Prediction of Infinite Dilution Volatilities of Polar Organic Solutes in Paraffinic Hydrocarbons

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ABSTRACT

Removal of trace organic solutes from chemical products is an important operation in chemical, petrochemical, food and pharmaceutical industries. Most widely used purification processes, such as distillation, stripping and absorption, utilize the differences of the equilibrium vapor and liquid concentrations, requiring vapor-liquid equilibrium (or VLE) data or correlations for the system consisting of the trace solute and product.

However, accurate VLE data and/or their correlations are not usually available for the mixture at the temperature and concentration ranges of industrial importance. Group contribution methods such as UNIFAC and ASOG provide the activity coefficients of mono-functional chemicals with fair accuracy over a relatively small temperature range.

Equations of state with new mixing rules promise to be versatile for the correlation of VLE involving polar chemical mixtures, but no reliable prediction method has been reported yet.

This paper presents a correlation method for infinite dilution volatilities of polar chemicals in a wide variety of paraffinic solvents between the temperature range of about 293.2 and 413.2 K, with about 8% accuracy.

Key Words

Method, infinite dilution volatility, polar chemicals, separations, vapor-liquid equilibria, activity coefficients

1. INTRODUCTION

For effective removal of trace organic impurities by distillation, stripping or absorption, accurate infinite dilution volatilities of the solute are needed to determine the important separation process design variables, such as the number of equilibrium stages and the reboiler duty or solvent flow rate in absorption and extractive distillation.

Besides the process design considerations, the volatilities of organic compounds dissolved in hydrocarbons are important environmental concern. Lately, oxygenated polar chemicals such as alcohols and ethers are added to transportation fuels such as gasoline and diesel fuels in order to reduce the emission of air pollutants such as the oxides of nitrogen. However, the volatilities of the oxygenated additives should be considered, because they contribute to the vaporization loss of the fuels. Indeed, Reid Vapor Pressure (or RVP), a measure of fuel volatility is regulated by local state air quality management boards as well as US Environmental Protection Agency (or EPA). RVP is defined as the equilibrium pressure of the fuel, when they are flashed to a gas space equal to four times their original liquid volume (ASTM D323-94).

Previously, a general correlation has been reported for the infinite dilution volatilities of polar solutes in hydrocarbon solvents, which were approximately divided into two groups: one between C_4 and

C_7 and the second between C_{16} and C_{20} (Won, 1979). In the present work, a new modified Flory term is used in order to account for the effect of solvent molecular size, which ranges from C_6 to C_{30}, and a solute-specific relationship between the infinite dilution volatilities and temperature. Therefore, the new correlation covers larger solvent molecules up to C_{30} and the accuracy is improved to within about 8 %, while the previous correlation was limited to C_{20} and was reportedly accurate to within about 15%.

2. THERMODYNAMICS OF INFINITE DILUTION VOLATILITY

The infinite dilution volatility, H of solute i is defined by,

$$H(i,s) = \lim_{x_i \to 0} \left(\frac{f_i}{x_i} \right) \tag{1}$$

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

$$H(i,s) = \gamma_i^\infty f_i^S \tag{1-a}$$

At low pressures, the equation (1) can be simplified to,

$$H(i,s) = K_i^\infty P \tag{2}$$

where K_i^∞ is vapor-liquid equilibrium coefficient at infinite dilution of solute i.

At high pressures, the following approximation was necessary:

$$H(i,s) = K_i^\infty P \phi_i^\infty \tag{2-a}$$

where ϕ_i^∞ is the saturated fugacity coefficient of component i at infinite dilution, which was calculated by the virial equation of state with the coefficients correlated and published by Tsonopoulos (1974).

Inspection of equation (1-a) indicates that the infinite dilution volatility, H, is the fugacity (or escaping tendency) of a solute molecule surrounded entirely by solvent molecules and the infinite dilution activity coefficient is, in fact, the ratio of H to the saturated fugacity of the pure solute liquid. If the solvent molecules are chemically inert, i.e., nonpolar, the molecular interaction between the solute and solvent is the sum of the relatively simple nonpolar dispersion (or London) forces and, to a much lesser degree, induction forces due to permanent dipole moment of the solute. Therefore, H can be a simple, well-behaved property, which can be predicted from a simple pure solute property. An energy parameter of Redlich-Kwong equation of state was selected, because the equation of state parameters are simple, well-defined and physically meaningful (Won, 1979).

$$A_{RK} = 0.42\ (RT_c)^2\ T_c^{\ 0.5} / P_c \tag{3}$$

where Tc and Pc are the critical temperature in Kelvin and pressure in bar of solute and R is the gas constant.

