Thermodynamic Properties of Binary Mixtures of 1-Hexyne and Polar Organic Solvents

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Vapor-liquid equilibrium data for polar solvent-hydrocarbon mixtures are relatively plentiful for *paraffins and aromatics; they are somewhat less plentiful for olefins.* However, almost no data at all have been published for such mixtures wherein the hydrocarbon possesses a triple bond. This paper reports vapor-pressure measurements of binary mixtures of 1-hexyne with acetone, acetonitrile, dimethyl carbonate, nitroethane and dimethyl formamide in the temperature range 0 to 70°C. The results are compared with those for polar solvent-hydrocarbon mixtures *wherein the hydrocarbon is paraffinic, olefinic, or aromatic.*

Many experimental thermodynamic data have been obtained for mixtures of paraffins, olefins, and aromatics with polar organic solvents; a recent correlation of such data has been given by Weimer (*1*), who developed a technique for estimating activity coefficients of hydrocarbons at infinite dilution in polar organic solvents.

However, aside from solubility data for acetylene in various liquids, there are essentially no thermodynamic data for solutions of acetylenic hydrocarbons and organic solvents. Such thermodynamic data are of interest for immediate application to practical engineering problems, and for physicochemical understanding of the specific interaction which occurs between the π-electron system of the triple-bonded carbon atoms and the functional groups of the polar organic solvents.

In the present work, low-pressure vapor-liquid equilibrium data have been obtained in the range 0 to 70°C. for five binary systems: 1-hexyne with acetone, acetonitrile, dimethyl carbonate, nitroethane, and N,N-dimethyl formamide.

EXPERIMENTAL PROCEDURE

Vapor-liquid equilibria for the five systems studied were measured by the static method; the advantages and disadvantages of this method have been discussed by Scatchard and co-workers (*2*). A detailed description of the apparatus has been given previously (*3*); only a brief summary, along with minor modifications in equipment and technique, is presented here.

A schematic diagram of the apparatus is shown in Figure 1. The pure components were completely degassed in magnetically stirred stills by intermittently cooling and evacuating. Samples of each component were then transferred by freezing with liquid nitrogen into the all glass vapor-liquid equilibrium cell and isolated by a Teflon-seated bellows valve. Graded glass-metal seals joined valve and glass tubing. A thermocouple vacuum gauge, located in the transfer line, conveniently indicated that the pure components were well degassed; if properly degassed, the cell pressure decreased to a negligibly small value when transfer was interrupted by closing the stopcock located in the transfer line.

Following transfer, the cell was gradually warmed and thermostated (±0.01°C.) while approximately balancing the small mercury null-manometer with a reference pressure system. The sample was magnetically stirred to hasten equilibration which required less than 1 hr. Reference system pressure was measured with a Texas Instruments fused-quartz pressure gauge, periodically standardized against a mercury manometer. Null-manometer imbalance was measured with a Wild Heerbrugg cathetometer. To minimize meniscus effects the small-bore null-manometer used by previous workers (*3*, *4*) was replaced by the 18 mm. I.D. manometer shown in Figure 1. Replicate pressure readings were made until they consistently agreed to within ±0.04 mm. The pressure measurements (tabulated elsewhere) are given in mm mercury reduced to 0°C. and standard gravity and are the average of several readings.

Following measurements at the lowest temperature, the thermostat temperature was raised and measurements were repeated at the desired higher temperatures. Finally, the sample was transferred into the collection cell by freezing, and weighed. Again, the thermocouple vacuum gauge indicated when transfer was complete.

Samples were analyzed in triplicate with an Aerograph 1520 chromatograph. Although analysis of known samples indicated accuracy to be better than 0.3%, in most cases the largest experimental uncertainty was associated with the analysis.

Components of the highest purity commercially available were used in this work. In each case they were distilled at high reflux in a 10-plate Oldershaw column. Several cuts were analyzed by chromatography, and only those fractions of highest purity were used in the experimental work. These fractions were dried over Linde 3A molecular sieves and used immediately; however, since acetone reacts with common drying agents (*5*), it was used immediately following distillation. Pure-component properties are given in Table 1.

