pressures corresponding to equal mean free paths.

2. The activation of glass surfaces was studied under different conditions.

3. The adsorption of nitrogen on glass spheres at liquid air temperatures was studied. Different degrees of packing of the spheres was found to have no effect on the adsorption.

4. Similar to oxygen the adsorption isotherm of nitrogen at low pressures shows the unusual phenomenon of recession of the equilibrium pressure. A possible explanation for this behavior is suggested.

5. The application of various adsorption theories to the data is discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF BRITISH COLUMBIA]

The Mutual Solubilities of Hydrocarbons. I. The Freezing Point Curves of Dotriacontane (Dicetyl) in Propane and Butane

BY W. F. SEYER AND REID FORDYCE

A considerable amount of information exists concerning the mutual solubilities of hydrocarbons. Thus over thirty years ago Holde was familiar with the fact that light hydrocarbons when added to petroleum caused the asphalt portion to be precipitated. This idea was further extended by Kling[1] in 1922 and by S. V. Pilatt and M. Godlevicz[2] in 1932. This work established the fact that mutual solubility among hydrocarbons was governed largely by the molecular weights of solute and solvent. Already extensive use has been made of this knowledge to isolate and purify certain petroleum fractions by utilizing solvents of various selective powers. So far all the information which has been forthcoming has been of a qualitative nature; consequently before much more headway can be made along this line, quantitative measurements concerning the solubility relationships existing among simple systems of hydrocarbons must be made. The following pages deal with the results obtained from a study of the systems, dotriacontane (dicetyl, $C_{32}H_{66}$) and propane and dotriacontane and butane.

Materials.—The propane and butane were purchased from The Ohio Chemical & Manufacturing Company, Cleveland. These gases were listed C. P. and the butane was claimed to be free of propane but to contain a trace of isobutane, while an analysis of the propane failed to reveal any traces of either of the two isomeric butanes. The hydrocarbon, dicetyl, was synthesized from Eastman C. P. cetyl alcohol by the method first used by Kraft.[3] The hydrocarbon was recrystallized five times from ether until no change in melting point could be detected. The final melting point was 69.9° as measured by a standardized mercury thermometer. This agrees with the findings of Hildebrand and Wachter who have pointed out that the true melting point of the hydrocarbon must be in the neighborhood of 70°.[4]

Experimental Procedure

The time honored bulb method was considered the most practical one for the determination of the freezing points. In the present case this method was susceptible of considerable accuracy because of the "cloud effect"; *i. e.*, whenever a solution of dicetyl in either propane or butane was cooled beyond the limits of solubility a white suspension immediately developed. The phenomenon is apparently due to the formation of tiny crystals of the high molecular weight hydrocarbon. The point of appearance and disappearance of these crystals was extremely sharp and did not vary more than ±0.02° in any case. The difference between the two temperatures was never greater than 0.05°.

Thick-walled uniform bulbs, 2 cm. in diameter, were blown and to these were attached glass stems 9 cm. long and 2 mm. in diameter. Varying amounts of dotriacontane were introduced by first melting the hydrocarbon and then allowing it to run down a long stemmed funnel into the bulb proper. The bulbs, after weighing, were then sealed onto the apparatus outlined in Fig. 1, evacuated and the required amounts of butane or propane condensed in each. These gases were stored in two 5-liter flasks which served as gas holders and which were placed in an insulated box whose temperature could be controlled. Before allowing either of these two gases to diffuse into the systems, it was evacuated by means of a mercury vapor pump down to a pressure of the order of 0.001 mm. as measured by a McLeod gage. Knowing the volume of the apparatus and noting the pressure changes on the manometer, it was a simple matter to calculate the amounts of gases condensed in the bulbs before they were sealed and detached from the apparatus. The amounts of the hydrocarbons in each bulb were again measured by weighing the sealed bulb after the freezing point had been obtained, then breaking off the tip, allowing the gas to escape and then weighing again.

Besides the buoyancy correction one other one was con-

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[1] Kling, German Patent 362,458.

[2] S. V. Pilatt and M. Godlevicz, *Oel und Kohle*, **11**, 655 (1935).

[3] Kraft, *Ber.*, **40**, 4783 (1907).

