sodium hydroxide solution and poured through a sintered glass filter. Neutralization with glacial acetic acid precipitated 26.1 g. (93% yield) of brown solid, m.p. 187–188°.[20] Recrystallized from acetone, it melted at 192°

Anal.[21] Calcd. for C_9H_6ClNO: Cl, 19.74. Found: Cl, 19.45.

2-(4-Chloroanilino)-6-quinolinol Hydrochloride.—A solution of 6 g. (0.03 mole) of 2-chloro-6-quinolinol and 4 g. (0.031 mole) of *p*-chloroaniline in 150 ml. of butyl alcohol was heated at reflux temperature overnight. The solution was concentrated to about 40 ml. of residue which was treated first with ether and then with acetone to give 7.4 g. (74% yield) of yellow crystals, m.p. 223–225° dec. A sample was recrystallized from isopropyl alcohol, m.p. 227–228° dec.

Anal.[21] Calcd. for $C_{15}H_{11}ClN_2O \cdot HCl \cdot 1^1/_4H_2O$: C, 54.64; H, 4.43; Cl, 21.51. Found: C, 54.51; H, 3.79; Cl, 21.51.

2-(4-Chloroanilino)-5-(1-piperidylmethyl)-6-quinolinol (VII).—The procedure of compound VI was applied. After three hours at reflux temperature, the solution was evaporated to about 50 ml. whereupon cooling gave 2.7 g. (88% yield) of white crystals, m.p. 192–193°. Purification by means of ether in a Soxhlet extractor and recrystallization from alcohol raised the melting point to 199–200°.

Anal.[21] Calcd. for $C_{21}H_{22}ClN_3O$: C, 68.56; H, 6.03. Found: C, 68.65; H, 6.30.

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[20] Edinger, *Ber.*, **30**, 2420 (1897), reported 187° for which is presumed to be the same compound.

[21] By Mr. Charles Childs and staff, of Parke, Davis and Company.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY OF THE UNIVERSITY OF TEXAS]

The Compressibility of Pentene-1

BY H. O. DAY[1] WITH W. A. FELSING

The compressibility of pentene-1 has been determined over the temperature range of 80° to 225°. The data presented are accurate to 0.1–0.2%, except at the highest temperatures (200° and 225°); evidence of decomposition at these temperatures was found.

Introduction

This Laboratory has been interested for a number of years in the determination of some of the thermodynamic properties of pure, saturated hydrocarbons.[2] The present investigation presents data on the compressibility of an unsaturated hydrocarbon, pentene-1, for which no previous accurate compressibility data existed in the literature. The vapor pressures of this substance were presented in a recent publication.[3] It was hoped at the initiation of this problem that critical data could be determined for this substance; however, the polymerization rate at 200° or above becomes too great to allow for an accurate determination of a series of isotherms in the immediate vicinity of the critical point (near 201°).[3]

Method and Apparatus.—All compressibility data were determined by means of a dead-weight piston gage described elsewhere,[4] being a modification of the M. I. T. unit described by Beattie.[5]

TABLE I

COMPRESSIBILITY OF PENTENE-1

Specific volume, ml./g.	Pressure, atmospheres
80.00°	
1.7466	5.616
1.7404	13.518
1.7346	21.414
1.7273	31.918
1.7165	49.025
1.6871	101.529
1.6621	154.075
1.6404	206.705
1.6213	259.372
1.6046	311.814
125.00°	
1.9637	11.681
1.9597	13.530
1.9543	16.158
1.9442	21.426
1.9260	31.930
1.9003	49.036
1.8386	101.539
1.7940	154.084
1.7583	206.714
1.7286	259.381
1.7032	311.822
175.00°	
2.5135	27.094
2.5052	27.476
2.4269	31.930
2.3413	39.826
2.2738	49.032
2.1554	75.274
2.0816	101.531
1.9842	154.075
1.9195	206.704
1.8691	259.370
1.8290	311.810
225.00°	
7.1296	43.280
5.7037	47.306
4.7531	50.543
4.0741	53.600
3.5648	57.144
3.1687	62.144
2.8519	71.502
2.5926	87.225
2.3765	114.483
2.1937	159.762
2.0370	231.852
1.9262	311.712
100:00°	
1.8297	7.203
1.8230	13.529
1.8149	21.423
1.8045	31.927
1.7893	49.033
1.7488	101.537
1.7160	154.083
1.6889	206.711
1.6661	259.378
1.6467	311.819
150.00°	
2.1566	18.541
2.1427	21.439
2.1012	31.953
2.0496	49.048
1.9479	101.550
1.8822	154.095
1.8344	206.724
1.7968	259.391
1.7644	311.832
200.00°	
7.1296	36.415
5.7037	38.151
4.7531	39.090
4.0741	39.772
3.5648	40.680
3.1687	42.458
2.8519	46.718
2.5926	57.124
2.3765	78.066
2.1937	117.323
2.0370	185.302
1.9012	288.570
1.8775	311.790

The thermostat temperatures were controlled to ±0.005° by means of a platinum resistance thermometer in conjunction with a Mueller bridge and a photoelectric relay. The actual thermostat temperature was simultaneously determined by the resistance thermometer (calibrated by the National Bureau of Standards). The method of manipulation was described elsewhere.[4]

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[2] Felsing, Cuellar and Newton, THIS JOURNAL, **69**, 1972 (1947), reference 1.

