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EXCESS ENTHALPIES OF KETONE–TRIETHER MIXTURES. MEASUREMENT AND APPLICATION OF THE DISQUAC GROUP CONTRIBUTION METHOD

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ABSTRACT

Excess molar enthalpy H_m^E was measured, at atmospheric pressure and 298.15 K, for binary systems formed from mixtures of 2-heptanone, 2-nonanone, 4-heptanone and 5-nonanone with 3,6,9-trioxaundecane. The DISQUAC group contribution method for correlating and predicting the thermodynamic properties of liquid mixtures was used.

Calculated results derived from the model are in agreement with experimental excess molar enthalpies.

INTRODUCTION

Excess molar enthalpies for a number of mixtures of linear ketones with triether (3,6,9-trioxaundecane) at 298.15 K and atmospheric pressure have been reported. DISQUAC is a good model for excess molar enthalpy data for mixtures of binary ketones with ether [1].

The group contribution method provides a basis for estimating properties of systems outside the set of investigated binaries. A single binary containing a specific pair of structural groups suffices to determine the corresponding group parameters. These parameters can be employed to estimate the properties of any other binary or multicomponent system containing the same structural groups. When applicable, this approach saves a considerable amount of experimental measurement, since the number of structural groups is much smaller than the number of molecular species.

In the present work, the predictive ability of the proposed model is tested by comparing calculated results with our previous measurements of experimental excess molar enthalpies for mixtures of 2-heptanone, 2-nonanone, 4-heptanone and 5-nonanone with 3,6,9-trioxaundecane [2].

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EXPERIMENTAL

A standard Calvet microcalorimeter [3] was used to determine the excess enthalpies. The calorimeter was calibrated with measured electrical energy and thermostatted to ±0.005 K. The measurements were carried out at 298.15 K and atmospheric pressure.

All the chemicals used were from Fluka (purum 97%). Prior to actual measurements, all liquids were dried using a molecular sieve (Union Carbide Type 4A from Fluka).

RESULTS

The observed excess molar enthalpies H_m^E are given in Table 1. The binary H_m^E results have been fitted to polynomial eqn. (1) by least squares regression

$$H_m^E(\text{J mol}^{-1}) = x(1-x)\sum A_i(2x-1)^i \tag{1}$$

Values of the coefficients A_i and standard deviations $s(H_m^E)$ are given in Table 2.

For almost all the mixtures, $s[H_m^E/H_m^E(\text{max})] < 0.01$, where $H_m^E(\text{max})$ denotes the maximum value of the excess molar enthalpy with respect to mole fraction.

For all the systems investigated, the excess molar enthalpy is positive. For both symmetrical and asymmetrical ketones, H_m^E increases as the aliphatic chain of the ketone molecule increases.

Also, for the symmetrical ketones H_m^E values are larger than for the asymmetrical ketones, and the maximum value of H_m^E moves to greater values for the same mole fraction.

DISCUSSION

The DISQUAC model (a simple extension of Guggenheim–Barker quasi-lattice theory [4] to group surfaces [5–9] has been useful in interpreting the results of measurements of the excess properties of binary liquid organic mixtures.

The excess functions molar excess Gibbs energy G^E and molar excess enthalpy H^E each contain a dispersive and a quasi-chemical term. These are calculated independently and then simply added together

$$G^E = G_{\text{comb}}^E + G_{\text{int}}^{E,\text{dis}} + G_{\text{int}}^{E,\text{quac}} \tag{2}$$

$$H^E = H^{E,\text{dis}} + H^{E,\text{quac}} \tag{3}$$

TABLE 1

Excess molar enthalpies for mixtures of asymmetrical and symmetrical ketones with 3,6,9-trioxaundecane at 298.15 K by eqn. (1)

