A Random Contact Point Model for Second Virial Coefficients in Dilute Solutions

A simple latticelike random contact point model is presented to correlate and predict second virial (or pair interaction) coefficients of thermodynamic quantities in dilute solutions. With this model it is possible to correlate pair interaction coefficients in different solvents with one equation and a single set of group interaction parameters. Enthalpic pair interaction coefficients of alkanes and alkanols dissolved in ten different alkan-1-ols and water, and of amides dissolved in N,N-dimethylformamide, N-methylformamide, and water are discussed in terms of the model. Corresponding group interaction parameters in water, alkan-1-ols, and amides are found to be equal within experimental error. When applied to aqueous solutions, the model yields the empirical equations of Savage and Wood, which are thus given some theoretical basis. The model also provides values of the higher interaction coefficients on the basis of the pair terms.

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Introduction

Lattice (or cell) models and quasi-lattice theories have been used since long ago to describe the properties of liquids and solutions (Tompa 1956; Barker 1963; Kozak et al., 1968; Kruus 1977). Despite strong criticism by Hildebrand and Scott (1962) and remarks about restricted applicability by others (Williamson 1967; Kruus 1977), these types of models are widely used with reasonable results, since they illustrate many of the phenomena present in liquid mixtures in a simple way (Kruus, 1977, p. 88). Recently, one of us used such an approach to describe quantitatively the standard molar Gibbs free energy of transfer of ions from a reference solvent to solvent mixtures as a function of the composition (Marcus, 1983).

In the current paper, a latticelike additivity model is used to describe pair interaction coefficients (second virial coefficients), B_2^y, of thermodynamic quantities y in dilute solutions. Two additivity approaches for these quantities are currently used, namely Savage-Wood additive groups (SWAG) and excess group activity (EGA). When used for enthalpic pair interaction coefficients, the former gives (Savage and Wood, 1976)

$$B^h_{PQ} = \sum_i \sum_j n_{P,i} \cdot n_{Q,j} \cdot h_{ij}(\text{SWAG}) \qquad (1)$$

in which $n_{P,i}$ and $n_{Q,j}$ are the numbers of groups of type i on solute molecule P and of type j on solute molecule Q, respectively, and h_{ij}(SWAG) is an intensive term quantifying the $i - j$ interaction. In the excess group additivity approach, account is taken of the fact that if solute and solvent are identical, B_2^h is bound to be zero. This was accomplished (Bloemendal and Somsen, 1987b) by the specification that

$$B^h_{PQ} = \sum_i \sum_j [(n_{P,i} - n_{V,i})(n_{Q,j} - n_{V,j})]\, h_{ij}(\text{EGA}) \qquad (2)$$

where $n_{V,i}$ and $n_{V,j}$ respectively denote the numbers of groups i and j in the solvent molecules.

These approaches demand separate sets of group interaction parameters when different solvents contain the same interacting solute groups. On the other hand, it has been shown (Bloemendal, 1985; Bloemendal et al., 1985) that 49 enthalpic pair interaction coefficients of six different alkanes as solutes and 54 enthalpic pair interaction coefficients of ten different alkan-1-ols as solutes, all dissolved in ten different alkan-1-ols as solvents, can be described with a single empirical equation for each type of solute compounds. One adjustable parameter is used in each equation:

$$B^h_{PP}(\text{alkanes}) = A_0(M_w/M_V)r_0\,(r_0 - 1) \qquad (3)$$

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and

$$B^h_{PP}(\text{alkanols}) = A_1(M_w/M_V)(r_i - 1)^2 \qquad (4)$$

where M_w and M_V are the molar masses of water and the solvent, respectively, r_i is related to the number of C atoms in the solute, $n_{U,C}$, and the solvent, $n_{V,C}$: $r_i = (n_{U,C} + i)/(n_{V,C} + i)$ where $i = 0$ and 1 in Eqs. 3 and 4 respectively, and A_0 and A_1 are fitting parameters. The molar mass of water in Eqs. 3 and 4 originated from historical grounds and can be included in the fitting parameters. Henceforth, $n_{X,i}$ is the number of groups of type i in a molecule of type X; properties of the solvent are designated with subscript V and those of the solute with subscript U.

The random contact point model (RCP) presented in this paper gives a single equation to describe pair interaction coefficients of different types of solute compounds in different solvents with a single set of parameters.