On the other hand, the infinite dilution activity coefficient depends on the saturated liquid fugacity, which can be strongly influenced by complicating intermolecular forces such as hydrogen bonding and electron donor-acceptor complex formation among the polar solute molecules in their pure liquid state (Prausnitz , 1969: Pimentel and McClellan, 1960).

Figure 1 shows the infinite dilution volatilities, H, of paraffinic hydrocarbons, aliphatic alcohols and acetates in n-hexadecane as a function of temperature-dependent pure solute parameter, Y_{RK}.

The temperature-dependent pure solute parameter, Y_{RK}, was defined by,

$$Y_{RK} = 10^6 A_{RK} / T^{2.5} \quad (4)$$

where A_{RK} is the energy parameter of the Redlich-Kwong equation of state and T is the absolute temperature in K.

Figure 2 presents the infinite dilution activity coefficients, γ^∞, of the same solute as a function of Y_{RK}. Figure 1 shows that H of such chemically diverse compounds as alcohols, acetates and paraffins forms a relatively narrow band, while γ^∞ in Figure 2 could differ by a factor of 50 or more at the same solute Y_{RK}.

3. EFFECT OF SOLVENT MOLECULAR SIZE ON INFINITE DILUTION ACTIVITY COEFFICIENT

The effect of molecular size differences on the excess thermodynamic properties, especially excess Gibbs energy of liquid mixtures has long been the subject of numerous investigators. In general, the research focuses on the athermal solution model suggested by Flory (1953) and by Staverman (1953), who used liquid molar volume as the molecular size or lattice size. Recent papers by Kikic et al (1980) and by Won (1989) point out that the original Flory and Staverman models appreciably overestimate the effect of the molecular size differences on the excess Gibbs energy. These papers also propose the use of an exponent to the characteristic molecular sizes such as liquid molar volume, Hildebrand's or Bondi's molecular size. The exponents are less than one as anticipated. Kikic investigated the excess Gibbs energy of binary mixtures consisting of C_5 (and C_6) and larger molecules ranging from C_{12} to C_{30} and suggested Staverman's model using Bondi's molecular size raised to the 2/3 power. Won (1989) investigated the solubilities of large molecules ranging from C_{28} to C_{36} in solvents ranging from n-pentane to n-dodecane (C_{12}) and recommended Flory's model using Hildebrand's liquid molar volume raised to the 2/3 power. Hildebrand's molar volume, defined as the saturated liquid molar volume at the temperature where the equilibrium vapor volume is 100 liters per mole, is difficult to calculate for many polar molecules.

Therefore, liquid molar volumes at 293.2K were used in this work. The effect of solvent molecular size on H can then be expressed by the following equation,

$$Ln(H(\iota,C_n)) = Ln(H(\iota,C_m)) + Ln(V_r) + V_s(1.0-V_r) \quad (5)$$

where $V_r = (VC_n / VC_m)^q$ (6-a)

$V_s = (V_i / VC_n)^q$ (6-b)

In the above equations, H(ι,Cn) and H(ι,Cm) are the infinite dilution volatilities of solute ι in paraffin solvent containing n carbon atoms and m carbon atoms VCn and VCm are the liquid molar volumes of C_n and C_m at 293.15K and q is the exponent to be determined. The second and third terms on the right hand side of equation(5) represent the modified Flory model. n-Hexadecane was chosen as the reference solvent, because many new accurate experimental data for a wide variety of polar solutes are available in n-Hexadecane. In other word, m is in most cases 16.