TABLE 1. PURE-COMPONENT PROPERTIES

Component	T, °C.	Vapor pressure, mm. mercury obs.	Vapor pressure, mm. mercury lit.	Refractive index, n_D^{25} obs.	Refractive index, n_D^{25} lit.
1-hexyne	71.3	760.0	760.0	1.3962	1.3957
acetone	45	511.4	511.8	1.3562	1.3563
acetonitrile	45	208.26	208.32	1.3417	1.3416
dimethyl carbonate	45	139.58	139.73	1.3665	1.3670
nitroethane	45	57.82	57.89	1.3899	1.3894
N,N-dimethyl formamide	70	42.24	41.0-42.1	1.4281	1.4269

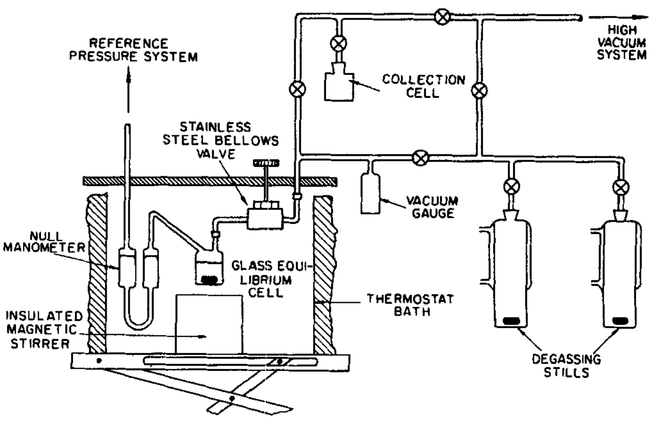

Fig. 1. Total pressure apparatus.

DATA REDUCTION

The total pressure-composition data were reduced to obtain excess Gibbs energies by a numerical technique similar to that initially described by Barker (6). The technique, based on the Gibbs-Duhem equation, is briefly outlined below.

For each isotherm, initial values were assumed for the parameters A, B, C, ... in a particular expression for the molar excess Gibbs energy, g^E:

$$n_T g^E = f(A, B, C, \ldots, n_1, n_2) \tag{1}$$

Activity coefficients were computed from Equation (1) according to

$$RT \ln \gamma_i = \left(\frac{\partial\, n_T g^E}{\partial n_i} \right)_{T,P,n_j \neq n_i} \tag{2}$$

where n_T is the total number of moles in solution, n_i is the number of moles of component i, R is the gas constant, and T is the absolute temperature. For thermodynamic consistency, Equation (1) must satisfy the Gibbs-Duhem relation:

$$\sum_i n_i \, d \ln \gamma_i = 0 \tag{3}$$

A calculated total pressure P of the binary mixture at a given composition was computed by

$$P_{\text{calc}} = \frac{x_1 \gamma_1 f_1^o}{\varphi_1} + \frac{x_2 \gamma_2 f_2^o}{\varphi_2} \tag{4}$$

where x_i is the liquid mole fraction, φ_i is the vapor-phase fugacity coefficient, and f_i^o is the reference fugacity of component i. The reference fugacity is given by the product of the saturation (vapor) presure P_i^s, the fugacity coefficient at saturation φ_i^s, and the Poynting correction:

$$f_i^o = P_i^s \varphi_i^s \exp\left[v_i (P - P_i^s)/RT\right] \tag{5}$$

For each component, the vapor composition y_i is given by

$$y_i = \frac{x_i \gamma_i f_i^o}{P \varphi_i} \tag{6}$$

Vapor-phase fugacity coefficients, φ_i, were calculated from the correlation of O'Connell (6); they deviated only slightly from unity.

