

Solubility of Sulfur Hexafluoride in Fluorocarbon Liquids

Heinz Jaster¹ and Phillip G. Kosky

Corporate Research and Development, General Electric Co., Schenectady, N.Y. 12301

Solubilities of SF₆ in several fluorocarbon liquids were measured over a temperature range of 235–373K. The data are presented in terms of Henry's parameter which varied with temperature according to $b = aT^m$ where m varied from solvent to solvent between 5.05 and 7.47. The data were compared to the corresponding states solubility theory of Prausnitz and Shair. The data indicated a marked deviation from this theory for those fluorocarbons containing chlorine. With data from five solvents, the solubility parameter for SF₆ was 6.16 (cal/cm³)^{1/2} at 298K.

SF₆ is a dielectric gas of manifest importance to the electrical industry. Many of its properties are available (2). An increasing application of SF₆ is in conjunction with fluorocarbon liquid coolants. This implies a need for knowledge of SF₆'s solubility in those liquids. We are aware of some data on the solubility of SF₆ with various solvents (3). However, the number of solvents for which data exist and the range of temperature were insufficient to draw general conclusions.

One can predict the solubility of nonreacting gases in liquids by related methods (4, 7). The solubility of gas in liquid solvents is most conveniently expressed by Henry's law:

$$P_2 = bx_2 \quad (1)$$

in which x_2 is the equilibrium mole fraction of the dissolved gas, P_2 is the gas partial pressure in contact with the liquid, and b is Henry's parameter. Equation 1 is valid for low pressure for which the Poynting correction may be neglected. For high pressures the extended form, due to Krichevsky-Kasarnovsky (5), must be used. Thus, Equation 1 implies that b is a function of temperature only.

Thermodynamic schemes to predict the solubility of gas in a liquid solvent generally calculate the free energy changes necessary to form a hypothetical liquid. This liquid is then mixed with the solvent for which process the free energy change is calculable. Since the latter process mixes two liquids of like volumes, one may apply the regular solution theory (3), assuming no change of volume.

Then according to ref. 4:

$$\frac{f_2^g}{x_2} = f_2^f \exp \left\{ \frac{V_2^f (\delta_1 - \delta_2)^2}{RT} \phi_1^2 \right\} \quad (2)$$

in which f_2^g is the fugacity of the gas initially in the system and which is condensed to the hypothetical pure liquid state, f_2^f . V_2^f is the partial molar volume of 2 in the hypothetical liquid state. The volume fraction, ϕ_1 , and the solubility parameter, δ_1 , are, respectively, given by

$$\phi_1 = \frac{x_1 V_1^f}{x_2 V_2^f + x_1 V_1^f} \quad (3)$$

$$\delta_1 = \left(\frac{h_{fg} - RT}{V_1^f} \right)^{1/2} \quad (4)$$

The volume fraction of liquid is very close to unity for data presented in this work. Here, h_{fg} is the molar latent heat of vaporization.

¹ To whom correspondence should be addressed.

At low-pressure conditions

$$f_2^g = P_2 \quad (5)$$

Hence, Equation 2 becomes

$$b = f_2^f \exp \left\{ \frac{V_2^f (\delta_1 - \delta_2)^2}{RT} \right\} \quad (6)$$

To solve for b , three independent properties are required: f_2^f , V_2^f , and δ_2 . Prausnitz and Shair (4) have shown that a useful correlation exists for f_2^f :

$$\frac{f_2^f}{P_c} = fn\{T_r\} \quad (7)$$

A further useful result is that $V_2^f (\delta_1 - \delta_2)^2$ is temperature independent and that it need only be specified at one convenient temperature, here taken as 298K. The value of V_2^f may be estimated in several ways, for example, ref. 6. A major objective of this paper is the independent measurement of δ_2 as determined by solubility measurements.

The liquid fluorocarbons tested were a series of commercially available fluids. They are tabulated below.

Formula	Chemical name	Commercial name	Purity
C ₈ F ₁₆ O	Perfluoro-2-butyltetrahydrofuran	FC-75*	~95 mol % C ₈ F ₁₆ O
?	?	FC-82*	?
?	?	FC-88*	?
C ₆ F ₁₄	Isomeric perfluorohexane	...	54%–2,3-Perfluorodimethylbutane 39%–2-Perfluoromethylpentane 7%– <i>n</i> -Perfluorohexane
CCl ₂ F–CClF ₂	Trichlorotrifluoroethane	R-113	?
CClF ₂ –CClF ₂	Dichlorotetrafluoroethane	R-114	?

