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Treatment of Liquid–Liquid Phase Equilibria. Hydrocarbon–Perfluorocarbon Mixtures

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Abstract: Methods are developed for treating critical miscibility and phase equilibria in binary liquid systems according to the theory of solutions presented previously. These methods are applied to the critical solution behavior of four hydrocarbon–perfluorocarbon systems as follows: methane–carbon tetrafluoride, *n*-hexane–perfluoro-*n*-hexane, *n*-heptane–perfluoro-*n*-heptane, and methylcyclohexane–perfluoromethylcyclohexane. The interaction parameter X_{12} characterizing each mixture is evaluated from the observed critical solution temperature (UCST). Critical compositions calculated according to theory agree very well with those observed. In conformity with a previous observation, the theory underestimates the large excess volumes characteristic of hydrocarbon–perfluorocarbon mixtures by a factor of 2. Excess enthalpies and excess free energies are fairly well reproduced by theory. Excellent agreement with observed enthalpies and free energies is achieved by using the observed excess volumes in place of those calculated according to theory.

A theory of solutions recently published[1] relates the thermodynamic properties of liquid mixtures to the properties of the pure components as manifested in the parameters characterizing their equations of state. The theory stems from a simple statistical mechanical model that is sufficiently versatile to permit its application to mixtures of molecules differing in size and shape. The usual "corresponding states" assumption of equivalence of the functional form of the intermolecular potentials for the several pairs of species is avoided. Excess quantities for mixtures of nonpolar molecules have been treated recently[2] on this basis. The properties of liquid *n*-alkanes and their binary mixtures were interpreted previously according to a version of the theory appropriate for homologous chain molecules.[3,4]

Parameters required for interpretation of results for binary liquid mixtures in this manner[1–4] consist of the characteristic molar volume v*, the characteristic temperature T^*, and characteristic pressure p^* for each of the components and, in addition, a single parameter X_{12} characterizing the liquid pair. The latter parameter is of the usual form for representing the difference between contact interactions of unlike and like neighbors. The characteristic quantities v*, p^*, and T^* can be determined for each liquid from equation-of-state data, *e.g.*, from the molar volume v, the thermal expansion coefficient α, and the thermal pressure coefficient γ of the pure component. The interaction parameter X_{12} may be evaluated from any of several properties of the mixture, *e.g.*, from its excess enthalpy.

In the preceding paper[2] virtually all of the binary liquid mixtures of nonpolar molecules for which adequate experimental information is available were treated according to the theory referred to. The generally favorable concurrence with experiment has encouraged further investigations of applications of the theory to the interpretation of properties of solutions. In this paper we present a general treatment of critical miscibility in binary mixtures based on this theory of solutions. The treatment is applicable to both upper and lower critical solution temperature (UCST and LCST) phenomena, and to the analysis of the binodial curves describing heterogeneous liquid equilibria in

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[1] P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
[2] A. Abe and P. J. Flory, *ibid.*, **87**, 1838 (1965).
[3] P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, **86**, 3507 (1964).
[4] P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, **86**, 3515 (1964).

the temperature–composition plane. The methods presented are applied to the UCST's and critical liquid miscibility for hydrocarbon–perfluorocarbon mixtures.

Lower critical miscibilities (LCST's) in mixtures of polyethylene with a lower *n*-alkane were considered in a previous paper.[4] Treatment of these systems was simplified by the condition $\varphi_2^c = 0$ which prevails in the limit of infinite molecular weight for the solute. The present analysis of critical miscibilities is more general, being free of restrictions to special cases. The calculations required for its application are consequently somewhat more complicated.

Theory

The Critical Solution Temperature. The chemical potential of component 1 of a binary mixture is given by

$$(\mu_1 - \mu_1{}^0) = (\mu_1 - \mu_1{}^0)_{\text{comb}} + p_1{}^*\text{v}_1{}^*\{3\tilde{T}_1 \ln [(\tilde{v}_1{}^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1{}^{-1} - \tilde{v}^{-1})\} + (\text{v}_1{}^* X_{12}/\tilde{v})\theta_2{}^2 \quad (1)$$

according to the theoretical treatment presented previously.[1] Here $(\mu_1 - \mu_1{}^0)_{\text{comb}}$ represents the combinatorial contribution. Subscripts 1 and 2 designate the components of the mixture. The characteristic and reduced quantities are specified by the use of * and ~, respectively; *viz.*, $\tilde{T} = T/T^*$, $\tilde{p} = p/p^*$, and $\tilde{v} = \text{v}/\text{v}^*$, where v is the molar volume. In accordance with previous definitions,[1,2] X_{12} is the interaction parameter characterizing the liquid pair, and θ_2 is the surface site fraction of component 2 in the mixture (see eq 23 and 16 of ref 1). Thus, the contribution of the contact interaction energy to the enthalpy of mixing is given by $N_1\text{v}_1{}^*\theta_2X_{12}/\tilde{v}$, where N_1 is the number of molecules of component 1 in the mixture, and $\tilde{v}$ is the reduced volume of the mixture (see eq 34′ of ref 1). The site fraction θ_2 is related to the hard-core volume fractions φ_1 and φ_2 according to

$$\theta_2 = \varphi_2/[(s_1/s_2)\varphi_1 + \varphi_2]$$

where s_1/s_2 is the ratio of surface sites per segment for molecules of the respective components. The analysis does not require a precise value for s_1/s_2. Hence, this quantity may be obtained with ample accuracy from estimates of the surface-to-volume ratios for the two species of molecules. It will not be treated as an adjustable parameter.