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
x 2-heptanone + 3,6,9-trioxaundecane							
0.1293	30	0.3965	77	0.6448	78	0.8639	40
0.1991	47	0.4642	81	0.7342	68	0.9011	31
0.2486	57	0.5224	84	0.7428	64	0.9552	16
0.2937	63	0.5500	82	0.7958	56		
0.3546	74	0.6105	80	0.8327	45		
x 4-heptanone + 3,6,9-trioxaundecane							
0.0686	40	0.3634	184	0.5807	202	0.7633	155
0.1422	86	0.4032	196	0.6015	200	0.8201	131
0.2442	138	0.4517	200	0.6530	192	0.8577	108
0.2667	152	0.5096	207	0.6924	182	0.8624	102
0.3052	166	0.5188	205	0.7393	163	0.9031	77
						0.9544	42
x 2-nonanone + 3,6,9-trioxaundecane							
0.0656	46	0.3432	177	0.5376	196	0.8046	123
0.1403	96	0.3954	190	0.5937	189	0.8581	97
0.2090	131	0.4466	196	0.6534	176	0.9363	49
0.2359	145	0.4752	195	0.6635	176		
0.2961	165	0.5005	198	0.7361	154		
x 5-nonanone + 3,6,9-trioxaundecane							
0.0976	114	0.3036	283	0.5352	332	0.7295	272
0.1474	166	0.3230	292	0.5940	324	0.7569	257
0.1632	183	0.3520	303	0.6120	324	0.8120	212
0.1978	211	0.4543	333	0.6521	309	0.8653	163
0.2518	251	0.5131	335	0.6664	306	0.9031	124

TABLE 2

Coefficients A_i and standard deviations $s(H_m^E)$ for excess molar enthalpies for mixtures of ketones with 3,6,9-trioxaundecane at 298.15 K by eqn. (1)

	A_i (J mol^{-1})				
	A_0	A_1	A_2	A_3	$s(H_m^E)$
2-heptanone	332.0	30.3	−48.4	26.1	1
4-heptanone	823.4	67.2	−63.5	115.6	2
2-nonanone	787.9	−21.5	9.6	54.1	1
5-nonanone	1041.4	−358.9	150.0	−104.6	2

where $G_{\text{int}}^{\text{E,dis}}$ and $H^{\text{E,dis}}$ are the dispersive terms, and $G_{\text{int}}^{\text{E,quac}}$ and $H^{\text{E,quac}}$ are the quasi-chemical terms. $G_{\text{comb}}^{\text{E}}$ is the Flory–Huggins combinatorial term, given by

$$G_{\text{comb}}^{\text{E}} = RT \sum x_i \ln\frac{\rho_i}{x_i} \tag{4}$$

where ρ_i and x_i are the volume fraction and molar fraction of component i. $G_{\text{int}}^{\text{E,dis}}$, $G_{\text{int}}^{\text{E,quac}}$, $H^{\text{E,dis}}$ and $H^{\text{E,quac}}$ are given by different equations, as shown in other published works [1,10,11].

All theoretical equations are functions of the parameters $g_{\text{st}}^{\text{dis}}$, $h_{\text{st}}^{\text{dis}}$, $g_{\text{st}}^{\text{quac}}$ and $h_{\text{st}}^{\text{quac}}$, which are the interchange dispersive and quasi-chemical parameters of contact of molecules (s, t).

The importance of DISQUAC is especially evident in mixtures containing three or more types of groups of different polarities. For example, systems of mixtures of ketones with triether are regarded as having three types of surface

(i) Type a: aliphatic groups (CH_3– or –CH_2–)
(ii) Type e: oxygen group (–O–)
(iii) Type c: carbonyl group (–CO–)

These surfaces generate three pairs of contacts: (a, e), (a, c) and (c, e). The interchange parameters for the (a, e)-contact have been adjusted previously [12], using experimental G^{E} and H^{E} values for mixtures of *n*-alkanones with ether. It was necessary to apply the dispersive approximation of the theory, with a coordination number $z = \infty$ (as for non-polar systems), in order to reproduce the shape of the G^{E} and H^{E} curves.

The interchange parameters for the (a,c)-contact have also been adjusted previously [5,6]. Here a quasi-chemical approximation of the theory was used (the group (a, c) is a polar contact), with a coordination number $z = 10$.

