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

Liquid–Vapor Equilibria in Fluorocarbon Systems[1]

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Using the dew point–bubble point technique, the following systems have been found to be ideal within experimental limits: (1) cyclo-C_5F_{10}–n-C_5F_{12}, (2) cyclo-C_5F_{10}–n-C_6F_{14}, (3) SF_6–n-C_5F_{12}, (4) A–n-C_5F_{12}, (5) n-C_6F_{14}–$(C_4F_9)_3N$, (6) n-C_6F_{14}–perfluoro-C_6-cyclic ether ($C_6F_{12}O$). The system n-C_6F_{14}–C_2F_5COOH shows marked positive deviation from Raoult's law behavior. The dew point–bubble point technique made this work possible, but it was not found to give as good experimental results as are obtained using an equilibrium still.

Introduction

Because of low intermolecular forces, fluorocarbons and many of their derivatives behave in general as poor solvents for hydrocarbons and their derivatives. Papers[2-4] dealing with the solvent properties of fluorocarbons have shown that these substances act substantially in the manner predicted from the theory developed by Hildebrand[5] and Scatchard.[6] Both from this theory and the general similarity of the various fluorocarbons one may predict that fluorocarbons and their derivatives should form substantially ideal solutions. One purpose of the present work was to test this prediction quantitatively. Liquid–vapor equilibria have been studied for several systems using the dew point–bubble point technique in a manner similar to that of Feller and McDonald.[7] This method offered two important advantages over the more conventional ways of measuring liquid–vapor equilibria: (1) small quantities of materials were required, (2) mixtures of known composition could be used, thereby eliminating a need for analysis.

In the common procedure for studying a liquid–vapor equilibrium one samples and analyzes the liquid and the vapor existing together at equilibrium. From several such measurements at the same temperature for mixtures of various compositions one can draw a pressure *vs.* composition graph for the whole system with curves for liquid and for vapor compositions. In the dew point–bubble point method one slowly compresses a known gaseous mixture of the two components at constant temperature and determines the following: (1) the dew point pressure (the pressure at which the liquid first appears as the pressure is increased); (2) the bubble point pressure (the pressure at which the last bubble of gas disappears leaving only a liquid phase). By using several mixtures of different compositions it is possible to construct a pressure *vs.* temperature graph like that obtained with an equilibrium still.

For the purpose of this research the dew point–bubble point technique really made the work practical. The supplies of fluorocarbons were very small and analysis of mixtures of small quantities of fluorocarbons would have been very difficult. Certain disadvantages of the method were found, however; the dew point and bubble point pressures could not always be measured with the desired precision. These pressures were determined by plotting pressure *vs.* volume for a particular mixture being compressed. Ordinarily a sharp break in the curve occurred at the dew point pressure. In some cases, however, the break was so slight that it was difficult to locate on the graph. The greatest difficulty, however, was found in establishing the bubble point pressure. A trace of a permanent gas such as nitrogen or air could cause a small bubble of gas to remain even at pressures well above the true bubble point pressure. This required thorough removal of nitrogen or air from the sample. Even when air had been thoroughly removed the bubble point pressure was difficult to establish when one component was much more volatile than the other. In the opinion of the authors this method is not likely to give as reliable data for determining activity coefficients as may be obtained using an equilibrium still.

Experimental

Materials.—The pure fluorocarbons perfluorocyclopentane, perfluoro-n-pentane and perfluoro-n-hexane were available as the result of earlier studies in this Laboratory.[8,9] A supply of sulfur hexafluoride was also available, but the gas was further purified by prolonged contact with sodium hydroxide solution followed by drying and fractional distillation. Spectroscopically pure argon was used directly as it came from the Linde Air Products Company. The other three materials were obtained from the Minnesota Mining and Manufacturing Co. All of them were subjected to careful fractional distillation. In the case of pentafluoropropionic acid a fraction boiling between 96.90 and 96.95° at 760 mm. was used. The selected cut of triperfluorobutylamine, $(C_4F_9)_3N$, boiled between 179.0 and 179.7° at 768 mm. pressure, and the selected cut of perfluoro-C_6-cyclic ether distilled between 55.1 and 55.7° at 765 mm. The latter material was a mixture of isomeric cyclic ethers of the empirical formula $C_6F_{12}O$. It contained $C_2F_5CF(CF_2)_3O$, $CF_3CF(CF_2)_4O$ and probably other isomers.