4. EFFECT OF TEMPERATURE ON THE INFINITE DILUTION VOLATILITIES

Using the same form of the equation representing the effect of temperature on the infinite dilution volatility, H, reported earlier (Won, 1979), a new equation is developed which is applicable to the temperature range from 293.2 to 413.2 K and to solvents ranging from C_6 to C_{30}.

$$Ln(H(\iota,Cn)) = a - bY_{RK} + c / (Y_{RK} + d) + Ln(V_r) + V_s(1.0-V_r) \quad (7)$$

5. RESULTS AND DISCUSSION

The experimental data of four aliphatic alcohols, one ketone, methyl ethyl ketone acetonitrile and methylene chloride in several paraffinic solvents were fitted to the above equation. Table 1 presents the constants a,b,c,d,q and A_{RK} parameters of the seven solutes. It is interesting to note that the parameter q for aliphatic alcohols increases with the molecular size of solute, while it was generally treated as a constant in the previous papers (Kikic, 1980:Won, 1989). The molecular size dependence of their parameter q is not apparent for the remaining non-alcoholic solutes.

Table 1
Molecular parameter of polar solute in paraffinic solvent

Solute	A_{RK}	No. of Data	q	a	b	c	d	std D %	max D %
Methanol	206	15	0.45	3.16	0.01268	215	92.1	9	25
Ethanol	270	24	0.55	3.44	0.01759	309	224	8	23
n-Propanol	365	24	0.65	3.41	0.01617	188	277	8	20
n-Butanol	482	25	0.75	2.85	0.01488	244	226	6	12
Butanone	449	21	0.7	2.7	0.01458	208	211	4	8
Acetonitrile	397	18	0.5	-4.084	-0.00109	2000	158	11	27
Methylene Chloride	257	22	1.0	-5.666	0.00429	2000	156	4	10

$$\text{std D} = \left(\sum^{N} (1 - H^{calc}/H^{exp})^2/N\right)^{0.5} \cdot 100$$

$$\text{max D} = \text{max ABS } (1 - H^{calc}/H^{exp}) \cdot 100$$

Table 2 presents the detailed comparisons between the results calculated by the new H method and the product of standard-state, pure-liquid fugacity and the activity coefficient at infinite dilution calculated by Pierotti's Method (1959) and by the group contribution method, UNIFAC, available in ASPEN PLUS Version 9.3 for four aliphatic alcohols and butanone (or methyl ethyl ketone) in paraffinic solvents ranging from pentane to perhydro squalene, a highly branched paraffinic isomer of $C_{30}H_{62}$.

Table 2

Comparison of calculated and measured values of Infinite Dilution Volatility, H/bar

Solute: Methanol

Solvent	T,K	Pierotti	UNIFAC	H Method	Data	Data Source
n-Hexane	308.2	17.1	5.24	15.7	20.4	Wolff et al (1968)
	348.2	29.0	19.2	28.3	37.8	
n-Heptane	293.2	14.0	2.62	11.6	10.4	Thomas et al (1982)
n-Octane	293.2	13.8	2.41	11.3	10.4	
n-Hexadecane	373.2	30.2	17.0	31.4	28.2	Comanita et al (1976)
	403.2	43.2	30.5	41.7	42.3	
	413.2	48.5	35.9	45.3	46.8	
	393.2	38.4	25.6	38.2	37.2	
n-Heptadecane	295.7	11.2	1.54	10.2	10.5	Martire & Riedl (1968)
	303.2	12.2	2.08	11.7	11.3	
	313.2	13.8	1.90	13.9	14.1	
	323.2	15.6	4.29	16.4	15.2	
n-Tetracosane	333.3	12.5	4.43	17.3	16.5	Alessi et al (1982)
	343.3	14.0	5.99	19.8	19.3	
	355.2	16.0	8.30	22.9	23.3	

