order to correlate these properties whose relation to molecular structure is known with the properties studied in this investigation. In this way it is hoped to arrive at a better correlation between the physical properties and the molecular structure.

Summary

An improved apparatus for the determination of viscosity of liquids has been described.

The viscosity, surface tension, vapor pressure and density of hexanols-1, -2 and -3, and 2-methylpentanol-1 and -4 have been determined at temperatures from 5° to their boiling points.

The boiling points, heats of vaporization and Rankine equation constants have been calculated from the vapor pressure measurements. They have been found to follow the Rankine equation closely.

The viscosity results have been discussed from the standpoint of the kinetic theory of viscosity. No quantitative results were obtained, but it has been found possible to give a qualitative explanation of the results in terms of different types of association.

The parachor, Eötvös constant, and critical temperature of each alcohol were calculated from the surface tension data. It has been found that no general conclusions could be drawn from the surface tension measurements.

Plans for further study have been outlined briefly.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF BRITISH COLUMBIA]

Mutual Solubilities of Hydrocarbons. II. The Freezing Point Curves of Dotriacontane (Dicetyl) in Dodecane, Decane, Octane, Hexane, Cyclohexane and Benzene

BY W. F. SEYER

It has been mentioned in a previous communication[1] that a quantitative study of the solubility relationships among simple hydrocarbon systems was highly desirable both from the theoretical and technical points of view. In this second paper on the subject there are given the freezing point data of six separate systems of dicetyl with some low molecular weight hydrocarbon. The hydrocarbons used were as follows: dodecane, decane, octane, hexane, cyclohexane and benzene. The purpose of investigating the last two was to find out whether ring structure would affect seriously the solubility of the dicetyl compared with that, say, of hexane.

Materials.—The dodecane, decane and hexane were obtained from the Eastman Kodak Co., and no other purification outside of drying over sodium was attempted. The dicetyl was prepared in the same manner as described previously except that the hydrocarbon was first recrystallized out of acetic acid and then out of ether.

It was found that in nearly all cases, if the dicetyl was first dissolved in glacial acetic acid, the acid became colored. This color could be removed readily by filtration through bone black. It would thus appear that in the treatment of the cetyl alcohol with hydrogen iodide as recommended by Kraft[2] some side reactions take place and that the products formed reacted with the glacial acetic acid, for it was found possible to raise the melting point of several samples of dicetyl which had been recrystallized only from ether by almost 0.2° by recrystallizing out of glacial acetic acid and then out of ether. For the preparation of the hydrocarbon two lots of cetyl alcohol from Eastman Kodak Co. were used. While in each case constant melting points were obtained, yet they differed by about 0.15° even after five recrystallizations from acetic acid and four from ethyl ether. The melting points were 70.0–70.1° for the first, and 70.1 to 70.2° for the second lot, both differing from that given by S. H. Piper and others[3] by about 0.6°. They give the transition point as 65.2–65.4° and state that it is a better criterion for indicating the purity of a paraffin than the melting points. Assuming this to be correct, it would indicate that our material was not pure but contained, calculated on the basis of their figures, about 5% of the next higher homolog.

In view of these findings, and that the long chain hydrocarbons separate out together to form mixed crystals, it becomes a question whether it is possible to prepare the pure hydrocarbon at all from cetyl alcohol, as it is probable that the lower member of the alcohol series will be present as well as the next higher.

The octane was prepared by the reaction as described by Lewis, Hendricks and Yohe.[4] The material had a refractive index $n^{20}\text{D}$ 1.3973, whereas the "International Critical Tables" give 1.3975. The cyclohexane was part

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[1] Seyer, THIS JOURNAL, **58**, 2029 (1936).

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

[3] Piper, Chibnall, Hopkins, Pollard, Smith and Williams, *Biochem. J.*, **25**, 2072 (1931).

[4] Lewis, Hendrick and Yohe, THIS JOURNAL, **50**, 1993 (1928).

of a lot which had been rectified in a special column and had a freezing point of 6.4°. The benzene was the ordinary C. P. variety and, after being subjected to three recrystallizations and dried, had a freezing point of 5.5°.

