[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Solubilities and Volume Changes Attending Mixing for the System: Perfluoro-*n*-hexane–*n*-Hexane

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The mutual solubility curve for the system: perfluoro-*n*-hexane–*n*-hexane and the volume changes attending mixing at 25, 35, 45 and 55° were determined. The critical solution temperature is 22.65° at 0.370 mole fraction perfluoro-*n*-hexane. Strong opalescence persists 4 to 5° above the consolute temperatures near the critical region. The temperatures at which phase separation occurred were confirmed by studying the thermal coefficient of expansion in this region. The volume changes are somewhat larger than expected and increase from 2.9% at 25° to 3.7% at 55°.

Introduction

Previous studies[1-9] of solutions of fluorocarbons and aliphatic hydrocarbons have shown that their mutual solubilities are lower than those predicted from the solubility parameters of these substances.[10] Large volume changes (2.5–4.5%) accompanying mixing have been reported to be symmetric about the mole fraction and to increase with increasing temperature.[2-5] The present investigation was undertaken to obtain a more detailed knowledge of the shapes of the volume of mixing curves.

When studying solutions of fluorocarbons and hydrocarbons, some workers[7] have reported the temperature at which opalescence was first noticed as the consolute temperature. For this system, and others[11] studied in our laboratory, phase separation occurs 4–5° below the temperatures at which opalescence is first observed. The temperatures at which phase separation was observed were verified by a study of the thermal coefficient of expansion as a function of temperature for two of the mixtures near the critical composition. Jura, Fraga, Maki and Hildebrand[12] carried out such a study for the system perfluoro-*n*-heptane–isooctane, and found a discontinuity in this property at the transition point between one and two phases.

Experimental

Materials.—Perfluoro-*n*-hexane was a portion of sample A previously described.[13] *n*-Hexane, Phillips Petroleum Company Pure Grade (99 mole %) was fractionated in a 90-plate column and a middle cut from the distillation plateau having a refractive index n^{20}D 1.3753 and a density at 25° of 0.65502 g./cm.^{3} (air saturated, 1 atm.) was used. The corresponding values reported by the National Bureau of Standards[14] are 1.37486 and 0.65482. The densities of degassed *n*-hexane were determined at 15, 25, 35 and 45° by the method previously described[13] for perfluoro-*n*-hexane, and are represented in this temperature interval by the equation $d = 0.67757 - 8.944 \times 10^{-4}t - 3.840 \times 10^{-7}t^2$, which was obtained from the data by the method of least squares.

Densities.—The densities of degassed liquid mixtures at their equilibrium vapor pressure were determined in sealed dilatometers at 25.05, 34.93, 44.91 and 55.00°. This procedure was selected in order to minimize the uncertainty in composition due to loses by evaporation, and to avoid the necessity for estimating the effect of dissolved air on the densities of mixtures. The procedure was especially desirable since the solubilities and partial molal volumes of gases are considerably larger in fluorocarbons[15-18] than in hydrocarbons. The dilatometers and temperature measurements have been described previously.[13]

Mixtures were prepared by transferring appropriate quantities of each of the degassed liquids from weighing tubes to a five liter mixing bulb in which the liquids evaporated completely at room temperature. Mixing was facilitated by a vapor pump. Approximately 95% of the mixture was then condensed into the dilatometer at Dry Ice temperature and the remainder was condensed into a small tube. The temperatures at which phase separation occurred were determined for both samples as a check on the homogeneity of the sample.

Densities were calculated from the observed weights, corrected for the displacement of air by the sample and weights, and for the weight of the material in the vapor assuming that equilibrium was attained. Liquid–vapor equilibria data were used for the latter correction.[19] Volumes were corrected for the amount of material in the meniscus. Volume changes were calculated from the density data interpolated to even degrees.

For two of the samples, *viz.*, 0.3251 and 0.4135 mole fraction perfluoro-*n*-hexane, the densities were determined at approximately 1° intervals as the samples were slowly cooled from 30° to 4° below their consolute temperatures.

