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CALORIMETRIC STUDY OF MOLECULAR INTERACTIONS IN MIXTURES OF SUBSTANCES CONTAINING CARBONYL GROUPS

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ABSTRACT

A Tian–Calvet type calorimeter has been used to determine molar excess enthalpies, H^E, as a function of concentration at atmospheric pressure and 298.15 K for some binary liquid mixtures containing linear ketones with tetrachloromethane or benzene and linear diketones with *n*-heptane or cyclohexane.

The experimental H^E results are interpreted in terms of molecular interactions and of the "homoproximity effect".

INTRODUCTION

This work is part of a systematic study of the thermodynamic properties of liquid organic mixtures, the TOM Project [1–8], undertaken with the purpose of developing accurate group contribution models to be used to predict thermodynamic excess functions, molar excess Gibbs energy, G^E, and molar excess enthalpy, H^E. In previous studies [4–5], Kehiaian et al. applied the quasi-chemical group contribution theory in the form of the surface interaction version [6] to mixtures of *n*-alkanones + *n*-alkanes.

By investigating other solvents, the number of surface-type and, consequently, the number of interchange parameters are increased. To carry out a

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systematic study one should replace the n-alkane with other homogeneous solvents, i.e., those having only one type of surface. The most typical are, in order of increasing "activity", cyclohexane, benzene and tetrachloromethane.

The purpose of this work was to provide additional experimental H^E data for binary liquid mixtures of benzene or tetrachloromethane with ketones of general formula $CH_3(CH_2)_{s-1}$–CO–$(CH_2)_{t-1}CH_3$ (s, $t = 1, 2, 3, 4$) and of heptane or cyclohexane with diketones of general formula CH_3CO–$(CH_2)_u$–$COCH_3$.

The H^E of six of the present systems involving monoketones were previously determined by Kiyohara et al. [13]. We repeated such measurements in order to apply our treatment to a homogeneous set of results.

In polyfunctional molecules the proximity of two identical or different groups in a given molecule changes considerably the interaction parameters of the compounds. The existence of this "proximity effect" has been found previously in molecules containing the following pair of identical groups: –O–...–O– [9], –S–...–S– [10], $>$N–...–N$<$ [11] and Cl–...–Cl [12].

EXPERIMENTAL

Materials

The liquids used, Fluka 99.5 mol% pure, were subjected to GLC analysis and no purification was attempted.

Calorimetric measurements

The excess enthalpies, H^E, were measured with a Tian–Calvet ("CRMT") type calorimeter which was manually tilted. The batch mixing cell and the experimental procedure are described elsewhere [14]. The calorimeter was calibrated using the Joule effect and the calibration was repeated after each experiment. The precision of our H^E measurements was generally better than 1%, as can be seen from the standard deviation values reported in Table 1. The reliability of the apparatus and procedure adopted were checked by performing H^E measurements on the test system benzene + cyclohexane. Our results differed by less than 2% from literature data [15] over the entire composition range. Also, the agreement with results of Kiyohara et al. [13] on aliphatic ketones + CCl_4 or + benzene is within declared experimental uncertainties.

All measurements were taken at an average temperature of 298.15 ± 0.10 K. The experimental values, H^E, reported in Tables 2–4, were fitted to the smoothing equation

$$H^E = x_1 x_2 \sum_{i}^{N-1} a_i (x_i - x_2)^i \tag{1}$$

TABLE 1

Values of the coefficients a_i, eqn. (1), and standard deviations $\sigma(H^E)$, eqn. (2), at 298.15 K, for binary mixtures of ketones + CCl_4 or C_6H_6 and of diketones + C_7H_{16} or C_6H_{12}

