carbon Monoxide-Ethane Systems

D. B. TRUST and FRED KURATA

University of Kansas, Lawrence, Kansas

Low-temperature vapor-liquid phase data are reported for the carbon monoxide-propane and the carbon monoxide-ethane systems. The data for the carbon monoxide-propane system are reported at eight temperatures ranging from −125° to +50°C., with pressure up to 2,000 lb./sq. in. abs., those for the carbon monoxide-ethane system are reported at four temperatures from −100° to 0°C., with pressures ranging up to the critical locus. Liquid phase immiscibility was observed at low temperatures in both the carbon monoxide-ethane and the carbon monoxide-propane systems. The pressure-temperature loci for these two systems in liquid-liquid vapor equilibrium were determined.

This study was undertaken to provide additional low-temperature vapor-liquid phase data for the carbon monoxide-propane and the carbon monoxide-ethane systems. Limited vapor-liquid data have been previously reported for the carbon monoxide-propane system (*8*), but no data for the carbon monoxide-ethane system were found in the literature. Vapor-liquid data for the carbon monoxide-methane system have been reported (*6*). At low temperatures liquid phase immiscibility was observed in both the carbon monoxide-propane and the carbon monoxide-ethane systems. Pressure-temperature loci for these two systems are reported.

EXPERIMENTAL METHOD

The apparatus and method used in this study have been described previously (*4*). Samples of vapor and liquid were taken from a magnetically stirred, static equilibrium cell which was maintained in a constant-temperature bath. Bath temperatures were measured and controlled to within ± 0.05°C., and the pressures are believed to be within ±3 lb./sq. in. of reported values. Three vapor samples and three liquid were removed from the equilibrium cells and analyzed by gas chromatography. During sampling the pressure drop was never greater than 5 to 10 lb./sq.in.

A visual glass cell was used for determining the pressure-temperature loci in the region of liquid phase immiscibility.

The carbon monoxide used in this study was Matheson Pure Grade, with a purity of 99.8%. Impurities in the carbon monoxide were 0.17% nitrogen and 0.04% carbon dioxide. The propane and ethane were Phillips Instrument Grade and Pure Grade, respectively. Hydrocarbon purities, as determined by chromatographic analyses, were propane, 99.9% and ethane, 99.1%. Impurities in the propane were nitrogen, methane, and ethane. Impurities in the ethane were nitrogen and methane.

EXPERIMENTAL DATA

Carbon Monoxide-Propane System

Qualitatively, the phase behavior of the carbon monoxide-propane system is very similar to the nitrogen-propane system studied by Schindler (*3*). The vapor-liquid behavior of this system was studied from −125° to 50°C., at pressures up to 2,000 lb./sq. in. abs.

The experimental vapor-liquid data are given in Table 1. Figures 1 and 2 show the equilibrium constants of carbon monoxide and propane as functions of temperature and pressure. These figures represent experimental data rather than smoothed data.

Certain mixtures of carbon monoxide and propane exhibit retrograde condensation at all temperatures above the critical solution temperature, while they exhibit double retrograde be-

