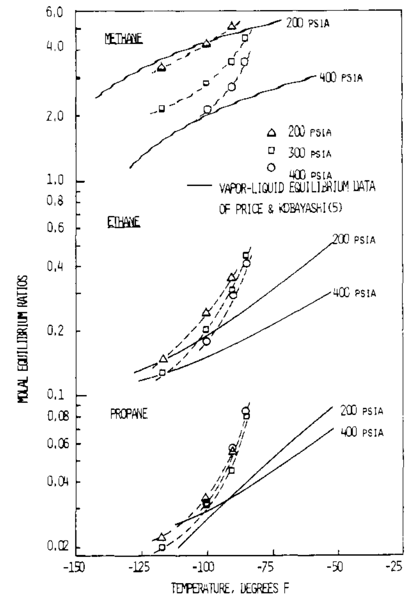

Figure 4. Molal equilibrium ratios for hydrocarbons in carbon dioxide–methane–ethane–propane system at $\phi = 0.28$

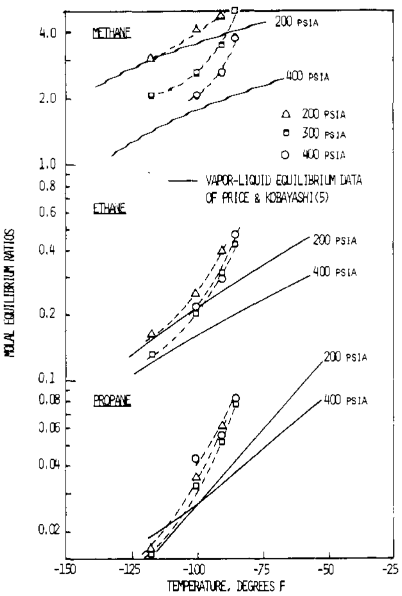

Figure 5. Molal equilibrium ratios for hydrocarbons in carbon dioxide–methane–ethane–propane system at $\phi = 0.68$

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Hydroxymethylabietanoic Acid and Derivatives: Dinitrile, Diamine, and Diisocyanate

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12-Hydroxymethylabietic acid is hydrogenated (nickel catalyst) to 12-hydroxymethylabietan-18-oic acid. Its conversion to 12-chloromethylabietan-18-oyl chloride and the syntheses of 12-cyanomethylabietan-18-nitrile, 12-(β-aminoethyl)abietan-18-amine, and 12-(β-isocyanatoethyl)abietan-18-isocyanate from 12-chloromethylabietan-18-oyl chloride are discussed. 12-Carboxymethylabietan-18-oic acid is readily prepared from 12-cyanomethylabietan-18-amide.

Recent efforts of the Naval Stores Laboratory and elsewhere have been directed toward making resin acid polyfunctional (*1*, *4-8*). In previous research, 12-hydroxymethylabiet-7,(8)-en-18-oic acid was converted to amino alcohols, dinitriles, diamines, and diisocyanates (*10*).

In the present work, 12-hydroxymethylabietan-18-oic acid (II) was prepared by hydrogenation of 12-hydroxymethylabietic acid (I), using a nickel catalyst. A more direct route for making nitrile, amine, and isocyanate derivatives than that reported by Watson et al. (*10*) was in the conversion of II to its 12-chloromethylabietan-18-oyl chloride (V) using Vilsmeier reagent (*9*). The acid chloride was readily converted to the amide (VI). Dehydration of VI with tosylchloride (*10*) provided the 12-chloromethylabietan-18-nitrile (VII); reaction of VI with sodium cyanide furnished 12-cyanomethylabietan-18-amide (VIII). The dinitrile, 12-cyanomethylabietan-18-nitrile (IX), was prepared either from VII by reaction with sodium cyanide or from VIII by dehydration (*10*). The diacid (X) was made by hydrolysis of VIII. Catalytic hydrogenation of IX over cobalt produced the diamine, 12-(β-aminoethyl)abietan-18-amine

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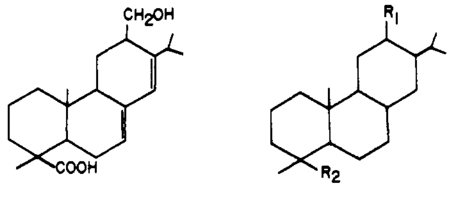
(XII) (*3*). The diisocyanate, 12-(β-isocyanatoethyl)abietan-18-isocyanate (XV) was prepared by interacting the diamine dihydrochloride with phosgene (*10*).

