Purification, Purity, and Freezing Points of 16 API Standard and API Research Hydrocarbons

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THIS INVESTIGATION is a continuation of the work of producing highly purified hydrocarbons of the API Standard and API Research series (*3*). The purification and determination of purity and freezing points of 16 hydrocarbons, which include three cycloparaffins, four monoolefins, one cyclo-olefin, six alkyl benzenes, and two alkylidene-cycloparaffins are described.

The final lots of material labeled API Standard are sealed in vacuum in glass ampoules and made available as API Standard samples of hydrocarbons through the American Petroleum Institute Samples and Data Office at the Carnegie Institute of Technology. The material labeled API Research is made available in appropriate small lots through the American Petroleum Institute Research Project 44 for loan to qualified investigators for the measurement of needed physical, thermodynamic, and spectral properties.

Table I gives the names of the compounds, details concerning the first and succeeding distillations, and the character of the plot of the freezing point of the hydrocarbon part of the distillate as a function of its volume.

The procedures followed in the process of purification and determination of purity were the same as in previous articles (*3*). Details of the distillation apparatus and operations have been described (*2*). Beginning July 1, 1957, determination of the purity of the best lot of each hydrocarbon completed is being made calorimetrically with the apparatus recently described (*1*). The compounds reported in this article were completed before this new apparatus was placed in formal service.

Figures 1 to 3 show graphically the results of some typical distillations and represent the cases where the purest material is, respectively, largely in the forepart of the distillation, in the middle of the distillation, and in the afterpart of the distillation. In each figure, plots are given for refractive index, boiling point, freezing point, and purity as a function of the volume of the hydrocarbon part of the distillate. As emphasized in the previous reports, the

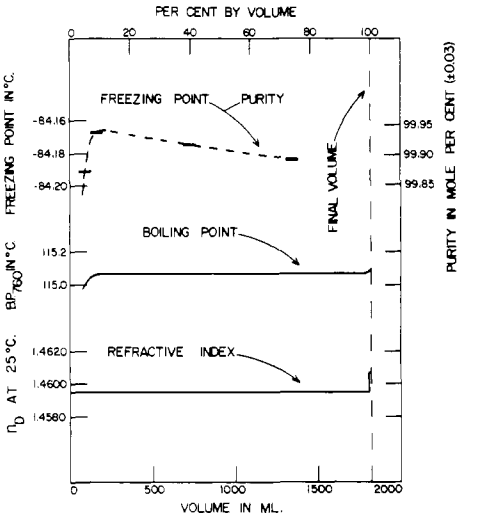

Figure 1. Results of azeotropic distillation of 1,2-dimethylcyclohexene with ethylene glycol monomethyl ether, methyl Cellosolve