[4] Hildebrand and Wachter, THIS JOURNAL, **51**, 2487 (1929).

sidered necessary. This was the amount of solvent present in the vapor phase. This amount of propane or butane is of course not effective in dissolving the dicetyl. Since this correction was small in any case, no great error was made in assuming the perfect gas law in the calculations. The values of the vapor pressures of butane at the various temperatures were calculated from the equation $\log_{10}p = 7.3948 - 1224.8/T$ given in the "International Critical Tables." The best values obtainable for the propane pressures over the temperature range of the investigation were those of A. W. Francis and G. W. Robbins[5] whose equation $\log_{10}p = 4.375 - 1010/T$ was used. The volume of vapor was found approximately by measuring the amount of water required to fill the vapor space in each bulb. Throughout the range of temperature covered by the investigation, the partial pressure of the dicetyl was so small it could be neglected and the total pressure was therefore sensibly equal to the vapor pressures of the low molecular weight hydrocarbons.

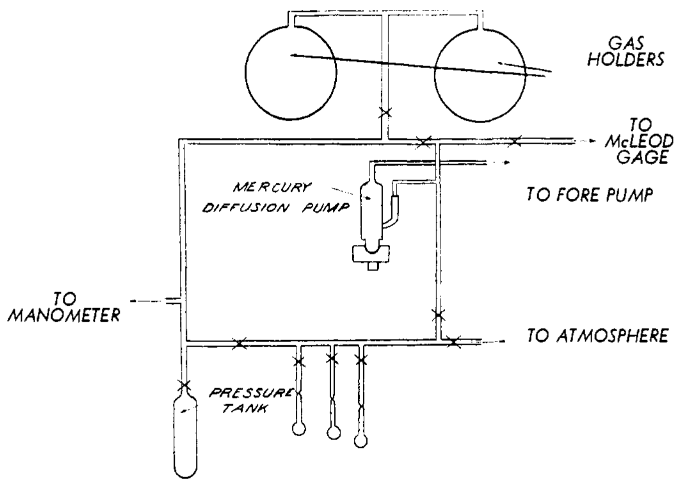

Fig. 1.—Condensing apparatus.

TABLE I

BUTANE–DOTRIACONTANE

Dotria-contane, g.	Butane, g.	Effective wt. of butane, g.	Mol. % dotria-contane	F. p., °C.
			0	−135.0[a]
0.0922	5.7882	5.7869	0.206	17.26
.0959	4.2977	4.2962	.288	20.02
.1241	4.9919	4.9902	.321	20.48
.0398	1.0640	1.0623	.482	24.09
.0447	0.6886	0.6866	.832	27.49
.1267	1.2102	1.2080	1.335	30.47
.1659	0.8931	0.8905	2.347	34.34
.2225	.8385	.8332	3.33	36.60
.3809	1.1587	1.1557	4.08	38.00
.3934	.8103	.8069	5.92	40.40
.3374	.6165	.6133	6.63	41.98
.4097	.6827	.6789	7.23	42.13
.4958	.7013	.6983	8.41	43.40
.4695	.4666	.4630	11.55	46.51
.6421	.3147	.3100	21.10	53.06
.6896	.3092	.3052	22.55	53.15
.7422	.2764	.2714	26.10	54.56
.7630	.1384	.1328	42.55	60.91
.4764	.0179	.0116	81.00	67.80
			100	69.90

[a] From "International Critical Tables."

The weights of dicetyl, of butane or propane, the effective weight, the molal concentration and the freezing points of these concentrations are given in Tables I and II.

In Fig. 1 the freezing point temperatures have been plotted against concentrations in mole per cent. It will be seen that in the neighborhood of 55° there is a slight change in curvature. From this point downward solubility changes rapidly with temperature. It would thus appear that there were two forms of the hydrocarbon and that at the above-mentioned temperature transition from one form into another takes place. Further evidence for the existence of two forms has been found by measuring the refractive index of the solid dicetyl at various temperatures below its melting point with the help of an Abbé refractometer. These figures are given in Table III.

TABLE II

PROPANE–DOTRIACONTANE

Dotria-contane, g.	Propane, g.	Effective wt. of propane, g.	Mol. % dotria-contane	F. p., °C.
			0	−189.9[a]
4.7368	4.6634	4.6581	0.16	22.30
0.1195	1.3401	1.3331	.87	34.03
.1195	1.0244	1.0181	1.136	35.70
.3107	1.1443	1.1361	2.61	39.31
.3107	0.6771	0.6688	4.36	42.13
.3661	.5434	.5374	6.27	44.13
.4769	.6398	.6309	6.92	44.30
.3661	.4381	.4289	7.72	45.80
.4769	.4628	.4543	9.28	46.81
.5617	.4180	.3831	12.54	49.72
.8449	.4895	.4895	14.46	50.53
.6388	.3309	.3207	16.45	52.63
.6583	.3222	.3113	17.15	52.90
.8449	.2393	.2272	26.70	57.90
.8527	.1663	.1545	35.0	59.88
.8787	.1135	.1015	45.80	62.42
1.2204	.1164	.1038	53.5	63.71
1.2716	.0952	.0824	60.3	64.54
			100	69.9

[a] From "International Critical Tables."

