Infinite Dilution Volatilities of Polar Solutes in Hydrocarbons

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Infinite dilution volatility data have been correlated for alcohols, esters, aldehydes, ketones, and sulfur containing hydrocarbon solutes in aliphatic hydrocarbon solvents over a wide temperature range using a temperature dependent energy parameter for the pure solute.

When a polar solute molecule is surrounded entirely by nonpolar molecules, polar molecular interactions such as hydrogen bonding do not play an important role. Therefore, a single, pure solute parameter is sufficient for correlation.

Calculated heats of solution at infinite dilution agree well with published calorimetric data.

SCOPE

The removal of trace organic solutes from hydrocarbon mixtures is an important separation process in chemical and energy related technology. Rational design of such processes requires quantitative estimates of the infinite dilution volatilities of organic solutes. While these estimates can often be made for nonpolar solutes, no correlations are available for polar solutes over a wide temperature range.

This work presents correlations, similar to the corresponding states framework, covering hydrocarbon and polar solutes in paraffinic solvents, from isobutane to high molecular weight polyethylene.

CONCLUSIONS AND SIGNIFICANCE

For effective removal of trace impurities by distillation, the infinite dilution volatility of the solute is needed to determine the number of stages and the reflux rate (or solvent flow rate in absorption and in extractive distillation). The solute volatility at finite concentrations, if needed, can be predicted with reasonable accuracy if its infinite dilution volatility is known.

The volatilities (and heats of solutions) of various polar solutes in a given paraffinic solvent are nearly the same when compared at the same temperature and at the same energy parameter. This energy parameter A_{RK} is related to the polarizability of the solute molecule. The correlation for predicting infinite dilution volatilities also provides the process engineer with a useful tool for extrapolating data beyond the temperature range covered by most experiments, typically, 298° to 400°K.

Literature data for infinite dilution volatilities are often subject to appreciable uncertainties due to experimental difficulties in obtaining data at highly dilute region and also due to the uncertainties in the extrapolating data to infinite dilution. It is not uncommon to find data that differ by 30% at similar conditions.

Therefore, if serious disagreement is observed between experimental results and those calculated from this correlation, preference should not immediately be given to the experimental value. The correlation presented in this work appears to be accurate within about ± 15%.

Chemical process design typically requires quantitative estimates of fluid phase equilibria for mixtures containing trace impurities. However, reliable fluid phase equilibrium data for impurities at high dilution are not plentiful. Most of the available experimental data have been obtained at finite concentrations. When such data are extrapolated to infinite dilution, the results are subject to considerable uncertainty.

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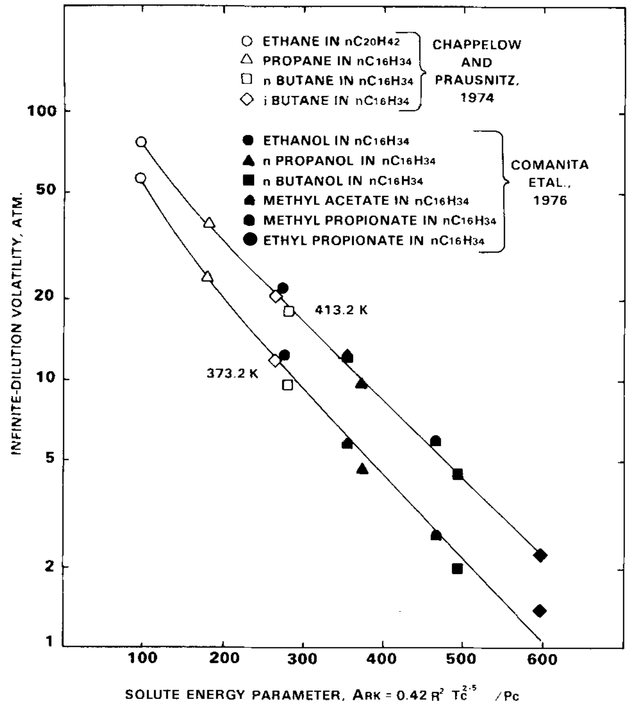

Fig. 1. Infinite dilution volatilities of organic solutes in $nC_{16}H_{34}$ (or in $nC_{20}H_{42}$) as a function of solute energy parameter A_{RK} at two temperatures.