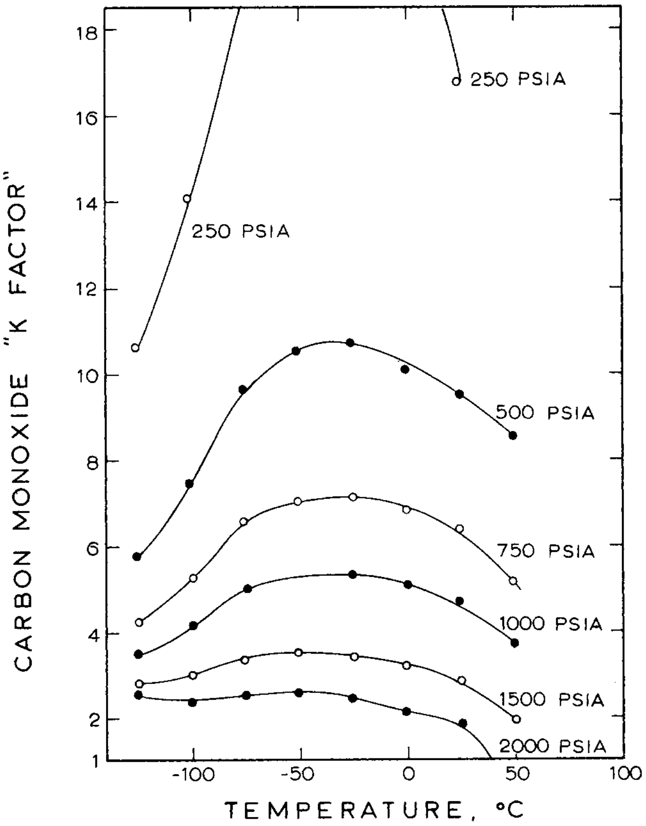

Fig. 1. *K* values for carbon monoxide in the carbon monoxide-propane system.

D. B. Trust is with Esso Research and Engineering, Florham Park, New Jersey.

havior below the critical solution temperature of −138.7°C. This latter phenomenon, as described by Katz and Kurata (2), is one in which two liquid phases are condensed or vaporized in a retrograde manner.

The liquid phase data of Widdoes and Katz (8) cannot be compared directly to those of this study because of the absence of a common temperature in the two investigations. However, comparisons of interpolated data show that the concentration of carbon monoxide in the liquid phase as reported by Widdoes and Katz is nearly twice as great as that determined in this study at −20°C. A large portion of this discrepancy can probably be attributed to the use of the Orsat method of analysis used in the Widdoes and Katz study, and to the larger pressure drops which occurred during sampling in their study.

Liquid phase immiscibility has previously been reported for the carbon monoxide-propane system (5). However, only two points on the three-phase locus were reported. The three-phase locus for the carbon monoxide-propane system is shown in Figure 3, and the data are tabulated in Table 2. At −179.5°C. a density inversion was observed for the two liquid phases. Above −179.5°C. the carbon monoxide-rich liquid phase was less dense than the propane-rich liquid phase; below −179.5°

Table 1. Vapor and Liquid Compositions of the Carbon Monoxide-Propane System

Pressure, lb./sq.in.abs.	$T = -125$°C. Mole % CO Liquid	$T = -125$°C. Mole % C_3H_8 Vapor	$T = -100$°C. Mole % CO Liquid	$T = -100$°C. Mole % C_3H_8 Vapor	$T = -75$°C. Mole % CO Liquid	$T = -75$°C. Mole % C_3H_8 Vapor
200	6.85	0.06	—	0.45	—	1.72
250	8.52	—	—	—	—	1.42
300	—	0.06	—	—	—	—
400	13.9	0.08	—	0.19	—	0.88
500	18.1	0.13	13.5	—	10.4	0.80
600	—	0.18	—	0.27	—	—
750	—	—	19.3	—	—	—
800	25.0	0.27	—	0.39	—	—
1,000	—	0.93	23.8	0.65	19.6	1.21
1,200	30.9	—	—	—	—	—
1,250	—	—	27.8	1.10	—	—
1,500	34.2	—	33.4	—	28.9	2.08
1,600	—	—	—	2.19	—	—
1,800	36.7	—	—	2.98	—	—
2,000	38.3	3.66	40.1	3.76	37.8	3.51
2,200	—	—	42.6	4.72	—	—
2,300	41.0	—	—	—	—	—
2,500	—	5.06	—	—	—	—

Pressure, lb./sq.in.abs.	$T = -50$°C. Mole % CO Liquid	$T = -50$°C. Mole % C_3H_8 Vapor	$T = -25$°C. Mole % CO Liquid	$T = -25$°C. Mole % C_3H_8 Vapor	$T = 0$°C. Liquid Mole % CO	$T = 0$°C. Vapor Mole % C_3H_8
200	—	—	—	22.6	2.3	41.4
250	—	5.36	—	—	—	—
300	—	—	—	16.8	—	—
400	—	3.30	—	12.1	5.7	26.6
500	9.2	—	8.6	10.0	—	22.2
600	—	2.59	—	—	9.1	—
750	13.8	—	—	—	—	17.7
800	—	2.58	13.8	—	12.3	—
1,000	18.3	2.72	17.2	7.35	16.2	15.4
1,200	—	3.10	21.1	7.88	21.4	14.8
1,600	29.1	4.20	—	8.91	28.2	—
1,700	—	—	—	—	—	16.1
1,800	—	4.69	32.5	9.22	32.5	—
2,000	36.3	3.53	36.3	11.00	37.8	20.0