Below 55° it was extremely difficult to get accurate readings on the instruments although the temperatures were kept constant to within one-half of a degree for some hours. When, however,

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[5] Francis and Robbins, This Journal, **55**, 4339 (1933).

TABLE III

Refractive index	Temp., °C.
1.4364 (liquid)	70
1.4738	65
1.5010	60
1.5464	57.5
1.5573	55
1.5597	50
1.5605	45
1.5632	40
1.5676	30

the figures are plotted against temperature as in Fig. 2, it is quite evident that two forms of the hydrocarbon exist and that the transition point is in the vicinity of 55°. This of course is what one should expect from the observations of Carpenter,[6] Rhodes[7] and others.

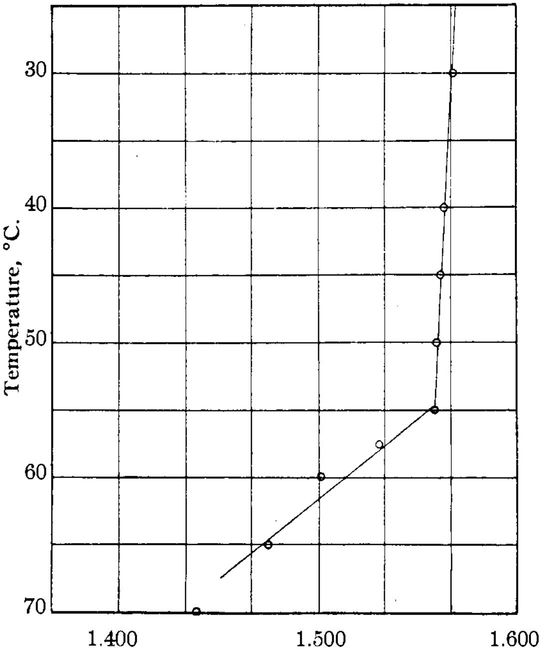

Fig. 2.

The solubility curves of the dotriacontane in propane and butane coincide until a concentration of about 50% is reached; from here on they diverge until a very low concentration is reached at temperatures below 30°. It is obvious from the shape of the curves that the solubility of the high molecular weight hydrocarbon falls off to extremely low values at low temperatures.

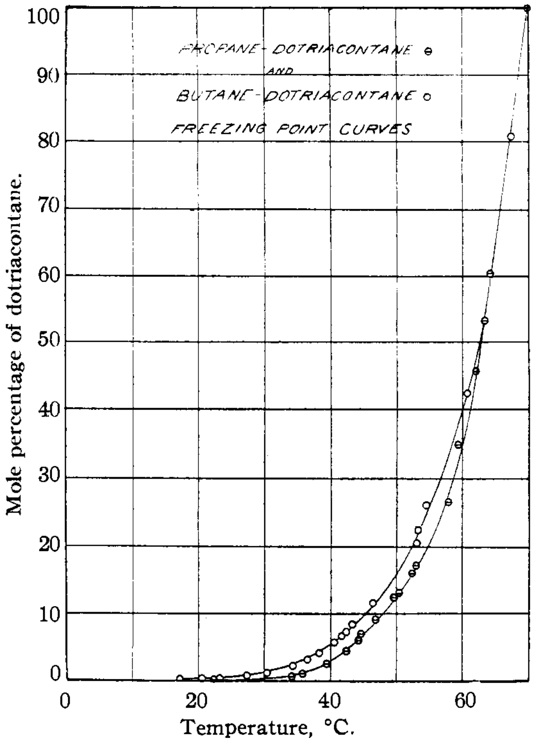

Fig. 3.—Freezing point curves: ⊖, propane–dotriacontane; ○, butane–dotriacontane.

Summary

1. The freezing points of solutions of dotriacontane (dicetyl) in propane and in butane have been found.

2. The curves constructed from the freezing point data indicate the occurrence of two forms of the high molecular weight hydrocarbon. Change of refractive index with temperature shows this to be the case and that the transition temperature is about 55°.

VANCOUVER, CANADA RECEIVED JUNE 18, 1936

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[6] J. A. Carpenter, *J. Inst. Petroleum Tech.*, **12**, 288 (1926).

[7] F. H. Rhodes, C. W. Mason and W. R. Sutton, *Ind. Eng. Chem.*, **19**, 935 (1927).