Random Contact Point Model

As in the SWAG and EGA approaches, it is assumed that the solute and solvent molecules can be regarded as consisting of independent interacting groups. In quasi-lattice theories, each particle of a solution is considered to be surrounded by Z neighboring particles (Marcus, 1983). This restricts the applicability of these models to particles of approximately equal size. In order to allow for different sizes of molecular groups, we assume in the model presented here that each interacting group i has $f(a)_i$ contact sites, where $f(a)_i$ is a function of the size of the groups. A comparable approach, sometimes called cell theory, is often used in polymer chemistry (Tompa, 1956; Kruus, 1977; van der Schee and Lyklema, 1984). If a molecule of the solvent or the solute has n_i groups of type i, it will have $F_i = n_i \cdot f(a)_i$ contact points of this type. In our model, only pair interactions are considered. This means that the interactions between three groups are to be considered as the sum of the contributions from the pair interactions.

For a binary system at solute molality m in a solvent of molar mass M_V kg · mol^{-1}, the excess value per kg of solvent of a thermodynamic quantity Y over that at infinite dilution is $Y^E(m)$. This can be expressed as (Cassel and Wood, 1974; Bloemendal and Somsen, 1983; and references in these papers)

$$Y^E(m) = B^y_2 m^2 + B^y_3 m^3 + B^y_4 m^4 + \cdots \qquad (5)$$

where B^y_n denotes the nth interaction or virial coefficient of the thermodynamic quantity Y. We will consider $Y^E(m)$ as the difference in Y between the above-mentioned system with the groups at random distribution, $Y^R(m)$, and the same but hypothetical system without solute-solute interactions, $Y^I(m)$. Hence

$$Y^E(m) = Y^R(m) - Y^I(m) \qquad (6)$$

As is shown in the appendix,

$$Y^E(m)/m^2 = B^y_2 + B^y_3 m + B^y_4 m^2 + \cdots = \frac{\sum_k \sum_{k>l} [(F_{U,k} \cdot \Sigma F_V - F_{V,k} \cdot \Sigma F_U)(F_{U,l} \cdot \Sigma F_V - F_{V,l} \cdot \Sigma F_U)\Delta y_{kl}]}{(m \cdot \Sigma F_U + \Sigma F_V/M_V)(\Sigma F_V)^2} \qquad (7)$$

where the abbreviated notation ΣF_X is used to denote $\Sigma_i F_{X,i}$, the summations are taken over all types of groups, and the group interaction parameter is given by

$$\Delta y_{kl} = y_{kl} - (1/2)(y_{kk} + y_{ll}) \qquad (8)$$

y_{ij} being the molar contribution to Y of an $i - j$ interaction. A series expansion of the righthand side of Eq. 7 gives

$$B^y_2 + B^y_3 m + B^y_4 m^2 + \cdots = \frac{\sum_k \sum_{k>l} [(F_{U,k} \cdot \Sigma F_V - F_{V,k} \cdot \Sigma F_U)(F_{U,l} \cdot \Sigma F_V - F_{V,l} \cdot \Sigma F_U)\Delta y_{kl}]}{(\Sigma F_V)^3/M_V} \cdot [1 - (\Sigma F_U/\Sigma F_V/M_V)m + (\Sigma F_U/\Sigma F_V/M_V)^2 m^2 - \cdots] \qquad (9)$$

Hence,

$$B^y_2 = \frac{\sum_k \sum_{k>l} [(F_{U,k} \cdot \Sigma F_V - F_{V,k} \cdot \Sigma F_U)(F_{U,l} \cdot \Sigma F_V - F_{V,l} \cdot \Sigma F_U)\Delta y_{kl}]}{(\Sigma F_V)^3/M_V} \qquad (10)$$

This result implies that B^y_2 values can be expressed in terms of molar group parameters Δy_{kl}, which are related to the difference in Y between like-unlike and like-like interactions. For n molecular groups in the system, $\Sigma_i i - n = \Sigma_i (i - 1)$ parameters, with i running from 1 to n, are to be used. This is n less than in the EGA approach.

From Eq. 10 it apears that

$$B^y_4 = -[\Sigma F_U/(\Sigma F_V/M_V)] \cdot B^y_3 = [\Sigma F_U/(\Sigma F_V/M_V)]^2 \cdot B^y_2 \qquad (11)$$

Hence, if for a binary system on the molecular level only pair-

wise interactions are considered, a molal expansion of an excess thermodynamic quantity Y leads to a sign oscillation of the B_n^y values. This implication of the random contact point model has already been indicated by Wood et al. (1978). The RCP predicts that the magnitude of the B_n^y values decreases with $\Sigma F_U/(\Sigma F_V/M_V)$. Conversely, if these values do not obey this relationship, three-body interactions or deviations from random contacts may be appreciable.

In order to determine absolute values of Δy_{kl}, it is essential to know the function $f(a)$. This will be a (lattice or cell) constant times a function that gives the number of cells occupied by a molecular group of specified size. Even if this latter function were known, only relative values of Δy_{kl} can be obtained, since the coefficients in Eq. 10 involve the constant $f(a)^3$ in the denominator and $f(a)^4$ in the numerator.