Pressure, lb./sq.in.abs.	$T = +25$°C. Mole % CO Liquid	$T = +25$°C. Mole % C_3H_8 Vapor	$T = +50$°C. Mole % CO Liquid	$T = +50$°C. Mole % C_3H_8 Vapor
300	—	56.0	—	—
400	4.8	44.8	—	—
500	—	—	4.5	58.5
600	8.4	31.7	6.4	54.4
750	—	—	—	48.6
800	—	28.0	10.7	—
1,000	16.3	25.2	15.3	43.9
1,200	20.0	24.0	20.0	41.6
1,500	—	24.0	—	43.2
1,600	28.5	—	32.3	47.9
1,700	—	—	35.4	62.3
1,800	33.3	—	—	—
2,000	38.4	29.3	—	—

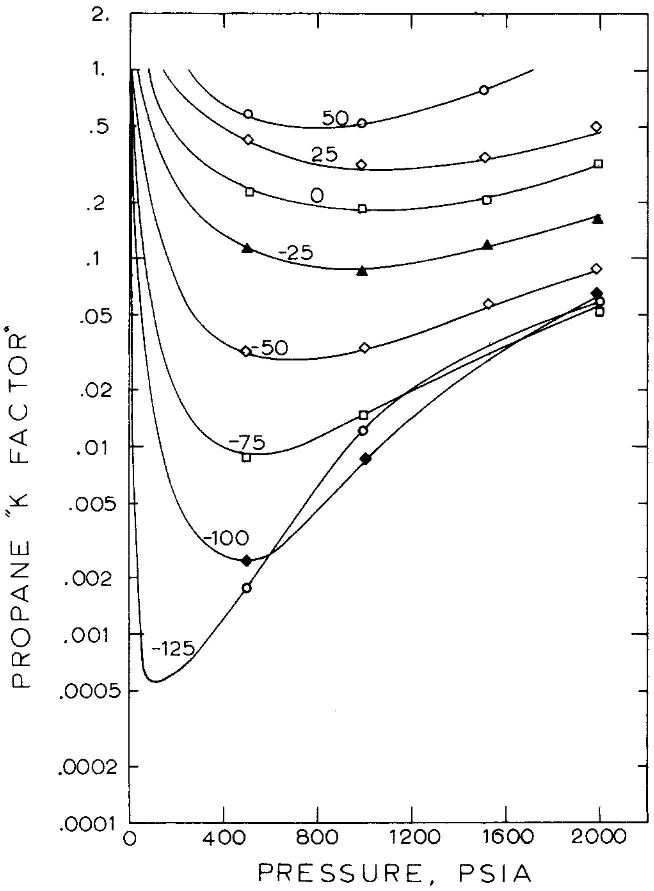

Fig. 2. *K* values for propane in the carbon monoxide-propane system.

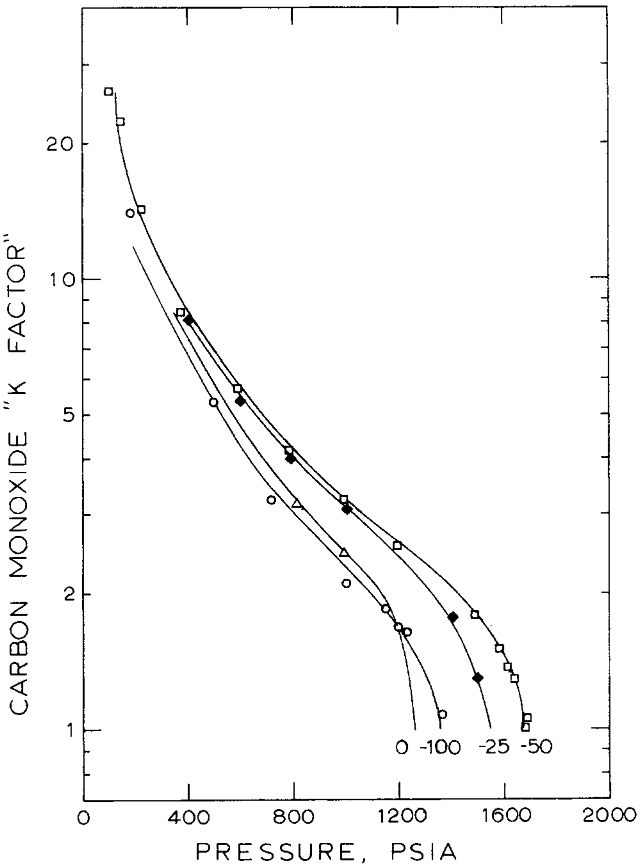

Fig. 4. *K* values for carbon monoxide in the carbon monoxide-ethane system.