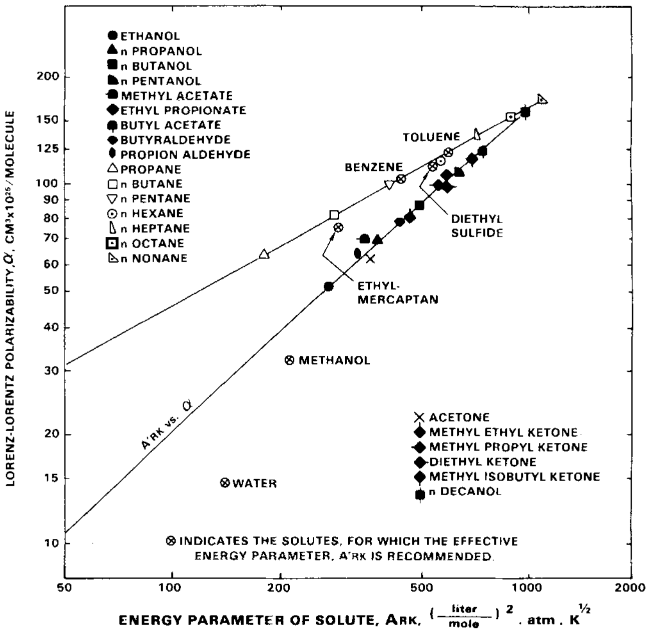

Fig. 2. Relation between the Redlich-Kwong energy parameter A_{RK} and Lorenz-Lorentz polarizability α.

Despite uncertainties in the experimental data, a general relation appears to exist between the temperature dependent solute parameter and the infinite dilution volatilities. The infinite dilution volatility, H of solute i is defined by

$$H_i = \lim_{x_i \to 0} \left(\frac{f_i}{x_i} \right) \qquad (1)$$

For supercritical solutes, the infinite dilution volatility is known as Henry's coefficient. For subcritical solutes, the infinite dilution volatility H_i is the product of infinite dilution activity coefficient γ_i^∞ and the saturated fugacity f_i^s of pure liquid i:

$$H_i = \gamma_i^\infty \cdot f_i^s \qquad (2)$$

Table 1. Infinite Dilution Volatilities in Hydrocarbon Solvents and Energy Constants, A_{RK} for Ten Organic Solutes

	Infinite dilution volatilities,* atm at 373.2°K	at 413.2°K	Energy constants, A_{RK} $(l/mole)^2 \cdot$ atm °K$^{1/2}$
Ethanol	12.1	22.1†	273
n-propanol	4.6	9.7†	372
n-butanol	1.96	4.5†	490
Methyl acetate	5.8	12†	355
Methyl propionate	2.6	6†	466
Ethyl propionate	1.4	3.45†	596
Ethane	55.7	77.5**	96.1
Propane	23.3	37.7**	179
n-butane	9.7	18.2**	282
i-butane	12.1	20.9**	266

* In *n*-hexadecane or *n*-eicosane solvent.
† Comanita, Greenkorn, and Chao (1976).
** Chappelow and Prausnitz (1974).

Molecular consideration of the dissolution process leads to a simple solution model from which the characteristics of a correlating parameter can be deduced. When a solute molecule is present in a nonpolar solvent at infinite dilution, such complicating intermolecular forces as polar, complex formation, and hydrogen bond formation play relatively insignificant roles. The primary molecular interactions between solute and solvent are the sum of nonpolar dispersion (London) forces and, to a much lesser degree, induction forces. This work postulates that the solvent may be considered as a continuous, polarizable medium.

The saturated fugacity f_i^s of pure polar solute is, however, influenced strongly by complicating intermolecular forces such as hydrogen bonding. Therefore, the correlation of activity coefficients of polar solutes is highly specific to the chemical nature of the solutes, that is, the type and the location of the functional groups in a solute molecule (Pierotti, 1959; Wilson and Deal, 1962; Derr and Deal, 1969; Fredenslund et al., 1975; Nitta et al., 1977).

A MEASURE OF ATTRACTION FORCES BETWEEN A SOLUTE AND PARAFFIN SOLVENT

A measure of attraction forces between a polar solute and nonpolar solvents is sought that satisfies the following conditions: the parameter should be readily available, or can be calculated from readily available literature data; the parameter should be applicable to polar as well as nonpolar solutes; and the parameter, when properly used, should provide a consistent method for predicting the effect of temperature on infinite dilution volatilities. The first condition dictates that the parameter should be a pure solute property. The second condition appears contrary to the first because most of the pure compound properties of a polar chemical are affected by polar, hydrogen bond, or complex formation energies

