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DARC ANALYSIS OF BINARY MIXTURES. EXCESS ENTHALPIES OF KETONE + ALKANE AND KETONE + ALCOHOL SYSTEMS

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ABSTRACT

The excess enthalpies of the series 2-butanone + *n*-alkane, 2-pentanone + *n*-alkane, 2-hexanone + *n*-alkane and 2-hexanone + *n*-alcohol at 298.15 K have been separately correlated using DARC methods, with excellent fit.

INTRODUCTION

The thermodynamic properties of organic liquid mixtures depend on various kinds of complex interaction among the molecules present, even when all the components are non-electrolytes. Prediction of these properties can be based not only on theories of the statistical mechanics of the liquid state, but also, more phenomenologically, on the adaptation by Mulet and co-workers [1,2] of the DARC system originally developed by Dubois and co-workers for pure compounds [3–7], which distinguishes topologically distinct positions within a graph [8] associated with a molecule or family of molecules. The present work reports the results of applying Mulet and co-workers' "topological analysis of mixtures" method to the excess enthalpies of ketone + alkane and ketone + alcohol mixtures.

DESCRIPTION OF THE METHOD

In the DARC (description, automatization, restitution, correlation) system, a linear molecule is associated with a tree (in the graph-theoretical sense) of which the nodes represent the non-H atoms of the molecule, the branches represent bonds, and the root is an atom or group of atoms chosen with a particular purpose in mind. When considering the structural depen-

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dence of physical properties within a family of molecules considered as having the same root (from which the property in question is considered to emanate), the family is associated with the union of the graphs of its individual members, and the magnitude of the property is regarded as being a linear function of node occupancy

$$I = I_0 + \langle \vec{T}(E) | \vec{I}^{(m)} \rangle \tag{1}$$

where I is the value of a thermodynamic property or a simple function of this property. I_0 is the value of I when $\vec{T}(E) = 0$, $\vec{I}^{(m)}$ is the information vector (I_0 and the components of $\vec{I}^{(m)}$ are characteristic coefficients estimated from the relevant experimental data for m suitable members of the family), and the "topological vector" $\vec{T}(E)$ is a vector listing the occupancy of nodes in the environment E, E being a subset of non-root nodes selected according to certain flexible rules. In calculating physical properties, the DARC method thus seeks to take into account possible differences among the contributions of molecular components with different topological relationships to the root. If the property in question is considered as being generated by the molecule as a whole, rather than by a particular group, then instead of the above "monofocal" approach, a "polyfocal" approach is used, such that it is a kind of average graph that is associated with each molecule. The topological vector becomes the sum of the topological vectors of all the graphs obtained by taking each atom of the molecule in turn as root.

When the DARC system is generalized for the analysis of liquid mixtures [1,2], the topological vector $\vec{T}$ used is the sum of the topological vectors $\vec{T}_j$ of the components of the mixture weighted by a characteristic factor S_j.

$$\vec{T} = \sum \vec{T}_j S_j \tag{2}$$

In the present work we use [2] $S_j = \log X_j$, where X_j is the mole fraction of the component j in the liquid mixture.

For analysis of the composition-dependence of the properties of a single mixture whose components have a single functional group or some other special feature, it is also recommended [1,2] that each $\vec{T}_j$ vector be reduced to just two components: $\vec{T}_{j,1}$ is proportional to the average degree of connection of the molecule's atoms, and is obtained by counting, for each atom in the molecule, the number of non-H atoms to which it is bound, and summing the results; $\vec{T}_{j,2}$ is the number of non-H atoms outside the special feature.

APPLICATION TO KETONE+ALKANE AND KETONE+ALCOHOL MIXTURES

This methodology was applied to the logarithmic excess enthalpies ($I = \log H^E$) of the series 2-butanone + n-alkane, 2-pentanone + n-alkane, 2-

TABLE 1

Components of topological vectors

Compound	T_1	T_2
2-Butanone	8	2
2-Pentanone	10	3
2-Hexanone	12	0
n-Pentane	8	0
n-Hexane	10	0
n-Heptane	12	0
n-Octane	14	0
n-Decane	18	0
1-Hexanol	12	5
1-Heptanol	14	6
1-Octanol	16	7
1-Nonanol	18	8
1-Decanol	20	9

hexanone + *n*-alkane and 2-hexanone + *n*-alcohol at 298.15 K. For the first two of these series we used the experimental data of Kiyohara and co-workers [9,10], and for the others our own recently reported data [11]. In obtaining $\vec{\mathbf{T}}_{j,2}$, the terminal Me–CO–group was taken as the root of the graphs for the ketones, and the terminal $-CH_2OH$ group as the root for the alcohols. For the alkanes, $\vec{\mathbf{T}}_{j,2}$ was taken as zero because these do not have a specific functional group. Table 1 lists the values of $\vec{\mathbf{T}}_{j,1}$ and $\vec{\mathbf{T}}_{j,2}$ for each of the compounds considered.

