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THERMODYNAMICS OF KETONES AND DIETHER MIXTURES: ANALYSIS IN TERMS OF GROUP CONTRIBUTION (DISQUAC)

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ABSTRACT

The purpose of this paper is to present a general quasichemical theory in terms of group surface interactions, and to calculate the excess molar enthalpy of mixtures of ketones and diether (1,2-dimethoxyethane). The model used in this paper, DISQUAC (Dispersive-Quasichemical model), is a simple extension of Guggenheim–Barker quasi-lattice theory. Calculated results derived from the model are in good agreement with experimental excess molar enthalpies for all the systems investigated. Possible sources of discrepancy and ways of refining the model are discussed.

INTRODUCTION

Since it is practically impossible to predict quantitatively the chemical contribution to the thermodynamic excess functions, one has to adjust a few parameters for each binary system in order to describe the properties of mixtures. A significant saving of adjustable parameters can be realized for classes of organic molecules which are ensembles of distinct functional groups. For that purpose, one needs a solution model or, at least, some more or less empirical equations. The different group-contribution methods proposed so far depend on the choice of the models and of equations.

The objective of this paper is to present the general theory, in the group surface version [1–5] by using a theory which is essentially identical to the Guggenheim–Barker quasi-lattice theory [6]. The originality of our approach lies mainly in the systematic determination of interaction parameters and the comparison of experimental enthalpy data of mixtures of ketones and diether.

THEORY

In the DISQUAC model [7,8] there are two contributions: a quasichemical and a dispersive contribution. The fundamental supposition of the

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DISQUAC model is to get two interaction terms in the thermodynamic functions by addition of two contributions: (1) dispersive contribution ($G_{\text{int.}}^{\text{E,disp.}}$, $H^{\text{E,disp.}}$), (2) quasichemical contribution ($G_{\text{int.}}^{\text{E,quac.}}$, $H^{\text{E,quac.}}$).

The excess Gibbs free energy and the excess enthalpy are given by the following

$$G^{\text{E}} = G_{\text{comb.}}^{\text{E}} + G_{\text{int.}}^{\text{E,disp.}} + G_{\text{int.}}^{\text{E,quac.}} \tag{1}$$

$$H^{\text{E}} = H^{\text{E,disp.}} + H^{\text{E,quac.}} \tag{2}$$

where $G_{\text{int.}}^{\text{E}}$ is the term of interaction and $G_{\text{comb.}}^{\text{E}}$ is the Flory–Huggins combinatorial term

$$G_{\text{comb.}}^{\text{E}} = RT \sum_i x_i \ln \frac{\rho_i}{x_i} \tag{3}$$

where ρ_i is the volume fraction of component i. The dispersive contribution for excess Gibbs free energy and the excess enthalpy at the zero approximation is [9]

$$G_{\text{int.}}^{\text{E,disp.}} = \tfrac{1}{2} \sum_i (q_i x_i) \sum_i \sum_j \xi_i \xi_j g_{ij}^{\text{disp.}} \tag{4}$$

$$H^{\text{E,disp.}} = \tfrac{1}{2} \sum_i (q_i x_i) \sum_i \sum_j \xi_i \xi_j h_{ji}^{\text{disp.}} \tag{5}$$

where q_i is the surface of contact of molecule i, x_i is the molar fraction of the component i in the mixture, ξ_i is the surface fraction of component i in the mixture and

$$g_{ij}^{\text{disp.}} = -\tfrac{1}{2} \sum_s \sum_t (\alpha_{si} - \alpha_{sj})(\alpha_{ti} - \alpha_{tj}) g_{st}^{\text{disp.}} \tag{6}$$

$$h_{ij}^{\text{disp.}} = -\tfrac{1}{2} \sum_s \sum_t (\alpha_{si} - \alpha_{sj})(\alpha_{ti} - \alpha_{tj}) h_{st}^{\text{disp.}} \tag{7}$$

where α_{si} is the surface fraction of type s on a molecule of type i and $g_{st}^{\text{disp.}}$ and $h_{st}^{\text{disp.}}$ are two interchange dispersive parameters of contact (s, t).