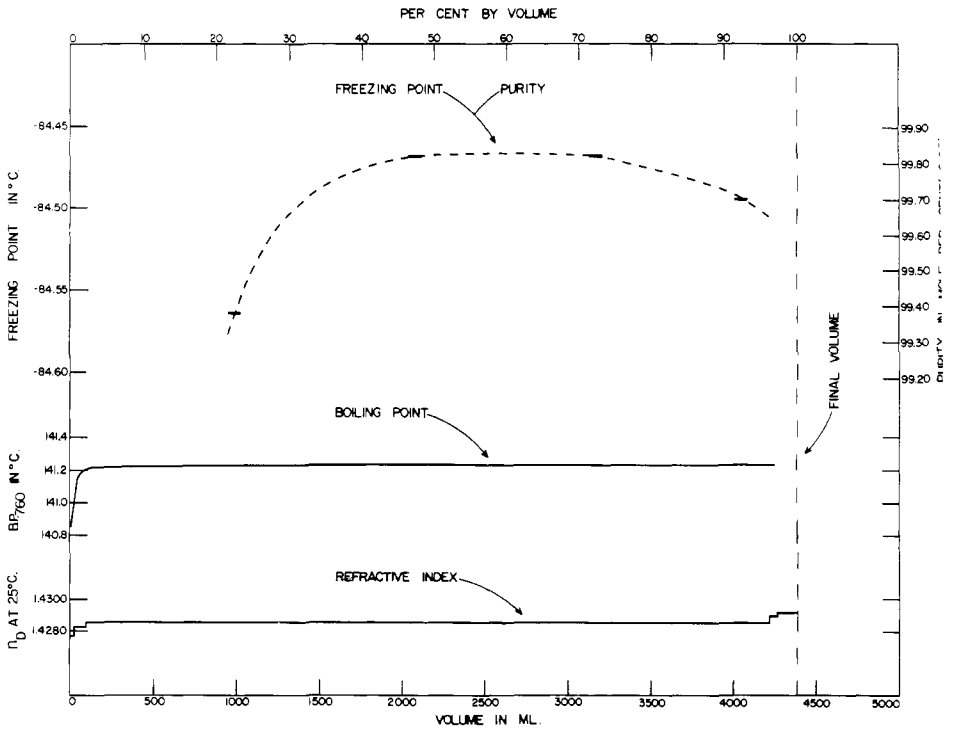

Figure 2. Results of regular distillation of 1,*cis*-3,*trans*-5-trimethylcyclohexane

Table I. Information on the Purification of 16 API Standard and API Research Hydrocarbons

Compound[a]	Hydrocarbon Charged for Distillation		Distillation[b]				
	Vol., l.	Purity, mole %	Kind[c]	Azeotrope-forming substance[d]	Rate of collection of distillate, ml./hr.	Time of distillation, hr.	Location[e]
1-Methyl-1-ethyl-cyclohexane	4.33	...	Reg.	...	4	1272	M
	1.76[f]	...	Azeo.	Cell	4	1296	M
	1.76[f]	...	Azeo.	Cell	4	1272	M
	2.16[h]	...	Azeo.	Cell	7	816	M
	1.82	...	Azeo.	Me Cell	5	1272	M
1,*cis*-3,*cis*-5-Trimethyl-cyclohexane	5.70	99.36 ± 0.10	Reg.	...	9	790	A
	3.00	99.91 ± 0.04	Azeo.	Me Cell	7	936	F
1,*cis*-3,*trans*-5-Trimethyl-cyclohexane	4.85	99.5 ± 0.1	Reg.	...	4	1584	A
	2.95	99.78 ± 0.08	Azeo.	Me Cell	4	1392	A
5-Methyl-*trans*-2-hexene	5.30	99.63 ± 0.10	Reg.	...	4	1320	M
	3.70	99.89 ± 0.07	Azeo.	Ethyl alcohol	9	672	M
2-Methyl-*trans*-3-hexene	3.98	99.66 ± 0.12	Reg.	...	4	960	A
	2.60	99.82 ± 0.12	Azeo.	Ethyl alcohol	7	648	M
3-Methyl-2-ethyl-1-butene	5.44	...	Reg.	...	4	1368	M
	2.89	...	Azeo.	Ethyl alcohol	7	1200	M
	1.90	...	Azeo.	Ethyl alcohol	7	504	M
2,5-Dimethyl-2-hexene	4.12	...	Reg.	...	9	552	M
	3.12	...	Azeo.	Me Cell	4	1076	M
	2.10	...	Azeo.	Me Cell	5	720	M