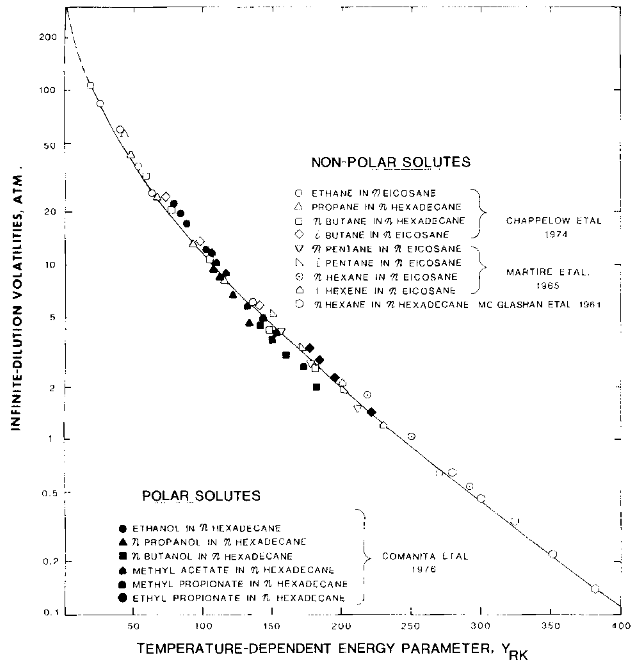

Fig. 3. The effect of temperature dependent energy parameter. Y_{RK} on the infinite dilution volatilities of organic solutes.

in addition to nonpolar dispersion energy. This second condition suggests that the parameter should be composed of two or more pure compound constants such that the contribution of polar forces would cancel out. To satisfy the third condition, the relation between the parameter and the infinite dilution volatility should take some form of a corresponding states principle.

ENERGY PARAMETER A_{RK}

Macroscopic corresponding state theory in its simplest form offers a set of reducing parameters: Tc, Pc, and Zc (or ω). The combinations of the parameters can be found from analytical forms of corresponding state correlations, namely, equations of state. The energy parameter of the Redlich-Kwong equation of state is selected because of its simple relation with the fluid critical constants. The energy parameter of the Redlich-Kwong equation of state A_{RK} is

$$A_{RK} \equiv 0.42 \frac{R^2 Tc^{2.5}}{P_c} \qquad (3)$$

Figure 1 shows the effect of A_{RK} on the infinite dilution volatilities of four hydrocarbons (Chappelow and Prausnitz, 1974) and six oxygenated polar solutes (Comanita et al., 1976) at 373° and 413°K. High boiling solvents $nC_{16}H_{34}$ and $nC_{20}H_{42}$ are chosen because the data in these solvents are considered to be of high accuracy. Figure 1 shows that the infinite dilution volatilities of three chemically different types of solutes are a smooth function of a single, pure component parameter A_{RK}. This energy parameter appears to satisfy the first two conditions. Table 1 presents the infinite dilution volatilities and energy parameters of four paraffins and six polar solutes shown in Figure 1. Critical constants were obtained from a property data bank (Reid et al., 1977).

Ethanol and isobutane exhibit similar infinite dilution volatilities in hexadecane solvent even though their natural volatilities (or the ratio of their vapor pressures) at 373°K differ by a factor of twenty. This can be explained by the similar energy parameters of the two solutes.

EFFECTIVE ENERGY PARAMETER A'_{RK}

Methane and methanol solutes deviate from the general trend, probably because they are the first members of homologous series. Also water, aromatic, and sulfur containing aliphatic hydrocarbon solutes do not follow the general relations shown in Figure 1. These exceptions lead to a study of the fundamental nature of the energy parameter A_{RK}.

According to the theory of intermolecular forces (Rutgers, 1954; Prausnitz, 1969), the dispersion force is proportional to the solute polarizability α.

The solution model employed in this work postulates that the attraction energy of any solute in a nonpolar solvent at infinite dilution is entirely due to dispersion force. Therefore, the polarizability α for polar as well as nonpolar molecules can be calculated from the readily available refractive index η by the Lorenz-Lorentz relation:

$$\alpha = 10^{25} \times \frac{\eta^2 - 1}{\eta^2 + 2} \cdot \left(\frac{3}{4\pi N} \right) \cdot V \qquad (4)$$

Refractive index and liquid density are taken from CRC Handbook (1970-71). For normally gaseous solutes, Vogel's group contribution (Vogel, 1948) is used for the calculation of α. Figure 2 shows that there are two relations between the polarizability α and the energy parameter; one for chainlike solutes and the other for polar solutes and compact molecules. The two relations can be represented by

TABLE 2. DATA SOURCES FOR INFINITE DILUTION VOLATILITIES IN n-HEXADECANE AND IN n-EICOSANE

Source	Solutes	Solvent	Experimental method
McGlashan and Williamson (1961)	n-hexane	n-hexadecane	Static cell
Chappelow and Prausnitz (1974)	Ethane, iso-butane, propane, n-butane	n-eicosane n-hexadecane	Static cell
Martire and Pollara (1965)	n-pentane, iso-pentane, n-hexane, 1-hexene	n-eicosane	Gas chromatographic
Lenoir, Renault, and Renon (1971)	Ethane, propane, n-butane, iso-butane	n-hexadecane	Gas chromatographic
Comanita, Greenkorn, and Chao (1976)	Methanol, ethanol, propanol, 1-butanol, methyl acetate, methyl propionate, ethyl propionate	n-hexadecane	Gas chromatographic