An interesting point in the RCP model emerges, when it is applied to a solvent that may be considered as a single interacting group, v. In that case the coefficients of Δy_{kl} in Eq. 10 can be simplified to $\Sigma_k \ \Sigma_{k>l}(F_{U,k} \cdot F_{U,l})/(F_v/M_v)$, when neither k nor l is identical with v, and to $-\Sigma_k(F_{U,k} \cdot F_U)/(F_v/M_v)$ when l is the same as v. Hence

$$B_2^y = \sum_{k\neq v} \sum_{l\neq v>k} [F_{U,k} \cdot F_{U,l} \cdot \Delta y_{kl}/(F_v/M_v)] - \sum_{k\neq v} \sum_{l\neq v} [F_{U,k} \cdot F_{U,l} \cdot \Delta y_{kv}/(F_v/M_v)] \quad (12)$$

Equation 12 may be rewritten in the form

$$B_2^y = 2 \sum_k \sum_{l>k} [F_{U,k} \cdot F_{U,l}(y_{kl} + y_{vv} - y_{kv} - y_{lv})/(2F_v/M_v)] + \sum_k [(F_{U,k})^2 (y_{kk} + y_{vv} - 2y_{kv})/(2F_v/M_v)] \quad (13)$$

When one selects for F_U the number of groups of type U [i.e., setting $f(a) = 1$], Eq. 13 is the same as the Savage and Wood equation, Eq. 1, where the interaction parameter y_{kl} (SWAG) equals $(y_{kl} + y_{vv} - y_{kv} - y_{lv})/(2F_v/M_v)$. Thus the Savage and Wood approach for aqueous systems (where $H_2O = v$) may be considered as a special case of the RCP model.

Applications

We have applied the random contact point model (RCP) described in the previous section to correlate enthalpic pair interaction coefficients, that is, with $Y = H$ and $y = h$. These coefficients pertain to a large set of n-alkanes and n-alkan-1-ols dissolved in n-alkan-1-ols, of amides dissolved in N,N-dimethylformamide (DMF) and in N-methylformamide (NMF), and of amides, alkanols, and alkan-polyols dissolved in water. To this end, literature data on B_2^h were fitted by means of a multiple linear regression analysis to Eq. 10. An analysis of higher interaction coefficients in terms of Eq. 11 has been carried out for the amidic solvents DMF and NMF.

The size-dependent function $f(a)_i$ was taken as the ratio of the van der Waals surfaces, given by Bondi (1964), to the van der Waals surface of a CH_2 group. The methylene group was selected as a reference for convenience. Since $f(a)_i$ also comprises the unknown lattice constant Z, the coefficients Δy_{kl}(RCP) given in the tabulated results should be considered as

$$\Delta y_{kl}(\text{RCP}) = Z \cdot S(\text{CH}_2) \cdot \Delta y_{kl} \quad (14)$$

where $S(CH_2)$ denotes the numerical value of the van der Waals surface of a methylene group. Relative van der Waals surfaces are presented in Table 1.

Table 1. Relative van der Waals Surfaces of Molecular Groups, S^r*

Group	S^r	Group	S^r
CH_3	1.57	$CONH_2$	2.47
CH_2	1.00	CONH	1.92
CH	0.42	CON	1.36
C	0.00	H_2O	1.67

*Data of Bondi (1964); $S^r(CH_2) = 1$

Alcoholic systems

Forty-nine enthalpic pair interaction coefficients of six n-alkanes (ethane, propane, butane, pentane, nonane, and decane) and 54 B_2^h values of ten n-alkan-1-ols (C_1 to C_{10}) as solutes in ten n-alkan-1-ols (C_1 to C_{10}) as solvents have been published (Bloemendal, 1985; Bloemendal et al., 1985). It has been shown in these publications that different values of the group interaction parameters are found with the SWAG and EGA equations for each alkanolic solvent.