Solubility.—The temperature at which phase separation occurred was determined for each of the samples prepared for density measurements. Although very pronounced opalescence was observed near the critical region, by the use of a microscope it was easy to observe the tiny droplets which either sank or rose to the surface when the new phase appeared. Transition temperatures were reproducible to 0.02°.

Results

The densities of the mixtures and corresponding volume changes are shown in Tables I and II. The shapes of the curves were studied by fitting power series equations of the form

$$\Delta V = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 \ldots] \quad (1)$$

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(1) J. H. Hildebrand, B. B. Fischer and H. A. Benesi, THIS JOURNAL, **72**, 4348 (1950).

(2) J. H. Simons and R. D. Dunlap, *J. Chem. Phys.*, **18**, 335 (1950).

(3) J. H. Simons and J. W. Mausteller, *ibid.*, **20**, 1516 (1952).

(4) R. D. Dunlap, R. V. Digman and J. Vreeland, Abstracts, 124th Meeting of the American Chemical Society, Chicago, Ill., Sept. (1952).

(5) R. D. Dunlap and D. M. Smyth, Abstracts, 124th Meeting of the American Chemical Society, Chicago, Ill., Sept. (1952).

(6) R. L. Scott and N. Thorp, *J. Phys. Chem.*, **60**, 670 (1956).

(7) G. J. Rotariu, R. J. Hanrahan and R. E. Fruin, THIS JOURNAL, **76**, 3752 (1954).

(8) J. B. Hickman, *ibid.*, **72**, 6154 (1955).

(9) D. N. Campbell and J. B. Hickman, *ibid.*, **75**, 2879 (1953).

(10) J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," 3rd Edition, Reinhold Publ. Corp., New York, N. Y., 1950.

(11) J. Vreeland and R. D. Dunlap, *J. Phys. Chem.*, **61**, 329 (1957).

(12) G. Jura, D. Fraga, G. Maki and J. H. Hildebrand, *Proc. Nat. Acad. Sci.*, **39**, 19 (1953).

(13) R. D. Dunlap, C. J. Murphy, Jr., and R. G. Bedford, THIS JOURNAL, **80**, 83 (1958).

(14) F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," National Bureau of Standards, United States Department of Commerce, Circular 461, U. S. Govt. Printing Office, Washington, D. C., 1947.

(15) J. Chr. Gjaldbaek and J. H. Hildebrand, THIS JOURNAL, **71**, 3147 (1949).

(16) J. Chr. Gjaldbaek and J. H. Hildebrand, *ibid.*, **72**, 1077 (1950).

(17) J. H. Hildebrand, *J. Phys. Chem.*, **58**, 671 (1954).

(18) F. W. Reeves and J. H. Hildebrand, THIS JOURNAL, **79**, 1313 (1957).

(19) R. D. Dunlap, R. G. Bedford, J. C. Woodbrey and S. D. Furrow, "Liquid-Vapor Equilibria for the System Perfluoro-*n*-hexane–*n*-Hexane" (to be published).

TABLE I

THE DENSITIES AND VOLUME CHANGES ATTENDING MIXING AT 25°

Mole fraction n-C_7F_{14}	Density, g./cm.^{3}	ΔV, cm.^{3}/mole exptl.	ΔV exptl. − ΔV calcd. 1-Constant eq.	2-Constant eq.	3-Constant eq.	4-Constant eq.
0.0000	0.65496					
.0846	.7711	1.83	0.27	0.30	0.02	0.06
.1373	.8396	2.56	.17	.21	− .09	− .06
.1777	.8888	3.19	.24	.28	.03	.03
.3251	1.0578	4.34	− .09	− .06	− .02	− .07
.4135	1.1495	4.80	− .10	− .08	.10	.06
.4854	1.2208	4.88	− .16	− .17	.05	.05
.5427	1.2757	4.83	− .18	− .20	.02	.01
.5795	1.3102	4.69	− .23	− .26	− .12	− .08
.8069	1.5064	3.58	.43	.39	.02	.03
.8995	1.5843	2.29	.46	.43	.03	− .01
1.0000	1.6717					
$\sigma = \pm\sqrt{\frac{\Sigma d^2}{n-1}}$			$\sigma = \pm 0.28$	$\sigma = \pm 0.28$	$\sigma = \pm 0.06$	$\sigma = \pm 0.05$