Table 3. Data Sources for Infinite-Dilution Volatilities of Polar Solutes in C_4 to C_7 Solvents

SOLUTE In isobutane solvent*	Temp, °K	Source
Methyl acetate	298	Won (1974)
Ethyl acetate	298	Won (1974)
Butyl acetate	298	Won (1974)
Acetone	298	Won (1974)
Methyl ethyl ketone	298	Won (1974)
Diethyl ketone	298	Won (1974)
Methyl isobutyl ketone	298	Won (1974)
Butyraldehyde	298	Won (1974)
Valeraldehyde	298	Won (1974)
In n-pentane solvent†		
Acetone	309	Lo et al. (1962)
Acetone	373	Cunningham (1974)
Propion aldehyde	373	Cunningham (1974)
Methyl acetate	373	Cunningham (1974)
n-butanol	303	Ronc and Ratcliff (1976)
n-pentanol	303	Ronc and Ratcliff (1976)
Methanol	308	Tenn and Missen (1963)
In hexane solvent†		
Methanol	308, 323, 333, 348	Wolff and Hoppel (1968)
Ethanol	342	Sinor and Weber (1960)
n-butanol	342	Govindaswami et al. (1976)
n-butanol	303	Ronc and Ratcliff (1976)
n-pentanol	303, 323	Ronc and Ratcliff (1976)
n-pentanol	298	Sayegh and Ratcliff (1976)
iso-pentanol	298	Sayegh and Ratcliff (1976)
n-butanol	333	Hanson and Van Winkle (1967)
Methyl ethyl ketone	333	Hanson and Van Winkle (1967)
In *n*-heptane solvent†		
Ethanol	371	Van Ness et al. (1967*a*)
Ethanol	303	Ronc and Ratcliff (1976)
n-propanol	303, 318, 333	Van Ness et al. (1976*b*)
i-propanol	303, 318, 333	Van Ness et al. (1976*b*)
Acetone	338	Maripuri and Ratcliff (1972)
Vinyl acetate**	331	Swamy and Van Winkle (1965)
Acetone	331	Willock and Van Winkle (1970)

* Distribution coefficient K_i at high dilution. The infinite dilution volatility $\overset{\infty}{\gamma}_i f_i^s$ is calculated by $\overset{\infty}{\gamma}_i f_i^s \simeq \overset{\infty}{K}_i \overset{\infty}{\gamma}_{i/A} P_i^s$, where $\overset{\infty}{\gamma}_{i/A}$ is the activity coefficient of solute *i* in water at infinite dilution calculated by the correlation of Pierotti et al. (1959).

† Vapor-liquid equilibrium data.

** Solvent is 2,4-dimethyl pentane.

$$\ln A'_{RK} = A_1 + A_2 \ln \alpha \tag{5}$$

where $A_1 = -2.219$, $A_2 = 1.785$ for chainlike molecules, and $A_1 = 1.214$, $A_2 = 1.118$ for polar molecules and compact molecules.

However, the use of the effective energy parameter A'_{RK} is recommended only for methanol, water, aromatic hydrocarbon, and sulfur containing aliphatic hydrocarbon solutes. For other solutes, the energy parameter A_{RK} is recommended because of the following:

1. If one chooses the polarizability α as a correlation parameter, one would need two relations between the infinite dilution volatilities and the polarizabilities; one for chainlike solutes and the other for polar and compact molecules. As shown in Figure 1, the infinite dilution volatilities of most solutes follow a single correlation with the energy parameter A_{RK}.

2. Beside this simplicity in the correlation, the energy parameters A_{RK} of the isomers, iso and normal butanes and propanols, correctly reflect their differences in the infinite dilution volatilities, while the polarizabilities α of the isomers are nearly the same.

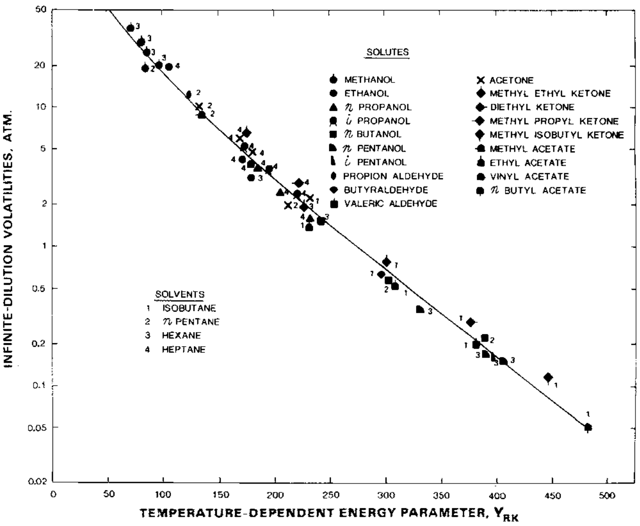

Fig. 4. Infinite dilution volatilities of polar organic solutes in C_4 to C_7 aliphatic hydrocarbon solvents.