If the component molecules are globular, or nearly spherical, in form and preferably do not differ greatly in size, then the combinatorial contribution to the chemical potential may be represented by the ideal mixing expression

$$(\mu_1 - \mu_1{}^0)_{\text{comb}} = RT \ln x_1 \quad (2)$$

where x_1 is the mole fraction of component 1. If one, at least, of the components (*e.g.*, component 2) is a chain molecule, then according to polymer solution theory we have

$$(\mu_1 - \mu_1{}^0)_{\text{comb}} = RT\{\ln \varphi_1 + (1 - r_1/r_2)\varphi_2\} \quad (3)$$

where r_1 and r_2 represent the numbers of segments in the respective molecules so defined that $r_1/r_2 = \text{v}_1{}^*/\text{v}_2{}^*$.

With the aid of the reduced equation of state[1]

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \quad (4)$$

which prescribes the isobar for $p = 0$, the chemical potential given by eq 1 can be treated as a function of the temperature and composition only. The critical temperature and composition for liquid–liquid miscibility is given by the simultaneous solution of the equations

$$(\partial\mu_1/\partial\varphi_2)_{T,p} = 0 \quad (5)$$

$$(\partial^2\mu_1/\partial\varphi_2{}^2)_{T,p} = 0 \quad (6)$$

From the combinatorial part of eq 1, we find

$$(1/R)[\partial(\mu_1 - \mu_1{}^0)_{\text{comb}}/\partial\varphi_2]_{T,p} = y\tilde{T} \quad (7)$$

and

$$(1/R)[\partial^2(\mu_1 - \mu_1{}^0)_{\text{comb}}/\partial\varphi_2{}^2]_{T,p} = z\tilde{T} \quad (8)$$

where *y* and *z* are given according to eq 2 for ideal mixing by

$$y = -(x_2/\varphi_1\varphi_2)T^*$$

$$z = -[\varphi_2 - \varphi_1 + 2(x_1/x_2)\varphi_2](x_2/\varphi_1\varphi_2)^2T^*$$

and according to eq 3 for polymer solutions by

$$y = -[(\varphi_2/\varphi_1) + (x_2\varphi_1/x_1\varphi_2)]T^*$$

$$z = -\varphi_1{}^{-2}T^*$$

Differentiation of the residual[1] part of the chemical potential (*i.e.*, the second and third terms of the right-hand member of eq 1) and use of the reduced equation of state (eq 4) yields

$$(1/R)[\partial(\mu_1 - \mu_1{}^0)^R/\partial\varphi_2]_{T,p} = a/\tilde{v} + b(\alpha T)/\tilde{v} \quad (9)$$

where

$$a = 2(X_{12}\text{v}_1{}^*/R)(\theta_1/\varphi_1)(\theta_2/\varphi_2)\theta_2$$

$$b = \{(p_1{}^*\text{v}_1{}^*/R)[(T^*/T_1{}^*) - 1] + (X_{12}\text{v}_1{}^*/R)\theta_2{}^2\}[(1/T^*)(\text{d}T^*/\text{d}\varphi_2)]$$

and α is the thermal expansion coefficient of the mixture. By further differentiating we obtain

$$(1/R)[\partial^2(\mu_1 - \mu_1{}^0)^R/\partial\varphi_2{}^2]_{T,p} = f/\tilde{v} + g(\alpha T)/\tilde{v} + h(\alpha T)^2(1 + \alpha T)/\tilde{v} \quad (10)$$

where

$$f = 2(X_{12}\text{v}_1{}^*/R)(\theta_1\theta_2/\varphi_1\varphi_2)^2\{1 + 2[\varphi_2 - (\theta_2/\theta_1)\varphi_1]\}$$

$$g = [(p_1{}^*\text{v}_1{}^*/RT_1{}^*)(\text{d}T^*/\text{d}\varphi_2) + 2a][(1/T^*)(\text{d}T^*/\text{d}\varphi_2)] + b\{-2[(1/T^*)(\text{d}T^*/\text{d}\varphi_2)] + [(\text{d}^2T^*/\text{d}\varphi_2{}^2)/(\text{d}T^*/\text{d}\varphi_2)]\}$$

$$h = -(4/3)b[(1/T^*)(\text{d}T^*/\text{d}\varphi_2)]$$

From the composition dependence of the characteristic temperature for the mixture

$$(\text{d}T^*/\text{d}\varphi_2) = (T^*/p^*)\{p_2{}^*[1 - (T^*/T_2{}^*)] - p_1{}^*[1 - (T^*/T_1{}^*)] - X_{12}(\varphi_1 - \theta_2)(\theta_2/\varphi_2)\}$$

and

$$(\text{d}^2T^*/\text{d}\varphi_2{}^2) = 2(T^*/p^*)\{X_{12}(\theta_1/\varphi_1)(\theta_2/\varphi_2)^2 - [(p_2{}^*/T_2{}^*) - (p_1{}^*/T_1{}^*)](\text{d}T^*/\text{d}\varphi_2)\}$$

where

$$p^* = \varphi_1p_1{}^* + \varphi_2p_2{}^* - \varphi_1\theta_2X_{12}$$

and

$$T^* = p^*/(\varphi_1p_1{}^*/T_1{}^* + \varphi_2p_2{}^*/T_2{}^*)$$

(see eq 25 and 27 of the earlier paper[1]). Substitution of eq 7 and 9 in 5 and of eq 8 and 10 in 6, and use of the relation

$$\tilde{T}\tilde{v} = (\alpha T)/(4\alpha T + 3) \quad (11)$$

(see eq 4 above and eq 41 of ref 1) yields

$$3a + (y + 4a + 3b)(\alpha T) + 4b(\alpha T)^2 = 0 \quad (12)$$

and

$$3f + (z + 4f + 3g)(\alpha T) + (4g + 3h)(\alpha T)^2 + 7h(\alpha T)^3 + 4h(\alpha T)^4 = 0 \quad (13)$$