We expected that the (c, e)-contact would also require a dispersive treatment, with $z = \infty$ (random mixing). For the fitting of g_{ce} we used the experimental G^{E} data of Abbot [13]. The parameter h_{ce} we fitted about our own experimental H^{E} data for the system of 2-butanone with di-*n*-butyl ether [2].

In the classic Guggenheim–Barker quasi-lattice model, z is assumed to be the same for all the contacts. This is, of course, not the case for systems such as ketones with ether, which consist of polar and non-polar groups.

We applied DISQUAC [9], considering the (a, e)- and (c, e)-contacts as entirely dispersive and the (a, c)-contact as entirely quasi-chemical.

As in other works [14,15], we assumed, for the 'steric' effect, that the interchange energy parameters are a function of

$$C_{\text{ce},2}^{\text{R}} = C_{\text{ce},2}^{\ominus}\left(1 + n^{\text{e}}\sigma_{\text{ce},2}^{\text{e}} + n^{\text{p}}\sigma_{\text{ce},2}^{\text{p}} + n^{\text{b}}\sigma_{\text{ce},2}^{\text{b}} + \dots\right) \tag{5}$$

where $C_{\text{ce},2}^{\ominus} = h_{\text{ce}}^{\text{dis}}/RT^{\ominus}$ is the interchange parameter of the component base (2-propanone) and n^{e}, $n^{\text{p}}, \dots$ are the numbers of carbon atoms in the

TABLE 3

Interchange parameters. Aliphatic–oxygen groups ($z = \infty$)

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

TABLE 4

Interchange parameters. Aliphatic–carbonyl groups ($z = 10$)

	$g_{ac}^{dis}/RT^{\ominus}$	$g_{ac}^{quac}/RT^{\ominus}$	$h_{ac}^{dis}/RT^{\ominus}$	$h_{ac}^{quac}/RT^{\ominus}$
2-heptanone	0.000	8.097	0.000	9.830
2-nonanone	0.000	8.097	0.000	9.830
4-heptanone	0.000	7.680	0.000	8.999
5-nonanone	0.000	7.680	0.000	8.999

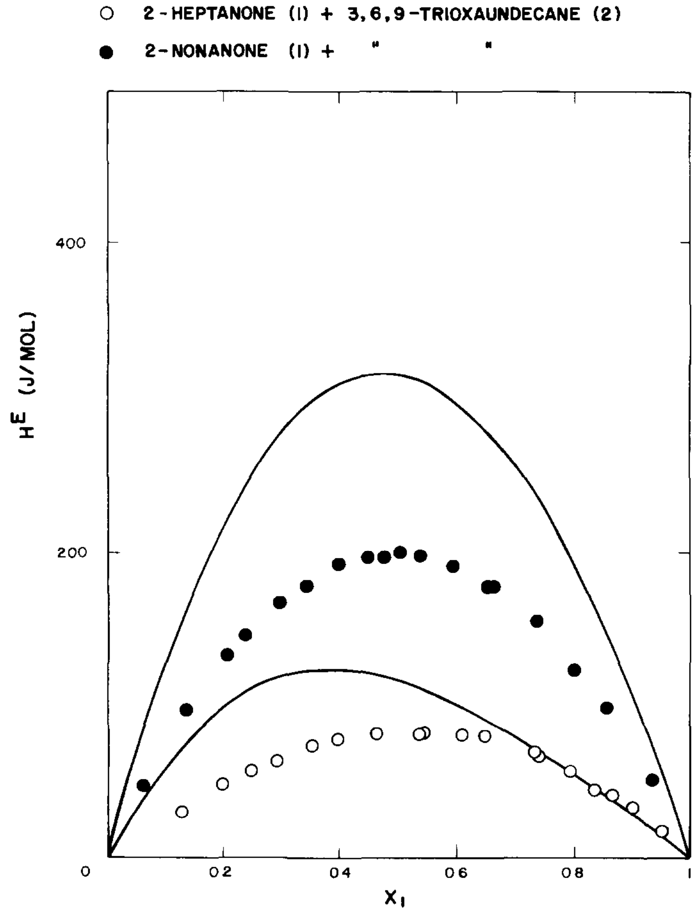

Fig. 1. Comparison of theoretical with experimental values for molar excess enthalpies h^E of mixtures of asymmetrical ketones (1) with 3,6,9-trioxaundecane (triether) (2). Full lines, predicted values; points, experimental results.