THE EFFECT OF TEMPERATURE ON THE INFINITE DILUTION VOLATILITIES

The effect of temperature on the infinite dilution volatility can be investigated by the application of the corresponding state principle to the energy parameter A_{RK} (and A'_{RK}).

A temperature dependent parameter Y_{RK} is defined by

$$Y_{RK} = 10^6 \times \frac{A_{RK}(\text{or } A'_{RK})}{T^{2.5}} \tag{6}$$

$$= 0.42 \times 10^6 \frac{R^2}{P_c T_R^{2.5}} \tag{6a}$$

where

$$T_R = \frac{T}{T_c} \tag{7}$$

Equation (6*a*) is applicable to solutes other than water, methanol, sulfur containing hydrocarbons, and aromatic solutes. Figure 3 shows the relation between the infinite dilution volatilities and the temperature dependent parameters Y_{RK} for fourteen solutes.

Solutes in Figure 3 include eight hydrocarbons, three alcohols, and three esters. The experimental temperature range for the six polar solutes is 373° to 413°K, while that for hydrocarbon solutes extends from 393° to 475°K. These data were fitted to an empirical equation similar to the Antoine equation for vapor pressure:

$$\ln H = a - bY_{RK} + \frac{c}{Y_{RK} + d} \tag{8}$$

Variables H and Y_{RK} at a given temperature are specific to each solute, but their relation as represented by Equation (8) is applicable to any solute investigated in this work. Table 2 presents the source of the infinite dilution volatility data and a brief description of the experimental

Table 4. Constants in Equation (8)

Solvents	Constants a	 b	 c	 d	
n-hexadecane n-eicosane	2.384	0.0126	221	67.2	For all solutes
iso-butane, n-pentane, Hexanes, Heptanes	3.00	0.0132	211.6	80.7	For polar solutes
Low-density polyethylene	2.25	0.0158	201.9	89.7	For linear solutes
	2.89	0.0145	140.2	98.4	For compact solutes

Table 5. Experimental and Calculated Partial Molar Heats of Mixing at Infinite Dilution $\Delta\bar{h}m^{\infty}$ for Five Solutes in n-Heptane

Solute	Temp, °K	$\Delta\bar{h}m^{\infty}$, cal/mole Predicted	 Experimental
Methanol	303	5 798	5 615*
	318	5 725	5 544
Ethanol	283	5 886	5 694†
	318	5 754	5 586
	348	5 485	5 287
n-propanol	303	5 908	5 570**
	318	5 860	5 475
	333	5 780	5 380
iso-propanol	303	5 705	5 557**
	318	5 543	5 460
	333	5 425	5 410
Acetone	283	2 180	—
	318	2 290	—
	348	2 230	—

* Extrapolated results of Savini et al. (1965).
† Van Ness et al. (1967*a*).
** Van Ness et al. (1967*b*).

methods. Constants a, b, c, and d, obtained by fitting the data, are shown in Table 4.

TESTS OF THE SOLUTION MODEL

The solution model is tested with a limited number of mixture data which, nevertheless, cover a broad range of chemical types and temperatures. First, experimental infinite dilution volatilities of organic solutes in butane through heptane are correlated by the temperature dependent energy parameter Y_{RK}. This correlation is then compared with the results calculated from the infinite dilution activity coefficient correlation of Pierotti et al. (1959) for alcohol and ketone solutes and also with the results calculated from the UNIFAC correlation (Fredenslund et al., 1975). Secondly, a correlation for infinite dilution heat of solution is derived. The calculated heats of solution are compared with the results of calorimetric heats of mixing and heats of vaporization. Finally, infinite dilution volatilities of various types of organic solutes in high molecular weight polyethylene solvent are correlated.

INFINITE DILUTION VOLATILITIES OF SOLUTES IN LOW MOLECULAR WEIGHT PARAFFIN SOLVENTS

Accurate experimental data for infinite dilution volatilities of solutes in low molecular weight paraffins are scarce. Until recently, vapor-liquid equilibrium data have been taken at finite concentration, and when these data are extrapolated to infinite dilution, the uncertainties of the calculated values are, in general, much larger than those of experimental data at finite concentration. Ebulliometric method (Null, 1970; Wong and Eckert, 1971) and the gas chromatographic retention-time method (Martire, et al., 1965) appear to be accurate methods for determination of infinite dilution volatilities. Such data are not plentiful in the open literature.