Table 2 (continued)
Solute: Ethanol

Solvent	T,K	Pierotti	UNIFAC	H Method	Data	Data Source
n-Hexane	298.2	4.09	2.21	3.8	4.36	Park et al (1987)
	304.8	4.73	2.94	4.57	4.32	Thomas et al (1982)
	322.6	6.88	5.96	7.05	6.56	
n-Heptane	293.2	3.6	1.67	3.19	3.01	
	298.2	4.05	2.11	3.71	3.87	Park et al (1987)
	303.2	4.52	2.61	4.27	3.36	Ronc (1976)
	371.2	16.8	25.2	16.3	21.1	Van Ness (1967, a)
n-Octane	293.2	3.58	1.63	3.13	2.97	Thomas (1982)
n-Decane	298.2	3.87	1.43	2.99	3.31	Park et al (1987)
n-Hexadecane	298.2	3.33	1.35	3.07	2.73	
	317.2	4.94	2.96	5.03	5.19	Alessi et al (1982)
	373.2	13.6	16.0	13.8	12.3	Comanita (1976)
	393.2	18.4	24.8	17.8	17.4	
	403.2	21.2	30.0	19.9	20	
	413.2	24.3	35.8	22.1	22.4	
n-Heptadecane	295.7	3.05	1.13	2.79	2.84	Martire (1968)
	303.2	3.58	1.61	3.46	3.36	
	313.2	4.40	2.43	4.48	4.73	
	323.2	5.37	3.56	5.66	5.81	
	333.2	6.51	5.05	6.98	7.11	
	343.2	7.84	7.01	8.44	9.51	
n-Tetracosane	333.3	4.68	5.07	6.21	6.39	Alessi (1982)
	343.3	5.57	5.44	7.53	7.88	
	355.4	6.83	7.81	9.25	8.95	

Table 2 (continued)
Solute: n-Propanol

Solvent	T,K	Pierotti	UNIFAC	H Method	Data	Data Source
n-Hexane	301.	1.33	0.72	1.30	1.31	Thomas et al (1982)
	315.3	2.01	1.43	2.01	2.06	
	331.8	3.10	2.91	3.06	3.17	
	340.3	3.81	4.03	3.7	3.93	
n-Heptane	303.2	1.41	0.77	1.37	1.58	Van Ness (1967, b)
	333.2	3.18	2.94	3.08	3.67	
	333.2	3.18	2.94	3.08	3.26	Pividal & Sandler (1990)
	353.2	5.09	6.08	4.68	4.57	
n-Hexadecane	312.2	1.52	0.82	1.44	1.21	Alessi et al (1982)
	317.2	1.74	1.03	1.66	1.62	
	373.2	6.21	7.41	5.33	4.59	Comanita (1976)
	393.2	8.91	12.33	7.11	6.8	
	403.2	10.5	15.40	8.06	8.25	
	413.2	12.3	19.85	9.05	9.7	
n-Heptadecane	295.7	0.92	0.35	0.84	0.778	Martire (1968)
	303.2	1.14	0.51	1.08	1.04	
	313.2	1.51	0.83	1.45	1.43	
	323.2	1.97	1.29	1.91	1.96	
	333.2	2.53	1.93	2.43	2.51	
	343.2	3.19	2.82	3.03	3.21	
	353.2	3.99	3.99	3.69	4.12	
n-Tetracosane	333.3	1.85	1.53	2.11	2.08	Alessi et al (1982)
	343.3	2.31	2.22	2.64	2.58	
	355.2	2.98	3.35	3.33	3.29	

Table 2 (continued)
Solute: n-Butanol

Solvent	T,K	Pierotti	UNIFAC	H Method	Data	Data Source
n-Hexane	301.0	.41	0.2	0.38	0.37	Thomas et al (1982)
	315.3	.67	0.44	0.65	0.64	
	331.8	1.13	0.97	1.1	1.13	
	340.3	1.45	1.41	1.41	1.43	
n-Heptane	353.2	2.05	2.25	1.88	2.04	Pividal & Sandler (1990)
	373.2	3.35	3.25	2.89	2.92	
n-Hexadecane	312.2	.51	0.27	0.44	0.43	Alessi et al (1982)
	317.2	.60	0.35	0.52	0.56	
	373.2	2.77	3.17	2.22	1.96	Comanita (1976)
	393.2	4.22	5.66	3.17	3.03	
	403.2	5.11	7.33	3.7	3.74	
	413.2	6.11	9.27	4.27	4.51	
n-Heptadecane	295.7	.27	10.0	0.22	0.21	Martire & Riedl (1968)
	303.2	.36	0.16	0.30	0.29	
	313.2	.51	0.27	0.44	0.43	
	323.2	.70	0.45	0.62	0.59	
	333.2	.95	0.71	0.84	0.83	
	343.2	1.27	1.07	1.1	1.11	
	353.2	1.65	1.57	1.41	1.51	
n-Tetracosane	324.2	.55	0.37	0.53	0.5	Alessi et al (1982)
	333.3	.71	0.56	0.71	0.74	
	343.4	.94	0.86	0.92	0.98	
	355.2	1.27	1.35	1.23	1.31	