	1.70	...	Azeo.	Isopropyl alcohol	7	960	M
1,2-Dimethylcyclohexene	1.96[f]	99.85 ± 0.05	Azeo.	Me Cell	9	528	F
	1.96[f]	99.85 ± 0.05	Azeo.	Me Cell	9	528	F
1-Methyl-2-*n*-propylbenzene	4.14[f]	96.6 ± 0.2	Reg.	...	4	1416	A
	4.14[f]	96.6 ± 0.2	Reg.	...	4	1104	A
	3.03[h]	99.77 ± 0.08	Azeo.	Me Carb	9	672	M
1-Methyl-3-*n*-propylbenzene	2.94[f]	99.4 ± 0.1	Reg.	...	7	504	F
	2.94[f]	99.4 ± 0.1	Reg.	...	7	600	F
	3.60[h]	99.91 ± 0.05	Azeo.	Me Carb	9	744	F
1-Methyl-4-*n*-propylbenzene	3.82[f]	98.3 ± 0.2	Reg.	...	4	1128	A
	3.82[f]	98.3 ± 0.2	Reg.	...	4	1008	A
	2.51[i]	99.5 ± 0.1	Azeo.	Me Carb	7	812	A
	2.50[i]	99.5 ± 0.1	Azeo.	Me Carb	7	984	A
1,2-Dimethyl-4-ethylbenzene	3.85	99.5 ± 0.1	Reg.	...	4	1224	A
	2.81	99.75 ± 0.09	Azeo.	Me Carb	7	768	A
1,3-Dimethyl-4-ethylbenzene	3.68[f]	97.1 ± 0.2	Reg.	...	9	600	A
	3.68[f]	97.1 ± 0.2	Reg.	...	7	696	A
	2.93[h]	99.79 ± 0.09	Azeo.	Me Carb	4	1272	A
1,4-Di-*tert*-butylbenzene	4.13	...	Xtln.[g]	...	...	...	...
Ethylidenecyclopentane	1.94	98.4 ± 0.1	Azeo.	Me Cell	7	600	A
	1.30	...	Azeo.	Me Cell	7	480	M
Ethylidenecyclohexane	2.27[f]	...	Azeo.	Me Cell	7	1008	A
	2.27[f]	...	Azeo.	Me Cell	7	744	A
	1.60[k]	...	Azeo.	Me Cell	5	1080	A
	2.75[j]	99.4 ± 0.1	Azeo.	Me Cell	7	1080	A
	1.05[k]	99.4 ± 0.1	Azeo.	Me Cell	5	528	A
	1.05[k]	99.4 ± 0.1	Azeo.	Me Cell	5	528	A