Experimental Procedure.—The bulb method as previously described was utilized for all the systems.[1] There was, however, a difference in the procedure of loading the bulbs, inasmuch as all the materials used, excepting the dicetyl, were liquids at room temperature, these could therefore be introduced by merely running them in through a long stemmed funnel. The contents of the bulbs were then frozen with "dry-ice" and sealed to a vacuum line. By alternately evacuating and filling with hydrogen several times it was thought all air in the bulb would be removed. After a final evacuation the bulbs were sealed so that upon melting the hydrocarbons would be under their own vapor pressure. As mentioned before, the freezing points with propane and butane were very sharp and the difference between them and the melting points did not exceed 0.1°. Unfortunately, this difference began to increase as the molecular weights of the solutes increased. Thus with the dodecane the difference amounted to 0.25°. A haze also seemed to persist for some time in the bulbs even after the last crystal had disappeared and even after the temperature was several degrees above the melting of the dicetyl.

The mole concentrations, the effective mole concentrations wherever corrections were necessary, and the freezing points are given in the six tables.[5]

TABLE I

DODECANE–DICETYL

Dicetyl, g.	Dodecane, g.	Mole % dicetyl	F. p., °C.
....	....	0.00	−12.0
0.0241	2.3064	.39	23.3
.0252	1.1740	.81	28.1
.1012	1.8471	2.04	34.9
.1014	1.2854	2.90	36.8
.1402	1.1959	4.24	40.2
.1581	0.9009	6.22	42.8
.2418	.9409	8.83	45.6
.2466	.5458	14.60	49.9
.2526	.4579	17.20	51.3
.3029	.4644	19.80	52.7
.3236	.3989	23.96	54.3
.3527	.3446	27.90	55.7
.4439	.3895	30.15	56.6
.4733	.2887	38.25	58.7
.4731	.2072	46.30	60.7
.4837	.1794	51.00	61.5
.5081	.1364	58.40	62.9
.7157	.1326	67.20	64.7
.9449	.1279	73.60	65.8
1.0400	.0814	82.80	67.6
....	....	100.00	70.1

TABLE II

DECANE–DICETYL

Dicetyl, g.	Decane, g.	Mole % dicetyl	F. p., °C.
....	....	0.00	−32.0[a]
0.0283	1.4509	.61	26.4
.0450	0.8474	1.65	32.7
.0672	.4455	4.54	40.0
.0876	.5049	5.18	40.9
.0725	.2788	7.59	43.9
.1221	.2661	12.63	48.4
.3652	.5644	16.96	50.9
.3219	.3107	24.61	54.9
.5499	.4345	28.55	55.9
.6333	.2545	43.99	59.0
.9349	.2286	56.34	62.4
.9883	.1560	66.67	64.4
1.1156	.0590	85.66	67.4
....	....	100.00	70.1

[a] "International Critical Tables," Vol. I, p. 224.

TABLE III

OCTANE–DICETYL

Dicetyl, g.	Octane, g.	Mole % dicetyl	F. p., °C.
....	....	0.00	−56.5[1]
0.0252	2.4801	.26	18.8
.0241	1.1787	.52	23.3
.1014	3.2020	.80	26.3
.1012	2.3802	1.07	28.3
.3527	4.6436	1.89	32.5
.1581	1.6561	2.43	34.5
.2466	1.8642	3.24	36.6
.2418	1.3850	4.24	38.6
.2526	0.9885	6.07	41.5
.2461	.7236	7.93	43.9
.3848	1.0041	8.95	44.5
.3029	0.6903	10.00	45.7
.4837	.8617	12.70	47.6
.5081	.7236	15.10	49.4
.6107	.7508	17.95	51.0
.4439	.3834	22.70	53.3
1.0400	.6216	30.10	56.1
0.4733	.2185	38.40	58.1
.9449	.3278	42.20	59.5
.4731	.1320	49.80	61.2
.7157	.0858	68.00	65.2
....	....	100.00	70.1

TABLE IV

HEXANE–DICETYL

Dicetyl, g.	Hexane, g.	Effective wt. of hexane	Mole % dicetyl	F. p., °C.
....	....	....	0.00	..
0.0403	2.0098	2.0049	.37	26.2
.2277	3.0228	3.0184	1.42	31.8
.2277	3.0125	3.0082	1.42	31.8
.1258	0.9129	0.9070	2.58	35.2
.5961	2.6894	2.6845	4.07	37.8
.2615	0.7764	0.7719	6.08	40.9
.5961	1.4409	1.4349	7.35	42.4
.3063	0.5591	0.5531	9.57	44.5
.6727	.6565	.6523	16.46	49.4
1.1882	.5659	.5584	28.91	55.7
0.4260	.0998	.0946	46.25	60.5
.5390	.1215	.1098	48.40	61.2
.6064	.0636	.0607	65.62	64.1
.7412	.0517	.0401	77.93	66.5
.8245	.0279	.0184	89.54	68.3

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(5) The author was assisted in this work, by the following students: A. M. Ames, Herman Nemetz and L. R. Gould.