Mixtures		a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$
2-Propanone	+ CCl_4	671	−919	487	−206		0.65
	+ C_6H_6	585	−141	−0.3	46	41	0.64
2-Butanone	+ CCl_4	−317	−933	392	−466	409	0.49
	+ C_6H_6	−201	−151	131	−104	104	0.43
2-Pentanone	+ CCl_4	−516	−821	468	−412	348	0.45
	+ C_6H_6	−292	−142	118	−107	134	0.82
3-Pentanone	+ CCl_4	−653	−821	521	−187		1.01
	+ C_6H_6	−521	−141	188	−129	46	0.37
2-Hexanone	+ CCl_4	−390	−1003	629	162		0.76
	+ C_6H_6	−683	47	162	−121		0.75
2,3-Butanedione	+ C_7H_{16}	6745	−450	−661	30	1685	0.31
	+ C_6H_{12}	7097	−1626	1031	−1849	1418	0.35
2,4-Pentanedione	+ C_7H_{16}	3727	−1497	702	15	452	0.43
	+ C_6H_{12}	4173	−967	828	−971	537	0.72
2,5-Hexanedione	+ C_7H_{16} [a]						

[a] Eqn. (19) not applicable because of the presence of the miscibility gap.

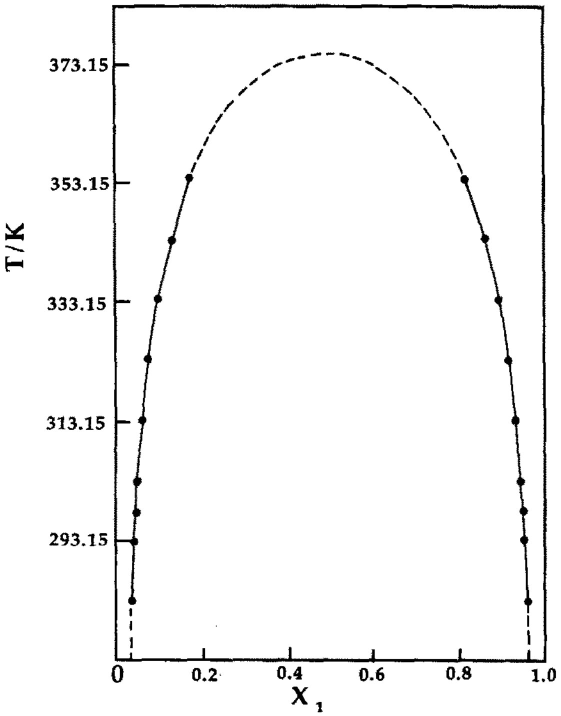

Fig. 1. Liquid–liquid phase diagram of 2,5-hexandione (1) + C_7H_{16} mixtures.

TABLE 2

Experimental values of the excess enthalpy, H^E, at 298.15 K for binary mixtures of ketones of the general formula $CH_3(CH_2)_{s-1}$–CO–$(CH_2)_{t-1}CH_3$ (1) + tetrachloromethane, CCl_4 (2)

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
CH_3COCH_3					
0.0531	102	0.2927	238	0.7017	76
0.1016	166	0.4014	209	0.7582	55
0.1384	199	0.5088	165	0.7991	40
0.1982	230	0.6011	120	0.8906	15
$CH_3CH_2COCH_3$					
0.0497	69	0.3977	−25	0.7100	−136
0.1102	100	0.5112	−85	0.7898	−128
0.1470	100	0.5984	−117	0.9016	−79
0.1900	90	0.6621	−132	0.9433	−48
0.2705	51				
$CH_3(CH_2)_2COCH_3$					
0.0498	44	0.3970	−78	0.7030	−167
0.0995	60	0.5151	−135	0.7512	−161
0.1503	55	0.6029	−160	0.7999	−148
0.1967	40	0.6400	−165	0.8974	−98
0.2993	−17				
$CH_3CH_2COCH_2CH_3$					
0.0477	29	0.4161	−123	0.7103	−190
0.0950	38	0.4906	−158	0.8052	−158
0.1469	33	0.5770	−187	0.8947	−100
0.2238	−1	0.6385	−195	0.9402	−62
0.3199	−62				
$CH_3(CH_2)_3COCH_3$					
0.0497	19	0.4662	−203	0.8025	−195
0.0982	21	0.5031	−224	0.8977	−110
0.1495	9	0.5906	−254	0.9502	−56
0.3005	−85	0.7107	−245		