If all of the characteristic quantities T_i^*, p_i^*, and v_i^* are known for the respective pure components, assignment of a value to a single parameter, namely, the interaction parameter X_{12}, permits the evaluation of the quantities y, a, and b of eq 12, and of z, f, g, and h of eq 13, all referring to a given composition specified by φ_2. In other words, we have two equations for two variables, αT and φ_2. (It is possible, in principle, to employ either $\tilde{T}$ or $\tilde{v}$ in place of αT in eq 12 and 13 as a variable descriptive of temperature. However, use of αT is preferable because the final expressions obtained take simpler forms than those derived for the other variables.) The appropriate solution, $(\alpha T)^c$ and φ^c, of eq 12 and 13 may be found graphically as illustrated in Figure 1 for the n-hexane–perfluoro-n-hexane system.

Analysis of the Temperature–Composition Binodial Curve. As Hildebrand and his co-workers[5] have shown in their investigations of solubility parameters, use of liquid–liquid solubility data offers a simple means to evaluate the contact interaction parameter X_{12}, or its analog in previous theories.

Let the phases in equilibrium be designated A and B. Then

$$\mu_{1A} = \mu_{1B}$$

and

$$\mu_{2A} = \mu_{2B}$$

Introducing eq 1 for the μ_1's in the first relation and similar expressions for the μ_2's in the second, we obtain

$$(\mu_{1A} - \mu_{1B})_{\text{comb}} + p_1^* v_1^* \{3\tilde{T}_1 \ln [(\tilde{v}_B^{1/3} - 1)/(\tilde{v}_A^{1/3} - 1)] + (\tilde{v}_B^{-1} - \tilde{v}_A^{-1})\} + v_1^* X_{12}[(\theta_{2A}^2/\tilde{v}_A) - (\theta_{2B}^2/\tilde{v}_B)] = 0 \quad (14)$$

and

$$(\mu_{2A} - \mu_{2B})_{\text{comb}} + p_2^* v_2^* \{3\tilde{T}_2 \ln [(\tilde{v}_B^{1/3} - 1)/(\tilde{v}_A^{1/3} - 1)] + (\tilde{v}_B^{-1} - \tilde{v}_A^{-1})\} + v_2^* X_{12}(\varphi_{1A}/\varphi_{2A})(\theta_{2A}/\theta_{1A})[(\theta_{1A}^2/\tilde{v}_A) - (\theta_{1B}^2/\tilde{v}_B)] = 0 \quad (15)$$

By subtracting eq 15 from eq 14, we have

$$[(\mu_{1A} - \mu_{1B}) - (\mu_{2A} - \mu_{2B})]_{\text{comb}} + 3T(p_1^* v_1^*/T_1^* - p_2^* v_2^*/T_2^*) \ln [(\tilde{v}_B^{1/3} - 1)/(\tilde{v}_A^{1/3} - 1)] + (p_1^* v_1^* - p_2^* v_2^*)(\tilde{v}_B^{-1} - \tilde{v}_A^{-1}) + X_{12}\{[v_1^* \theta_{2A}^2 - (\varphi_{1A}/\varphi_{2A})(\theta_{2A}/\theta_{1A}) v_2^* \theta_{1A}^2]/\tilde{v}_A - [v_1^* \theta_{2B}^2 - (\varphi_{1B}/\varphi_{2B})(\theta_{2B}/\theta_{1B}) v_2^* \theta_{1B}^2]/\tilde{v}_B\} = 0 \quad (16)$$

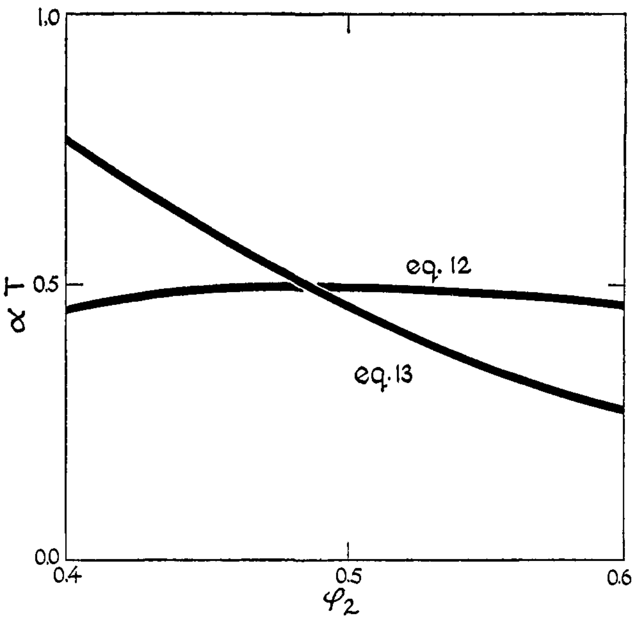

Figure 1. Curves calculated according to eq 12 and 13 for the system n-hexane–perfluoro-n-hexane with X_{12} = 13.9 cal cc^{-1}, the value which is required to match the observed UCST (*cf.* Table II).

where the combinatorial contributions are given by

$$[(\mu_{1A} - \mu_{1B}) - (\mu_{2A} - \mu_{2B})]_{\text{comb}} = RT \ln (x_{1A}x_{2B}/x_{1B}x_{2A})$$

for solutions to which the ideal combinatory entropy is applicable, and by

$$[(\mu_{1A} - \mu_{1B}) - (\mu_{2A} - \mu_{2B})]_{\text{comb}} = RT\{\ln (\varphi_{1A}\varphi_{2B}/\varphi_{1B}\varphi_{2A}) + [2 - (r_1/r_2) - (r_2/r_1)](\varphi_{2A} - \varphi_{2B})\}$$

for polymer solutions.