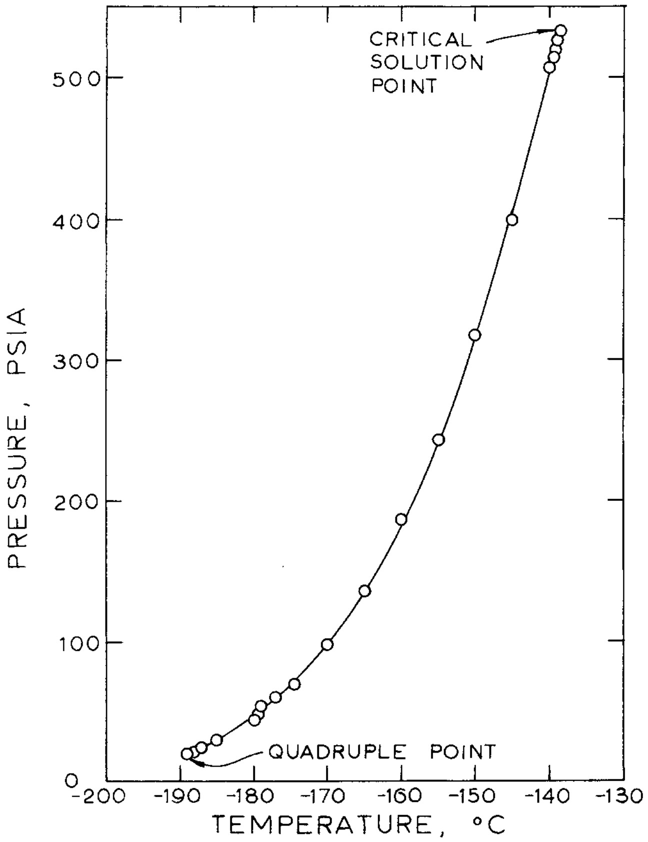

Fig. 3. Liquid-liquid vapor locus for carbon monoxide-propane system from quadruple point to critical solution point.

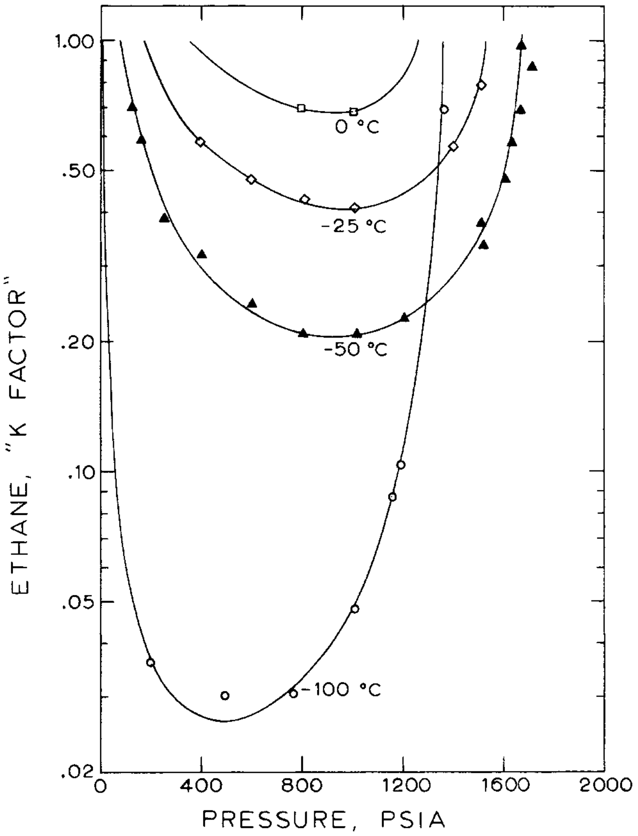

Fig. 5. *K* values for ethane in the carbon monoxide-ethane system.