(Properties are tabulated in Appendix I). *These compounds (or mixtures) are manufactured by 3M Co. 3M will not specify composition nor purity. However, FC-75 appears to be approximately 95% mole solution of the ether quoted above. Its thermodynamic properties are extensively available (8). Other information is supplied by the manufacturer under "Fluorinert Electronic Liquids," Catalogues, 3M, St. Paul, Minn.

Experimental

The apparatus shown as Figure 1 was constructed of hermetically sealed copper pipe. It consisted of a known gas measuring volume (of about 1 l.) and the test cell proper. The test cell of known volume (about 1 l.) was maintained in a thermostat which could be operated in a temperature range between a dry ice bath in trichloroethylene and boiling water. The test cell pressure was measured via a pressure transduc-

er of small volume which was used as a null detector. The pressure was measured against an external gas source as indicated in the schematic. Corrections were made as necessary for barometric pressure changes. The apparatus was initially evacuated, and the test cell filled with a known volume of liquid and the measuring cylinder with a known pressure of SF₆. A charge of gas was admitted to the test cell through isolation valves. The number of moles transferred was calculated from the initial and final pressures and temperatures of the measuring cylinder (assuming ideal gas behavior). Mixing in the test cell was accomplished with a fluorocarbon polymer-coated magnetic stirrer. After equilibrium was attained for the system, the test cell pressure and temperature were recorded. For all fluorocarbon liquids tested, except CCl₂F-CClF₂ (R-113), we also measured the vapor pressure, π , of

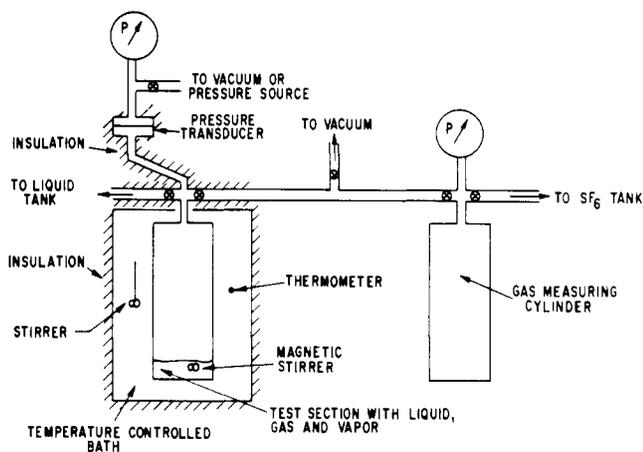


Figure 1. Solubility test cell

the pure liquid prior to gas addition to the test cell. Then, at a given temperature the partial pressure of gas in the mixture at pressure P was taken to be as given by Dalton's law, $P_2 = P - \pi(T)$.

The volume available for the gas phase was calculated from the original volume of liquid in the cell, its density-temperature relationship, and the fact that the volumetric fraction of gas, ϕ_2 , in the liquid phase was negligibly small. Hence, once again by use of the ideal gas law, the number of moles of gas (and of solvent) in the gaseous phase were calculated. Finally, knowing the initial molar inventory of solvent and gas, we calculated the number of moles of gas and solvent in the liquid phase and hence x_2 . Thus, b could be calculated at each temperature from Equation 1 (Appendix II).

To check experimentally that the value of b was independent of total pressure at a given temperature, for most solvents, the measurements were repeated using an increased charge of SF₆ without changing the liquid charge. For reference purposes, the total number of moles of gas per unit test cell volume is denoted by n_2''' and of solvent by n_1''' . In practice, the test cell total pressure varied from 100 to 1500 torr depending on n_2''' and T .

Results

The basic results of this investigation are given in Figures 2-6 and Appendix III. In all cases, b (torr) is plotted vs. T (K) on log-log coordinates for each set of data pertaining to one solvent: $b = aT^m$ with a , m given in each figure and b was independent of n_2''' and hence of P in the tested range.

A few additional data points are also quoted for R-114 which was not investigated in detail.

The data for the first five solvents cited were deemed to be of sufficient internal consistency to calculate the solubility parameter for SF₆. Referring to Equation 6, to compute δ_2 we