TABLE V

CYCLOHEXANE–DICETYL

Dicetyl, g.	Cyclohexane, g.	Effective wt. of cyclohexane	Mole % dicetyl	F. p., °C.
....	....	....	0.00	..
0.0403	1.5147	1.5118	.49	19.2
.1258	2.3602	2.3588	.98	22.2
.1625	1.4179	1.4151	2.09	28.0
.1625	1.1968	1.1899	2.48	29.1
.2293	1.1098	1.1078	3.71	33.2
.2615	0.7526	0.7501	6.10	37.0
.5961	1.4259	1.4225	7.25	38.4
.3063	0.5421	0.5386	9.59	41.1
.1258	.1770	.1720	12.01	43.2
.6727	.6598	.6571	16.04	47.0
1.1882	.6153	.6091	26.69	53.1
0.4260	.1204	.1170	40.46	58.3
.5390	.1036	.0961	51.14	60.5
.6064	.0666	.0645	63.70	62.8
.8245	.0140	.0070	95.64	69.7
....	....	....	100.00	70.2

TABLE VI

BENZENE–DICETYL

Dicetyl, g.	Benzene, g.	Effective wt. of benzene	Mole % dicetyl	F. p., °C.
....	....	....	0.00	5.5
0.0403	1.5544	1.5502	0.44	26.8
.2277	2.7539	2.7510	1.41	33.2
.2401	1.6946	1.6906	2.40	36.0
.2293	1.1672	1.1648	3.29	37.7
.1258	0.4872	0.4830	4.31	39.3
.2615	.7789	.7759	5.51	40.8
.5961	1.7040	1.7001	5.72	41.1
.1625	0.3677	0.3617	7.52	42.4
.3063	.5553	.5514	8.77	44.0
.6727	.6624	.6596	15.01	48.3
1.1882	.6592	.6526	24.53	52.9
1.3111	.4269	.4235	34.91	56.9
0.5390	.0673	.0587	63.77	62.6
.6064	.0412	.0388	73.02	65.6
.8245	.0138	.0064	91.18	68.6
.7412	.0122	.0036	97.27	69.3
....	....	....	100.00	70.3

Discussion of Results

By plotting mole concentrations against temperature for each system a series of curves is obtained as shown in Fig. 1. To emphasize the change in curvature as one proceeds from the dicetyl–hexane system to the dicetyl–dodecane system, the curves have been placed in pairs. Similarly, the dicetyl–6-carbon atom systems also have been grouped together. Inspection of the paraffin series reveals the tendency for all the curves to coincide, from the melting point of dicetyl on, until the concentration of this substance falls to about 40 mole per cent. Whether the freezing point curves of the dicetyl–6-carbon atom systems coincide between the melting point and transition point of the dicetyl cannot be decided from the present figure. It is hoped that by using purer dicetyl than at present available this question will be decided in the near future.

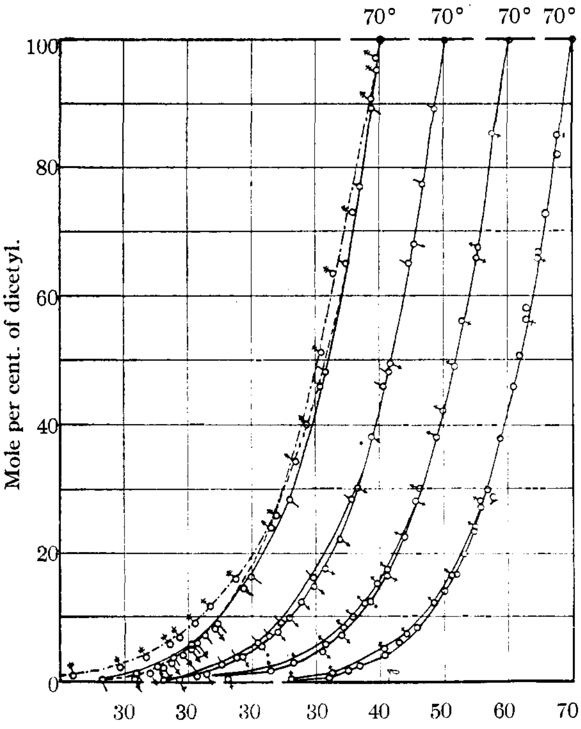

Fig. 1.—⊙, Dodecane-dicetyl; ȯ, decane-dicetyl; ô, octane-dicetyl; ó, hexane-dicetyl; $\overset{+}{\circ}$, cyclohexane-dicetyl; $\overset{\uparrow}{\circ}$, benzene-dicetyl.