C. the propane-rich liquid phase was less dense than the carbon monoxide-rich liquid phase. The temperature for the density inversion determined in this study is the same as that reported by Stein (*5*).

Carbon Monoxide-Ethane System

The vapor-liquid data for the carbon monoxide-ethane system are given in Table 3. Figures 4 and 5 show the equilibrium constants for carbon monoxide and ethane as a function of temperature at various pressures. These *K* value plots were constructed from experimental data. The phase behavior of this system is similar to that of the nitrogen-ethane system reported by Eakin (*1*).

The pressure-temperature locus for the three-phase region is shown in Figure 6, and the data are given in Table 4. Since the two liquid phases become identical at the critical solution point for the carbon monoxide-ethane system, the critical solution point of this system differs from that of the carbon monoxide-propane system in which the carbon monoxide-rich liquid becomes identical with the vapor phase. In the carbon monoxide-ethane system the carbon monoxide-rich liquid is

TABLE 2. THREE-PHASE LOCUS; CARBON MONOXIDE-PROPANE SYSTEM

Temp., °C.	Pressure, lb./sq.in.abs.
−189.05	18.4*
−188.0	20.8
−187.0	23.3
−185.0	28.7
−180.0	44.0
−179.5	47.0
−179.0	53.0
−177.0	58.5
−175.0	68.5
−170.0	99
−165.0	135
−160.0	185
−155.0	243
−150.0	317
−145.0	400
−140.0	507
−139.5	514
−139.0	527
−138.9	528
−138.72	533†

* Quadruple point.
† Critical solution point.

TABLE 3. VAPOR AND LIQUID COMPOSITIONS OF THE CARBON MONOXIDE-ETHANE SYSTEM

	T = −100°C.		*T* = −50°C.	
Pressure, lb./sq.in.abs.	Mole % CO Liquid	Mole % C_2H_6 Vapor	Mole % CO Liquid	Mole % C_2H_6 Vapor
125	—	—	1.17	69.4
200	6.96	3.41	—	—
250	—	—	4.36	37.9
400	—	—	8.37	29.2
500	18.6	2.16	—	—
600	—	—	13.8	21.1
750	—	—	19.7	16.8
1,000	42.8	2.73	25.8	16.0
1,200	56.9	5.43	32.4	15.1
1,300	—	—	—	—
1,350	82.8	11.7	—	—
1,500	—	—	44.4	21.0
1,600	—	—	51.1	23.6
1,700	—	—	63.6	32.3

	T = −25°C.		*T* = 0°C.	
Pressure, lb./sq.in.abs.	Mole % CO Liquid	Mole % C_2H_6 Vapor	Mole % CO Liquid	Mole % C_2H_6 Vapor
400	5.56	54.8	—	—
500	—	—	3.72	—
600	10.6	43.1	6.01	—
800	15.7	35.7	11.6	61.4
1,000	21.9	31.8	17.6	56.7
1,400	35.9	36.3	—	—
1,500	43.2	44.4	—	—

TABLE 4. THREE-PHASE LOCUS DATA; CARBON MONOXIDE-ETHANE SYSTEM

Temp., °C.	Pressure, lb./sq.in.abs.
−187.8	19.8*
−180.0	43.0
−178.0	47.0
−175.0	62.0
−174.0	69.0
−173.0	72.0
−172.6	72.5†

* Quadruple point.
† Critical solution point.