Procedure.—Before making a run, a dry mixture of the desired composition and size was made up by weight in a glass bulb closed by a stopcock. The whole of the sample was transferred to a graduated gas buret and while the sample was held at −183° the remaining trace of air, if present, was removed by pumping. The sample was then allowed to evaporate and the buret was later placed in a water-bath at constant temperature. When making pressure *vs.* volume measurements, it was common practice to start with the buret nearly filled with gas and to gradually decrease the volume from time to time by forcing mercury into the bottom of the buret. Sufficient time was allowed to pass to permit equilibrium to be established at each vol-

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[1] Summary of the Ph.D. thesis of M. M. Newcome, University of Washington, 1954.

[2] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 3928 (1948).

[3] R. L. Scott, *ibid.*, **70**, 4090 (1948).

[4] J. H. Hildebrand and D. R. F. Cochran, *ibid.*, **71**, 22 (1949). Later papers illustrate the same point.

[5] J. H. Hildebrand, "Solubility of Non-Electrolytes," 2nd Ed., A. C. S. Monograph Series 17, Reinhold Publ. Corp., New York, N. Y., 1936, p. 73.

[6] G. Scatchard, *Chem. Revs.*, **8**, 321 (1931).

[7] M. Feller and H. J. McDonald, *Anal. Chem.*, **22**, 338 (1950).

[8] E. J. Barber, L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4241 (1951).

[9] V. E. Stiles and G. H. Cady, *ibid.*, **74**, 3771 (1952).

ume observed. The pressure of the gas was read with a precision of 0.1 mm. of mercury using a cathetometer focused on a mercury manometer. When the pressures and volumes so obtained were plotted as a graph, the dew point and bubble point pressures could be recognized. These were recorded with a precision of 0.1 mm. and with a single sample were usually reproducible to within 1.0 mm. While most of the dew point and bubble point pressures probably were accurate within about 1 mm., there is reason to feel that some of the bubble points were as much as 5 mm. too high. The most satisfactory runs were those in which the dew point pressure was reached when the volume of gas had been reduced to about 50 to 70% of the volume of the buret.

Results

Observed dew point and bubble point pressures are contained in Tables I to VII. Six of the systems turned out to be ideal within experimental limits. In these cases the ideal bubble point and dew point pressures are given for comparison. These ideal values involve the assumptions that Raoult's law is obeyed by each component and that the vapors act as ideal gases. When calculating ideal dew point pressures the assumption was made that the first drop of liquid to appear was an ideal solution in equilibrium with vapor of the composition of the sample in question. Vapor pressures for the pure components were taken from the literature.

TABLE I

THE SYSTEM CYCLO-C_5F_{10}–n-C_6F_{12}

Mole fraction C_5F_{10}	Dew point pressure, mm. Obsd.	Ideal	Bubble point pressure, mm. Obsd.	Ideal
	At 25.0°			
0.000	646.5[a]			
.238	684.7	683.1	691.1	691.1
.506	728.0	729.3	740.5	741.1
.695	767.5	765.9	778.5	776.4
1.000	833.4[a]			
	At 15.0°			
0.000	435.0[a]			
.238	457.8	460.9	464.9	467.3
.506	493.8	494.0	503.6	503.4
.713	525.8	523.2	533.9	531.4
1.000	569.6[a]			
	At 9.6°			
0.000	346.6[a]			
.238	376.6	368.0	372.4	373.2
.506	396.8	395.3	402.3	403.1
.713	421.9	419.6	429.7	426.2
1.000	458.3[a]			

[a] Vapor pressures of the pure components are taken from E. J. Barber and G. H. Cady, *J. Phys. Chem.* **60**, 504 (1956).