where x_1 is the mole fraction of the ketone or diketone and x_2 that of benzene, tetrachloromethane, *n*-heptane or cyclohexane. Values of the standard deviations $\sigma(H^E)$ are given by

$$\sigma(H^E) = \left[\sum\left(H^E_{sm} - H^E_{exp}\right)^2/(N-n)\right]^{\frac{1}{2}} \qquad (2)$$

where N is the number of experimental points and n is the number of coefficients a_i. The values for the coefficients a_i and the standard deviations $\sigma(H^E)$, determined by least-squares analysis, are reported in Table 1.

TABLE 3

Experimental values of the excess enthalpy H^E at 298.15 K for binary mixtures of ketones of the general formula $CH_3(CH_2)_{s-1}$–CO–$(CH_2)_{t-1}CH_3$ (1) + benzene, C_6H_6 (2)

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
CH_3COCH_3					
0.1011	63	0.4483	148	0.7042	111
0.2035	107	0.5024	146	0.8044	81
0.2997	135	0.5519	142	0.9077	43
0.4018	147	0.5950	134		
$CH_3CH_2COCH_3$					
0.0997	9	0.3935	−39	0.7021	−51
0.2013	−5	0.5004	−50	0.8044	−40
0.3052	−24	0.5983	−55	0.8976	−23
$CH_3(CH_2)_2COCH_3$					
0.0189	3	0.2871	−41	0.7000	−70
0.0493	5	0.3944	−60	0.8025	−53
0.0900	2	0.5017	−73	0.8978	−31
0.1951	−19	0.5896	−77		
$CH_3CH_2COCH_2CH_3$					
0.0273	−2	0.3968	−115	0.7870	−94
0.0995	−18	0.4910	−130	0.8915	−54
0.1820	−47	0.6048	−130	0.9457	−29
0.2951	−88	0.7059	−115		
$CH_3(CH_2)_3$–CO–CH_3					
0.1012	−50	0.3995	−165	0.7044	−135
0.1978	−100	0.5000	−170	0.7983	−100
0.3007	−140	0.6021	−160	0.9026	−53

Liquid–liquid equilibrium measurements

Mixtures of CH_3–CO–$(CH_2)_n$–$COCH_3$ + *n*-heptane show partial miscibility for $u \geqslant 2$ at 298.15 K.

The liquid–liquid equilibrium (LLE) for the mixture of 2,5-hexanedione ($u = 2$) + *n*-heptane was investigated in the temperature range 283.15–353.15 K using a glass reactor equipped with a thermostatted jacket and helical stirring. The stirring speed was measured by means of a stroboscope; the contact between the two fluids was started in nitrogen and fine dispersion of the two fluids was reached only at a stirring speed of 1600 r.p.m. After a contact time of about 30 min, the mixtures were allowed to stand so that the two phases could form; after drawing off an aliquot of each, the composition was determined by gas-chromatography. The GC instrument used was a Hewlett–Packard 5700 A equipped with a 2.0-m-long column packed with Durapack. Helium was used as carrier gas and the column temperature was 473.15 K.

TABLE 4

Experimental values of the excess enthalpy H^E at 298.15 K for binary mixtures of diketones of the general formula $CH_3CO\text{-}(CH_2)_n\text{-}COCH_3$ (1) + C_7H_{16} or C_6H_{12} (2)