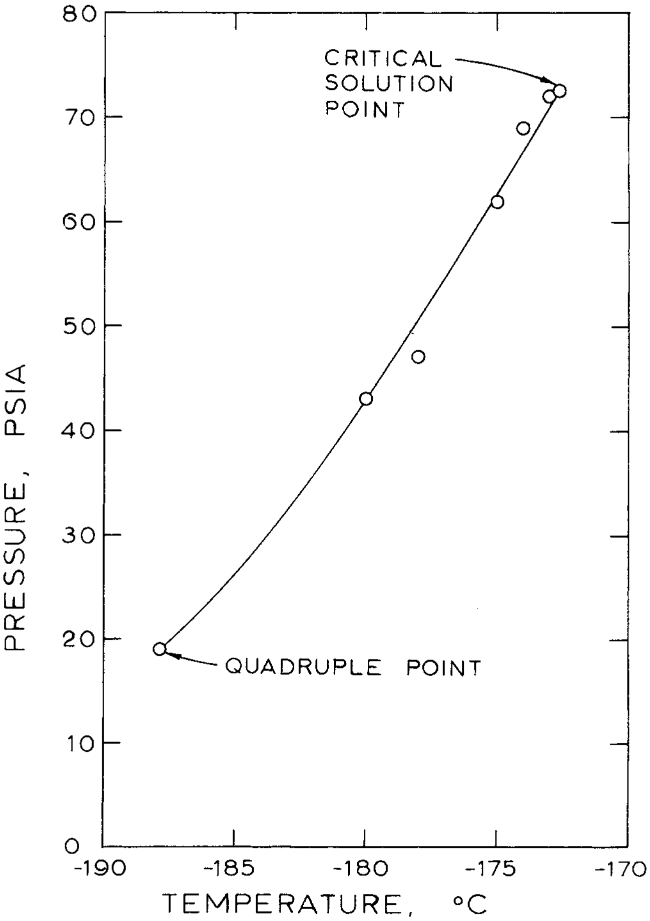

Fig. 6. Liquid-liquid vapor locus for carbon monoxide-ethane system from quadruple point to critical solution point.

more dense than the ethane-rich liquid over the entire three-phase region.

DATA ANALYSIS

Isothermal vapor and liquid composition data for the carbon monoxide-propane system were fitted to empirical equations in the form of power series in pressure. The mathematical form of the vapor and liquid polynomials, as well as the least-squares constants, are presented by Trust (*7*).

The average standard deviation of the experimental liquid phase data from the curve was 0.28 mole % carbon monoxide. For the vapor phase the average standard deviation of the experimental data from the curves was 0.40 mole % propane.

The experimental data for the carbon monoxide-ethane system were not fitted to equations.

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NOTATION

P = pressure, lb./sq.in.abs.
T = temperature, °C.
X = liquid phase composition, mole %
Y = vapor phase composition, mole %

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Precipitate Flotation of Chromium

DIBAKAR BHATTACHARYYA, J. ANDREW CARLTON, and ROBERT B. GRIEVES

University of Kentucky, Lexington, Kentucky

A three-stage process of reduction of acid chromate ($HCrO_4^-$), with $NaHSO_3$ followed by precipitation of Cr(III) with NaOH followed by flotation with an anionic surfactant, provides 97% removal of chromium from aqueous suspensions containing 48.3 mg./liter Cr (0.929 mM). The required dosage of surfactant (sodium laurylsulfate) is 0.093 mole SLS/mole Cr, compared to a dosage of 1.1 mole cationic surfactant/mole Cr, used to ion float soluble acid chromate. The precipitate flotation process is pH dependent: below pH 6.3, soluble chromium species become appreciable and the flotation results agree with calculated soluble chromium concentrations; above pH 9.7, the charge of the precipitate is reversed, as indicated by surface potential measurements. The optimum pH range for flotation is 7.0 to 8.8. The effect of initial surfactant concentration on the flotation efficiency is established. Small quantities of calcium enhance the flotation of Cr, while higher concentrations, 0.5 mM and greater, decrease flotation efficiency. For suspensions with a doubled chromium concentration (96.6 mg./liter), the optimum pH range for flotation is lowered and narrowed to 6.3 to 6.5, indicating modifications in particle surface characteristics validated by measurements of surface potential and surfactant adsorption. Eighty-seven percent flotation is achieved at a 0.093 mole/mole ratio.

The precipitate flotation technique has received attention from a number of investigators, beginning with the work of Skrylev and Mokrushin (*1*) and that of Baarson and Ray (*2*). A number of studies have been carried out (*3* to *6*), including an excellent group of papers by Pinfold et al. (*7* to *12*) and another by Rubin et al. (*13* to *15*). Grieves and Bhattacharyya (*16*) have investigated the separation of complexed cyanide by precipitate flotation. The present study involves the precipitate flotation of chromium from aqueous suspension as chromic hydroxide. Grieves et al. (*17* to *20*) have investigated the ion flotation technique for the removal of chromium (as soluble acid