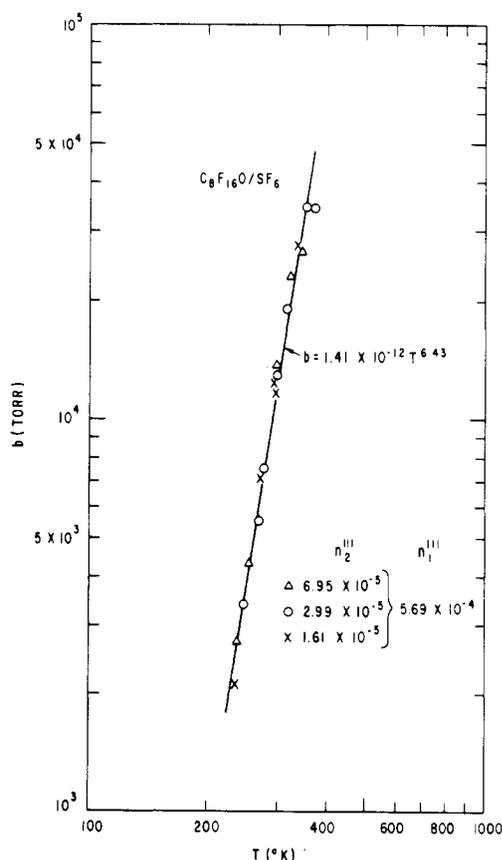


Figure 2. Henry's parameter for C₈F₁₆O/SF₆ solutions

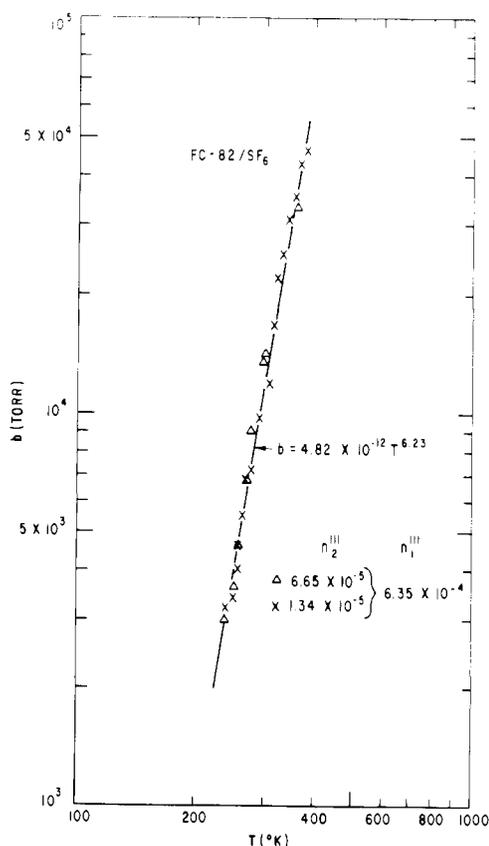


Figure 3. Henry's parameter for FC-82/SF₆ solutions

need to know three independent quantities, b , f_2^f , and V_2^f . $V_2^f(\delta_1 - \delta_2)^2$ is temperature independent and can be evaluated at any convenient state (taken here as 298K). Thus, Equation 6 can be solved using one measured value of b at 298K for each of three solvents, i.e., b' , b'' , and b''' for which the solubility parameters δ_1 were calculated from Equation 4 as δ_1' , δ_1'' , and δ_1''' , respectively. We first eliminate V_2^f from the equations since it is not dependent on the solvent properties. After algebraic simplification

$$\delta_2 = \frac{1}{2} \left\{ \frac{\delta_1' + \delta_1''(1 - \beta) - \beta\delta_1'''}{1 - \beta} \right\} \quad (8)$$

where

$$\beta = \left(\frac{\delta_1'' - \delta_1'''}{\delta_1' - \delta_1'''} \right) \frac{\ln(b'/b'')}{\ln(b''/b''')}$$

Use of Equation 8 has eliminated the need for an explicit value for f_2^f while still retaining the thermodynamic relationship, Equation 2. For the five solvents intensively investigated, three solvents can be chosen in $5! / 3!2! = 10$ ways, which resulted in

$$\delta_2 = 6.16 \text{ (cal/cm}^3\text{)}^{1/2} \text{ (average)}$$

with

$$\sigma = 0.64 \text{ (cal/cm}^3\text{)}^{1/2} \text{ (standard deviation)}$$

The standard deviation, σ , is heavily weighted by those combinations containing R-113 which, as will be shown, behaved atypically. However, eliminating the six combinations containing R-113 yields

$$\delta_2 = 6.15 \text{ (cal/cm}^3\text{)}^{1/2} \text{ (average)}$$

$$\sigma = 0.06 \text{ (cal/cm}^3\text{)}^{1/2}$$

While, theoretically at least, V_2^f can be calculated by a

method similar to that used for δ_2 , it transpires that a more accurate estimate can be obtained by using the correlation of Prausnitz (6). From his results

$$V_2^f = 103 \text{ cm}^3/\text{g-mol @ 298K}$$

which favorably compares to the value of $104 \text{ cm}^3/\text{g-mol}$ quoted in ref. 3.

Using Equation 6, f_2^f can be calculated as a function of temperature and the results cast in the form of Equation 7. Data for the six solvents cited are plotted in Figure 7 on which the corresponding states relationship of ref. 4 is also drawn. The Prausnitz and Shair curve may be represented by the following functional relationship:

$$\frac{f_2^f}{P_c} = 0.693 T_r^{(4.987 - 2.758 \ln T_r)} \quad (9)$$

for $2.5 \geq T_r \geq 0.7$.