Table 2 (continued)
Solute: Butanone

Solvent	T,K	Pierotti	UNIFAC	H Method	Data	Data Source
n-Hexane	298.2	.55	0.66	0.52	0.54	Park et al (1987)
	298.2	.55	0.66	0.52	0.53	Thomas (1982)
	315.3	1.01	1.27	0.99	1.02	
	331.8	1.67	2.19	1.7	1.77	
	340.3	2.11	2.84	2.17	2.27	
n-Heptane	298.2	.55	0.63	0.51	0.51	Park et al (1987)
n-Octane	293.2	.45	0.49	0.40	0.39	
iso-Octane	293.2	.44	0.49	0.4	0.37	
	298.2	.53	0.59	0.49	0.51	
n-Decane	298.2	.53	0.55	0.47	0.51	
n-Hexadecane	298.2	.48	0.42	0.41	0.39	
	333.3	1.49	1.38	1.41	1.44	Arnold (1980)
	363.2	3.11	3.06	3.14	3.21	
	393.2	5.62	5.67	6.13	6.33	
	423.2	9.20	10.6	10.9	11.1	
n-Octacosane	353.4	2.33	2.31	1.92	1.82	Weldlich (1985)
	373.5	3.61	3.50	3.12	2.93	
	393.4	5.27	5.28	4.81	4.6	
perhydro	298.2	.27	0.26	0.31	0.32	Nitta et al (1982)
Squalene	323.2	.59	0.65	0.77	0.73	

Table 2
Solute: Methylene Chloride

Solvent	T,K	UNIFAC	H Method	Data	Data Source
n-Heptane	293.2	0.65	1.12	1.02	Thomas (1982)
Iso-Octane	293.2	0.60	1.04	1.00	
n-Octane	293.2	0.61	1.05	1.01	
n-Hexadecane	293.2	0.38	0.70	0.70	Abraham (1990)
	293.2	0.38	0.70	0.73	Chien (1981)
	303.2	0.56	0.97	1.00	
	313.2	0.79	1.33	1.33	
n-Octadecane	293.2	0.35	0.64	0.65	Chien (1981)
	303.2	0.51	0.89	0.94	
	313.2	0.72	1.21	1.26	
	323.2	0.99	1.64	1.69	
n-Eicosane	326.4	1.0	1.67	1.81	Martire (1965)
	347.3	1.76	2.97	2.98	
	367.1	2.80	4.87	4.58	
Per Hydro	303.2	0.34	0.60	0.63	Sewell (1970)
Squalene	313.2	0.47	0.82	0.83	
	323.2	0.65	1.11	1.12	
	326.4	0.70	1.18	1.20	Martire (1965)
	333.2	0.87	1.48	1.44	Sewell (1970)
	347.3	1.26	2.16	2.15	Martire (1965)
	367.1	1.99	3.55	3.48	

Table 2
Solute: Acetonitrile

Solvent	T,K	UNIFAC	H Method	Data	Data Source
n-Hexane	294.95	3.02	3.07	2.92	Thomas (1982a)
	322.85	7.16	5.74	5.64	
	332.25	9.23	7.07	6.50	
	340.85	11.5	8.52	7.93	
n-Heptane	293.15	2.61	2.88	2.92	
Iso-Octane	293.15	2.41	2.81	3.07	
n-Octane	293.15	2.39	2.82	3.05	
n-Hexadecane	293.15	1.49	2.43	1.92	Abraham (1980)
	305.25	2.22	3.19	3.59	Alessi (1982a)
	315.35	3.02	4.01	4.42	
n-Octadecane	324.15	3.52	4.71	5.61	
	334.55	4.58	5.92	6.53	
	343.65	5.80	7.21	7.86	
	353.15	7.20	8.83	9.29	Harris (1969)
	353.65	7.28	8.92	9.25	Alessi (1982a)
Per Hydro	298.15	2.23	2.27	2.09	Nitta (1982)
Squalene	323.15	3.02	3.98	3.77	
	353.15	4.70	7.61	6.13	Harris (1969)

For methanol solute, the root-mean-squared (or standard) deviation of the infinite dilution volatilities calculated by H method is 11%. The deviation is reduced to less than 7%, if we subtract the two data points in n-hexane, which were underestimated by 23 and 25%. UNIFAC also underestimates these data by a factor of two to four.