A successive approximation method may be used to evaluate X_{12} from eq 16. In the first approximation, additive reduced volumes $\tilde{v}_A^0$ $(= \varphi_{1A}\tilde{v}_1 + \varphi_{2A}\tilde{v}_2)$ and $\tilde{v}_B^0$ $(= \varphi_{1B}\tilde{v}_1 + \varphi_{2B}\tilde{v}_2)$ may be introduced for $\tilde{v}_A$ and $\tilde{v}_B$, respectively. The parameter X_{12} may then be calculated from the concentrations observed for the pair of phases coexisting in equilibrium at a given temperature. In the next approximation, the reduced volumes, $\tilde{v}_A$ and $\tilde{v}_B$, computed from the X_{12} thus obtained are used. Further iteration is not required, as the result converges rapidly.

Application to Hydrocarbon–Perfluorocarbon Systems

Listed in Table I are the experimental molar volumes v, thermal expansion coefficients α, and thermal pressure coefficients γ for the pure liquid components of the several binary mixtures considered. Inasmuch as the parameters v*, p^*, and T^* invariably display minor trends with temperature,[2,3] it is desirable that they be determined from values of v, α, and γ measured near the temperature of interest. To this end, the temperature selected for each pure liquid approximates that for the observed UCST of the mixture of which the liquid is a constituent.

Our method is necessarily limited to those systems for which the required equation-of-state data for the pure components are available. The scarcity of accurate data of this nature restricts its present application. The n-hexane–perfluoro-n-hexane system is the only one of the systems here considered for which all of the

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(5) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 142.

Table I. Parameters for Pure Liquids

Liquid	T, °K	v, cc mole^{-1}	$\alpha \times 10^3$, deg^{-1}	γ, cal cc^{-1} deg^{-1}	$\tilde{v}$	v*, cc mole^{-1}	T^*, °K	p^*, cal cc^{-1}	C, molecule^{-1}
CH_4	107	37.2[a]	3.29[a]	0.414[b]	1.2836	29.0	1720	73.0	0.619
CF_4	107	48.9[a]	2.59[a]	(0.58 ± 0.6)[c]	1.2331	39.7	1956	(94 ± 10)	(0.70 ± 0.08)
n-C_6H_{14}	298	131.57[d]	1.378[d]	0.194[e]	1.3203	99.65	4448	101	1.14
n-C_6F_{14}	298	202.23[f]	1.802[f]	0.150[e]	1.3917	145.32	3976	86.4	1.59
n-C_7H_{16}	323	152.31[d]	1.319[d]	0.175[g]	1.3295	114.56	4742	100	1.22
n-C_7F_{16}	323	235.1[h]	1.68[h]	0.136[i]	1.3946	168.6	4292	85.4	1.69
c-$CH_3C_6H_{11}$	319	131.57[j]	1.178[j]	0.204[k]	1.2988	101.30	4965	110	1.13
c-$CF_3C_6F_{11}$	319	202.6[l]	1.64[l]	0.152[m]	1.3843	146.4	4299	92.9	1.59

[a] I. M. Croll and R. L. Scott, *J. Phys. Chem.*, **62**, 954 (1958). [b] J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworths Publications, Ltd., London, 1959, p 56. [c] Estimated from the solubility parameter ($\delta = 7.6$ cal$^{1/2}$ cc$^{-1/2}$ at 110°K) reported by N. Thorp and R. L. Scott, *J. Phys. Chem.*, **60**, 670 (1956), by assuming the validity of the semiempirical relation between internal pressure and cohesive energy density $T\gamma \cong (\partial E/\partial V)_T = n(\Delta E^v/V)$, with $n = 1.1 \pm 0.1$ as found by Hildebrand and Scott ref 5, Chapter 6. [d] "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 29. [e] R. D. Dunlap and R. L. Scott, *J. Phys. Chem.*, 66, 631 (1962). [f] R. D. Dunlap, C. J. Murphy, Jr., and R. G. Bedford, *J. Am. Chem. Soc.*, **80**, 83 (1958). [g] Estimated by extrapolation from experimental thermal pressure coefficients reported between 19 and 36° by W. Westwater, H. W. Frantz, and J. H. Hildebrand, *Phys. Rev.*, **31**, 135 (1928). Thermal pressure coefficients calculated from the available compressibility data from various sources fall within ±2% of this value: ref 3, Table I. [h] Calculated from the equation ρ (g cc^{-1}) = 1.7892 − 0.00277t, derived from the density value 1.72006 g cc^{-1} measured at 25° by D. N. Glew and L. W. Reeves, *J. Phys. Chem.*, **60**, 615 (1956), and the temperature coefficient -2.77×10^{-3} g cc^{-1} deg^{-1} reported between 20 and 30° and between 25 and 45°, respectively, by G. D. Oliver, S. Blumkin, and C. W. Cunningham, *J. Am. Chem. Soc.*, **73**, 5722 (1951), and by T. M. Reed, III, and T. E. Taylor, *J. Phys. Chem.*, **63**, 58 (1959); T. M. Reed, III, "Fluorine Chemistry," Vol. V, J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1964, p 162. [i] Estimated by extrapolation of thermal pressure coefficients reported between 14 and 42° by E. B. Smith and J. H. Hildebrand, *J. Chem. Phys.*, **31**, 145 (1959). Thermal pressure coefficients calculated from sound velocity measurements between 20 and 60° by R. T. Lagemann, W. E. Woolf, J. S. Evans, and N. Underwood, *J. Am. Chem. Soc.*, **70**, 2994 (1948), with the aid of heat capacity data reported by R. M. Yarrington and W. B. Kay, *J. Phys. Chem.*, **61**, 1259 (1957), are about 10% lower than the Smith–Hildebrand values throughout the temperature range studied. [j] L. Massart, *Bull. Soc. Chim. Belges*, **45**, 76 (1936). [k] Estimated from the thermal pressure coefficient at 25° deduced from compressibility measurements by K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.*, **65**, 183 (1961), assuming a temperature coefficient $(\partial\gamma/\partial T)$ similar to that for cyclohexane (see Table I of ref 2). The γ value estimated from sound velocity and its temperature coefficient reported at room temperature by W. Schaaffs, *Z. Physik. Chem.*, **194**, 28 (1944), is lower by about 2% at 46°. The heat capacity data required in the latter estimation were taken from G. S. Parks, H. M. Huffman, and B. Thomas, *J. Am. Chem. Soc.*, **52**, 1032 (1930), and D. R. Douslin and H. M. Huffman, *ibid.*, **68**, 173, 1704 (1946). [l] R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, 603 (1951). [m] Estimated by extrapolation of the thermal presssure coefficients obtained between 13 and 41° by Smith and Hildebrand (footnote *i*) and also from sound velocity measurements between 20 and 60° by Lagemann, *et al.* (footnote *i*), with the aid of the heat capacity data reported by Yarrington and Kay (footnote *i*). The mean of these estimates was chosen.