This curve has been extrapolated to $T_r = 0.53$ in Figure 7.

Data for the four nonchlorinated solvents, FC-75, FC-82, FC-88, and isomeric perfluorohexane, agree reasonably well with the corresponding states theory using the quoted values of δ_2 and V_2^f . However, the data for the chlorinated refrigerant liquids (R-113 and R-114) lie considerably away from the theory.

Discussion

Hildebrand et al. (3) have shown that SF_6 behaves atypically in a group of solvents ranging from hydrocarbons to fluorinated chlorocarbons (Figure 8.5 loc. cit.). The effects are most apparent in these new data for the chlorinated refrigerants R-113 and R-114 which lie respectively 100% above and 70% below the corresponding states theory of ref. 4. Since the properties of these fluids are well documented (7), we did not repeat their vapor-pressure curves. A simple back calculation showed, however, that the uncertainty in vapor

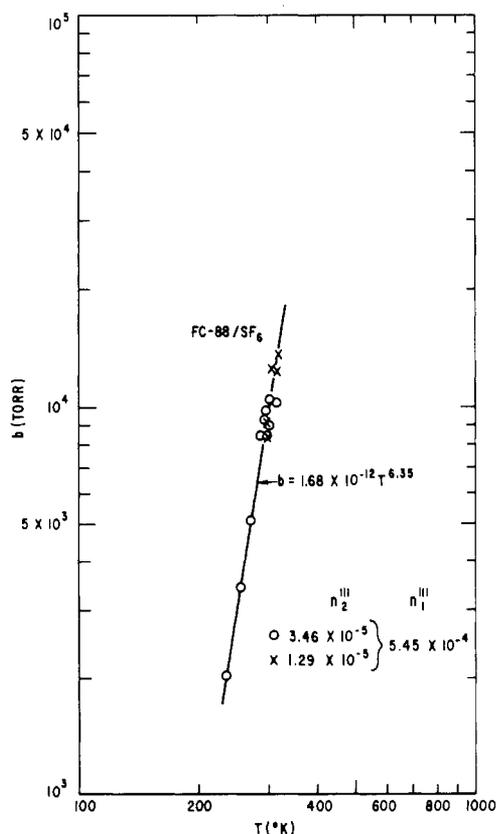


Figure 4. Henry's parameter for FC-88/SF₆ solutions

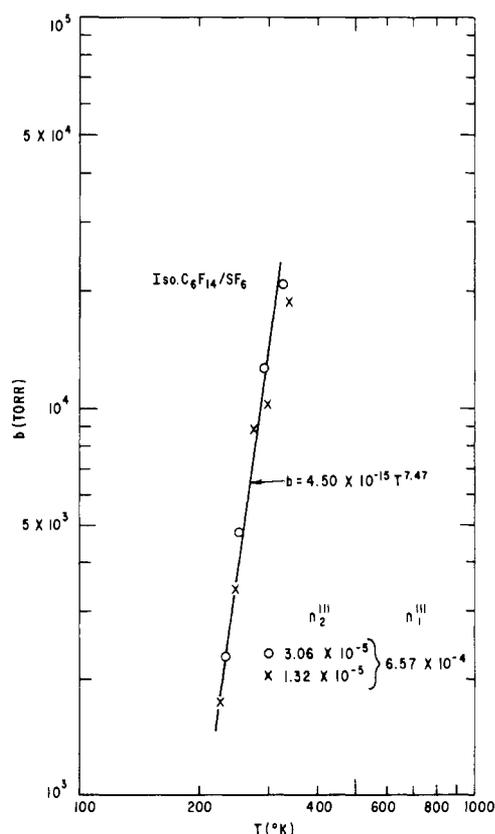


Figure 5. Henry's parameter for C₆F₁₄/SF₆ solutions

pressure was less than the necessary change to assign these points to the reference corresponding states curve. For example, in the case of R-113, the vapor pressure would have to be increased by a factor of ~ 2.4 .

A single datum point quoted in ref. 3, Appendix 3, has been plotted in Figure 6 of this work and shows remarkable agreement with our data for R-113.