Two molecular groups, alkyl (CH, CH_2, or CH_3) and hydroxyl (OH), were employed in order to apply the random contact point model to these data. This calculation yields one adjustable enthalpic group interaction parameter, $\Delta h_{\text{alkyl,OH}}$(RCP) which is the same for all the solvents. The results of this approach are compared in Table 2 with those of the empirical relations, Eqs. 3 and 4, published previously (Bloemendal, 1985; Bloemendal et al., 1985). It appears that the results with the RCP for the alkan-1-ols as solutes are slightly better than those with the empirical equation, whereas those for the n-alkanes as solutes are somewhat worse. However, with RCP the fitting parameter has a physical meaning. The positive sign of $\Delta h_{\text{alkyl,OH}}$(RCP) could be expected, since a hydrogen bond is lost when a pair of OH · · · OH and CH_2 · · · CH_2 interactions is replaced by two OH · · · CH_2 interactions. In addition, it is possible with the RCP model to describe both alkanes and alkan-1-ols as solutes with a single equation. The quality of this

Table 2. Fit Results for Enthalpic Pair Interaction Coefficients in n-Alkan-1-ols as Solvents*

Solutes	Eq.	σ**	R	Fit Parameter
n-Alkanes	3	42	0.97	−15.1 ± 0.5†
	RCP	83	0.90	4.4 ± 0.3‡
n-Alkan-1-ols	4	38	0.98	−24.3 ± 0.4†
	RCP	33	0.98	5.8 ± 0.2‡
n-Alkanes + n-alkanols	RCP	66	0.93	5.0 ± 0.2‡

*The range of the data fitted is from near zero to −936 J · kg · mol^{-2}
**J · kg · mol^{-2}; †J · kg · mol^{-2}; ‡kJ · mol^{-1}

description is slightly less than that with the two empirical equations. The F-statistic of the RCP, for 103 B_2^h values ranging from near zero to -936 J · kg · mol^{-2}, is 689. Table 2 also indicates that the values of $\Delta h_{\text{alkyl,OH}}$(RCP) from the two separate RCP fits for the two kinds of solutes and the combined fit agree reasonably well.

Amidic systems

An extensive set of pair interaction coefficients of amides and related compounds in N,N-dimethylformamide (DMF) has been measured (Bloemendal and Somsen, 1987a and references therein). It was concluded from these results that several deviations from random group interactions do occur. These include dependence on neighboring groups (Bloemendal et al., 1986), preferential orientation of interacting molecules (Bloemendal and Somsen, 1984, 1985), and structural discrimination (Kent et al., 1985). It is therefore expected that simple models, such as the one presented here, will give only a rough correlation, but it is of interest to see how well it is in fact applicable.

Several sets of interacting groups might be selected, and we made an RCP fit with three groups: alkyl (CH, CH_2, or CH_3), amide (CON), and amide with N-bonded hydrogen atoms (CONH or $CONH_2$). This yields three group interaction parameters. The results of this fit are compared in Table 3 with those found for SWAG and EGA (Bloemendal, 1985). It appears that the results of the RCP model are superior to those of the SWAG model and are comparable with those of the EGA model. The RCP fit can be further improved when it is realized that the contribution to B_2^h of hydrogen bonding from N-bonded hydrogen atoms (H_N) to the amide group of formamide (CON_f) differs significantly from that of other amide groups (Bloemendal et al., 1986b). In order to account for this, we have also fitted the data with four group interaction parameters, namely those concerning the alkyl · · · CON, alkyl · · · H_N, CON · · · H_N, and CON_f · · · H_N interactions. The results of this fit are also included in Table 3. The corresponding group interaction parameters are presented in Table 4.

A less extensive set of 19 B_2^h values of amides was measured in the solvent N-methylformamide (NMF) (Bloemendal, 1985). This set of data is too small for a statistically significant fit with four parameters. However, we made an RCP fit of the combined data in DMF and NMF, using the same four group interaction parameters as above. The results of this fit can also be found in Tables 3 and 4. The statistics are comparable with those in DMF. When the group interaction parameters of both fits are compared, it appears that those of the DMF and the DMF + NMF data agree reasonably well, with the exception of that of the CON · · · H_N interaction, which has a large statistical uncertainty in DMF. In order to illustrate the quality of the RCP correlation for the combined sets of data, we compare in Figures 1 and 2 the calculated B_2^h values with the experimental ones in DMF and NMF, respectively. Reasonable agreement between the calculated and experimental values is noted, with a few cases of clear deviations.

Deviations are noted in Figure 1 for the unsubstituted amides in DMF. In these systems there exists a preferential mutual orientation of the interacting solute molecules (Bloemendal and Somsen, 1984), which is incompatible with the basic assumption of the RCP model. It may also be noted that the deviations in the highly structured solvent NMF are larger than those in DMF, but also that in the former solvent the trends are correctly predicted. Thus, the RCP model permits the correlation of enthalpic pair interaction coefficients of simple amide solutes both in the highly structured NMF and the much less and differently structured DMF (Kopecni et al., 1981) with a single set of four fitting parameters, despite a breakdown of the basic assumption of the model.