primary parameters have been determined with satisfactory accuracy in the vicinity of the critical solution temperature. For other systems, it has been necessary to obtain at least one of the primary parameters by extrapolation from measurements at lower temperatures. The thermal pressure coefficient of carbon tetrafluoride was estimated from its energy of vaporization (see footnote *c* of Table I) and hence is subject to a larger error than for other entries in Table I.

As is well known, the molar volumes of the perfluorocarbons exceed those for the corresponding hydrocarbon analogs (see Table I). The thermal expansion coefficient of carbon tetrafluoride is less than that of methane, but its thermal pressure coefficient (estimated; see Table I) exceeds that of methane. For all of the other hydrocarbon–perfluorocarbon pairs, both α and γ display the reverse order; that is, the fluorocarbon has the larger thermal expansion coefficient and the smaller thermal pressure coefficient.

Reduced volumes, $\tilde{v}$, and characteristic quantities, v*, T^*, and p^*, all computed from the aforementioned experimental data according to the procedure described in previous papers,[2,3] are included in Table I. The parameter $C = p^*\text{v}^*/RT^*$, which is identified in the theory as one-third of the number of external degrees of freedom of a molecule, is given in the last column. For the perfluorocarbons other than CF_4, the value of C considerably exceeds unity.[2] For the corresponding hydrocarbons, C is only slightly greater than unity.

Values of the interaction parameter X_{12} found through solution of eq 12 and 13 by trial to give agreement with the observed UCST's are recorded in Table II. The hard-core volume ratio $r_1/r_2 = \text{v}_1^*/\text{v}_2^*$ and the ratio of the surface contact sites s_1/s_2 needed for the calculations are given in the third and fourth columns. In accordance with the procedure adopted in the previous investigation,[2] molecules such as CH_4, CF_4, c-$CH_3C_6H_{11}$, and c-$CF_3C_6F_{11}$ have been treated as spheres, and the n-alkanes and perfluoro-n-alkanes as right cylinders for the purpose of assigning approximate values to s_1/s_2. Computations for all of the systems were carried out using the expressions for y and z given above for ideal mixing contributions from the combinatorial entropy. None of the components departs markedly from spherical form, and the ratio r_2/r_1 of the hard-core molar volumes v* does not exceed 1.5 for any pair. Hence, the ideal solution approximation for $(\mu_1 - \mu_1^0)_{\text{comb}}$ should be ligitimate. Critical compositions calculated from the values of X_{12} given in the fifth column are presented in the sixth column of Table II, where they may be compared with observed values in the last column.

Molar excess volumes v^{E}, heats of mixing H^{E}, and excess free energies G^{E} for equimolar mixtures, calculated[2] from the parameters given above, are compared in Table III with the experimental values found at temperatures in the neighborhood of the UCST's. The excess free energies G^{E} have been included for completeness; the comparison of calculated with observed values does not offer a critical test of theory, however, owing to proximity to the critical temperature where G^{E} tends to be of the order of $RT/2$.

CH_4–CF_4. All characteristic quantities used in the calculations were estimated at a temperature slightly

Table II. Interaction Parameters X_{12} Calculated from the Observed UCST's and Comparison of Calculated and Observed Critical Compositions

System 1, 2	UCST obsd, °K	r_1/r_2	s_1/s_2	X_{12}, cal cc^{-1}	Critical composition x_2(crit) Calcd	Obsd
CH_4, CF_4	94.5[a]	0.730	1.11	14.0	0.43	0.43[a]
n-C_6H_{14}, n-C_6F_{14}	295.9[b]	0.686	1.16	13.9	0.392	0.370[b]
n-C_7H_{16}, n-C_7F_{16}	323.2[c]	0.679	1.16	13.3	0.394	0.356[c]
c-$CH_3C_6H_{11}$, c-$CF_3C_6F_{11}$	319.0[d]	0.692	1.13	14.2	0.385	~0.40[d]

[a] Croll and Scott, footnote *a*, Table **I**. [b] R. G. Bedford and R. D. Dunlap, *J. Am. Chem. Soc.*, **80**, 282 (1958). [c] J. H. Hildebrand, B. B. Fisher, and H. A. Benesi, *ibid.*, **72**, 4348 (1950); B. G. Kyle and T. M. Reed, III, *ibid.*, **80**, 6170 (1958). [d] D. E. L. Dyke, J. S. Rowlinson, and R. Thacker, *Trans. Faraday Soc.*, **55**, 903 (1959).