For the other methanol data below 355K, UNIFAC severely underestimates data by a factor of three to five.

For ethanol solute, the standard deviation of the H method is about 8 % for 24 data points and maximum deviation is 25%. UNIFAC underestimates the infinite dilution volatility data below about 355 K by a factor of about two, but then overestimates the data above about 371 K. The standard deviations of H method for normal propanol, butanol and butanone (or MEK) data are 8.1, 5.1 and 4.4 %. The maximum deviations for the three solutes are 19,13 and 8 %, respectively.

UNIFAC consistently underestimates the infinite dilution volatilities of n-propanol and butanol below about 355 K and overestimates above that temperature.

For Butanone, the standard deviation of H method is 4.4 %, while the maximum deviation is 8 %. UNIFAC overestimates the data in n-hexane by about 20 % and underestimates the data in per hydro squalene by about 20 %. Pierotti's correlation coefficients were fitted as a function of temperature for the purpose of the comparison. For oxygenated solutes, Pierotti's correlation provides reasonable estmates of

the inifinite dilution volatilities. Pierotti did not provide coefficients for acetonitrile and methylene chloride. UNIFAC slightly overestimates acetonitrile data in n-hexane and underestimates them in large molecules. All methylene chloride data were underestimated by UNIFAC.

The saturated pure liquid fugacities reported by Comanita et al (1976) were used for alcohols above 373K. For the alcohols at other temperatures and other solutes, the vapor pressures which were correlated and published by AIChE DIPPR801 or by Reid et al (1987) were used.

6. CONCLUSION

The new correlation uses four constants, a,b,c and d to represents the effect of temperature and one constant, q to represents the effect of solvent molecular size on the infinite dilution volatilities of a solute.

To use this method for prediction purpose, the infinite dilution volatility data of the solute in one reference solvent are needed as a function of temperature to determine the four constants a to d, and one additional data point at one temperature in a solvent, whose molecular size is very different from the reference solvent to determine the constant q.

The standard deviations defined by average root-mean-squared deviation for all the data are about 8%, while the maximum deviations between the calculated values and data appear to be about 20 to 25 % for alcohols. Considering that the experimental data accuracy of the infinite dilution activity coefficient data are within about 30% (Prausnitz, 1996), the agreement between the data and the new correlation is considered satisfactory for engineering design purpose.

UNIFAC played an instrumental role in the prediction of complex VLE of polar multi-component mixtures, typically found in chemical reaction products. However, we should not take into granted the infinite dilution volatilities(or activity coefficients) of alcohols and other polar solutes in paraffins calculated by UNIFAC available in commercial softwares.

7. LIST OF SYMBOLS

A_{RK} = energy constant defined by equation (3), (liter/mole)2bar$(K)^{0.5}$
a,b,c,d = constants in equation (7)
Cn = molecules containing n carbons
f = fugacity, bar
H = infinite dilution volatility, bar
K = vapor-liquid equilibrium coefficient
P = pressure, bar
q = quotient used in equations (6-a) and (6-b)
R = gas constant, 0.08313 liter bar/mole K
T = absolute temperature, K
V = molar volume of liquid at 293.15K, cc/mole
Y_{RK} = temperature-dependent energy parameter defined by equation (4), (liter/mole K) 2 bar

7.1 Greek Letters

γ = activity coefficient
ϕ = fugacity coefficient

7.2 Subscripts

c = critical constants
i = component i
r = relative to a reference solvent, usually n-hexadecane
RK = Redlich-Kwong equation of state
s = relative to solvent

7.3 Superscripts

∞ = infinitely dilute state
L = liquid state
s = saturated state

Acknowledgment

The author wishes to express his appreciation to Mr. R.A. Barneson and Dr.J.M.Prausnitz for helpful discussion and to the management of Fluor Daniel, Inc. for permission to publish this work.