For each isotherm, the squared deviations

$$\left(\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right)^2$$

corresponding to each experimental composition were found, and a nonlinear regression on the parameters A, B, C, ... was carried out to minimize the sum of squared deviations. This procedure was necessarily iterative, and calculations were carried out on a high-speed computer.

Since the vapor space was small, the true liquid-phase composition, x_i, was essentially the same as the measured composition; however, small corrections were applied to account for changes in liquid composition due to vaporization. A more detailed discussion of the calculation techniques has been given elsewhere (7).

RESULTS

The experimental data were fitted using several algebraic expressions for f in Equation (1); representative results are shown in Table 2. Of the two-parameter expressions, the best fit was given by the Wilson equation; however, significant improvement in each case was obtained by using the three-parameter Redlich-Kister expression. Best-fit constants for the three-parameter Redlich-Kister equation are given in Table 3 for each system, along with standard percent deviation of $\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{calc}}}$ and limiting activity coefficients, γ_2^∞, for 1-hexyne at infinite dilution in each solvent. Figure 2 shows observed and calculated total pressures for a typical isotherm for the 1-hexyne-acetonitrile system.

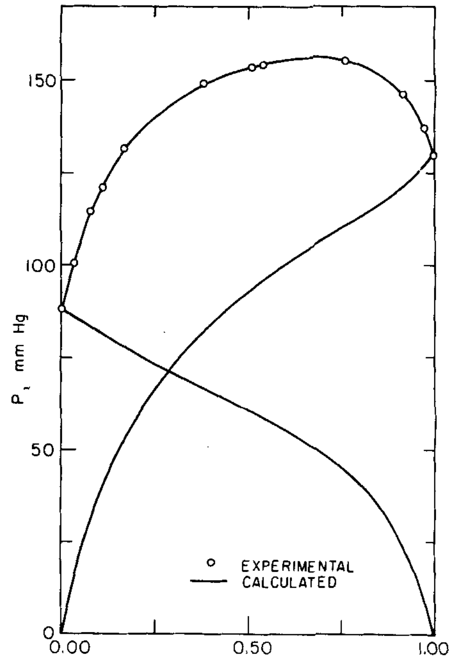

Fig. 2. Total and partial pressures of acetonitrile (1)-1-hexyne (2) at 25°.

Calorimetric heat-of-mixing data have been reported by Anderson, et al. (8) for the 1-hexyne-nitroethane system; their results along with excess Gibbs energy and corresponding excess entropy are shown in Figure 3. Heat of mixing can also be found by differentiation of excess Gibbs energy with respect to temperature:

$$h^E = -T^2 \left[\frac{\partial \frac{g^E}{T}}{\partial T} \right]_{P,n_1,n_2} \tag{8}$$

TABLE 2. COMPARISON OF EQUATIONS FOR EXCESS GIBBS ENERGY SYSTEM 1-HEXYNE(2)—ACETONITRILE(1), 25°C.

Equation	Standard deviation in P, %
Redlich-Kister (2-Parameter):	
$\frac{g^E}{RT} = x_1 x_2 [a + b(x_1 - x_2)]$	1.10
van Laar:	
$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\alpha}{x_1 + \beta x_2} \right)$	1.10
Wilson:	
$\frac{g^E}{RT} = -x_1 \ln (x_1 + \Lambda_{12} x_2)$ $- x_2 \ln (x_2 + \Lambda_{21} x_1)$	0.71
Redlich-Kister (3-Parameter):	
$\frac{g^E}{RT} = x_1 x_2 [a + b(x_1 - x_2) + c(x_1 - x_2)^2]$	0.35