Table III. Comparison of Calculated and Observed Excess Thermodynamic Quantities for Equimolar Mixtures

System 1, 2	T, °K	V^E, cc mole^{-1} Calcd	Obsd	H^E, cal mole^{-1} Calcd	Obsd	G^E, cal mole^{-1} Calcd	Obsd
CH_4, CF_4	107	0.39	0.88[a]	116		90	86[b]
n-C_6H_{14}, n-C_6F_{14}	298	2.33	4.84[c]	416	516[d]	288	325[d,e]
n-C_7H_{16}, n-C_7F_{16}	323	2.7	5.7[f,g]	460		314	313[f]
c-$CH_3C_6H_{11}$, c-$CF_3C_6F_{11}$	319	1.8	7.3[h]	428	670[h]	309	331[h]

[a] Croll and Scott, footnote *a*, Table I. [b] Observed at 110.5°K by Thorp and Scott, footnote *c*, Table I. [c] Bedford and Dunlap, footnote *b*, Table II. [d] A. G. Williamson and R. L. Scott, *J. Phys. Chem.*, **65**, 275 (1961). [e] R. D. Dunlap, R. G. Bedford, J. C. Woodbrey, and S. D. Furrow, *J. Am. Chem. Soc.*, **81**, 2927 (1959). [f] R. L. Scott, *J. Phys. Chem.*, **62**, 136 (1958). [g] T. M. Reed, III, "Fluorine Chemistry," Vol. V, J. H. Simons, Ed. Academic Press Inc., New York, N. Y., 1964, Chapter 2, p 215. [h] Observed at 65° by Dyke, *et al.*, footnote *d*, Table II.

higher than the observed UCST (94.5°K) of the system. The effect of this difference of temperature on the characteristic parameters does not exceed the experimental error, however. Alteration of γ for CF_4 by ±10% from the value quoted in Table I does not affect the value of X_{12} significantly. This insensitivity to γ is a consequence of the small values of αT and $(1/T^*)(dT^*/d\varphi_2)$, *ca.* 0.3 and 0.2, respectively, in the vicinity of the UCST. It follows that terms beyond the first in eq 9 and 10 contribute little. The first terms in these equations do not depend on the characteristic pressure p^*, and hence on γ, apart from the small dependence of the reduced volume $\tilde{v}$ on p^*. The approximation involved in the estimation of γ for CF_4 therefore has little effect.

It is to be noted that higher terms in eq 9 and 10 and the corresponding terms in eq 12 and 13 assume greater importance in the vicinity of lower critical solution temperatures (LCST's). These often occur at temperatures approaching the vapor–liquid critical temperature of one of the components; hence αT is large.

Agreement between theory and experiment is satisfactory for the critical concentrations (Table II) and excess free energies (Table III). The calculated excess volumes, however, are about half of those observed. Changes of ±10% in γ for CF_4 alter the calculated excess volumes by about ±0.1 cc mole^{-1}. The heat of mixing and excess free energy are affected negligibly (<1 cal mole^{-1}).

n-C_6H_{14}–n-C_6F_{14}. This system has been studied in detail by Dunlap, Scott, and their co-workers,[6] who reported excess volumes, heats of mixing, excess free energies, and critical solution properties. Thermal pressure coefficients for both pure liquids are also taken from their publication.[7]

The result X_{12} = 13.9 cal cc^{-1} (Table II) calculated from the critical solution temperature in conjunction with the equation-of-state parameters for the components is 18% lower than the value, 17.0 cal cc^{-1}, calculated previously[2] from the experimental enthalpy of mixing at 308°K and the equation-of-state parameters. Adoption of the latter value for X_{12} yields a calculated UCST higher by 40° than that observed. The effect on the critical composition (−0.01 in φ_2^c) is insignificant.

The discrepancy of about 20% between the calculated and observed heats of mixing (see Table III) appears to be related to the low estimate of the excess volume (48% of the observed value). Use of the observed reduced volume $\tilde{v}_{obsd}$ = 1.4021 in place of $\tilde{v}_{calcd}$ = 1.3816 in eq 34 of ref 1 increases the "equation-of-state" contribution to the calculated heat of mixing from 137 to 256 cal mole^{-1}. The net increase of 119 cal mole^{-1} raises the calculated heat of mixing to 535 cal mole^{-1} in virtual agreement with observation.

The calculated excess free energy agrees reasonably well with that observed (Table III). As may be seen from the expression for G^R ($\equiv G^E$ since the combinatory entropy is taken to be ideal) given by eq 37 of ref 1, the excess free energy depends strongly on the contact interaction term but varies little with the reduced volume. Use of $\tilde{v}_{obsd}$, coupled with X_{12} = 13.9 cal cc^{-1}, in the aforementioned equation yields G^E (calcd) = 290 cal mole^{-1}, which differs insignificantly from the value, 288 cal mole^{-1}, given in Table III.