Table 3 presents the literature data on infinite dilution volatilities used in this work. Figure 4 shows the correlation between the temperature dependent energy parameter Y_{RK} and the infinite dilution volatilities for mixtures listed in Table 3. The solid line shown in Figure 4 is determined by fitting the experimental infinite dilution volatilities to Equation (8). The constants in Equation (8) are presented in Table 4.

HEATS OF SOLUTION AT INFINITE DILUTION

A measure of the effect of temperature on the infinite dilution volatility is the heats of solution at infinite dilution $\bar{h}_s^{\infty}$:

$$\Delta\bar{h}_s^{\infty} = h^o - \bar{h}^{\infty} \tag{9}$$

The heats of solution $\bar{h}_s^{\infty}$ can be derived from Equation (8) using the Gibbs-Helmholtz relation:

$$\Delta\bar{h}_s^{\infty} = RT^2\left(\frac{d\ln H}{dT}\right) \tag{10}$$

Substitution of Equation (8) into Equation (10) yields

$$\Delta\bar{h}_s^{\infty} = 2.5RT\left[b + \frac{c}{(Y_{RK}+d)^2}\right]Y_{RK} \tag{11}$$

The heat of solution $\Delta\bar{h}_s^{\infty}$ is related to the partial molar heats of mixing $\Delta\bar{h}_m^{\infty}$ by

$$\Delta\bar{h}_s^{\infty} = (h^o - h^L) - \Delta\bar{h}_m^{\infty} \tag{12}$$

The first term in Equation (12) represents the enthalpy of condensation of pure solute. The second term is the partial molar heat of mixing for the liquid solute.

Table 5 presents infinite dilution partial molar heats of mixing $\Delta\bar{h}_m^{\infty}$ calculated from Equations (11) and (12). The enthalpy of condensation $h^o - h^L$ is approximated by the heat of vaporization. For comparison purpose, the calorimetric results (Savini et al., 1965; Van Ness et al., 1967*a*, *b*) are also presented. In all cases, the agreement between experimental and calculated values is considered good. Table 5 also presents the partial molar heats of mixing of acetone in n-heptane. For this mixture, experimental data are not available. The small values of $\Delta\bar{h}_m^{\infty}$ for acetone solute are anticipated owing to the absence of such strong hydrogen bonding among acetone molecules compared to alcohols.

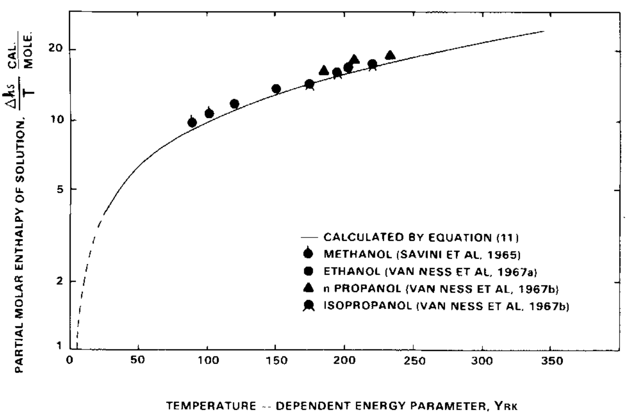

Fig. 5. Effect of temperature dependent energy parameter Y_{RK} on the enthalpy of solution of organic solutes in *n*-heptane at infinite dilution.

The partial molar heats of mixing $\overline{\Delta h}_m^{\infty}$ depend very much on the chemical type of the solute. On the other hand, the partial molar heats of solution $\overline{\Delta h}_s^{\infty}$ in paraffin solvents are a general function of the temperature dependent energy parameter Y_{RK}.

Figure 5 shows the effect of the temperature dependent energy parameter Y_{RK} on $\overline{\Delta h}_s^{\infty}/T$. The solid line in Figure 5 represents the results calculated from Equation (11). For comparison purpose, Figure 5 also presents the results ($\overline{\Delta h}_s^{\infty}/T$) calculated from the calorimetric heats of mixing $\overline{\Delta h}_m^{\infty}$ and the heats of vaporization for four alcohol solutes in *n*-heptane. The agreement between experimental and calculated results is good.

INFINITE DILUTION VOLATILITIES OF SOLUTES IN HIGH MOLECULAR WEIGHT POLYETHYLENE

Since the solution model postulates that there will be a simple relation between the temperature dependent energy parameters and the infinite dilution volatilities of any solutes in any solvents that do not exhibit specific chemical interaction with the solute molecule, solubility data in high molecular weight polyethylene solvent offer a good test of the solution model.