Table 3. Fit Results for Enthalpic Pair Interaction Coefficients in Amides as Solvents*

Approach	Solvent	n_{data}	n_{pm}	σ**	R	F
SWAG	DMF	33	3	115	0.953	99
EGA	DMF	32	3	89	0.974	171
RCP	DMF	32	3	92	0.971	160
RCP	DMF	32	4	60	0.988	294
RCP	NMF + DMF†	51	4	64	0.978	261

*The range of the data fitted is from $-1{,}050$ to 100 J · kg · mol^{-2}
**J · kg · mol^{-2}
†The range of the data fitted is from $-1{,}050$ to 182 J · kg · mol^{-2}

Table 4. Values of Δh_{kl}(RCP)* for Fits of Amide Solvent Systems Using Four Parameters

Solvent	Alkyl, CON	Alkyl, H_N	CON, H_N	CON_f, H_N
DMF	7.0 ± 0.3	−0.5 ± 2.9	−0.9 ± 7.0	11 ± 4
DMF + NMF	6.8 ± 0.3	1.0 ± 1.5	10 ± 4	13 ± 3

*kJ · mol^{-1}; see Table 3 for the quality of the fits

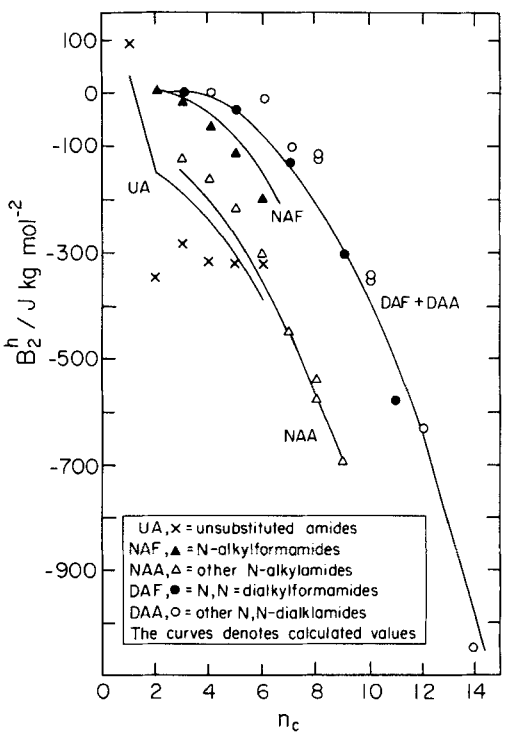

Figure 1. B_2^h values for several amides dissolved in DMF.
Symbols: experimental values
n_C = number of carbon atoms in solute molecules

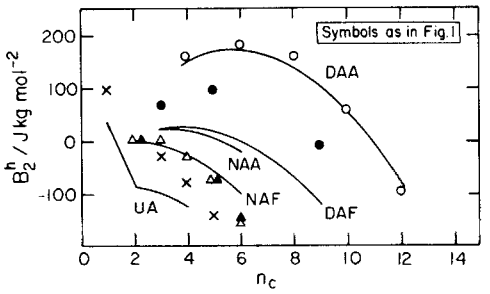

Figure 2. B_2^h values for several amides dissolved in NMF.

Values of B_2^h for more complicated compounds, N-acetyl amino-acid amides, were obtained in DMF by Kent et al. (1985). Since structural discrimination was found to occur in these solutions, it is not surprising that the RCP model fails to yield reasonable predictions of these coefficients. The fit obtained with the RCP model is comparable with that of the SWAG model and considerably worse than with the EGA model.

It was shown above, Eq. 11, that when pairwise interactions only are considered, the B_n^y values follow a trend with alternating signs and decreasing magnitudes as n increases. Such trends were found for the B_n^h values of amides in DMF and NMF. We therefore compare the experimental values of B_3^h with those calculated from B_2^h by means of Eq. 11 in Figures 3 and 4. In the latter figure absolute values are shown, since in NMF some of the triplet coefficients are negative. In most cases the deviations of the predicted from the experimental B_3^h values are <25%. Some extremely large deviations are found for the unsubstituted amides dissolved in DMF, and these were excluded from Figure 3. These deviations can again be explained in terms of the breakdown of the basic assumption of randomness of the RCP model for these systems.