The observed miscibility data[8] for this system provide an alternative basis for evaluation of X_{12} through use of eq 16. Thus, from the observed compositions of the equilibrium at 20° and at 15° we find X_{12} = 14.6 cal cc^{-1} at 293°K and 15.2 cal cc^{-1} at 288°K. These values are only slightly greater than the one obtained from the observed critical solution temperature. It follows that the form of the temperature–composition binodial defined by experiment is also consistent with the present theory.

n-C_7H_{16}–n-C_7F_{16}. Although the difference between the calculated and observed critical composition for this system is the largest among those included in Table II, the discrepancy amounts to only 0.04 in x_2^c. The behavior of this mixture resembles that for the n-hexane–

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(6) See Table III, footnotes *c*, *d*, and *e*.
(7) See Table I, footnote *e*.
(8) See Table III, footnote *c*.

perfluoro-*n*-hexane system, according to the data presented in Table III.

c-$CH_3C_6H_{11}$–c-$CF_3C_6F_{11}$. In the previous paper a value of 21.5 cal cc^{-1} for the interaction parameter X_{12} was deduced from the observed heat of mixing for this system at 338°K. The value, 14.2 cal cc^{-1}, given in Table II is lower by 34%. Calculated excess quantities are compared in Table III with those observed at the somewhat higher temperature, 338°K: The use of $\tilde{v}_{obsd}$ in place of $\tilde{v}_{calcd}$ in eq 34 and 37 of ref 1 raises the "equation-of-state" contributions to H^E and G^E by 285 and 18 cal $mole^{-1}$, respectively. The thus calculated excess enthalpy, 713 cal $mole^{-1}$, compares favorably with the value observed. Hence, as has been found for the *n*-hexane–perfluoro-*n*-hexane mixture, the discrepancy between observed and calculated excess enthalpies appears to be related to the inaccuracy of the theory in its representation of the excess volumes for hydrocarbon–perfluorocarbon mixtures.

The Berthelot Relationship. Failure of the Berthelot geometric mean rule for hydrocarbon–fluorocarbon and related systems has been pointed out by Clegg, Rowlinson, and Sutton,[9] and by Scott.[10] The comparison of present results with those calculated from the Berthelot relationship

$$\Delta\eta/\eta_{11} = [1 - (\eta_{22}/\eta_{11})^{1/2}]^2 = X_{12}/p_1^*$$

is presented in Table IV, which corresponds to Table IV of the previous paper[2] for the systems there considered.

Table IV. Comparison of Interaction Parameters Calculated from the Berthelot Relation with Those Observed

System 1, 2	T, °K	$\eta_{22}/\eta_{11} = (s_1p_2^*/s_2p_1^*)$	$\Delta\eta/\eta_{11} = X_{12}/p_1^*$		η_{12}(obsd)/η_{12}(calcd)
			Calcd $\times 10^3$	Obsd $\times 10^3$	
CH_4, CF_4	94.5	1.43	38	192	0.94
n-C_6H_{14}, n-C_6F_{14}	296	0.99	0	138	0.93
n-C_7H_{16}, n-C_7F_{16}	323	0.99	0	133	0.93
c-$CH_3C_6H_{11}$, c-$CF_3C_6F_{11}$	319	0.95	1	129	0.93

Values of the interaction parameter X_{12} calculated in this manner and scaled by the factor $1/p_1^*$ are given in the fourth column of Table IV; the same quantities deduced from experimental results as detailed above are given in the fifth column. Shown in the third column are the ratios η_{22}/η_{11}. The interaction parameter η_{11} for the hydrocarbon component is slightly greater than η_{22} for all systems with the exception of CH_4–CF_4, for which η_{11} exceeds η_{22} by a considerable margin. The gross inadequacy of the Berthelot geometric mean rule as applied to these systems is apparent from comparison of columns four and five of Table IV. Observed and calculated parameters η_{12} are compared in the sixth column. Those *observed* are consistently lower by 6–7% than the geometric mean values, $\eta_{12}(\text{calcd}) = \sqrt{\eta_{11}\eta_{22}}$.

Concluding Remarks

The theory of solutions[1] employed in the present paper for the interpretation of phase equilibria was shown previously[2] to reproduce observed excess volumes v^E for various binary mixtures of simple, nonpolar molecules with remarkable accuracy. Its representation of the excess entropies although less satisfactory was favorable. The only significant exceptions to these generalizations were found to occur for hydrocarbon–perfluorocarbon systems. For these the excess entropies were well reproduced, whereas the excess volumes were considerably underestimated. The present investigation confirms and extends these observations.

The most striking achievement of the theory here presented is the remarkably accurate prediction of critical compositions for the four systems investigated. The calculated compositions are insensitive to the precise value of the interaction parameter. They are determined principally by the ratio r_1s_1/r_2s_2. The approximate form of the binodial curve in the heterogeneous region of thetemperature–composition diagram appears to be in accord with theory, as judged by the application of eq 16 to the hexane–perfluorohexane system. More detailed comparisons of theory with experimental binodials for various systems clearly should be carried out.

Self-consistent treatment of a binary mixture with limitation to only one arbitrary parameter (X_{12}) for that mixture dictates use of the calculated excess volume in the deduction of other properties from the theory. Since the hydrocarbon–fluorocarbon mixtures are exceptional in the disparity between calculated and observed excess volumes, calculations carried out using the observed excess volumes seemed nevertheless to be of interest. Excess enthalpies calculated on this basis for the second and fourth mixtures in Table III differ from those observed by only a few per cent. A close connection between the enthalpy of mixing at constant pressure and the volumetric properties of mixtures is apparent.[1–4]

The interaction parameters X_{12} for the four hydrocarbon–fluorocarbon systems are virtually identical (Table II). This observation confirms the significance of X_{12} as a measure of intermolecular interaction energies for the groups involved, without reference to the molecules of which they are a part. It further indicates that the theory takes satisfactory account of equation-of-state contributions, which otherwise would affect the apparent numerical value of the contact interaction term.