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
$CH_3CO\text{-}COCH_3 + C_7H_{16}$					
0.0991	657	0.3643	1581	0.5714	1633
0.1429	877	0.4287	1665	0.6906	1392
0.2503	1296	0.5193	1679	0.9103	548
0.2983	1436				
$CH_3CO\text{-}COCH_3 + C_6H_{12}$					
0.0571	619	0.3216	1727	0.6571	1497
0.1072	1000	0.3929	1792	0.7786	1091
0.1786	1365	0.4643	1796	0.8571	754
0.2504	1592	0.5571	1708	0.9286	402
$CH_3CO\text{-}CH_2\text{-}COCH_3 + C_7H_{16}$					
0.0714	382	0.3857	973	0.7277	636
0.1561	683	0.5101	924	0.8571	385
0.2950	930	0.6286	792	0.9360	193
$CH_3CO\text{-}CH_2\text{-}COCH_3 + C_6H_{12}$					
0.0715	432	0.4357	1060	0.6987	815
0.1431	709	0.5020	1042	0.8105	574
0.2273	904	0.6008	961	0.9046	315
0.3214	1021				
$CH_3CO\text{-}(CH_2)_2\text{-}COCH_3 + C_7H_{16}$					
0.0143	252	0.3100	550 [a]	0.9531	490
0.0286	429	0.4964	535 [a]	0.9588	409
0.0454	576	0.7222	514 [a]	0.9856	187

[a] Phase heterogeneity points.

TABLE 5

Data of liquid–liquid equilibria at various temperatures for the 2,5-hexanedione (1) + *n*-heptane mixture. X_{11} is the molar fraction of diketone in the diketone-rich phase; X_{12} is the molar fraction of diketone in the *n*-heptane-rich phase

T (K)	X_{11}	X_{12}
283.15	0.0395	0.9620
293.15	0.0438	0.9572
298.15	0.0466	0.9523
303.15	0.0509	0.9485
313.15	0.0610	0.9397
323.15	0.0804	0.9258
333.15	0.1016	0.8993
343.15	0.1321	0.8684
353.15	0.1730	0.8172

The liquid–liquid equilibrium data are reported in Table 5 (see also Fig. 1).

DISCUSSION

Mixtures with monoketones

The substitution of a $-CH_2-$ group in *n*-alkane with a $-CO-$ group influences the intermolecular forces as a result of two oppositely acting effects, one, weakening, due to smaller dispersion forces exerted by the $-CO-$ groups, compared to the $-CH_2-$ groups, and another, strengthening, due to electrostatic interactions between the C=O bond dipoles.

Although a detailed interpretation of all our results, in terms of DISQUAC, an extended quasi-chemical group contribution theory [3,16] will be the subject of a future article, a preliminary qualitative discussion of several features of the present work seems justified. First, we note the pronounced

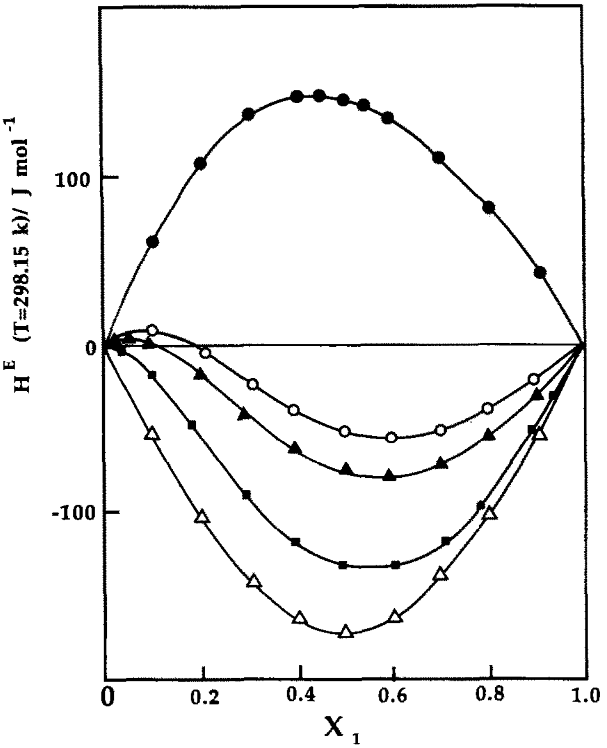

Fig. 2. Molar excess enthalpies H^E, at 298.15 K, of ketone (1)+C_6H_6 (2) mixtures vs. x_1, the mole fraction of ketone. Experimental results: ●, 2-propanone, ○, 2-butanone ▲, 2-pentanone; △, 2-hexanone; ■, 3-pentanone. Curves calculated from eqn. (1) with coefficients from Table 1.