Table 3*. Excess Gibbs Energies for Mixtures of Organic Solvents(*1*) and 1-Hexyne(2)

$$\frac{g^E}{RT} = x_1 x_2 \left[a + b(x_1 - x_2) + c(x_1 - x_2)^2\right]$$

Solvent	T, °C.	a	b	c	Standard % deviation in $\left(\frac{P_{exp} - P_{calc}}{P_{exp}}\right)$	γ_2^∞
acetone	0	0.44329	—0.12173	0.14460	0.31	1.59
	25	0.47461	—0.10345	0.08405	0.16	1.58
	55	0.48607	—0.14660	0.41358	0.43	1.46
acetonitrile	0	1.42131	—0.08275	0.23530	0.37	4.8
	25	1.34348	—0.08470	0.22165	0.35	4.4
	55	1.25026	—0.16128	0.19418	0.71	3.6
dimethyl carbonate	5	0.53873	0.04106	0.02879	0.17	1.84
	25	0.50222	0.03111	0.01169	0.08	1.73
	55	0.49805	—0.00352	0.08194	0.21	1.78
nitroethane	25	1.06437	—0.11747	0.08261	0.51	2.8
	45	1.03985	—0.15427	0.11293	0.43	2.7
	70	0.97327	—0.13879	0.08446	0.47	2.5
N,*N*-dimethyl formamide	45	0.85194	—0.24867	0.13018	1.42	2.1
	70	0.86230	—0.23011	0.11200	1.18	2.1

* Detailed P-T-x data are to be tabulated in: H. G. Harris, dissertation, University of California, Berkeley.

For the four systems in which data were taken at three temperatures, differentiation was performed at mid-temperature of a parabolic fit of excess Gibbs energy versus temperature. Results of this calculation for each of the four systems are given in Table 4. Considering the large uncertainty introduced by differentiation, the 95 cal./g. mole value for 1-hexyne-nitroethane compares favorably with the more precise calorimetric measurements of Anderson, et al., who find the mid-concentration heat of mixing to be about 130 cal./g. mole.

Table 4. Heats of Mixing from Excess Gibbs Energies

Solvent	h^E, cal./g.mole at $x = 0.5$
acetone	− 40
acetonitrile	135
dimethyl carbonate	50
nitroethane	95

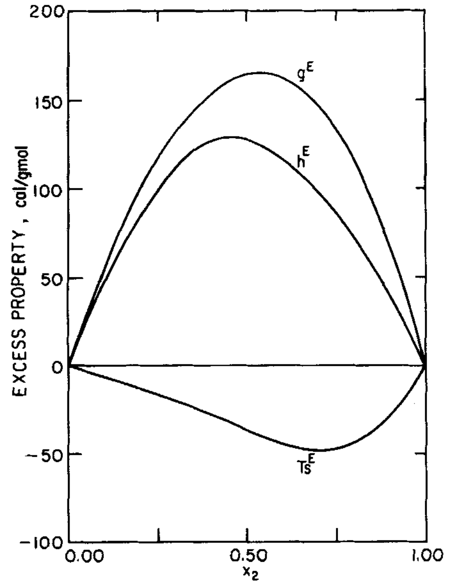

Fig. 3. Thermodynamic excess properties of nitroethane (*1*)-1-hexyne (2) at 45°C.

DISCUSSION

Since extraction processes most frequently operate with excess solvent, a comparison of the limiting activity coefficients of hydrocarbons at infinite dilution in the solvent gives a relevant measure of solvent selectivity. Table 5 presents limiting activity coefficients for hydrocarbons typical of four major classes. The most striking difference is that between 1-pentene and 1-hexyne, in which γ^∞ for the olefin is twice, or more, that of 1-hexyne. Since limiting activity coefficients of hydrocarbons in polar solvents increase somewhat with molecular weight, differences between 1-hexene and 1-hexyne would be even larger. This result reflects the considerably greater interaction between the solvent polar group and a triple bond than with a double bond.

Differences between limiting activity coefficients for benzene and 1-hexyne are small. In three solvents γ^∞ for benzene is somewhat lower, whereas in acetone it is about the same as that for 1-hexyne. No data are available for γ^∞ of benzene in dimethyl carbonate, and the estimated value is subject to considerable uncertainty.

Table 5. Activity Coefficients of Infinitely Dilute Hydrocarbons in Polar Organic Solvents at 25°C.