In the case of the FC-XX fluids, there was considerable deviation from the nominal vapor-pressure curve; from our

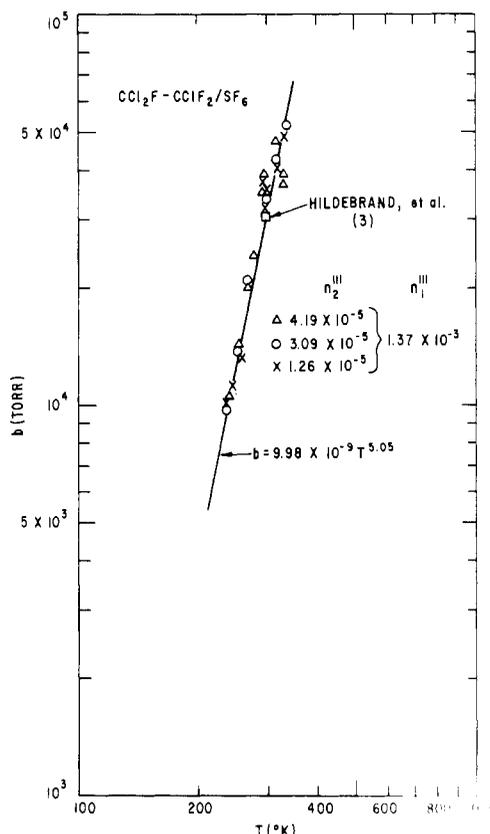


Figure 6. Henry's parameter for $\text{CCl}_2\text{F}-\text{CClF}_2/\text{SF}_6$ solutions

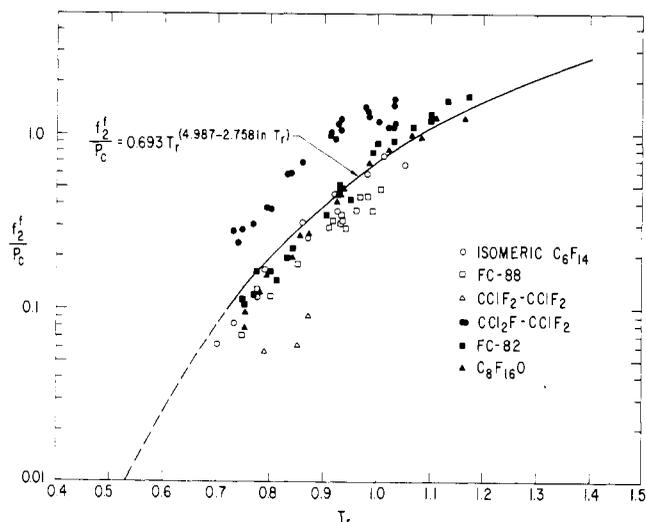


Figure 7. Corresponding states representation of solubility data

smoothed vapor-pressure curve we used the Clausius-Clapeyron equation to compute h_{fg} at 298K so that errors were minimized both for the direct measurement of b and for δ_1 .

Deviations from the reference corresponding states curve are not explainable by our neglect of the volumetric fraction ϕ_1 in Equation 2. Using a worst case example, f_2^f would differ from our quoted results by a factor of ~ 0.99 since $\phi_1 \sim 0.98$ at highest gas concentrations.

It proved impossible to obtain consistent values of V_2^f from the experimental data. The reason is simple:

$$\frac{V_2^f}{RT} = \frac{\ln(b'/b'')}{(\delta_1' - \delta_1'')(\delta_1' + \delta_1'' - 2\delta_2)} \quad (10)$$

Small errors in δ_1' , δ_1'' , and δ_2 very strongly affect the computed value of V_2^f . This is most strongly the case where δ_1' , δ_1'' , and δ_2 have similar magnitudes.

Conclusions

Henry's parameter, b (torr), for SF_6 is given by

$$b = 1.41 \times 10^{-12} T^{6.43} \quad \text{for } \text{C}_8\text{F}_{16}\text{O}$$

$$b = 4.82 \times 10^{-12} T^{6.23} \quad \text{for FC-82}$$

$$b = 1.68 \times 10^{-12} T^{6.35} \quad \text{for FC-88}$$

$$b = 4.50 \times 10^{-15} T^{7.47} \quad \text{for iso-}\text{C}_6\text{F}_{14}$$

$$b = 9.98 \times 10^{-9} T^{5.05} \quad \text{for } \text{CCl}_2\text{F}-\text{CClF}_2$$

for $373\text{K} > T > 235\text{K}$.

At 298K the solubility parameter for SF_6 is $\delta_2 = 6.16$ (cal/cm³)^{1/2}.