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Figure 1, Infinite Dilution Volatilities as a Function of Molecular

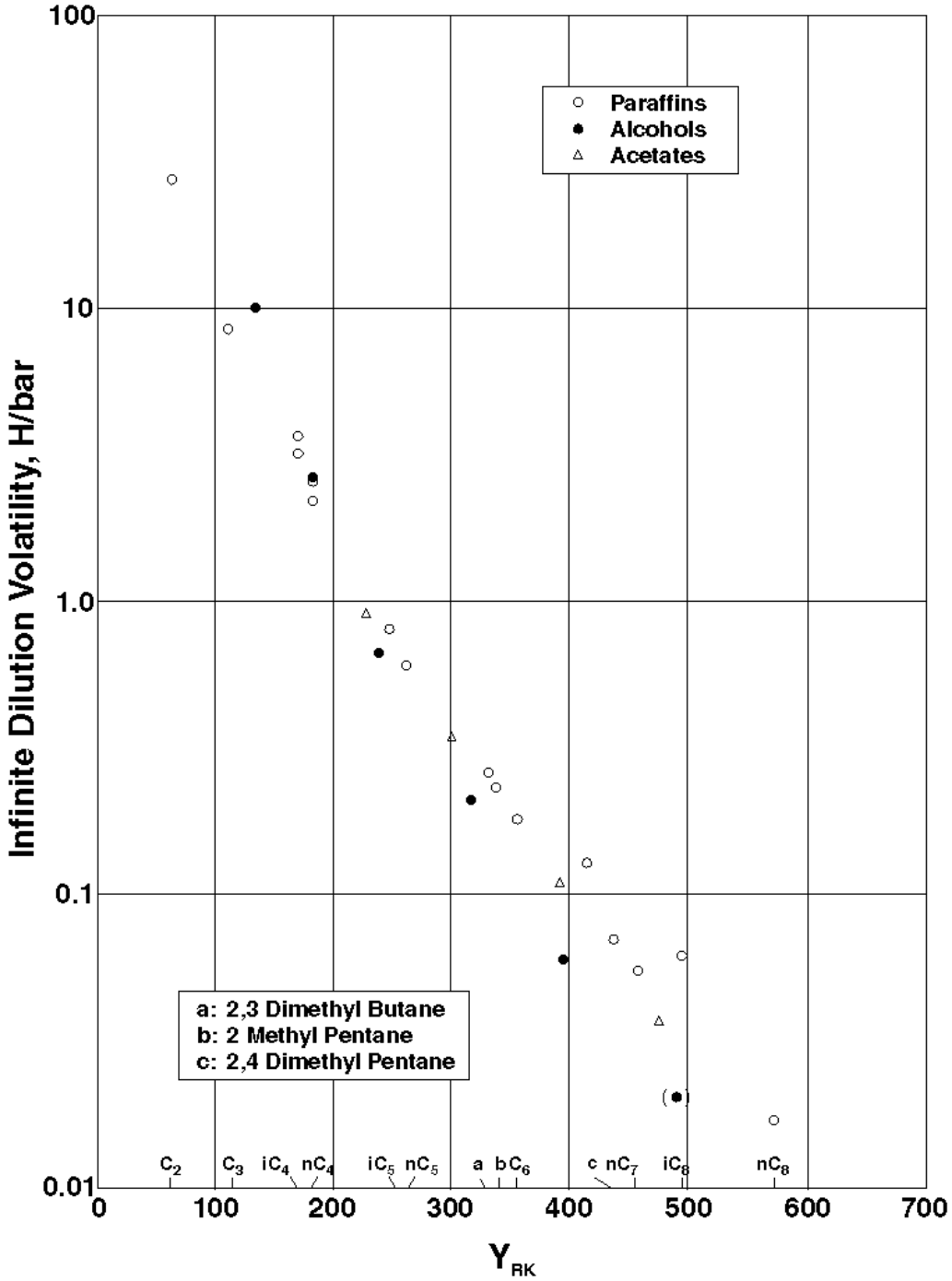

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