[3] Day and Nicholson with Felsing, *ibid.*, **70**, 1784 (1948).

[4] Kelso with Felsing, *ibid.*, **62**, 3132 (1940); *Ind. Eng. Chem.*, **34**, 161 (1942).

[5] Beattie, *Proc. Am. Acad. Arts and Sci.*, **69**, 389 (1934).

Material Used.—The sample of pentene-1 was obtained from the Phillips Petroleum Company; it was part of the large batch which had been reported by the National Bureau of Standards to have a purity of 99.34 ± 0.4 mole per cent., based upon freezing point data. It had a normal boiling point of 30.07 ± 0.02°. Before being loaded into the bomb, the material was de-gassed and fractionally distilled under a vacuum at −65°.

The Accuracy Attained.—The compressibility data are believed to be accurate to 0.1 to 0.2% at all temperatures up through 175°. However, at the two highest temperatures, the isotherms are estimated, by an extrapolation of the accurate lower temperature isotherms, to be in error by 0.2 to 1% for the 200° isotherm and by 2% for the 225° isotherm.

The reality of polymerization was demonstrated by an investigation of the vapor pressures. At 175°, with a total specific volume (volume of liquid plus volume of gas divided by the total number of grams of material) of 3.2938 ml./g., the vapor pressure was 27.056 atmospheres, and with a total specific volume of 2.8362 ml./g., the vapor pressure was 27.061 atmospheres; this difference of 0.005 atmospheres is probably due to experimental error and to the presence of a small amount of impurity. However, after these measurements, the temperature was raised to and kept at 195° for several hours and at 200° for several hours. On cooling to 175° and adjusting again to the same total specific volumes as before, the vapor pressures were found to be 27.003 and 27.030 atmospheres, respectively. These vapor pressure values are not only considerably lower, but they show a greater difference for the two total specific volumes. These facts were considered as evidence that the material was no longer pure pentene-1 and that some polymerization had taken place.

The Experimental Data.—The compressibilities are presented in Table I at the various constant temperatures.

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The Separation of Rare Earths by Ion Exchange. VI. Conditions for Effecting Separations with Nalcite HCR and One-tenth Per Cent. Citric Acid–Ammonium Citrate Solutions

BY F. H. SPEDDING, E. I. FULMER, J. E. POWELL, T. A. BUTLER AND I. S. YAFFE

Procedures have been developed for the successful separation of the rare earths using a high capacity resin, Nalcite HCR, and 0.1% citrate solution. The high capacity resin proved to be definitely superior to a low capacity resin, Amberlite IR-100, for the separation of the heavy rare earths. Gram quantities of Er, Ho and Dy have been obtained in purities greater than 99%. The process proved to be equally efficient when stepped up 50-fold to a pilot plant scale separation of the more abundant rare earths.

I. Introduction

Previous communications from this Laboratory[1–7] have dealt only with the use of the low capacity resins, Amberlite IR-1 and IR-100, for the separation of rare earths by ion exchange on a macro scale. Although Amberlite IR-1 proved to be undesirable due to its relative high solubility, IR-100 was found to give satisfactory separations over a rather wide range of conditions and has been successfully employed for the separation of certain rare earths from their mixtures. Harris and Tompkins[8] have stated that Dowex 50 resin is superior to the Amberlite resins IR-1 and IR-100 for rare earth separations; their comparison appears to be based on experiments performed on yttrium and cerium mixtures, using 5% citrate solutions in the *p*H range 2.75 to 3.3. Recent investigations,[4,6] using 0.1% citrate solutions, resulted in elution curves which differed significantly from those previously reported. The present communication deals with the use of the high capacity resin, Nalcite HCR, with 0.1% citrate solutions.

II. Materials, Apparatus and General Procedures

Unless otherwise noted, the materials, apparatus and procedures are the same as those previously given.[5]

1. **Resin.**—Nalcite High Capacity Resin, a sulfonated copolymer of styrene and divinylbenzene, was used in all experiments described in this paper; according to a private communication from the Dow Chemical Co., the National Aluminate Corporation is licensed to distribute Dowex 50 resin under the trade name Nalcite HCR. Resin particles of −40 + 50 mesh size were used in the 22-mm. and the 40-mm. i.d. columns, and −30 + 40 mesh size in the 6-inch i.d. columns.

2. **Resin Beds.**—Each of the 40-mm. columns contained 450 g. of air-dried resin which gave a bed height of 60 cm. in the NH_4^+ cycle and 63 cm. in the H^+ cycle. Each 6-inch column was loaded with 9 kg. of resin, which gave a bed height of 30 in. in the H^+ cycle. The conditioning of the resin has been previously described.[5]

3. **Eluant.**—The eluting solution was 0.1% citrate, based on anhydrous citric acid; the concentration of the eluant was, therefore, 9.4% greater in citric acid than that used in previous investigations[6] in which the concentration was based on the monohydrate.

4. **Recovery of the Heavy Rare Earths.**—Certain properties of the heavy rare earths make them more difficult to recover than the light rare earths; for example, the complexing action with citrate ions is increased; the oxalates are more soluble; and the rate of precipitation[9] is slower,

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(7) F. H. Spedding, *Discussions Faraday Soc.*, No. 7, 214 (1949).

(8) D. H. Harris and E. R. Tompkins, THIS JOURNAL, **69**, 2792 (1947).

(9) D. S. Martin and C. Crouthamel, *ibid.*, **72**, 1382 (1950).