Cpd	R_1	R_2	Mp, °C
II	CH_2OH	$COOH$	242-43
III	CH_2OH	CO_2CH_3	147-48
IV	CH_2OCOCH_3	CO_2CH_3	83
V	CH_2Cl	$COCl$	. . .
VI	CH_2Cl	$CONH_2$	168-71
VII	CH_2Cl	CN	125
VIII	CH_2CN	$CONH_2$	. . .
IX	CH_2CN	CN	170-71
X	CH_2CO_2H	CO_2H	236-39
XI	$CH_2CO_2CH_3$	CO_2CH_3	130-31
XII	$CH_2CH_2NH_2$	CH_2NH_2	108-10
XIII	$CH_2CH_2NHCONHC_6H_5$	$CH_2NHCONHC_6H_5$	197-98
XIV	$CH_2CH_2NH_2\cdot HO_2CC_6H_3\text{-}(NO_2)_2$	$CH_2NH_2\cdot HO_2CC_6H_3\text{-}(NO_2)_2$	261-64
XV	CH_2CH_2NCO	CH_2NCO	82-3
XVII	$CH_2CH_2NHCONHC_6H_{11}$	$CH_2NHCONHC_6H_{11}$	235-40

Scheme 1



I II - XVII

EXPERIMENTAL

Gas-liquid partition chromatography (GLPC) was carried out on an F&M 700 chromatograph using a 6-ft W-98 silicone Hewlett-Packard column. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. Nmr spectra were run on a Varian A-60 spectrometer. Analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are all uncorrected. Elemental analyses (C, H, N, Cl) in agreement with the theoretical values have been obtained and were submitted for review.

12-Hydroxymethylabietan-18-oic Acid (II). A mixture of I (100 grams), Girdler G-69 nickel on kiesulguhr (10 grams), and 1-butanol (400 ml) was charged into a 1780-ml stainless steel bomb, hydrogen was added (2000 psig), and the batch was heated to 200° C and maintained at that temperature for 22 hr. The mixture was cooled, removed from the bomb, heated with charcoal (10 grams), and filtered through a pressure filter. Hydroxy acid II (51.7 grams) crystallized on cooling the filtrate, was removed; the mother liquor was evaporated almost to dryness, refluxed with acetone (ca. 50 ml), cooled, and filtered; yield of II, 32.9 grams; total yield, 84.6%. Tests for presence of unsaturation with tetranitromethane were negative and the nmr spectra did not have a signal for a vinyl or allylic proton. Removal of acetone from the filtrate gave a residue (5 grams) containing II with traces of another product.

Methyl, 12-Hydroxymethylabietan-18-oate (III). This ester was prepared for analysis purposes by standard procedures (CH_2N_2); GLPC showed only one component; infrared bands at 2.79 (OH) and 5.8 (CO). The mass spectrum showed a parent ion at a mass of 350, appropriate for the tetrahydro structure $C_{22}H_{38}O_3$. The nmr spectrum was also in accord with the saturated skeletal structure.

Methyl, 12-Acetoxymethylabietan-18-oate (IV). This derivative was prepared from III (*1*) for analysis purposes; the GLPC chromatogram had a single peak; infrared bands at 5.75 (acetate) and 5.8 (CO, ester).

12-Chloromethylabietan-18-oyl Chloride (V). Hydroxy acid II (33.6 grams; 0.1 mole), chloroform (100 ml), DMF (20 ml), and thionyl chloride (48 grams; 0.4 mole) were refluxed for 1 hr (*2, 9*). The reaction mixture was cooled, and the excess thionyl chloride was removed under vacuum. The residue was taken up in ether and washed with water and dried. Evaporation of the ether gave V in quantitative yield; infrared bands showed absorptions at 5.6 (CO, acid chloride), 14.25, and 14.85 (C—Cl). This crude material was used, without purification, for the preparation of VI.

12-Chloromethylabietan-18-amide (VI). A benzene solution of V was stirred into excess ammonium hydroxide containing about 1% pyridine, and the mixture cooled overnight in a refrigerator. The solid was removed by filtration, washed, and taken up in ether. The ether solution was washed with very dilute hydrochloric acid, sodium carbonate solution, and water and dried. Evaporation of ether gave VI; yield, 34.3 grams (97%); infrared absorptions at 2.85, 2.95 (NH, amide), 6.05 (CO, amide), and 13.7-13.95 (C—Cl).

12-Chloromethylabietan-18-nitrile (VII). Dehydration of VI was accomplished with *p*-toluenesulfonyl chloride (*10*); infrared bands at 4.5 (CN) and 13.33-14.29 (C—Cl).

12-Cyanomethylabietan-18-amide (VIII). A mixture of VI (20 grams; 0.06 mole), sodium cyanide (12 grams; 0.24 mole), DMF (250 ml), and DMSO (10 ml) was refluxed for 48 hr. The mixture, after cooling, was extracted with chloroform, washed with water, dilute hydrochloric acid, and again with water and dried. After removal of the solvent, 17.5 grams (90.2%) of a solid was obtained; infrared absorption at 2.85, 2.95 (NH, amide), 4.48 (CN), and 6.06 (CO, amide). This was used, without purification, for the preparation of the dinitrile IX by dehydration.