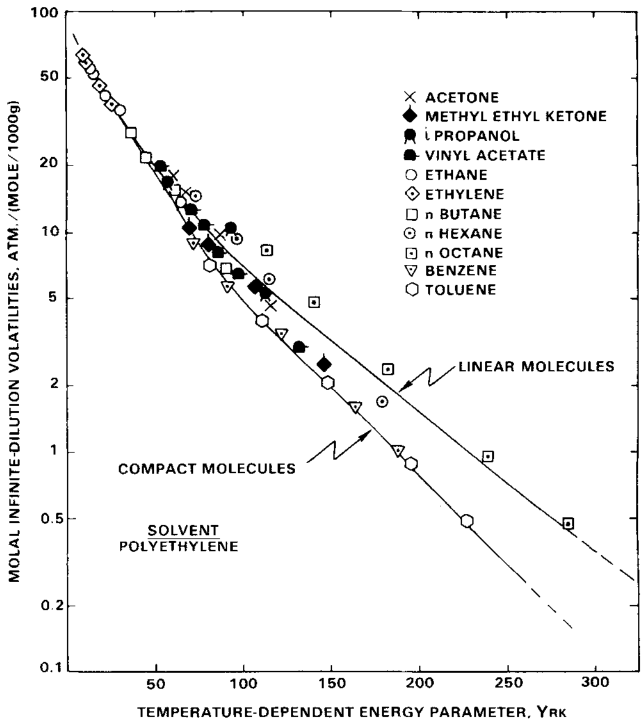

Fig. 6. The effect of temperature dependent energy parameter Y_{RK} on the molal infinite dilution volatilities of organic solutes in low density polyethylene.

The molecular weight of such polyethylene is, however, not definitely known. Therefore, a molal Henry's coefficient is defined

$$H^m = \lim_{m \to 0} \left(\frac{f}{m} \right) \tag{13}$$

where m = g mole solute/1 000g solvent.

Figure 6 shows that there are two distinct relations between the molal Henry's coefficients and the temperature dependent parameters, one for linear and the other for compact solutes. The solutes with polar functional group show results closer to those of compact molecules. This distinction of the molecular shape becomes more appreciable as the temperature decreases and as the solute molecular size increases. The data in polyethylene solvent are reported elsewhere (Liu and Prausnitz, 1976; Maloney and Prausnitz, 1976).

Table 6a. Use of Effective Energy Parameter A'_{RK} for the Infinite Dilution Volatilities of Methanol, Water, Mercaptan, Sulfide, and Aromatic Hydrocarbon Solutes

Solute	Energy parameter A_{RK}	A'_{RK}	T, °K	H*	H†	H_{EXP}
Methanol	211	162	373	14	27	28**
			413	27	43	46
Water	140	68	278	10-12	35-40	25-110††
			293	15-17	45-50	35-105
Ethyl mercaptan	292	420	373	9.2	4.1	4.96***
			413	15.5	7.8	9.60
Diethyl sulfide	532	660	373	2.0	1.0	1.06***
			413	4.2	2.3	3.27
Benzene	441	600	326	1.2	0.37	0.36†††
			367	3.2	1.17	1.23
Toluene	596	720	326	0.38	0.15	0.12†††
			367	1.2	0.58	0.52

* Calculated by Equation (8) using A_{RK}.
† Calculated by Equation (8) using A'_{RK}.
** Comanita et al. (1976) in *n*-hexadecane.
†† Black et al. (1948) in *n*-butane and *n*-heptane.
*** Turek et al. (1976) in *n*-hexadecane.
††† Martire and Pollara (1965) in *n*-eicosane.

Table 6b. Experimental and Calculated Infinite Dilution Activity Coefficients of Polar Solutes in Paraffin Solvents

Solute	Solvent	Temp, °K	Infinite dilution activity coefficient γ^∞ calculated by UNIFAC(a)	Pierotti et al(b)	H_i/f_i^s(d)	Experimental
Methanol	*n*-hexadecane	373	5.3	8.6	9.0(e)	8.6(1)
		413	4.1	4.1(c)	4.5(e)	4.9
Methanol	*n*-hexane	308	19	62(c)	68(e)	73(2)
		348	13	17(c)	21(e)	25
Ethanol	*n*-heptane	303	47	43(c)	48	41(3)
		371	23	8(c)	8	10(4)
n-propanol	*n*-heptane	303	18	38(c)	49	41(5)
		333	14	16	20	18
iso-propanol	*n*-heptane	303	18	26(c)	28	31(5)
		333	13	12	12	14
n-pentanol	*n*-hexane	298	15	38	49	47(6)
iso-pentanol	*n*-hexane	298	15	38	43	38
Acetone	Isobutane	298	7	7	6.2	7.4(7)
	n-pentane	309	6.1	6.2(c)	5.3	5(8)
		373	4.3	3.4	2.6	3(9)
	2.4-dimethyl butane	331	5.1	4.9(c)	4.1	4.4(10)
Propionaldehyde	*n*-pentane	373	3.4	—*	2.9	3.2(9)
Methyl acetate	*n*-pentane	373	2.9	—*	2.8	2.7(9)