In quest of an explanation for the exceptionally large excess volumes exhibited by the hydrocarbon–fluorocarbon mixtures, we note first that the parameter C, which ostensibly represents one-third of the number of intermolecular degrees of freedom, is on the order of 1.5 for the fluorocarbons other than CF_4 compared with 1.0 to 1.2 for other simple molecules,[2] including the hydrocarbons other than methane. This departure may reflect a difference in liquid structure which could conceivably account for the behavior peculiar to mixtures in which one of the components is a fluorocarbon. On the other hand, CF_4 does not display a large value of C, yet it conforms with other

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[9] H. P. Clegg, J. S. Rowlinson, and J. R. Sutton, *Trans. Faraday Soc.*, 51, 1327 (1955).

[10] See Table III, footnote *f*.

fluorocarbons in exhibiting a much larger excess volume than is predicted by theory.[11]

Alternatively, the discrepancies noted may be related to the large positive values of X_{12} for the hydrocarbon–perfluorocarbon systems. Thus, the theory may become inaccurate when applied to *any* system for which X_{12} is large. In opposition to this hypothesis, it is to be observed that the previous investigations of solutions[2] offer no intimation of a disparity between observed and calculated excess volumes which increase with X_{12}.

Among nonpolar mixtures for which adequate equation-of-state data for the pure components are available, the hydrocarbon–perfluorocarbon systems appear unfortunately to be unique in being characterized by large positive interactions X_{12}. It is difficult therefore to reach a decision between alternative explanations attributing the error in the calculated excess volumes to a peculiarity of the fluorocarbons on the one hand or to the large values of X_{12} for their mixtures with hydrocarbons on the other. Detailed experimental studies on systems exhibiting LCST's would be informative in this connection.

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(11) An inverse dependence of the intermolecular energy E_0 on the volume V has been assumed in the derivation[1,3] of eq 1. If instead we write $E_0 = -\text{constant}/V^m$ with $m > 1$ (*ca.* 1.3 for n-C_6H_{14}–n-C_6F_{14}), the calculated excess volume is increased and values calculated for other excess quantities also are brought into better agreement with observation. The parameter C, then given by $C = (\gamma v/R)/[1 + 3m + 3/\alpha T]$, is diminished somewhat as well. However, representation of the equation of state for both the fluorocarbon and the hydrocarbon components is rendered less satisfactory by such revision, which would also entail introduction of an additional parameter. For these reasons we have not made use of this device.

A Kinetic Study of the Photochemical Reaction of Phenanthrenequinone with Olefins

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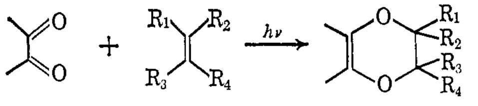
Abstract: Quantum yields at 405 mμ for the addition of phenanthrenequinone to stilbene, diphenylethylene, and triphenylethylene in benzene solution are independent of the olefin concentration over a wide range but vary with the structure of the olefin. *cis*-Stilbene and *trans*-stilbene react at different rates but give rise to a common product. This reaction is accompanied by *cis–trans* isomerization for which $\Phi_{CS\rightarrow TS} \approx \Phi_{TS\rightarrow CS}$. The system reaches a stationary *trans/cis* isomer ratio of 0.7 ± 0.05, which is close to that reported for some photostable, high-energy sensitizers, but which in this case represents a balance between the rates of isomerization and adduct formation. Measurements with α,α'-stilbene-d_2 indicate a kinetic isotope effect for adduct formation. The results are consistent with the formation of the spectroscopic triplet state of *trans*-stilbene by classical energy transfer and of a short-lived common association complex between triplet quinone and the *cis*- or *trans*-olefin, which is partitioned between decay to a nonspectroscopic excited state and collapse to adduct. The intersystem-crossing efficiency for phenanthrenequinone is inferred to be unity.

Phenanthrenequinone (PAQ) adds photochemically to olefins. This is a general reaction for certain 1,2-diketones which was first reported by Schönberg and Mustafa[1] and which has been carried out on a preparative basis with a large number of olefins. The reaction yields adducts of structure I (eq 1). It was established by Pfundt and Schenck that only excitation of PAQ leads to adduct I; separate excitation of the olefin produces no conversion of PAQ.[2,3] On the basis of limited kinetic measurements, these authors propose a mechanism in which an excited state of PAQ forms a biradical intermediate with the olefin. Adduct is postulated to result from the interaction of this intermediate with a second, ground-state PAQ molecule.[3]



(1)

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PAQ has a triplet energy of 48.8 kcal/mole,[4] and it was anticipated and found that, with the stilbenes, adduct formation is accompanied by *cis–trans* isomerization. Sensitized olefin isomerization is well documented, but the detailed mechanism of this process can by no means be regarded as established.[5] The question arises as to whether there is a relation between adduct formation and isomerization and whether, in general, olefin-sensitizer intermediates participate in the isomerization brought about by low-energy sensitizers. The detailed kinetic study of the reaction of PAQ with stilbene and with two other phenyl-substituted ethylenes was undertaken to firmly establish a mechanism for the addition reaction and to shed light on the role of

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(1) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 387 (1944).

(2) G. O. Schenck, O. Neumüller, and R. Koch, *Strahlentherapie*, **114**, 22 (1961).

(3) G. Pfundt, Doctoral Dissertation, Göttingen, 1962.

(4) This value was obtained from the emission spectra of PAQ in aliphatic hydrocarbons at 77°K; *cf.* N. A. Shcheglova, D. N. Shigorin, and M. V. Gorelik, *Zh. Fiz. Khim.*, **39** (4), 893 (1965).

(5) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964). This paper cites earlier references.