For a binary system the quasichemical contribution is

$$G_{\text{int}}^{\text{E,quac.}} = x_1 \mu_{\text{int,1}}^{\text{E,quac.}} + x_2 \mu_{\text{int,2}}^{\text{E,quac.}} \tag{8}$$

where μ_i^{E} is the excess molar chemical potential of component i,

$$\mu_{\text{int,1}}^{\text{E,quac.}} = z q_i \sum \alpha_{si} \ln \frac{X_\alpha \alpha_{si}}{X_{si} \alpha_s} \quad (i = 1, 2, \ldots) \tag{9}$$

$$H^{\text{E,quac.}} = \tfrac{1}{2}(q_i x_i + q_2 x_2) \sum_s \sum_t (X_s X_t - (\xi_i X_{s1} X_{t1} + \xi_2 X_{s2} X_{t2})) \eta_{st} h_{st}^{\text{quac.}} \tag{10}$$

where

$$\eta_{st} = \exp(-g_{st}^{\text{quac.}}/zRT) \tag{11}$$

and $g_{st}^{\text{quac.}}$ and $h_{st}^{\text{quac.}}$ are the interchange quasichemical parameters of contact (s, t). z represents the number of possible orientations that can exist between two surfaces in contact. X_s and X_t we obtain from the following system of λ equations (λ is the number of surfaces, contacts or different functional groups)

$$X_s\left(X_s + \sum X_t \eta_{st}\right) = \alpha_s \quad (s,\ t = a,\ b, \ldots \lambda) \tag{12}$$

X_{si} and X_{ti} ($i = 1, 2$) are the solutions of eqn. (12) for $x_i = 1$.

Since we used independent determinations of both g^E and h^E at different temperatures, we have assumed a temperature dependence of the Gibbs energy interchange parameter g_{st} according to the equation

$$g_{st}(T)/RT = C_{st,1} + C_{st,2}\left((T^{\ominus}/T) - 1\right) \tag{13}$$

where $T^{\ominus}$ is a reference temperature (generally 298.15 K). The constants $C_{st,1}$ and $S_{st,2}$ are numbers (independent of the units chosen) which have the following significance

$$C_{st,1} = g_{st}^{\ominus}/RT^{\ominus} \tag{14}$$

$$C_{st,2} = h_{st}^{\ominus}/RT^{\ominus} \tag{15}$$

where $g_{st}^{\ominus} = g_{st}(T^{\ominus})$ and $h_{st}^{\ominus} = h_{st}$ (independent of T).

In the theory each type of molecule i is characterized by the following set of geometrical parameters: the total surface q_i, the molecular surface fractions α_{si} and the volume r_i. In order to account for the constitution of organic molecules realistically, we consider them as ensembles of identifiable structural units corresponding to the main chemical groups. Here we have adopted the method developed by Bondi [10,11].

In this more elaborate method each atom is considered to be spherical and the volume V_G and the surface A_G of a given group G, composed of various atoms, are calculated on the basis of the geometry of bonded atoms with interpenetrating surfaces. The fraction of surface (and therefore of volume) left for a possible contact is calculated from the covalent and the van der Waals radii [12,13]. As volume and surface units we arbitrarily decided to take the volume and surface of methane, CH_4 (Table 1). The volume r_i, the total surface q_i and the areas q_{si} were calculated additively using the corresponding group increments. The molecular surface fractions α_{si} were calculated as defined by the equation $\alpha_{si} = q_{si}/q_i$ (Table 2).

The thermodynamic properties must be studied in a systematic way with respect to the interactions of a given functional group. Each individual pair of group (st) is characterized by the two interaction parameters g_{st} and h_{st}. We have adjusted first g_{st} and then h_{st} for each class to fit eqns. (1) and (2) to the best available experimental data for G^E and H^E respectively. Only one pair of parameters g_{st} and h_{st} was adjusted since the key systems used contained only two types of surfaces. Throughout this study the different types of contact surfaces have been labelled with small letters: contact

TABLE 1

Relative group increments for molecular volumes $r_G = V_G/V_{CH_4}$ and areas $q_G = A_G/A_{CH_4}$ calculated using Bondi's method. ($V_{CH_4} = 17.12 \times 10^{-6}$ m^3 mol^{-1}, $A_{CH_4} = 2.90 \times 10^{-6}$ m^2 mol^{-1})

Group	r_G	q_G
CH_4	1.00000	1.00000
CH_3-	0.79848	0.73103
-CH_2-	0.59755	0.46552
-O-	0.21612	0.20690
-CO-	0.68344	0.55174