TABLE II

THE SYSTEM CYCLO-C_5F_{10}–n-C_6F_{14}

Mole fraction C_5F_{10}	Dew point pressure, mm. Obsd.	Ideal	Bubble point pressure, mm. Obsd.	Ideal
	At 25.0°			
0.000	219.2[a]			
.256	271.5	270.2	383.4	376.4
.503	352.6	348.3	539.1	528.1
.747	496.4	487.7	688.0	678.0
.909	663.3	664.1	780.8	777.5
1.000	833.4[b]			
	At 15.0°			
0.000	138.5[a]			
.256	171.9	171.8	254.6	248.9
.503	224.2	223.6	369.0	355.3
.747	320.5	318.6	468.2	460.5
1.000	569.6[b]			

[a] From reference 9. [b] See Table I.

TABLE III

THE SYSTEM SF_6–n-C_5F_{12} AT 25°

Mole fraction SF_6	Dew point pressure, mm. Obsd.	Ideal	Bubble point pressure, mm. Obsd.	Ideal
0.000	646.5[a]			
.051	681.7	679.9	1500	1528
.389	1045.1	1034.3		
.522	1323.8	1301.3		
1.000	17930[b]			

[a] See Table I. [b] Product Data Sheet #SX-6, "Sulfur Hexafluoride," General Chemical Div., Allied Chemical and Dye Corp., New York (about 1950).

TABLE IV

THE SYSTEM ARGON–PERFLUORO-n-PENTANE AT 25°

Mole fraction A	Dew point pressure, mm. Obsd.	Ideal
0.000	646.6[a]	
0.238	868	848
0.424	1153	1118
1.000		475000[a]

[a] The temperature 25° is far above the critical temperature of argon. To calculate the "ideal" dew point pressures a graph of log (vapor pressure) of argon *vs.* $1/T$ was extrapolated to 25° as suggested by Hildebrand (Hildebrand, "Solubility of Non-Electrolytes," 2nd Edition, Reinhold Publ. Corp., New York, N. Y., 1936, pp. 30, 31). An extrapolated pressure of 625 atm. was obtained.

TABLE V

THE SYSTEM n-C_6F_{14}–$(C_4F_9)_3N$ AT 25°[a]

Mole fraction n-C_6F_{14}	Bubble point pressure, mm. Obsd.	Ideal
0.000	*ca.* 1	
.104	24.8	23.7
.206	42.7	45.9
.398	87.3	87.8
.588	129.9	129.3
.614	137.4	134.9
.848	187.8	186.0
1.000	219.2[b]	

[a] Because of the low vapor pressure of one of the components, $(C_4F_9)_3N$, no dew point pressures were measured for the system in Table V. It is highly probable that they are substantially ideal. [b] See Table II.

TABLE VI

THE SYSTEM n-C_6F_{14}–PERFLUORO-C_6-CYCLIC ETHER AT 25°

Mole fraction $C_6F_{12}O$	Dew point pressure, mm. Obsd.	Ideal	Bubble point pressure, mm. Obsd.	Ideal
0.000	219.2[a]			
.155	222.7	221.0	224.4	222.5
.295	225.2	223.3	228.0	225.6
.545	230.1	227.2	233.2	231.0
.743	234.0	231.9	235.5	235.2
.754	234.1	232.2	235.7	235.5
.846	236.3	235.0	238.0	237.5
.871	236.8	235.8	238.7	238.0
1.000	240.8			

[a] See Table II.

TABLE VII

PART OF THE SYSTEM n-C_6F_{14}–C_2F_5COOH

Mole fraction n-C_6F_{14}	Dew point pressure, mm.	Bubble point pressure, mm.
0.000	30.0	
0.496[a]	142.6	183.0
0.755	174.7	201.5
1.000	219.2	

[a] Solutions of mole fraction less than 0.496 could not be used in the apparatus because no suitable stopcock grease was found for the gas buret.

Discussion

The close resemblance of the system argon–perfluoro-n-pentane to ideal behavior was to be expected because of the low polarizability of molecules of both substances and because of the general physical resemblance of the rare gases to the fluorocarbons.

The system perfluoro-n-hexane–pentafluoropropionic acid deviates greatly from ideality, the pressures being greater than ideal. This might be expected in the case of substances differing as these do. The deviation, however, is probably not as great as it appears to be, because polymerization of the acid causes its true mole fraction to be less than indicated in Table VII.