TABLE 5

Interchange parameters. Carbonyl–ether groups ($z = \infty$)

	$C^{\mathrm{dis}}_{\mathrm{ce},2} = h^{\mathrm{dis}}_{\mathrm{ce}}/RT^{\ominus}$	$C^{\mathrm{quac}}_{\mathrm{ce},2} = h^{\mathrm{quac}}_{\mathrm{ce}}/RT^{\ominus}$
2-heptanone	−2.31	0.00
2-nonanone	−1.05	0.00
4-heptanone	−0.97	0.00
5-nonanone	0.30	0.00

different levels around group (–CO–). Superscripts e, p and b represent (CH_3–CH_2–), (CH_3–CH_2–CH_2–) and (CH_3–CH_2–CH_2–CH_2–) respectively. $\sigma^{R}_{ce,2}$ is the increment alkyl group.

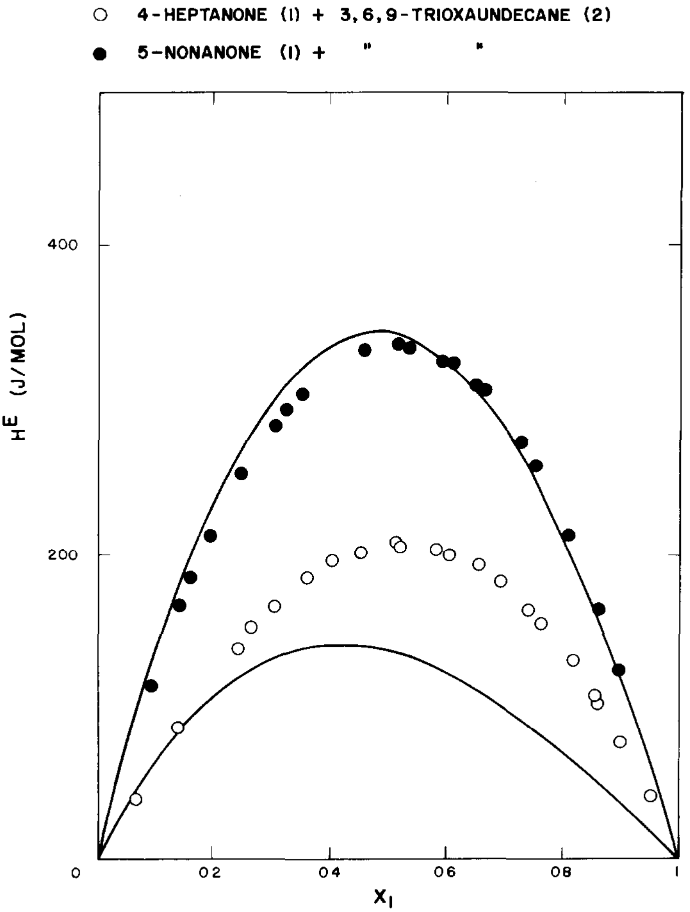

Fig. 2. Comparison of theoretical with experimental values for molar excess enthalpies H^{E} of mixtures of symmetrical ketones (1) with 3,6,9-trioxaundecane (triether) (2). Full lines, predicted values; points, experimental results.

We fitted the parameter σ_{ce}^{R} of eqn. 5

$$C_{ce,2}^{dis} = -6.183(1 - 0.222n^{e} - 0.200n^{p} - 0.102n^{b})$$

Using the parameters from Tables 3, 4 and 5, we compared theoretical and experimental excess enthalpies for binary mixtures of some asymmetrical and symmetrical ketones with 3,6,9-trioxaundecane (triether). The results are shown in Figs. 1 and 2.

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