The I_i parameters were estimated for each mixture by fitting eqn. (1) to the experimental data for four compositions (x_1, $1 - x_1$). The results are listed in the columns headed "(a)" in Table 2. Table 2 also compares the experimental values of H^E for $x = 0.5$ with those calculated using these parameters, and lists the root mean square (r.m.s.) deviations between the experimental values and both the present predictions and those obtained by fitting Redlich–Kister equations to all the experimental data.

In view of the systematic variation of the I_i parameters within each series of mixtures, they were fitted with quadratic functions of the number of carbon atoms n in the variable component of the series

$$I_i(n) = \sum_{j=0}^{2} A_{ij} n^j \tag{3}$$

The values of A_{ij} estimated by fitting eqn. (3) to the I_i data for all members of the series are listed in Table 3. The new I_i values calculated from eqn. (3) using these A_{ij} values, and the corresponding values of H^E ($x = 0.5$) and of the r.m.s. deviation from the experimental values are listed in Table 2 in the columns headed "(b)". The corresponding H^E–x curves for all the mixtures of the four series are shown in Fig. 1, together with the

TABLE 2

Components of I_i calculated by methods (a) and (b); experimental excess enthalpies for $x = 0.5$, together with values calculated by methods (a) and (b); and r.m.s. deviations of Redlich–Kister, (a) and (b) curves from the experimental values

Alkanone + n-alkane	n	I_0		I_1		I_2		H, $x = 0.5$ (J mol^{-1})			s		
		(a)	(b)	(a)	(b)	(a)	(b)	Exp.	(a)	(b)	R.–K.	(a)	(b)
2-Butanone	5	3.591	3.594	0.1199	0.1990	−0.0850	−0.0798	1159	1168	1172	1.0	16	12
2-Butanone	6	3.629	3.623	0.0938	0.0949	0.0363	0.0268	1252	1256	1238	1.3	8	18
2-Butanone	7	3.645	3.648	0.0746	0.0756	0.1136	0.1124	1338	1340	1334	1.5	12	11
2-Butanone	8	3.669	3.670	0.0631	0.0613	0.1696	0.1769	1408	1409	1437	1.5	9	33
2-Butanone	10	3.705	3.704	0.0470	0.0474	0.2449	0.2498	1545	1548	1539	1.5	–	12
2-Pentanone	5	3.523	3.520	0.1260	0.1245	−0.1616	−0.1579	966	969	972	0.6	8	10
2-Pentanone	6	3.549	3.556	0.0971	0.0997	−0.0595	−0.0662	1040	1043	1036	1.0	10	13
2-Pentanone	7	3.593	3.588	0.0800	0.0799	0.0084	0.0075	1135	1138	1129	1.1	8	11
2-Pentanone	8	3.616	3.616	0.0668	0.0650	0.0580	0.0633	1203	1205	1227	0.8	7	25
2-Pentanone	10	3.656	3.656	0.0497	0.0502	0.1225	0.1209	1335	1338	1331	0.9	8	9
2-Hexanone	6	3.548	3.547	0.1099	0.1083	−0.1273	−0.1257	949	949	957	6	10	11
2-Hexanone	7	3.564	3.561	0.0830	0.0842	−0.0492	−0.0529	1055	1057	1038	8	11	18
2-Hexanone	8	3.567	3.584	0.0655	0.0672	0.0012	0.0020	1132	1129	1138	8	16	14
2-Hexanone	9	3.638	3.618	0.0610	0.0574	0.0365	0.0389	1198	1202	1223	7	11	28
2-Hexanone	10	3.655	3.662	0.0533	0.0547	0.0594	0.0580	1268	1265	1254	6	7	18

Alkanone + n-1-alcohol	n	I_0		I_1		I_2		H, $x = 0.5$ (J mol^{-1})			s		
		(a)	(b)	(a)	(b)	(a)	(b)	Exp.	(a)	(b)	R.–K.	(a)	(b)
2-Hexanone	6	3.700	3.703	0.0903	0.0927	−0.0402	−0.0459	1431	1434	1437	8	13	14
2-Hexanone	7	3.725	3.717	0.1315	0.1254	−0.1578	−0.1446	1478	1482	1482	8	13	13
2-Hexanone	8	3.731	3.736	0.1490	0.1522	−0.2170	−0.2228	1545	1562	1558	9	23	20
2-Hexanone	9	3.761	3.761	0.1713	0.1730	−0.2747	−0.2804	1611	1608	1623	5	11	24
2-Hexanone	10	3.793	3.792	0.1892	0.1878	−0.3213	−0.3176	1688	1590	1574	8	12	21