It is of interest to compare the observed behavior of systems described by Tables I to VI with that predicted by the theory of Hildebrand[4] and Scatchard.[5] This theory results in the equation

$$RT \ln \gamma_1 = V_1\phi_2^2(\delta_1 - \delta_2)^2$$

in which the symbols have the following meanings: R is the gas constant, T the absolute temperature, γ_1 the activity coefficient of component 1, V_1 the molar volume of component, 1, ϕ_2 the volume fraction of component two in the liquid solution and δ_1 and δ_2 are the "solubility parameters" of the two components. A similar equation may be used to calculate the activity coefficient of the second component. From the two activity coefficients one may calculate the pressures of the components over a solution. To do this, δ for each component has first been calculated by the usual method: $\delta = (\Delta E_v/V)^{\frac{1}{2}}$. The quantity ΔE_v is the energy of vaporization per mole of the component at 25° and V is its molar volume when a liquid. Table VIII gives the calculated values of δ.

TABLE VIII

SOLUBILITY PARAMETERS AT 25°

Substance	C_5F_{10}	n-C_5F_{12}	n-C_6F_{14}	SF_6	$(C_4F_9)_3N$	$C_6F_{12}O$
δ	6.09	5.77	5.96	3.57	5.52	6.03

Since all of these values except that for sulfur hexafluoride are close to each other, the term $(\delta_1 - \delta_2)$ is small for mixtures of these substances, unless sulfur hexafluoride is one component. The systems as predicted by the theory are very close to ideal, as shown in Table IX.

TABLE IX

CALCULATED TOTAL PRESSURE (IN MM.) AT 25° FOR SYSTEMS AT LIQUID MOLE FRACTION 0.500

System	C_5F_{10}–C_5F_{12}	C_5F_{10}–C_6F_{14}	SF_6–C_5F_{12}	C_6F_{14}–$(C_4F_9)_3N$	C_6F_{14}–$C_6F_{12}O$
Ideal	740.0	526.3	9289	110.1	230.0
From eq. 1	745.3	527.1	12700	114.2	230.1

The system SF_6–n-C_5F_{12} is without question more nearly ideal than is predicted from the δ-values. In a case such as this, it is common practice to use the system to calculate an arbitrary δ-value for the component which seems to misbehave. To make the system in question ideal, δ for SF_6 would be 5.77. A value as low as 5.3 would still give reasonably good agreement with experiment. For other fluorocarbon systems involving sulfur hexafluoride a δ-value in this neighborhood should lead to better predictions than the value 3.57, given in Table VII.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Some Metal Complexes of Glycine and Valine[1]

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The formation constants of the nickel(II) and copper(II) complexes of glycine and valine at different temperatures have been measured. From these data, the enthalpy and entropy changes for the reaction $M^{2+} + 2A^- = MA_2$ have been calculated for M^{2+} = nickel(II) and copper(II) ions, and A^- = glycinate and valinate ions. Only data for the nickel chelates are in agreement with the "iceberg-forming tendency" of Frank and Evans and of Robinson. In 45% by weight dioxane, the entropy of formation of Ni(glycinate)$_2$ complex is much more positive than in aqueous medium, presumably in part because of "sorting-desorting" effect. A linear relationship exists between log k^N of nickel–glycine complexes and mole fraction of dioxane in the range $N_2 = 0$ to $N_2 = 0.323$, whereas the variation of pK_2^N of glycine with mole fraction of dioxane is not linear. The highest order cadmium complex of glycine is CdA_3^-; log $k_3 = 1.8$, compared to log $k_1k_2 = 8.1$. These values suggest that in the highest order complex, two glycinates are chelated, but the third is not chelated.

Introduction

For the purpose of obtaining a better understanding of the factors which cause complex formation to take place, it is desirable to consider the free energy change to be a consequence of the enthalpy and entropy changes accompanying complex formation and to measure the relative contribution of these factors.[2] Such a study is described herein for the nickel(II) and copper(II)

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[1] This investigation was supported by Grant No. NSF-G1926 from the National Science Foundation.

[2] C. G. Spike and R. W. Parry, THIS JOURNAL, **75**, 2726 (1953).