Appendix I. Solvent Properties

Vapor pressure $\pi = \exp\left\{-\frac{A}{T} + B\right\}$, torr

Liquid density $\rho_{lf} = a - bT$, g/cm³

MW of solvent M_1

Solubility parameter δ_1 of solvent at 298°K (Equation 4) (cal/cm³)^{1/2}

Solvent	A	B	a	b × 10 ³	M ₁	δ ₁
FC-75	4398.9	18.26	2.48	2.4	416	6.24
FC-82	4176.9	17.86	2.55	2.4	400	6.17
FC-88	3308.5	17.54	2.39	2.5	300	5.81
Iso-C ₆ F ₁₄	3758.5	17.96	2.60	2.9	338	5.93
R-113	3396.8	17.19	2.24	2.3	187	7.25
R-114	3010.1	17.51	2.29	2.8	170.9	8.58

Appendix II. Reduction of Experimental Data

The specification of Henry's parameter from the raw experimental data was made with three primary assumptions

1. Vapor-gas mixture obeys Dalton's law
2. Vapor-gas mixture obeys ideal gas laws
3. Change in volume of solvent on solution of solute is negligible

With these assumptions, the following relationships result:

$$P_2 = P - \pi(T) = bx_2 \quad (11-1)$$

$$F = \frac{n_2''' - \pi(T)/RT}{\rho_{lf}(T)/M_1 - \pi(T)/RT} \quad (11-2)$$

$$x_2 = \frac{n_2''' - P_2(1-F)/RT}{n_2''' - P_2(1-F)/RT + \rho_{lf}(T)F/M_1} \quad (11-3)$$

where F is the volume fraction of liquid (mass density ρ_{lf} , molecular weight M_1) in the test cell

Appendix III. Experimental Data

n_2'''	T	P	π	x_2	b
Solvent: FC-75					
Concn in test cell, $n_1''' = 5.69 \times 10^{-4}$ g-mol/cm ³					
1.61×10^{-5}	239.3	50.5	0.9	0.0232	2.14×10^3
	272.0	130.6	8.1	0.0174	7.04×10^3
	293.8	201.5	26.7	0.0139	1.26×10^4
	294.7	196.2	28.0	0.0145	1.16×10^4
	338.3	457.7	191.7	0.0095	2.80×10^4
2.99×10^{-5}	247.9	134.0	1.7	0.0388	3.40×10^3
	268.1	199.4	6.4	0.0345	5.59×10^3
	277.2	246.9	10.9	0.0314	7.52×10^3
	296.5	359.7	20.7	0.0254	1.30×10^4
	313.1	471.5	67.2	0.0213	1.90×10^4
	353.6	890.3	336.9	0.0153	3.62×10^4
	370.1	1154.0	586.5	0.0165	3.44×10^4
6.95×10^{-5}	239.5	247.6	0.9	0.0900	2.74×10^3
	253.1	361.1	2.4	0.0819	4.38×10^3
	298.4	810.7	33.7	0.0566	1.37×10^4
	325.1	1149.0	113.2	0.0441	2.35×10^4
	344.6	1380.9	243.9	0.0422	2.69×10^4
Solvent: FC-82					
Concn in test cell, $n_1''' = 6.35 \times 10^{-4}$ g-mol/cm ³					
1.34×10^{-5}	238.6	53.9	1.4	0.016	3.28×10^3
	247.0	57.5	2.6	0.016	3.43×10^3
	255.5	67.4	4.6	0.0155	4.05×10^3
	264.3	87.2	7.8	0.0144	5.51×10^3
	276.6	111.4	15.8	0.0134	7.14×10^3
	288.5	148.0	29.4	0.0121	9.80×10^3
	301.9	190.3	55.9	0.0114	1.18×10^4
	306.1	229.3	67.9	0.0096	1.68×10^4
	316.4	291.4	105.4	0.0084	2.21×10^4
	328.0	370.2	168.6	0.0079	2.55×10^4
	339.7	483.4	261.0	0.0071	3.13×10^4
	350.6	620.9	382.4	0.0067	3.56×10^4
	362.0	816.5	557.5	0.0060	4.32×10^4
	373.6	1069.1	796.4	0.0058	4.70×10^4
6.65×10^{-5}	238.8	233.6	1.4	0.0772	3.00×10^3
	247.0	274.8	2.6	0.0748	3.64×10^3
	255.4	334.2	4.5	0.0713	4.62×10^3
	266.5	454.0	9.0	0.0641	6.94×10^3
	277.5	560.5	16.6	0.0587	9.27×10^3
	295.3	739.3	41.1	0.0510	1.37×10^4
	296.7	753.8	43.9	0.0505	1.41×10^4
	297.3	769.1	45.3	0.0497	1.46×10^4
	320.6	1047.3	125.4	0.0381	2.42×10^4
	351.5	1546.1	394.9	0.0343	3.36×10^4
Solvent: FC-88					
Concn in test cell, $n_1''' = 5.45 \times 10^{-4}$ g-mol/cm ³					
1.29×10^{-5}	297.0	729.2	604.2	0.0138	9.20×10^3
	304.9	1065.3	910.6	0.0123	1.26×10^4
	312.7	1209.1	1052.4	0.0125	1.25×10^4
	320.5	1695.8	1528.2	0.0123	1.35×10^4
3.46×10^{-5}	238.6	148.4	39.6	0.0532	2.05×10^3
	255.4	265.3	97.8	0.0487	3.44×10^3