TABLE 2

Volumes r_i, total surfaces q_i and molecular surface fractions α_{si}, calculated from the relative group increments r_G and g_G given in Table 1

	r_i	q_i	α_{ai} [a]	α_{ei} [b]	α_{ci} [c]
2-Butanone	2.87790	2.47930	0.77750	0.00000	0.22250
2-Pentanone	3.47550	2.94480	0.81260	0.00000	0.18740
2-Hexanone	4.07300	3.41030	0.83820	0.00000	0.16180
2-Heptanone	4.67060	3.87590	0.85770	0.00000	0.14230
2-Octanone	5.26810	4.34140	0.87290	0.00000	0.12710
2-Nonanone	5.86570	4.80690	0.88520	0.00000	0.11480
3-Pentanone	3.47550	2.94480	0.81260	0.00000	0.18740
4-Heptanone	4.67060	3.87590	0.85770	0.00000	0.14230
5-Nonanone	5.86570	4.80690	0.88520	0.00000	0.11480
1,2-Dimethoxyethane	3.22430	2.80690	0.85258	0.14742	0.00000

[a] α_{ai} aliphatic chain; [b] α_{ei} oxygen group; [c] α_{ci} carbonyl group.

(a, e), aliphatic (CH_3- or -CH_2-) oxygen (-O-); contact (a, c), aliphatic (CH_3- or -CH_2-) carbonyl (-CO-); contact (e, c), oxygen (-O-) carbonyl (-CO-).

In the ketones and diether (1,2-dimethoxyethane) mixtures we determined all the interaction parameters reported in the study. First we considered mixtures of n-alkanes and ether and, using the experimental data for G^E and H^E, we fitted the parameters g_{ae} and h_{ae} respectively. This study was done by Kehiaian [14], who used $z = \infty$ (random mixing) and considered a dispersive contribution (Table 3). We then fitted the parameters g_{ac} and

TABLE 3

Interchange parameters for aliphatic-oxygen groups

$g_{ae}^{\text{dis}}/RT^{\ominus}$	$g_{ae}^{\text{quac.}}/RT^{\ominus}$	$h_{ae}^{\text{dis}}/RT^{\ominus}$	$h_{ae}^{\text{quac.}}/RT^{\ominus}$
15.73	0.00	29.04	0.00

TABLE 4

Interchange parameters for aliphatic–carbonyl groups ($z = 10$)

	$g_{ac}^{\text{dis}}/RT^{\ominus}$	$g_{ac}^{\text{quac.}}/RT^{\ominus}$	$h_{ac}^{\text{dis}}/RT^{\ominus}$	$h_{ac}^{\text{quac.}}/RT^{\ominus}$
2-Butanone	0.000	8.097	0.000	9.990
2-Pentanone	0.000	8.097	0.000	9.830
2-Hexanone	0.000	8.097	0.000	9.830
2-Heptanone	0.000	8.097	0.000	9.830
2-Octanone	0.000	8.097	0.000	9.830
2-Nonanone	0.000	8.097	0.000	9.830
3-Pentanone	0.000	8.680	0.000	9.319
4-Heptanone	0.000	7.680	0.000	8.999
5-Nonanone	0.000	7.680	0.000	8.999

TABLE 5

Interchange parameters for carbonyl–oxygen groups

$g_{ce}^{\text{dis}}/RT^{\ominus}$	$g_{ce}^{\text{quac.}}/RT^{\ominus}$	$h_{ce}^{\text{dis}}/RT^{\ominus}$	$h_{ce}^{\text{quac.}}/RT^{\ominus}$
1.320	0.000	−3.320	0.000

h_{ac}. Again, this study was carried out by Kehiaian et al. [1,2] who considered a quasichemical contribution $z = 10$ (Table 4).

For the fitting of g_{ce} we used the experimental G^{E} data of Abbot et al. [15]. The parameter h_{ce} we fitted about the experimental H^{E} data of the system measured by us (2-butanone + di-*n*-butylether) [16]. We have considered a dispersive contribution $z = \infty$ (Table 5).

RESULTS AND DISCUSSION

Tables 1–5 show the parameters calculated in accordance with the DISQUAC model.

Using exactly the same parameters as above, we compared theoretical and experimental excess enthalpies [16] for the ketones and diether mixtures. The comparison was carried out for asymmetrical and symmetrical ketones (Figs. 1 and 2).

With the systems 1,2-dimethoxyethane + 2-pentanone, 3-pentanone or 5-nonanone, the theory gave satisfactory agreement. However, with the system 1,2-dimethoxyethane + 4-heptanone, the theory shows a negative deviation with respect to the experimental data. Finally, with the systems 1,2-dimethoxyethane + 2-hexanone, 2-heptanone, 2-octanone or 2-nonanone, the theory shows a positive deviation with respect to the experimental data. Though the theory and experiment have a good agreement, there must be two different effects that the theory does not take into account.