Solvent	Hexane*	1-Pentene†	1-Hexyne	Benzene*
acetone	6.5	3.16	1.58	1.5§
acetonitrile	25.5	9.45	4.4	2.7
dimethyl carbonate	5.5‡	3.4‡	1.73	2.4‡
nitroethane	13‡	6.5‡	2.8	1.8
N,*N*-dimethyl formamide	17	7.18	2.1	1.4

* Reference *9*
† Reference *10*
‡ Estimated by Weimer's method (*1*)
§ Reference *5*

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Correlations for Adsorption of a Binary Gas Mixture on a Heterogeneous Adsorbent—the Methane-Ethane-Silica Gel System

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Correlations for the adsorption of a binary gas mixture on a heterogeneous adsorbent have been developed for both mobile and immobile models. Experiments determined the form for the expression of the surface heterogeneity, and only one dimensionless constant for the molecular size was required.

The correlations were tested by experimental data on the system methane-ethane-silica gel. For the same amount of adsorption the root-mean-square deviation of calculated versus experimental fugacity ranged from 4.1 to 5.2% for methane and from 2.7 to 3.4% for ethane at 5.0, 15.0, 25.0, and 35.0°C. for surface coverage ranging from zero to monolayer and for the complete composition range. The system at these conditions is classified as highly mobile based on examination of spreading pressure curves, both experimental and calculated based on the correlations.

The effect of surface heterogeneity of the adsorbent on the adsorption isotherms of gases has been studied by several investigators (*4, 5, 7, 11, 13*). The theories cover localized (immobile) and mobile adsorption, with and without lateral interactions among the adsorbates. Surface heterogeneity is usually given in terms of the probability distribution of the adsorptive energy on the surface of the adsorbent. Some mathematical expressions used for the distribution of the adsorptive energy have been a step function (*4*), a truncated sine function (*4*), exponential functions (*2, 13*), Gaussian functions (*11, 13*), and a log-normal function (*7*). The mathematical expression for a specific gas-solid system and the amount of the lateral interaction energy among adsorbates with respect to the total adsorptive energy are difficult to determine.

An empirical determination of the distribution function was first attempted by Sips (*12*). He assumed a Freundlich type adsorption isotherm and then determined the resulting expression for the surface heterogeneity. Honig and Hill (*6*) followed Sips' approach but still assumed a particular form for the adsorption isotherm.

In this work an empirical determination of the distribution function of the adsorptive energy has been made without assuming a particular type of adsorption isotherm. The adsorptive energy, including the lateral interaction among adsorbates, is assumed to be a function only of the surface coverage at a constant temperature, although the form of the function is not known. Isothermal derivations for both mobile and immobile adsorption models for binary gas mixtures have been made. Experimental data required are fugacity versus the amount of adsorption for both pure components for the pure state and fugacity versus the amount of adsorption ratio for the infinite dilution of one component in the other. These data are easily obtained by a chromatographic method (*8, 9*). Experimental data on the system methane-ethane-silica gel have been used to check the correlations at ambient temperatures up to about monolayer adsorption.

THEORETICAL

MOBILE ADSORPTION

Fundamental Formulations

The derivation by Hill (*3*) for the isotherm for mobile adsorption of a pure component was based on a van der Waals type formulation. The adsorbed phase has been defined elsewhere (*8*). When modifications are made for the application to a binary gas mixture of different molecular sizes and for a three-dimensional expression in place of the two-dimensional expression, the resulting partition function of the adsorbates in a mobile model is

$$Q_m = \left[j_{m,1}^{N_1} \, j_{m,2}^{N_2} / (N_1! \, N_2!) \right] (V - b_1 N_1 - b_2 N_2)^{N_1 + N_2} \exp\{[N_1 E_{m,1}(\theta_m) + N_2 E_{m,2}(\theta_m)]/(kT)\} \quad (1)$$

The surface coverage, θ, is defined by

$$\theta_m = (b_1 N_1 + b_2 N_2)/V \quad (2)$$

The chemical potential, μ, and the fugacity of a spe-

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