Aqueous systems

Lattice and cell models may be less appropriate from a theoretical point of view for a description of aqueous solutions, where molecular interactions depend strongly on the orientation of the molecules (Barker, 1963, p. 129). Nevertheless, such models

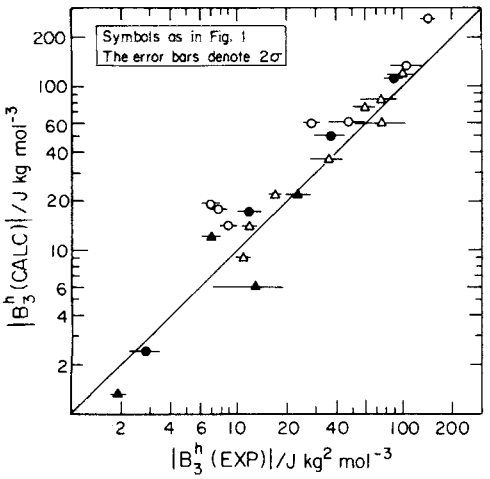

Figure 3. B_3^h in DMF: experimental values vs. values calculated on the basis of Eq. 11.

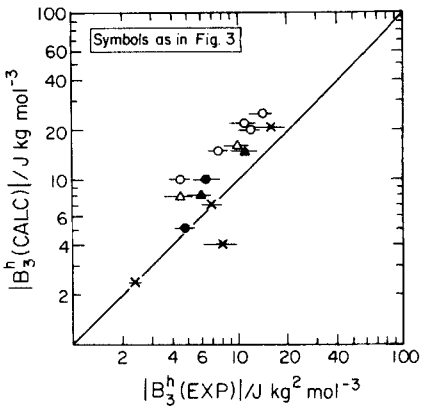

Figure 4. B_3^h in NMF: experimental values vs. values calculated on the basis of Eq. 11.

have extensively and often successfully been used for these types of systems (Kozak et al., 1968; Kruus, 1977; Marcus, 1983). We therefore tried our RCP model also on these systems. A large number of interaction coefficients, both of the enthalpy and the Gibbs energy, have been measured in water. A review was recently published by Suri et al. (1985). Some of these coefficients are for pairs of unlike solute molecules. As we will prove in another paper, the analog of Eq. 10 for unlike molecules P and Q, B_{PQ}^y, is given by

$$B_{PQ}^y = \sum_k \sum_{l>k} \{[(F_{P,k} \cdot \Sigma F_V - F_{V,k} \cdot \Sigma F_P) \cdot (F_{Q,l} \cdot \Sigma F_V - F_{V,l} \cdot \Sigma F_Q) + (F_{Q,k} \cdot \Sigma F_V - F_{V,k} \cdot \Sigma F_Q) \cdot (F_{P,l} \cdot \Sigma F_V - F_{V,l} \cdot \Sigma F_P)] \Delta y_{kl}\} \div [2\,(\Sigma F_V)^3 / M_V] \quad (15)$$

In that paper we will discuss the application of the RCP model to aqueous systems in detail, and compare its performance with that of other models. Here we restrict ourselves to the data on enthalpic interaction coefficients of alcohols (including polyols) and amides (including some small polypeptides). The water molecule is considered to be a single group. The van der Waals surface of this group was obtained from extrapolation of the Bondi (1964) data on ethers and alcohols to zero number of carbon atoms. From the former set a surface of 1.69 relative to that of CH_2 was found, and a surface of 1.65 from the latter set. The mean was used in the fits.

For the first fit, all the B_2^h data for alcohols and polyols collected by Suri et al. (1985) were used. As before, alkyl (CH, CH_2, or CH_3) and hydroxyl (OH) were selected as the interacting groups of the solutes. For the second fit, all the B_2^h values of amides and (poly-)peptides were used, except those for the largely deviating value of N-acetyl-L-alanyl-L-alanyl-L-alanine-amide (Blackbourne et al., 1980). As was indicated by Suri et al., only two solute functional groups, alkyl (CH, CH_2, or CH_3) and amidic (CON, CONH, or $CONH_2$), need to be selected in this case, since the contributions to B_2^h of CON, CONH, and $CONH_2$ in water are comparable. The results are collected in Table 5.

Table 5. Fit Results for Enthalpic Pair Interaction Coefficients in Water as Solvent

Solutes	n_{data}	Range of B_2^{h*}	σ*	R	F
Alcohols	40	−818 to 1,757	178	0.970	195
Amides	41	−1,499 to 3,920	220	0.979	295

	Δh_{kl}(RCP)**				
Solutes	CH_2,OH	OH,w	CH_2,w	CON,w	CH_2,CON
Alcohols	6.7 ± 1.5	4.2 ± 0.4	−3.1 ± 0.3	—	—
Amides	—	—	−3.0 ± 0.6	5.7 ± 0.7	8.3 ± 2.6