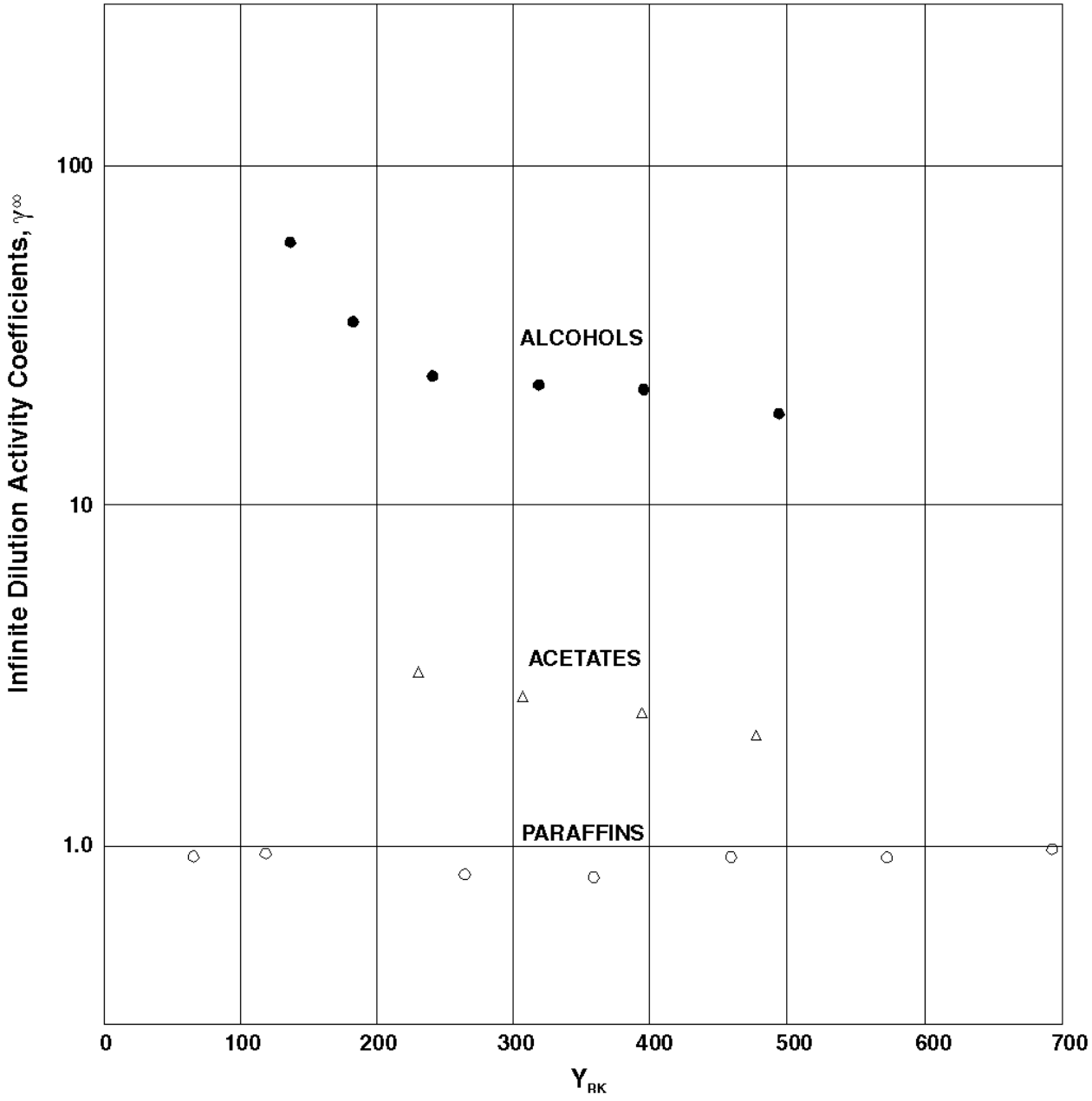
Figure 2, Infinite Dilution Activity Coefficients as a Function of Molecular Parameter, Y_{RK}



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