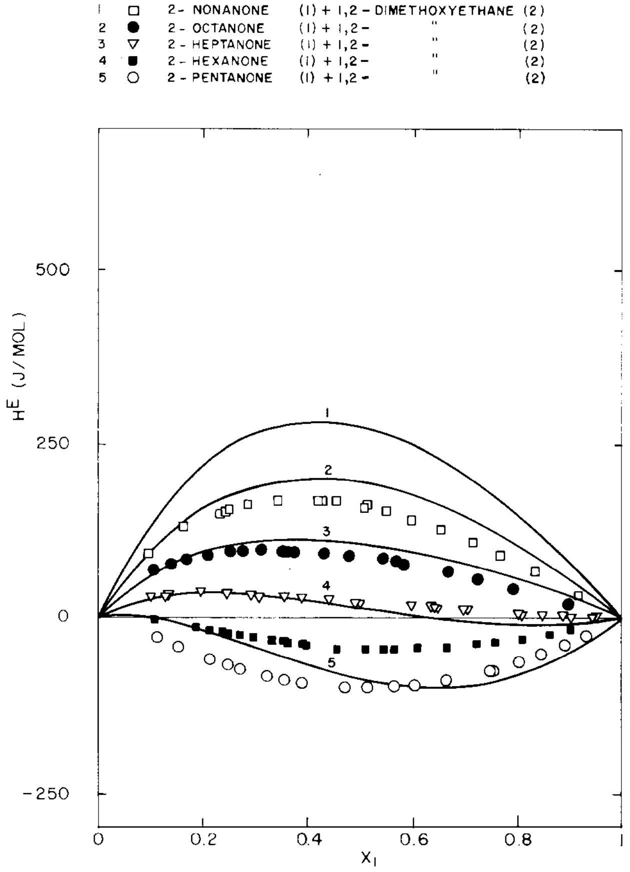

Fig. 1. Comparison of theory with experiment for the excess enthalpy h^E of asymmetrical ketones (1) + 1,2-dimethoxyethane(2) mixtures. Full lines, predicted values; points, experimental results (data of Rey [16]).

Systems with a negative deviation, whose characteristics are the same as the other types of systems, have recently been studied [17–21].

This effect is assumed to be of the "steric" type. The systems with positive deviation have an opposite effect, assumed to be of the "induction" type from the oxygen group and the carbonyl group. Our model does not describe this effect, but as in other works [17–20] we have assumed that the interchange energy parameters are a function of

$$C^{R}_{ce,2} = C^{\ominus}_{ce,2}\left(1 + n^{e}\sigma^{e}_{ce,2} + n^{p}\sigma^{p}_{ce,2} + n^{b}\sigma^{b}_{ce,2} + \left(n^{p} + n^{b}\right)\sigma_{\mathrm{ind.}}\right) \qquad (16)$$

where $C^{\ominus}_{ce,2}$ is the interchange parameter of the component base (2-propanone) and n^e, n^p,... are the number of carbon atoms in the different levels around the carbonyl group (–CO–); e, p and b are (CH_3–CH_2–), (CH_3–CH_2–CH_2–) and (CH_3–CH_2–CH_2–CH_2–) respectively (Fig. 3).