*J · kg · mol^{-2}
**kJ · mol^{-1}

The quality of the fits, as judged from the statistical R and F values, is comparable with those in the amidic solvents in Table 3. The values of $\Delta h_{alkyl,w}$(RCP) of both alcohol and amide fits in water agree perfectly. The negative sign of this term means that the adherence of two methylene groups in water is accompanied by a decrease in enthalpy. This is in accordance with the generally accepted ideas on hydrophobic interactions. Within the uncertainties, the value (6.7 ± 1.5) of $\Delta h_{alkyl,OH}$(RCP) obtained from the aqueous data agrees with that obtained from the combined fit (5.0 ± 0.2) and from the fit in alcoholic solvents of the alkanols as solutes (5.8 ± 0.2) as given in Table 2, and is not far from the value found with alkanes as solutes (4.4 ± 0.3). Similarly, the value (8.3 ± 2.6) of $\Delta h_{alkyl,CON}$(RCP) agrees with the values from Table 4 (6.8 ± 0.3 and 7.0 ± 0.3). These results indicate that with the RCP model, notwithstanding certain theoretical objections, the B_2^h values in aqueous and nonaqueous solutions can be related to each other. Remembering the exceptional role of water as a solvent (Franks, 1972–1981), this is a remarkable result.

Notation

A_0, A_1 = fitting parameters
$A_{kk} = C_{kk}/D$
$A_{kl} = C_{kl}/D$ for $k \neq l$
B_n^Y = nth virial (or interaction) coefficient of Y
B_{PQ}^Y = pair interaction coefficient of Y between molecules P and Q
C_{kl}/D = coefficient of y_{kl}, Eq. A5
$f(a)_i$ = number of contact sites of group i
F = F-statistic
$F_i = n_i \cdot f(a)_i$
h = enthalpy
$h_{kl}(X)$ = enthalpic group-interaction parameter between groups k and l in model X
I = total number of interaction sites per kg solvent
M = molar mass
m = molality
n_i, $n_{i,X}$ = number of groups of type i (in molecule X)
n_{data} = number of data in a fit
n_{pm} = number of parameters used in a fit
N_A = Avogadro's constant
$r_i = (n_{C,U} + i)/(n_{C,V} + i)$
R = multiple linear correlation coefficient
$S(CH_2)$ = van der Waals surface of a methylene group
S^r = van der Waals surface relative to that of a CH_2 group
y_{kl} = molar contribution of the interaction of groups k and l to Y
Y = any extensive thermodynamic quantity
Z = lattice constant
Δy_{kl} = defined in Eq. 8
Δy_{kl}(RCP) = defined in Eq. 14
σ = standard deviation
Σ = summation
$\Sigma F_X = \Sigma_i F_{X,i}$
$\forall_i$ = for all i

Subscripts

C = carbon atom
i, j, k, l = dummy variables
U = solute
V = solvent
w = water

Superscripts

E = excess over system at infinite dilution
h = enthalpic
I = ideal system without solute-solute interactions
R = system at random distribution of groups and contact points
y = for thermodynamic quantity Y

Appendix: Derivation of Eq. 7

The total number of groups in a solution of m moles of solute in one kg of solvent is $N_A \Sigma_i(m \cdot n_{U,i} + n_{V,i}/M_V)$, N_A being Avogadro's number. The total number of interaction sites in this system is

$$I = N_A \Sigma_i[f(a)_i (m \cdot n_{U,i} + n_{V,i}/M_V)] \tag{A1}$$

For a random distribution of groups and interaction sites, the probability for a certain group k that one of its contact sites will be occupied by a group l is $(m \cdot F_{U,l} + F_{V,l}/M_V)/I$, F_i being the product $n_i \ f(a)_i$. The number of $k - l$ interactions is thus $(1/2)[N_A(m \cdot F_{U,k} + F_{V,k}/M_V) \cdot N_A(m \cdot F_{U,l} + F_{V,l}/M_V)]/I$. Hence, the total value of Y of the system at random distribution will be

$$Y^R(m) = \frac{\left(\frac{1}{2}\right) \sum_k \sum_l [(m \cdot F_{U,k} + F_{V,k}/M_V)(m \cdot F_{U,l} + F_{V,l}/M_V) \cdot y_{kl}]}{(m \cdot \Sigma F_U + \Sigma F_V/M_V)} \tag{A2}$$

where y_{kl} is the molar contribution of a $k - l$ interaction to Y.

For the hypothetical system without solute-solute interactions, only solvent groups are available for interaction with a solute group k. Thus the contribution of solute-solvent interactions to Y for this system, $Y_{UV}^I(m)$, are

$$Y_{UV}^I(m) = \sum_k \sum_l [m \cdot F_{U,k} \cdot (F_{V,l}/\Sigma F_V) \cdot y_{kl}] \tag{A3}$$

In this case the factor (½) is omitted, because no interactions are counted twice.