n_2'''	T	P	π	x_2	b
Solvent: FC-88					
Concn in test cell, $n_1''' = 5.45 \times 10^{-4}$ g-mol/cm ³					
	270.9	436.5	206.0	0.0444	5.19×10^3
	290.2	791.2	463.5	0.0385	8.51×10^3
	292.5	853.3	507.5	0.0373	9.27×10^3
	296.3	937.1	586.3	0.0376	9.33×10^3
	296.4	919.5	587.5	0.0392	8.47×10^3
	296.5	936.0	589.9	0.0380	9.11×10^3
	296.6	954.1	592.4	0.0367	9.86×10^3
	296.8	959.3	596.1	0.0366	9.92×10^3
	305.5	1205.0	821.2	0.0366	1.05×10^4
	315.0	1530.8	1138.3	0.0380	1.03×10^4
Solvent: Iso-C ₆ F ₁₄					
Concn in test cell, $n_1''' = 6.57 \times 10^{-4}$ g-mol/cm ³					
1.32×10^{-5}	223.9	33.6	3.2	0.0173	1.75×10^3
	247.0	68.8	15.6	0.0156	3.41×10^3
	273.8	175.3	69.2	0.0120	8.84×10^3
	295.3	307.7	188.1	0.0117	1.02×10^4
	333.3	980.0	803.2	0.0094	1.89×10^4
3.06×10^{-5}	232.9	94.1	6.2	0.0380	2.31×10^3
	251.9	178.4	21.0	0.0330	4.77×10^3
	293.4	483.5	173.2	0.0244	1.27×10^4
	322.8	972.2	554.2	0.0200	2.09×10^4
Solvent: R-113					
Concn in test cell, $n_1''' = 1.37 \times 10^{-3}$ g-mol/cm ³					
1.26×10^{-5}	233.1	77.6	12.7	0.0063	1.03×10^4
	244.5	95.7	25.3	0.0062	1.13×10^4
	255.2	126.7	46.3	0.0060	1.34×10^4
	292.5	418.4	265.9	0.0040	3.81×10^4
	293.5	418.9	276.3	0.0044	3.24×10^4
	295.4	449.9	298.2	0.0041	3.70×10^4
	319.0	885.9	719.2	0.0041	4.07×10^4
	328.6	1176.5	990.9	0.0038	4.88×10^4
3.09×10^{-5}	235.7	171.2	14.9	0.0157	9.95×10^3
	249.2	233.8	33.4	0.0144	1.39×10^4
	264.3	337.7	74.0	0.0126	2.05×10^4
	291.0	609.2	250.0	0.0104	3.45×10^4
	296.7	713.7	314.5	0.0094	4.25×10^4
	312.8	992.9	576.0	0.0097	4.30×10^4
4.19×10^{-5}	238.4	238.9	17.6	0.0209	1.06×10^4
	249.5	303.1	33.9	0.0195	1.38×10^4
	266.9	444.8	84.5	0.0170	2.12×10^4
	290.4	734.3	244.0	0.0140	3.50×10^4
	294.9	817.1	292.9	0.0132	3.97×10^4
	312.0	1148.1	559.1	0.0123	4.79×10^4
	328.6	1551.4	989.1	0.0142	3.96×10^4
	329.0	1545.8	999.8	0.0147	3.71×10^4
Solvent: R-114					
Concn in test cell, $n_1''' = 8.56 \times 10^{-4}$ g-mol/cm ³					
1.16×10^{-5}	252.0	315.8	261.0	0.0101	5.43×10^3
	270.8	651.8	596.0	0.0106	5.27×10^3
	277.6	858.1	783.5	0.0097	7.69×10^3

Acknowledgment

We thank the 3M Co. for providing a sample of FC-82.

Nomenclature

a = constant
 b = Henry's parameter, torr
 f_i^j = fugacity of i in phase j , torr
 h_{fg} = latent heat of vaporization, cal/g-mol
 m = exponent
 n_i''' = molar concentration with respect to total volume, g-mol/cm³
 P, P_i = pressure, partial pressure, torr
 P_c = critical pressure of solute, torr
 R = gas constant, cal/g-mol K
 T, T_r = temperature, reduced temperature, K, 1
 V_i^l = partial molar volume in liquid phase, cm³/g-mol
 x_i = mole fraction in liquid phase

Greek

δ_i = solubility parameter (cal/cm³)^{1/2}
 $\pi(T)$ = vapor pressure at T , torr
 σ = standard deviation (cal/cm³)^{1/2}
 ϕ_i = volume fraction in liquid phase