Constants for the equation $\Delta V = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + A_3(x_1 - x_2)^3 \ldots]$

	A_0	A_1	A_2	A_3
1-Constant eq.	20.19			
2-Constant eq.	20.22	0.470		
3-Constant eq.	19.37	1.18	7.28	
4-Constant eq.	19.35	0.161	7.38	2.51

TABLE II

THE DENSITIES AND VOLUME CHANGES ATTENDING MIXING AT 35, 45 AND 55°

Mole fraction n-C_6F_{14}	35° Density, g./cm.^{3}	ΔV, cm.^{3}	$\Delta V - \Delta V_c$[a]	45° Density, g./cm.^{3}	ΔV, cm.^{3}	$\Delta V - \Delta V_c$	55° Density, g./cm.^{3}	ΔV, cm.^{3}	$\Delta V = \Delta V_c$
0.0000	0.64581			0.6354			0.62722[b]		
.0845	.7596	1.91	0.00	.7478	2.03	−0.04	.7356	2.22	−0.03
.1373	.8264	2.72	− .11						
.1776	.8742	3.43	.03	.8595	3.67	− .03	.8444	3.97	− .06
.3251	1.0385	4.81	.01	1.0194	5.23	− .01	.9997	5.75	.02
.4135	1.1278	5.34	.12	1.1064	5.82	.11	1.0846	6.36	.12
.4854	1.1974	5.43	.06	1.1742	5.94	.07	1.1504	6.52	.09
.5427	1.2515	5.32	− .06	1.2270	5.84	− .03	1.2017	6.41	− .03
.8070	1.4779	3.87	.06	1.4496	4.11	.00	1.4195	4.54	.01
.8995	1.5554	2.39	.02	1.5250	2.62	.08	1.4937	2.89	.08
1.0000	1.6413			1.6102			1.5783[c]		
			$\sigma = \pm 0.07$			$\sigma = \pm 0.06$			$\sigma = 0.07$

[a] $\Delta V - \Delta V_c$ is the difference between the change in volume calculated from the density data and that calculated from the least square power series equation with three constants. [b] The densities of the pure components at 55° were obtained from the density–temperature equations.

to the experimental data where x_1 is the mole fraction of the fluorocarbon. An equation having this form, and the effect of the constants on the shape of the curves has been discussed in detail by Scatchard.[20] The first constant determines the height of the curve at 0.5 mole fraction, the second constant skews the curve, and the third raises or lowers the sides depending on the sign.

The volume changes at 25° will serve to illustrate the desirability of the three-constant equation. Constants for the one-, two-, three- and four-constant equation were determined from the experimental data by the method of least squares. Deviations from the fitted curves are shown in Table I. The systematic trend in the deviations shown in columns 4 and 5 for the one- and two-constant equations disappears when three constants are used. The data do not justify the use of four constants.

Constants for the three-constant equation at 25, 35, 45 and 55° are shown in Table III. The volume changes and corresponding deviations from the fitted curves at 35, 45 and 55° are shown in Table II. When compared with the symmetric parabola, $\Delta V = A_0x_1x_2$, which has been used previously to describe the volume changes for solutions of fluorocarbons and hydrocarbons,[2–5] these curves are flatter, and slightly skewed toward the fluorocarbon. The volume change at $x = 0.5$ is in-

TABLE III

CONSTANTS FOR THE EQUATION

$\Delta V = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2]$

	A_0	A_1	A_2
25°	19.37	1.18	7.28
35°	21.52	1.11	5.97
45°	23.53	1.04	5.93
55°	25.79	1.38	6.51

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(20) G. Scatchard, *Chem. Revs.*, **44**, 7 (1949).

creasing at the rate of 0.053 cm.^{3} mole^{-1} deg.$^{-1}$. The percentage volume change, 100 ($\Delta V/V$), is 2.9 at 25° and increases 0.026% per degree. The maximum at 25° occurs at 0.524 mole fraction perfluoro-*n*-hexane and it approaches $x = 0.5$ as the temperature increases.