The solvent group sites used for solute-solvent interactions are not available for solvent-solvent interactions. For each solvent group k there are $N_A \cdot m \cdot \Sigma F_U \cdot (F_{V,k}/\Sigma F_V)$ such sites. Hence, the solvent-solvent part of Y for the hypothetical system, $Y^I_{VV}(m)$, is

$$Y^I_{VV}(m) = \left(\frac{1}{2}\right)\sum_k \sum_l [F_{V,k}(1/M_V - m \cdot \Sigma F_U/\Sigma F_V) \cdot F_{V,l}(1/M_V - m \cdot \Sigma F_U/\Sigma F_V) \cdot y_{kl}/\Sigma F_V \cdot (1/M_V - m \cdot \Sigma F_U/\Sigma F_V)] \quad \text{(A4)}$$

It follows from Eqs. 6 and A2 to A4 that

$$Y^E(m) = Y^R(m) - [Y^I_{UV}(m) + Y^I_{VV}(m)] = \left(\frac{1}{2}\right)\sum_k \sum_l \left\{\left[\frac{(m \cdot F_{U,k} + F_{V,k}/M_V)(m \cdot F_{U,l} + F_{V,l}/M_V)}{m\Sigma F_U + \Sigma F_V/M_V} - \frac{2m \cdot F_{U,k} \cdot F_{V,l}}{\Sigma F_V} - \frac{F_{V,k} \cdot F_{V,l} \cdot (\Sigma F_V/M_V - m \cdot \Sigma F_U)}{(\Sigma F_V)^2}\right] y_{kl}\right\} \quad \text{(A5)}$$

Let the coefficient of y_{kl} be denoted by C_{kl}/D, where

$$D = 2(m \cdot \Sigma F_U + \Sigma F_V/M_V)(\Sigma F_V)^2 \quad \text{(A6)}$$

Then for two similar groups

$$\begin{aligned} C_{kk} &= (mF_{U,k} + F_{V,k}/M_V)^2(\Sigma F_V)^2 - 2mF_{U,k} \cdot F_{V,k} \\ &\quad -(\Sigma F_V)(m\Sigma F_U + \Sigma F_V/M_V) \\ &\quad - F^2_{V,k}[(\Sigma F_V/M_V)^2 - (m \cdot \Sigma F_U)^2] \\ &= m^2 \cdot [F^2_{U,k}(\Sigma F_V)^2 - 2F_{U,k} \cdot F_{V,k} \cdot \Sigma F_V \\ &\quad \cdot \Sigma F_U + F^2_{V,k}(\Sigma F_U)^2] \\ &= m^2 \cdot [F_{U,k} \cdot \Sigma F_V - F_{V,k} \cdot \Sigma F_U]^2 \end{aligned} \quad \text{(A7)}$$

In the same manner, for two dissimilar groups

$$C_{kl} + C_{lk} = 2m^2 \cdot [F_{U,k} \cdot \Sigma F_V - F_{V,k} \cdot \Sigma F_U][F_{U,l} \cdot \Sigma F_V - F_{V,l} \cdot \Sigma F_U] \quad \text{(A8)}$$

Let us further define $A_{kk} = C_{kk}/D$ for $k = l$ and $A_{kl} = (C_{kl} + C_{lk})/D$ for $k \neq l$. From the fact that $y_{kl} = y_{lk}$ it follows that

$$Y^E(m) = \sum_k \sum_{l>k} A_{kl}\, y_{kl} \quad \text{(A9)}$$

However, the total number of interactions of every type of group is equal in the systems with and without solute-solute interactions. It is $N_A \cdot (m \cdot F_{U,k} + F_{V,k}/M_V)$ per kg of solvent for each k. Hence

$$\forall_k = \sum_{j \neq k} A_{jk} + 2\,A_{kk} = 0 \quad \text{(A10)}$$

Substitution of Eq. A10 in Eq. A9 yields

$$Y^E(m) = \sum_k \sum_{l>k} A_{kl}\left[y_{kl} - \left(\frac{1}{2}\right)(y_{kk} + y_{ll})\right] \quad \text{(A11)}$$

Substitution of Eqs. 5, A6, and A8 in Eq. A11, replacement of $y_{kl} - (1/2)(y_{kk} + y_{ll})$ by Δy_{kl}, and division by m^2 gives

$$Y^E(m)/m^2 = \frac{\sum_k \sum_{l>k} (F_{U,k} \cdot \Sigma F_V - F_{v,k} \cdot \Sigma F_U)(F_{U,l} \cdot \Sigma F_V - F_{v,l} \cdot \Sigma F_U)\Delta y_{kl}}{(m \cdot \Sigma F_U + \Sigma F_V/M_V)/(\Sigma F_V)^2} \quad \text{(A12)}$$

which is the same as Eq. 7.

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