(a) Fredenslund et al. (1975).
(b) Pierotti et al. (1959).
(c) Interpolation is made with respect to temperature.
(d) H_i is calculated by Equation (8). f_i^s is approximated by P_i^s when P_i^s is less than 1 atm and virial equation is used when P_i^s is greater than 1 atm.
(e) A'_{RK} is used.
* Original article of Pierotti et al. (1959) does not include necessary constants for aldehyde and ester solutes in parrafins.

(1) Comanita et al. (1976).
(2) Wolff et al. (1968).
(3) Ronc and Ratcliff (1976).
(4) Van Ness et al. 1967*a*).
(5) Van Ness et al. (1967*b*).
(6) Sayegh and Ratcliff (1976).
(7) Won and Prausnitz (1974).
(8) Lo et al. (1962).
(9) Cunningham (1974).
(10) Willock and Van Winkle (1970).

DISCUSSION

The infinite dilution volatilities of polar solutes in paraffin solvents are correlated by a temperature dependent energy parameter Y_{RK}. For methanol, water, aromatic, and sulfur containing aliphatic hydrocarbon solutes, the effective energy parameter A'_{RK} is recommended for the calculation of Y_{RK}. Table 6*a* presents the infinite dilution volatilities of these solutes calculated by the energy parameter A_{RK} and by the effective energy parameter A'_{RK}. For comparison purposes, the experimental results are also shown in Table 6*a*.

Table 6*b* presents the infinite dilution activity coefficients γ_i^∞ of nine polar solutes calculated by the correlation presented in this work and those calculated by the UNIFAC method (Fredenslund et al., 1975; Fredenslund et al., 1977).

Comparison of calculated results with experimental data shows that the infinite dilution volatility correlation represents well the experimentally observed effect of temperature on the infinite dilution activity coefficients. For example, the infinite dilution activity coefficient of methanol in *n*-hexane increases three times as temperature decreases from 348° to 303°K (Wolff et al., 1968).

It appears that the UNIFAC correlation underestimates the temperature effect on the infinite dilution activity coefficients of alcohols. For acetone, propionaldehyde, and methyl acetate solutes, the two correlations predict data equally well.

The infinite dilution activity coefficients calculated by the correlation of Pierotti et al. (1959) for ketone and alcohol solutes are in good agreement with the results calculated by the infinite dilution volatility correlation presented in this work. The Pierotti correlation does not provide infinite dilution activity coefficients in paraffins for solutes other than ketones and alcohols.

CONCLUSION

A new correlation is developed for the infinite dilution volatilities of polar solutes in nonpolar, paraffin solvents. This correlation, using only readily available, pure solute constants, predicts the infinite dilution volatilities of various solutes in paraffinic solvents within about 15%.

The good agreement between the experimental and the calculated heats of solution suggests that the correlation can be used to extrapolate the infinite dilution volatility data beyond the common experimental temperature range, typically 300° to 400°K.

NOTATION

A_{RK} = energy constant defined by Equation (3) (l/mole)^2·atm·°K$^{1/2}$
A'_{RK} = energy constant defined by Equation (5) (l/mole)^2·atm·°K$^{1/2}$
A_1, A_2 = constants in Equation (5)
a, b, c, d = constants in Equation (8)
FMW = formula molecular weight
f = fugacity (atm)
H = infinite dilution volatility (atm)
h = partial molar enthalpy (cal/mole)
K = unit of Kelvin temperature
m = molal concentration (g mole/1 000 g)
N = Avogadro number (6 023 × 10^{23}/mole)
P = pressure (atm)
R = gas constant, (0.08206 l·atm/mole·°K)
T = absolute temperature (°K)
V = molar volume of liquid at 293°K (cm^3/mole)

x = liquid mole fraction
Y_{RK} = temperature dependent energy parameter $(l/\text{mole}\cdot{}^\circ\text{K})^2\cdot\text{atm}$
α = polarizability ($\text{cm}^3 \times 10^{25}$/molecule)
γ = activity coefficient
η = refractive index of liquid measured by sodium D light at 293°K

Subscripts

c = critical constant
i = component i
m = molar quantity associated with liquid mixing process
RK = Redlich-Kwong equation of state
s = molar quantity associated with gas dissolution process

Superscripts

∞ = infinitely dilute state
o = ideal gas state at 1 atm
L = liquid state
m = molal concentration basis
s = saturated state

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