The question arises as to whether the volume changes for this and other fluorocarbon–hydrocarbon systems studied[2-5] are abnormally large. Although no experiments have been designed to determine the effect of pressure on the free energy of mixing directly, Hildebrand, Alder, Beams and Dixon[21] have studied the effect of pressure on the critical solution temperature for the system perfluoro-*n*-heptane–isoöctane. By inference that the excess free energy can be calculated from the critical solution temperature, the calculated volume change 2.6 cm.^{3}/mole is considerably lower than 4.9 cm.^{3} calculated from densities.[22]

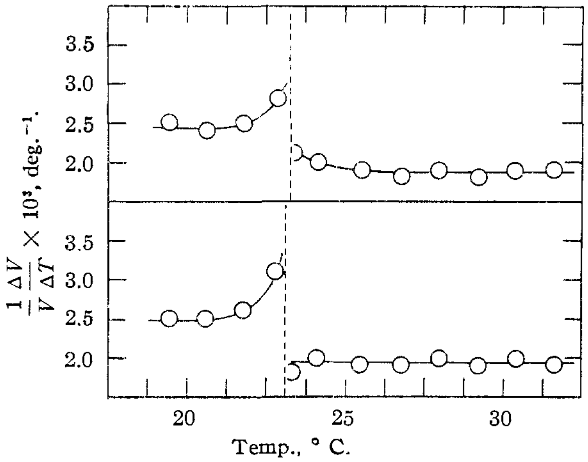

Fig. 1.—Thermal coefficients of expansion near the critical region showing discontinuities at the consolute temperatures for solutions of composition 0.3251 (upper curve) and 0.4135 mole fraction perfluoro-*n*-hexane.

If one uses the approximate relationship[23-25]

$$\frac{\Delta V}{V} = -\frac{\alpha T \Delta F^E}{E} \qquad (2)$$

where α, E and V are the thermal coefficient of expansion, potential energy and volume of the isolated components, respectively, and the excess free energy $\Delta F^E = 328$ cal. at $x = 0.5$ and 25° as determined from liquid–vapor equilibria,[19] the calculated volume change is 3.82 cm.^{3}. This is somewhat less than 4.84 calculated from the density measurements. (ΔF^E estimated from the critical solution temperature and composition is 286 cal.) Considering the approximations used in the derivation of equation 2, it is difficult to decide whether the large volume change is really abnormal.

The solubility data are shown in Table IV. The critical solution temperature and composition are 22.65° and 0.370 mole fraction n-C_6F_{14}, respectively. The solubility parameter difference, $\delta_2 - \delta_1$, calculated from Hildebrand's equation[26]

$$RT_c = \frac{2x_1x_2V_1^2V_2^2}{(x_1V_1 + x_2V_2)^3}(\delta_2 - \delta_1)^2 \qquad (3)$$

is 2.64. The solubility parameters of the pure components calculated from the energies of vaporization and molar volumes are 5.88 for the fluorocarbon and 7.32 for the hydrocarbon. The discrepancy between the difference, 1.44, and that calculated from equation 3 is not unusual for solutions of fluorocarbons and aliphatic hydrocarbons.[1-9]

TABLE IV

CONSOLUTE TEMPERATURES FOR THE SYSTEM PERFLUORO-*n*-HEXANE–*n*-HEXANE

Mole fraction n-C_6F_{14}	T, °C.	Mole fraction n-C_6F_{14}	T, °C.
0.0847	5.90	0.5427	20.95
.1373	15.93	.5795	19.49
.1778	19.45	.6137	17.97
.3251	22.60	.6663	14.89
.4135	22.51	.8068	− 1.58
.4854	21.92	.8994	−23.58

The thermal coefficients of expansion for two of the solutions near the critical composition are shown in Fig. 1. Although strong opalescence was observed 4–5° above the temperature corresponding to phase separation, these temperatures are confirmed by the location of the discontinuities. The molar volumes calculated from the densities of the two-phase mixture are shown in columns 2 and 4 of Table V. Corresponding values shown in columns 3 and 5 were calculated from the volume of mixing and the solubility curve. The compositions of the conjugate phases were determined graphically and corresponding molar volumes were obtained by a linear extrapolation of the volume of mixing below 25°.