[a] All starting materials were provided by the API Research Project 45 at the Ohio State University, Columbus, Ohio, except 1,4-di-*tert*-butylbenzene supplied by Esso Research and Engineering Co., Linden, N. J.
[b] All distillations were made in columns of 200 theoretical plates. See (2) for further details.
[c] Azeo, azeotropic; reg., regular.
[d] Cell for Cellosolve, ethylene glycol monoethyl ether; Me Cell, for methyl Cellosolve, ethylene glycol monomethyl ether; Me Carb, for methyl Carbitol, diethylene glycol monomethyl ether.
[e] General location of the purest material in the hydrocarbon part of the distillate as a function of its volume: F, fore or front of the distillate; M, middle part; A, afterpart.
[f] One of two similar distillations.
[g] Purified by fractional crystallization.
[h] Material having substantially the same composition from each of the preceding two distillations.
[i] One of two similar distillations of material having substantially the same composition from the first two distillations.
[j] Material having substantially the same composition from each of the preceding three distillations.
[k] One of two similar distillations of material having substabtially the same composition from the preceding distillation.

Table II. Freezing Points and Purity of 16 API Standard and API Research Hydrocarbons

Compound	Freezing Point in Air at 1 Atm., ° C. API Standard	Freezing Point in Air at 1 Atm., ° C. API Research	Freezing Point for Zero Impurity in Air at 1 Atm., ° C.	Cryoscopic Constant[a] A Mole Fraction/Deg.	Calcd. Amount of Impurity,[b] Mole % API Standard	Calcd. Amount of Impurity,[b] Mole % API Research
1-Methyl-1-ethylcyclohexane	...	...	...	...	(0.20 ± 0.15)[c]	(0.15 ± 0.10)[c]
1,*cis*-3,*trans*-5-Trimethylcyclohexane	−43.257	−43.250	−43.220 ± 0.020	0.0223	0.08 ± 0.04	0.07 ± 0.04
1,*cis*-3,*trans*-5-Trimethylcyclohexane	−84.463	−84.450	−84.430 ± 0.015	0.0463	0.15 ± 0.07	0.09 ± 0.07
trans-5-Methyl-2-hexene	−124.372	−124.370	−124.340 ± 0.020	0.0343	0.11 ± 0.07	0.10 ± 0.07
trans-2-Methyl-3-hexene	−141.590	−141.590	−141.560 ± 0.025	0.0368	0.11 ± 0.09	0.11 ± 0.09
3-Methyl-2-ethyl-1-butene	...	...	...	...	(0.20 ± 0.15)[c]	(0.15 ± 0.10)[c]
2,5-Dimethyl-2-hexene	...	...	...	...	(0.20 ± 0.15)[c]	(0.15 ± 0.10)[c]
1,2-Dimethylcyclohexene	−84.165	−84.159	−84.145 ± 0.010	0.0275	0.06 ± 0.03	0.04 ± 0.03
1-Methyl-2-*n*-propylbenzene	−60.325	−60.322	−60.305 ± 0.015	0.0392	0.08 ± 0.06	0.07 ± 0.06
1-Methyl-3-*n*-propylbenzene	−82.600	−82.598	−82.580 ± 0.015	0.0350	0.07 ± 0.05	0.06 ± 0.05
1-Methyl-4-*n*-propylbenzene	−63.730	−63.725	−63.695 ± 0.010	0.0315	0.11 ± 0.03	0.09 ± 0.03
1,2-Dimethyl-4-ethylbenzene	−66.964	−66.960	−66.930 ± 0.020	0.0341	0.12 ± 0.07	0.10 ± 0.07
1,3-Dimethyl-4-ethylbenzene	−62.920	−62.918	−62.880 ± 0.020	0.0352	0.14 ± 0.07	0.13 ± 0.07
1,4-Di-*tert*-butylbenzene	+ 77.577	+ 77.602	+ 77.610 ± 0.010	0.0214	0.07 ± 0.02	0.02 ± 0.02
Ethylidenecyclopentane	−126.594	−126.594	−126.575 ± 0.015	0.0334	0.06 ± 0.05	0.06 ± 0.05
Ethylidenecyclohexane	−92.478	−92.475	−92.440 ± 0.015	0.0378	0.14 ± 0.06	0.13 ± 0.06

[a] See (2) for experimental details and definition of cryoscopic constant.
[b] Values in this column, except as noted, were calculated using values of the cryoscopic constants and freezing points for zero impurity given in previous columns (2).
[c] Estimated by analogy with isomers subjected to similar purification.

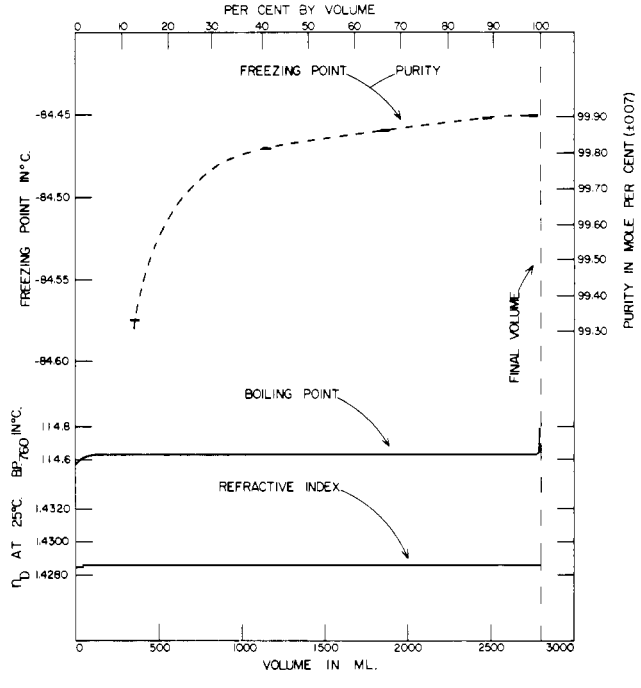

Figure 3. Results of azeotropic distillation of 1,*cis*-3,*trans*-5-trimethylcyclohexane with ethylene glycol monomethyl ether, methyl Cellosolve

blending of fractions of distillate for the preparation of material of the highest purity can be done safely only on the basis of the freezing points.

For all compounds listed in Table II, the freezing point, where given, was determined by observing time-temperature curves of the melting compound. Also given are the freezing point of the actual sample, the calculated value of the freezing point for zero impurity, the value of the cryoscopic constant determined from the lowering of the freezing point on the addition of a known amount of a suitable impurity (2), and the calculated amount of impurity in the API Standard and API Research materials.

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