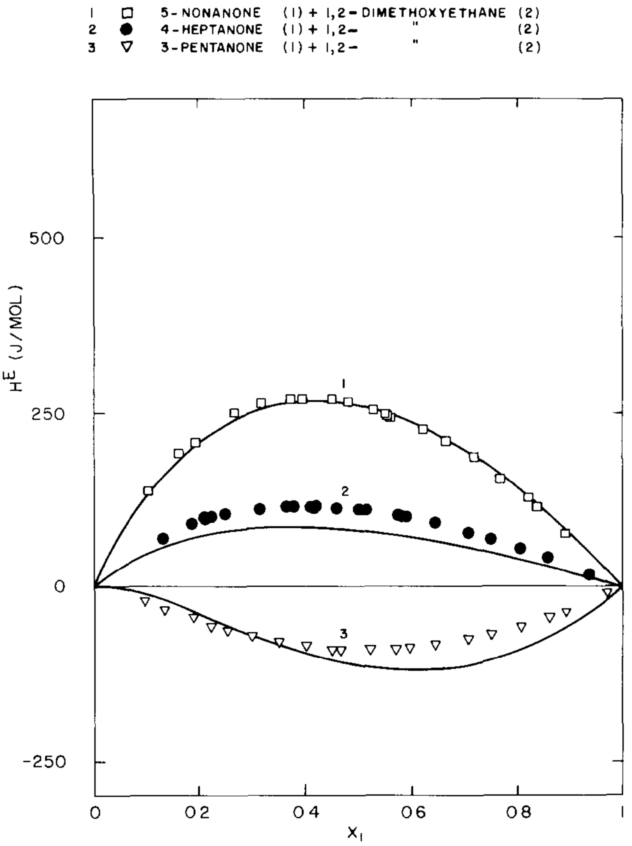

Fig. 2. Comparison of theory with experiment for the excess enthalpy h^E of symmetrical ketones(1) + 1,2-dimethoxyethane(2) mixtures. Full lines, predicted values; points, experimental results (data of Rey [16]).

The $\sigma_{ce,2}^{R}$ parameters account for the steric effect of the alkyl group increment in the equation and $\sigma_{ind.}$ accounts for the induction effect of the alkyl group increment. This preceding class was used for the calculation of the new interchange parameter h_{ce}^{dis}/RT of ketones and 1,2-dimethoxyethane mixtures.

We have fitted the parameter σ_{ce}^{R} of eqn. (16) by the standard method of linear regression, finding the parameter h_{ce}^{dis} with optimal fitting for each of the investigated ketones + monoether (di-*n*-butylether) systems [21].

The values of the parameter σ_{ce}^{R} are given in Table 6.

To calculate the parameter of induction effect σ_{ind} we do the following: after we have fitted the parameter h_{ce}^{dis} optimally for each system investigated, we take away the parameter h_{ce}^{dis} calculated for the same ketones and monoether (di-*n*-butylether) mixtures but where we have assumed a steric effect [21].

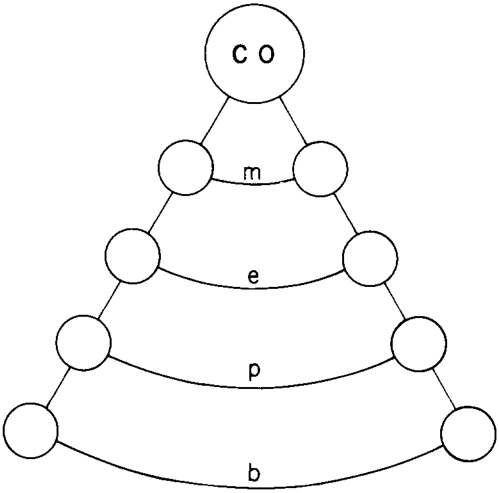

Fig. 3. Number of carbon atoms in the different levels around –CO– group. m, e, p and b are CH_2–, CH_3–CH_2–, CH_3–CH_2–CH_2–, and CH_3–CH_2–CH_2–CH_2– respectively.

TABLE 6

Parameters of alkyl group increment according to eqn. (16)

$h_{ce}^{\ominus,\mathrm{dis}}/RT = C_{ce,2}^{\ominus}$	σ_{ce}^{e}	σ_{ce}^{p}	σ_{ce}^{b}
−6.183	−0.222	−0.200	−0.102

TABLE 7

Parameter of alkyl group increment (induction effect) according to eqn. (16)

σ_{ind}
0.153

TABLE 8

Interchange parameters for carbonyl–ether groups

Molecule	$h_{ce}^{\mathrm{dis}}/RT^{\ominus}$	$h_{ce}^{\mathrm{quac.}}/RT^{\ominus}$
2-Pentanone	−4.52	0.00
2-Hexanone	−4.84	0.00
2-Heptanone	−5.16	0.00
2-Octanone	−5.47	0.00
2-Nonanone	−5.78	0.00
3-Pentanone	−3.44	0.00
4-Heptanone	−2.86	0.00
5-Nonanone	−3.49	0.00

The results are different values which follow a linear function of the type

$$h_{ce}^{\mathrm{dis}} = (n^{\mathrm{p}} + n^{\mathrm{b}})\sigma_{\mathrm{ind.}} \tag{17}$$

where n^{p}, b^{b} and $\sigma_{\mathrm{ind.}}$ are as before and we have fitted the parameter $\sigma_{\mathrm{ind.}}$ in the same way as before (Table 7).

The sign of parameter $\sigma_{\mathrm{ind.}}$ is opposite to that of the parameter for the steric effect of the alkyl group increment σ_{ce}^{R} in accordance with the first assumption.