TABLE V

VOLUME AS A FUNCTION OF TEMPERATURE FOR SOLUTIONS NEAR THE CRITICAL REGION

Temp., °C.	0.3251 mole fraction n-C_6F_{14} V, cm.^{3}/mole Exptl.	0.3251 mole fraction n-C_6F_{14} V, cm.^{3}/mole Calcd.	0.4135 mole fraction n-C_6F_{14} V, cm.^{3}/mole Exptl.	0.4135 mole fraction n-C_6F_{14} V, cm.^{3}/mole Calcd.
19.03	156.72	156.58	163.28	163.07
20.04	157.11	156.97	163.69	163.45
20.92	157.44	157.34	164.05	163.87
21.97	157.86	157.84	164.50	164.40
22.51[a]			164.78	164.71
22.60[a]	158.14	158.19		
22.84	158.22	158.26	164.88	164.81
23.81	158.53	158.53	165.21	165.10
25.00	158.88	158.87	165.58	165.47
35.00	161.82	161.77	168.76	168.64

[a] Consolute temperatures.

It is evident that the larger coefficients of expansion and the shapes of the curves below the consolute temperature result from the mixing and volume changes which take place as the temperature of the two-phase system is increased. Whereas general agreement between the observed and calculated molar volumes exists, substantiating the magnitude of the volume change and the accuracy of the solubility curve, the calculated volumes in each case are slightly less than those de-

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(21) J. H. Hildebrand, B. J. Alder, J. W. Beams and H. M. Dixon, *J. Phys. Chem.*, **58**, 577 (1954).

(22) R. D. Dunlap, unpublished data.

(23) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

(24) Ref. 10, p. 138.

(25) R. L. Scott, *Disc. Far. Soc.*, **15**, 47 (1953).

(26) See ref. 10, p. 253.

termined. The discrepancy, which exceeds the experimental error, may be significant but will require additional study before it can be explained.

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The Decomposition of Xanthate in Acid Solution

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A kinetic study of the decomposition of xanthate in acidified aqueous solutions using spectrophotometric measurements has shown that xanthate and xanthic acid are virtually in equilibrium and that the dissociation constant is 0.020 ± 0.001. The instability of xanthate solutions in the acid range is due to the monomolecular decomposition of xanthic acid with a rate constant of 4.3 ± 0.21 minute^{-1}.

The alkali metal xanthates, an important group of collectors for sulfide minerals, are known to be quite unstable in acidified aqueous solution. This presents a problem both in research and in plant operation with regard to the actual concentration of xanthate present in pulp solution.

The acid decomposition of xanthates has been studied by several investigators, all of whom assumed the reaction to be an ionic combination of xanthate and hydrogen ion to form xanthic acid with subsequent decomposition of the last-named compound into alcohol and carbon disulfide. Von Halban and his associates[1,2] studied the rate of decomposition by mixing xanthate solutions with hydrochloric acid, stopping the reaction at suitable time intervals by the addition of sodium carbonate and then analyzing the solutions by iodimetric titration. King and his associates[3-5] measured the rate from the increase in vapor pressure, primarily due to the formation of carbon disulfide. Cook and Nixon[6] attempted to follow the decomposition by measuring *p*H at different time intervals with a *p*H meter.

All of these investigators have assumed that xanthate and xanthic acid were in equilibrium. Using this assumption, they were able to calculate the dissociation constant for xanthic acid from the decomposition rate data. However, no experimental proof for this assumption has been given.

In the present paper it will be shown that the application of an ultraviolet spectrophotometer, particularly in the low *p*H range where the decomposition is extremely rapid, leads to an important implication as to the mechanism of the decomposition reaction.