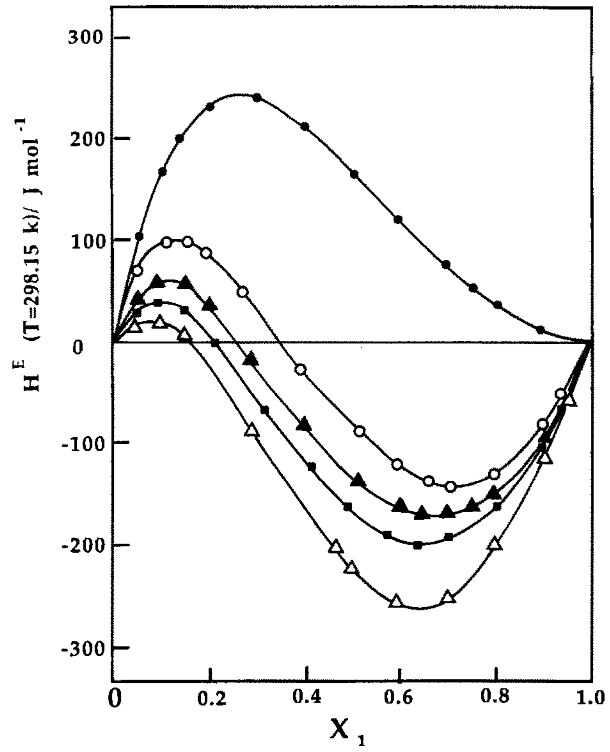

Fig. 3. Molar excess enthalpies H^E, at 298.15 K, of ketone (1) + CCl_4 (2) mixtures vs. x_1, the mole fraction of ketone. Experimental results: ●, 2-propanone; ○, 2-butanone; ▲, 2-pentanone; △, 2-hexanone; ■, 3-pentanone. Curves calculated from eqn. (1) with coefficients from Table 1.

decrease in H^E in each case when changing from cyclohexane [7] to benzene or tetrachloromethane as second component. Secondly, when comparing the excess enthalpy, say H^E ($T = 298.15$ K; $x_1 = 0.5$), of an n-alkanone (K_n) ($n = s + t$) + an active solvent (b, benzene or tetrachloromethane) with that pertaining to homomorphic alkane (A_n), the increment $\Delta = H^E(K_n) - H^E(A_n)$ is always a rather larger negative quantity.

The values for mixtures with benzene as second component are Δ ($n = 6$; $b = C_6H_6$) $= -740$ J mol^{-1} [17].

Thermodynamic excess properties of compounds containing the carbonyl group + benzene mixtures have been qualitatively discussed in terms of specific $n - \pi$ interactions [18]. The increments for mixtures with tetrachloromethane are of similar magnitude, that is to say Δ ($n = 6$; $b = CCl_4$) $=$ -535 J mol^{-1} [19]. Specific interactions of the n–σ type have been postulated for mixtures of tetrachloromethane with a polar compound, i.e., ether [20].

As shown in Figs. 2 and 3, the excess enthalpies decrease when the number of alkyl groups (s, t) of the ketone increases; this confirms the weakening of the dipole–dipole interactions (CO–CO) previously observed when using *n*-alkane or cyclohexane as solvent [3,4], and also confirms the existence of specific intermolecular interactions between the polar group (CO) and the π-electrons of benzene (n–π) or between CO and tetrachloromethane (n–σ).

The occurrence of oriented interactions between the ketone molecules is also confirmed by the S-shaped curves of H^E vs. x_1, which is positive at low alkanone concentrations and negative in the ketone-rich regions.