The curves as shown in Fig. 1 represent only part of the freezing point systems. It is apparent that at the temperatures of the freezing point of the low molecular weight hydrocarbons the solubility of dicetyl would be extremely small and the eutectic point, if such a point exists for this type system, would lie very close to the freezing point of the solvent. Preliminary work has shown that for the system dodecane–tetradecane there is a strong tendency to form a eutectic. Piper[3] and his co-workers, on the contrary, have found in their work that for binary mixture of high molecular weight paraffins there is no eutectic point and that the melting points of such mixtures are linear functions of the compositions. Upon cooling the melt, mixed crystals are formed.

This fact suggests an explanation as to why the freezing point curves of dicetyl tend to persist more and more as straight lines as the molecular weight of the solute increases. Thus let us suppose that in Fig. 1 the freezing point curve of tet-

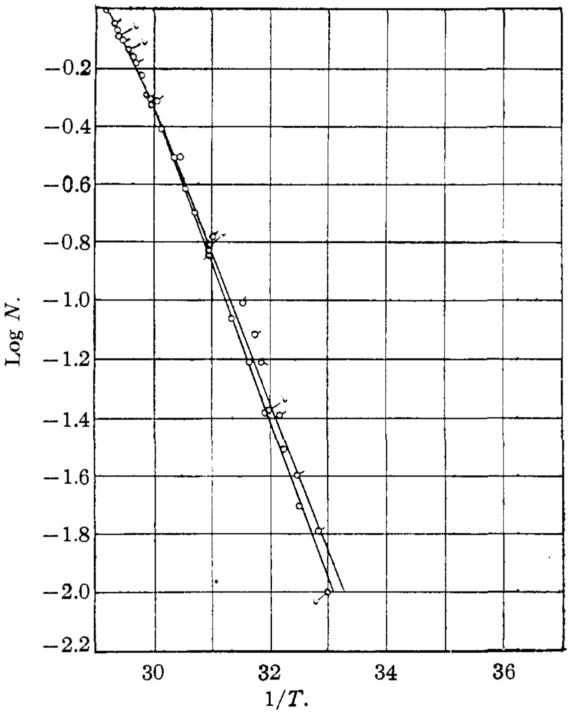

Fig. 2.—○, Dodecane; ○-, hexane; ○-, *i*-ideol.

radecane were to be superimposed upon that of dodecane. It is apparent that somewhere about the point (a) the curve would begin to deviate upward to a greater extent than dodecane. Finally, if the molecular weight of the solute became great enough, say equal to that of tetracosane, which has a m. p. of 51.9°, the freezing point curve would continue on a straight line from point (a) to (b), and that part of the curve tending to become asymptotic to the temperature axis would have disappeared completely.

The theoretical aspect of the solubility of long-chain hydrocarbons has been investigated recently by Hildebrand.[6] The curves in Fig. 2 would appear to support his arguments. Here ln N has been plotted against $1/T$ for the hexane and dodecane systems only. The other systems have been omitted in order to avoid a too great density of points. The points marked with an "i" have been calculated by means of the equation

$$\ln N = -\lambda_m \left\{ \frac{1}{T_m} - \frac{1}{T} \right\}$$

where the letters have the usual significance. The latent heat of fusion, λ_m, of the V form, stable between the m. p. of dicetyl, 70.1°, and its transition point, 63°, was calculated from the data of Garner and his co-workers to be equal to 17.6 kcal.[7] From the transition temperature downward the latent heat of the T form was taken to be 28.2 kcal. Practically all the points from the remaining paraffin systems fall between those of the hexane and dodecane lines.

Summary

1. The freezing point curves of four paraffin hydrocarbons with dicetyl have been studied, hexane, octane, decane and dodecane, also those of dicetyl–benzene and dicetyl–cyclohexane.

2. After a concentration of about 0.4 N is reached the solute appears to exert its influence in determining the shape of the freezing point curve and it is suggested this may be due to the separation of mixed crystals from the solution.

3. The experimental evidence supports the validity of Raoult's law.

VANCOUVER, CANADA RECEIVED JANUARY 18, 1938

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[6] Hildebrand, THIS JOURNAL, **59**, 794 (1937).

[7] Garner, van Bibber and King, *J. Chem. Soc.*, **111**, 1533 (1931).