Subscripts

1 = of the solvent
 2 = of the solute

Superscripts

f = in the liquid phase
 g = in the gaseous phase

Literature Cited

- (1) Du Pont Co., Freon Product Information, Bulletin 2, Wilmington, Del.
- (2) "Encyclopedia of Chemical Technology", J. G. Kirk and D. F. Othmer, Eds., 2nd ed., pp 9, 664, Wiley, New York, N.Y., 1970.
- (3) Hildebrand, J. H., Prausnitz, J. M., Scott, R. L., "Regular and Related Solutions", Van Nostrand Reinhold, New York, N.Y., 1970.
- (4) Prausnitz, J. M., Shair, F. H., *AIChE J.*, **7**, 682 (1961).
- (5) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria", p 357, Prentice-Hall, Englewood Cliffs, N.J., 1969.
- (6) Prausnitz, J. M., *AIChE J.*, **4**, 269 (1958).
- (7) Preston, G. T., Prausnitz, J. M., *Ind. Eng. Chem. Fundam.*, **10**, 389 (1971).
- (8) Yarrington, R. M., Kay, W. B., *J. Chem. Eng. Data*, **4**, 24 (1959).

Received for review February 14, 1975. Accepted August 6, 1975. Project supported by Corporate Research and Development of General Electric.

Excess Gibbs Energies of Binary Systems of Isopentanol and *n*-Pentanol with Hexane Isomers at 25°C: Measurement and Prediction by Analytical Group Solution Model

Selim G. Sayegh and Gerald A. Ratcliff¹

Department of Chemical Engineering, McGill University, Montreal, Que., Canada

Vapor-liquid equilibrium data were measured at 25°C for binary mixtures of *n*-pentanol with each of the five hexane isomers (*n*-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane) and also for isopentanol-*n*-hexane mixtures. Measurements were made with a total pressure static equilibrium still. The analytical group solution model of Ronc and Ratcliff gave good predictions of the excess free energy for all the systems studied. The presence of branched-chain molecules in these systems had only a small effect on excess free energies, and no modification of the group solution model to allow for molecular shape was necessary.

Group solution models have been successfully employed for representing the nonideality of liquid mixtures and for predicting thermodynamic and transport properties. The development of such models, starting from the early work of Langmuir (4) to date, has been extensively reviewed elsewhere (7, 8). Such work has largely been based on experimental data for straight-chain hydrocarbons and their derivatives. This paper is concerned with the effect of branched hydrocarbon chains on solution excess properties, in this case excess free energies, and the corresponding necessity to allow for molecular shape in the group solution models.

¹ To whom correspondence should be addressed.

Virtually no suitable excess free energy data on systems containing branched chain compounds are available in the literature. Experimental measurements were therefore made at 25°C on six binary systems, consisting of binary mixtures of *n*-pentanol with each of the five isomers of hexane and of isopentanol and *n*-hexane. The specifications of the materials employed are listed in Table I. The refractive indices were measured for each of the substances and were in good agreement with values reported in the literature. The hydrocarbons and the *n*-pentanol were used as purchased, whereas the isopentanol was dried over molecular sieves as the main impurity in it (0.7%) was stated by the manufacturer to be water.

Vapor-liquid equilibrium data were measured in a total pressure static equilibrium still. Descriptions of the apparatus, experimental technique, and the computational procedure have been reported elsewhere (7, 8).

Analytical Group Solution Model

The analytical group solution model for excess Gibbs free energy developed by Ronc (7) may be summarized by the following equations:

$$\log \gamma_i = \log \gamma_i^S + \log \gamma_i^G \quad (1)$$

$$\log \gamma_i^G = \sum_k N_{ki} (\log \Gamma_k - \log \Gamma_k^*) \quad (2)$$

Table I. Materials Used as Pure Components

Material	Supplier	Grade	Purity, mol %	Refractive index @ 25°C	
				Lit (7)	This work
<i>n</i> -Hexane	PPC ^a	Pure	99.4	1.37226	1.3725
2-Methylpentane	PPC	Pure	99.2	1.36873	1.3687
3-Methylpentane	PPC	Pure	99.4 wt %	1.37386	1.3739
2,2-Dimethylbutane	PPC	Pure	99.4	1.36595	1.3662
2,3-Dimethylbutane	PPC	Pure	99.3	1.37231	1.3723
<i>n</i> -Pentanol	MCB ^b	Chromato-quality	99.79	1.4081	1.4079
<i>i</i> -Pentanol (3-methyl-1-butanol)	Fisher Scientific	Reagent	99.25 (0.7% H ₂ O)	1.4051	1.4046

^a Phillips Petroleum Co. ^b Matheson Coleman & Bell.