Mixtures with diketones

The introduction of a second carbonyl group in an alkanone molecule increases the H^E values of mixtures with *n*-heptane in comparison with the H^E of the corresponding mixtures involving monoketones. It seemed interesting to estimate the enthalpic effect for mixtures with diketones on the assumption that the two –CO– groups in the bifunctional molecule are independent of each other. To this purpose we have used the quasi-chemical approximation of the lattice theory of solutions [21] following Kehiaian's

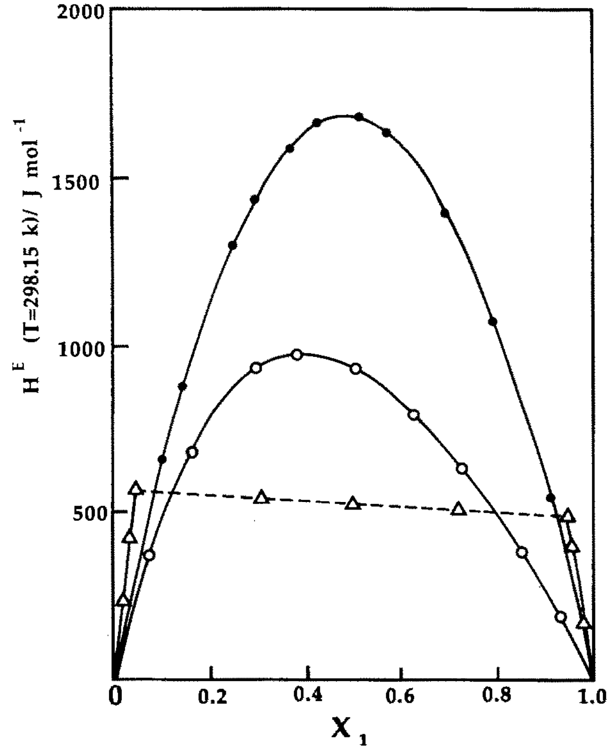

Fig. 4. Molar excess enthalpies H^E, at 298.15 K, of diketone (1)+C_7H_{16} (2) mixtures vs. x_1, the mole fraction of diketone. Experimental results: ●, 2,3-butanedione; ○, 2,4-pentanedione; △, 2,5-hexanedione. Curves calculated from eqn. (1) with coefficients from Table 1.

treatment [6]. The relevant aliphatic/carbonyl group interaction parameters were evaluated from monoketone + alkane [5,13].

The H^E ($x_1 = 0.5$) values obtained from these parameters, i.e., implicitly assuming the above hypothetical behaviour, are the following: 1474, 1373, 1240 J mol^{-1} for 2,3-butanedione, 2,4-pentanedione and 2,5-hexanedione, respectively in mixtures with *n*-heptane. These calculated values are to be compared with the experimental H^E ($x_1 = 0.5$)/J mol^{-1}: 1686, 931 and 2850 (extrapolated value).

The difference H^E (calc) – H^E (exp) for 2,4-pentandione + *n*-heptane is to be attributed, at least partially, to the high degree of enolization of diketone: the enol content is 78% in the pure liquid [22] and 92% in *n*-hexane [23]. For the other diketones, which exhibit low enol content in the pure liquid state [22], the difference H^E (calc) – H^E (exp) is certainly due to the existence of an important intramolecular interaction between the carbonyl groups or, in other words, to the strong influence of a –CO– group on the solvation of the other.

Similar conclusions can be reached for cyclohexane mixtures. In this case, H^E is higher (~ 100 J mol^{-1} at the maximum) than the corresponding values for *n*-heptane mixtures. That may be attributed to dispersive aliphatic–cycloaliphatic interactions. In this connection, it is worth remembering that for *n*-heptane + cyclohexane, H^E ($x_1 = 0.5$) at 298.15 K is about 240 J mol^{-1} [24].

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