TABLE 3

Parameters A_{ij} of eqn. (3)

Series	i	A_{i0}	A_{i1}	A_{i2}
2-Butanone	0	3.3990	0.0473	−0.0017
+ *n*-alkanes	1	0.3140	−0.0513	0.0025
	2	−0.9291	0.2225	−0.0105
2-Pentanone	0	3.2668	0.0623	−0.0023
+ *n*-alkanes	1	0.3231	−0.0521	0.0025
	2	−0.8856	0.1904	−0.0090
2-Hexanone	0	3.6712	−0.0504	0.0049
+ *n*-alkanes	1	0.4039	−0.0708	0.0036
	2	−0.9389	0.1893	−0.0090
2-Hexanone	0	0.0976	−0.0212	0.0027
+ *n*-1-alcohol	1	−0.2289	0.0715	−0.0030
	2	−0.9766	−0.2320	0.0102

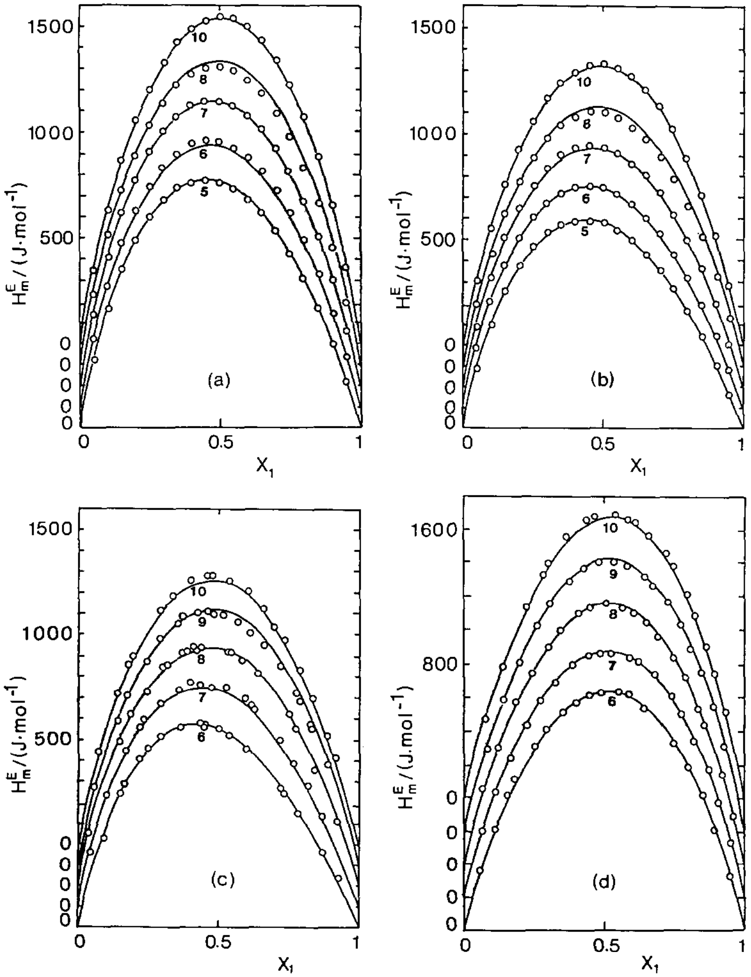

Fig. 1. Excess molar enthalpies H^E at 298.15 K for mixtures of the series 2-butanone + *n*-alkane (a), 2-pentanone + *n*-alkane (b), 2-hexanone + *n*-alkane (c) and 2-hexanone + *n*-alcohol (d): ○, experimental values; — — —, calculated curves.

experimental points. It can be seen that the fit achieved is very satisfactory considering the small number of data upon which the curves are based.

CONCLUSIONS

The method sketched above appears to be very useful for the prediction of excess functions over the whole range of compositions from a small number of experimental data. We would nevertheless point out that if, as in this study, it is logarithmic quantities that are to be predicted, the excess function must be positive over the whole range of compositions; and that the quadratics fitted using eqn. (3) allow interpolated prediction when data are unavailable for intermediate members of a series, but do not allow reliable extrapolation.

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