Since to get the parameters σ_{ce}^{R} and $\sigma_{\mathrm{ind.}}$ we have used eqn. (16), the new values for the interchange parameters $h_{ce}^{\mathrm{dis}}/RT^{\ominus}$ for all systems investigated are as shown in Table 8.

Using the same parameters as in Table 8, we have compared theoretical and experimental excess enthalpies for binary mixtures of ketones and

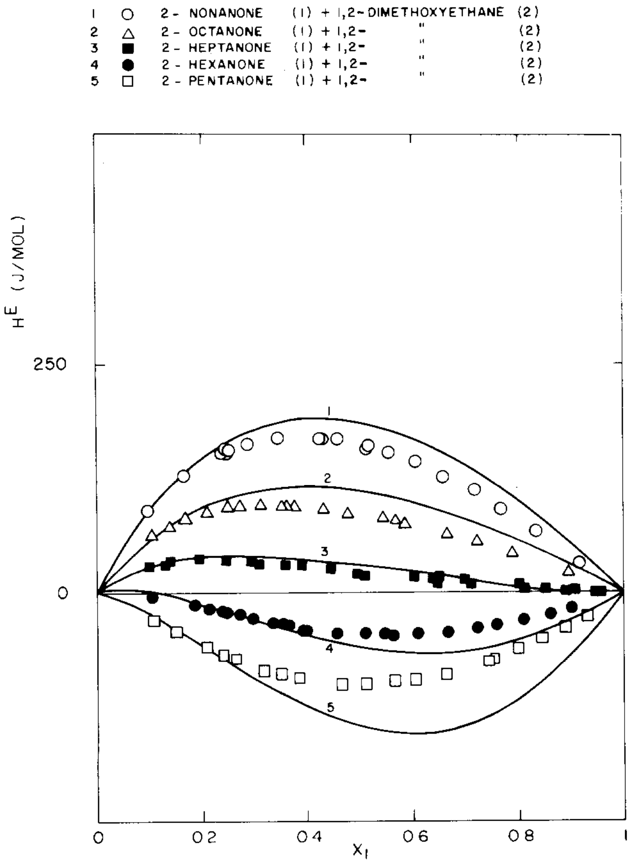

Fig. 4. Comparison of theory (assuming steric and induction effects and using the new parameters of Table 8) with experiment for the excess enthalpy h^{E} of asymmetrical ketones(1) + 1,2-dimethoxyethane(2) mixtures. Full lines, predicted values; points, experimental results. The agreement is better than in Fig. 1.

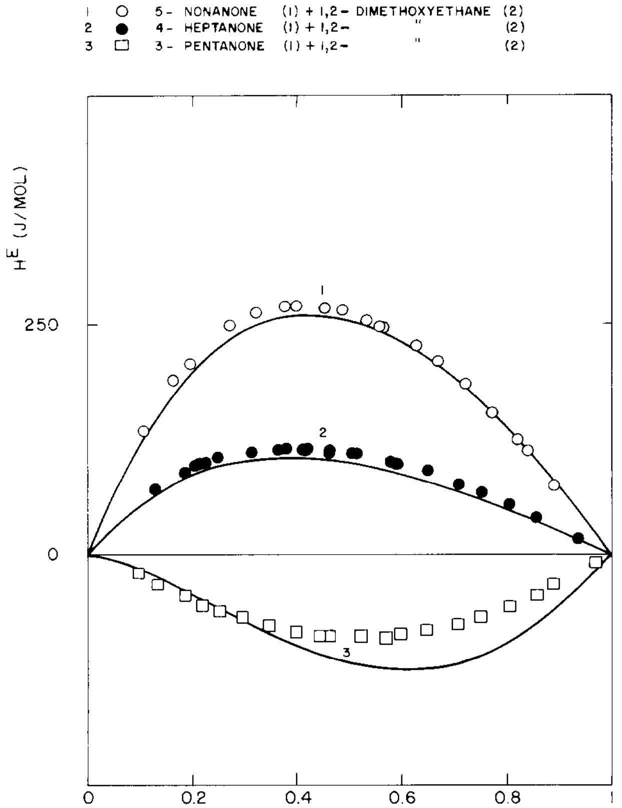

Fig. 5. Comparison of theory (assuming steric and induction effects and using the new parameters of Table 8) with experiment for the excess enthalpy h^E of symmetrical ketones(1) + 1,2-dimethoxyethane(2) mixtures. Full lines, predicted values; points, experimental results. The agreement is better than in Fig. 2.

diether (1,2-dimethoxyethane). Better agreement is obtained than before (as shown in Figs. 4 and 5).

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