Experimental

It has been reported by Hagihara[7] and by Bushell and Malnarich[8] that potassium ethyl xanthate in aqueous solution has a light absorption peak at a wave length of 301 mμ, this serving as a convenient basis for the colorimetric analysis of the substance.

The experimental procedure for the measurement of the decomposition rate consisted of mixing xanthate solutions with a known quantity of either hydrochloric or acetic acid, transferring the mixture to an absorption cell and measuring the optical density of the solution at suitable time intervals. Potassium ethyl xanthate used in this experiment was prepared in the usual manner[9] and a Beckman DU Quartz Spectrophotometer with a 1 cm. path-length quartz cuvette was used for the optical density measurements. All the experiments were made at room temperature, 23.5°.

It is possible that decomposition of xanthate may also be brought about by oxidation or by the action of alkali, and Taylor and Knoll[10] have listed the most probable reactions as

Oxidation:

$$4X^- + 2H_2O + O_2 \longrightarrow 2X_2 + 4OH^-$$

Action of alkali:

$$NaX + NaOH \longrightarrow CSONaSNa + C_2H_5OH$$

$$NaX + 2NaOH \longrightarrow CS(ONa)_2 + NaSH + C_2H_5OH$$

$$NaX + NaSH \longrightarrow CS(SNa)_2 + C_2H_5OH$$

Prior to the study of the decomposition of xanthate by acid, the extent of the effects of oxidation and of the addition of alkali were examined briefly.

Effect of Oxygen.—The decomposition of xanthate with atmospheric oxygen was tested by simultaneously agitating and aerating 2500 ml. of 7.5 × 10^{-5} mole per liter (12 mg. per liter) potassium ethyl xanthate solution in a Fagergren laboratory-type flotation machine.

Samples taken at approximately 10 minute intervals up to a total of 45 minutes of aeration showed no change in the optical density readings. This indicates that the decomposition of xanthate by oxidation is extremely slow and hence negligible in the following work.

Effect of Alkali.—The effect of alkali on the absorption spectrum of potassium ethyl xanthate solution was tested at *p*H values of approximately 6, 11 and 12; no change in the spectrum was noted. It was also shown that the addition of alkali to a xanthate solution stabilizes the compound to a large extent. In one experiment a solution containing approximately 3.1 × 10^{-5} mole per liter (5 mg. per liter) of potassium ethyl xanthate solution was left in volumetric flasks at *p*H 6.5 and 10.8 for a period of 8 days. The former solution at *p*H 6.5 showd 75% decomposition, that at *p*H 10.8 only 25%.

Effect of Acid. 1. Between *p*H 2.68–4.71.—In this *p*H range mixing was achieved by manual shaking in a 100-ml. volumetric flask. One milliliter of acid (0.1 and 0.2 *M* hydrochloric or 1 *M* acetic) was added to a flask which contained 100 ml. of 6.2 × 10^{-5} mole per liter (10 mg. per liter) potassium ethyl xanthate solution, and the mixture was

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(1) H. von Halban and A. Kirsch, *Z. physik. Chem.*, **82**, 325 (1913).

(2) H. von Halban and W. Hecht, *Z. Elektrochem.*, **24**, 65 (1918).

(3) C. V. King and E. Dublon, THIS JOURNAL, **54**, 2177 (1932).

(4) A. Chatenever and C. V. King, *ibid.*, **71**, 3587 (1949).

(5) M. L. Schochet and C. V. King, *ibid.*, **77**, 4745 (1955).

(6) M. A. Cook and J. C. Nixon, *J. Phys. Chem.*, **54**, 445 (1950).

(7) H. Hagihara, *Bull. Kobyashi Inst. Phys. Research, Japan*, **4**, 30 (1954).

(8) C. H. G. Bushell and M. Malnarich, *Trans. AIME*, **205**, 734 (1956).

(9) L. S. Foster, *Utah Eng. Exp. St. T. P.*, **5** (1929).

(10) T. C. Taylor and A. F. Knoll, *Trans. AIME*, **112**, 395 (1934).