12-Cyanomethylabietan-18-nitrile (IX). Dehydration of VIII, using the same procedure as for VII (*10*), gave IX in 90% yield; the GLPC curve had only one component; infrared absorption at 4.5 (CN). This was also made from VII following the procedure for VIII; yield, 88%.

12-Carboxymethylabietan-18-oic Acid (X). The diacid X was prepared by the hydrolysis of VIII in refluxing ethylene glycol with potassium hydroxide and treatment of the product with dilute hydrochloric acid; yield, 70%. A sample of X was converted to its methyl ester (XI) (CH_2N_2) for identification purposes; there was only one component in the GLPC chromatogram; infrared band at 5.85 (CO).

12-(β-Aminoethyl)abietan-18-amine (XII). Dinitrile (20 grams), Girdler cobalt (G-67RS) catalyst (4 grams), and *p*-dioxane (350 ml) were charged into a 1780-ml stainless steel bomb and chilled in Dry Ice/acetone. Liquid ammonia (25 ml) followed by hydrogen (2000 psig) was added to the mixture and the batch heated to 170-5° C. At the reaction temperature, hydrogen was pumped to 5000 psig and the heating continued for 7 hr. The bomb was cooled, ammonia was allowed to escape, and the clear liquid was filtered to remove the catalyst. Evaporation of the solvent left the amine as gray-white crystals; distillation, however, gave a snow-white material. Di-*N*-phenylurea derivative (XIII) and the 3,5-dinitrobenzoate (XIV) were made for identification purposes.

12-(β-Isocyanatoethyl)abietan-18-isocyanate (XV). The diisocyanate was prepared by treating the dihydrochloride salt of XII in refluxing *o*-dichlorobenzene with carbonyl chloride (*10*). The brown solid, left after removing the solvent, was distilled to get diisocyanate as a colorless liquid which immediately crystallized; the GLPC curve had only one component; strong infrared absorption at 4.45 (CNO). Di-*N*-phenylurea derivative (XVI) and di-*N*-cyclohexylurea derivative (XVII) were prepared for identification purposes.

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Relative Volatility of Propane–Propene System by Integration of General Coexistence Equation

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Experimental data on the propane–propene system ranging from –20° to 100° F and from 20 to 1600 psia are reported. They include vapor compressibility factors for pure propane and pure propene; liquid specific volumes for propane, propene, and three mixtures containing 0.25, 0.50, and 0.75 mole fraction propene; and vapor pressures for propane, propene, and mixtures containing approximately 0.17, 0.33, 0.50, 0.67, and 0.83 mole fraction propene. The data have an estimated probable error of ±0.1%. The experimental data are correlated, and relative volatilities are calculated by integration of a rigorous form of the isothermal general coexistence equation at –20°, 10°, 40°, 70°, and 100° F. By incorporating some literature data into the correlations, relative volatilities are also calculated at 130° F. The relative volatilities have an estimated probable error of ±0.005 unit.

Vapor-liquid equilibrium compositions of the propane–propene system under various conditions have been experimentally measured by several investigators (*2-4*, *8*, *9*); however, due to the physical similarity of these two chemicals, the effect of experimental error on column design is greatly magnified. The purpose of this work was to resolve the experimental differences in the literature data by developing improved relative volatility information on the propane–propene system.

The method chosen to accomplish this purpose was integration of the isothermal general coexistence equation to generate vapor-liquid equilibrium compositions from vapor pressure and pressure-volume-temperature data on the pure components and their mixtures. This method has the advantage of requiring neither vapor-phase compositions nor dew-point pressures, both difficult to determine experimentally. In lieu of these data, the method relies heavily on the requirement that the physical properties of coexisting phases at equilibrium satisfy the general coexistence equation.

THEORY

Previous investigators (*6*, *12*) have not applied the general coexistence equation to high-pressure isothermal P-x data for the purpose of generating P-y information. Consequently, it was necessary to derive a form of the equation for this purpose. Also, to perform the numerical integration, it was necessary to have analytical correlations for the vapor pressure, the liquid specific volume, and the vapor compressibility factor. The computer programs used are given by Manley (*7*).

High-Pressure Isothermal General Coexistence Equation. The starting point for the derivation is taken from Van Ness (*14*). For a single-phase binary system

$$VdP/RT_a = z_1 d(\ln \hat{f}_1) + z_2(\ln \hat{f}_2) \tag{1}$$

at constant temperature. Since the vapor and liquid fugacities are equal at equilibrium, writing Equation 1 for both phases and subtracting gives

$$\Delta' V/(y - x) = d[\ln (\hat{f}_2/\hat{f}_1)]/dP \tag{2}$$

where

$$\Delta' V = (V^V - V^L)/RT_a \tag{3}$$

Expanding the right-hand side of Equation 2 gives

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