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Excess enthalpies for binary mixtures of toluene, *p*-xylene or pseudocumene + methyl-*n*-alkyl ketones. Application of an extended cell model

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Abstract

Excess molar enthalpies H^E of the fifteen binary mixtures containing toluene, *p*-xylene or pseudocumene + five methyl-*n*-alkyl ketones at 298.15 K and atmospheric pressure are reported. The results confirm for *p*-xylene or pseudocumene + ketones the systematic behavior of H^E with respect to the chain length of the ketone, whereas for the toluene + 2-undecanone mixture, an inversion in the tendency of H^E has been noted (Patterson effect). The experimental data are examined by an extended cell model.

INTRODUCTION

This work was undertaken as part of a long program to provide accurate experimental information about the changes in the thermodynamic properties of a binary mixture which result from increased chain lengths in the molecular configuration of one of its components. For this purpose five methyl-*n*-alkyl ketones, namely 2-propanone, 2-butanone, 2-pentanone, 2-octanone and 2-undecanone, were taken into consideration.

Previous papers [1–3] report excess molar enthalpies H^E for the binary mixtures of the above ketones with halothane or naphthalene derivatives. Continuing this study, we have determined excess molar enthalpies for binary mixtures of three methyl-substituted benzene compounds, namely toluene, *p*-xylene and pseudocumene (1,2,4-trimethylbenzene) with the same ketones over the whole composition range, at atmospheric pressure and 298.15 K.

To our knowledge, excess enthalpy data for these fifteen binary systems have not previously been reported.

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EXPERIMENTAL

Apparatus

Molar excess enthalpies H^E were obtained by using an LKB flow microcalorimeter (Model 2107, Produkter AB, Bromma, Sweden). Fully automatic burets (ABU, Radiometer, Copenhagen, Denmark) were used to pump the pure liquids into the mixing cell. Details of the equipment and its operation have been described previously [4, 5]. Calibration was checked by determining the H^E at 298.15 K for the test system cyclohexane–hexane over the whole composition range. The agreement with the literature [6] is better than 0.5% over the central range of concentration.

Chemicals

Sources of the liquid compounds and purities specified by the manufacturers are summarized in Table 1. Liquids were used without further purification (stated purity $\geqslant$99%) with the exception of 2-octanone, which was distilled following the method of Collerson et al. [7]. Before use, liquids were stored in dark bottles over molecular sieves (Union Carbide, type 4A, 1/16 inch pellets).

Density measurements

Densities of pure compounds, also required for evaluating fluxes and, hence, mole fractions in the calorimetric measurements, were determined

TABLE 1

Sources, purities and densities ($T = 298.15$ K) of liquid compounds and comparison with literature data

Liquid	Source and Purity	ρ (g cm^{-3})	
		Obsd.	Lit.
Toluene	Aldrich, Research Grade 99.9%	0.862149	0.86219 [8]
p-Xylene	Aldrich, Research Grade 99.5%	0.856620	0.85661 [8]
Pseudocumene	Kodak, Research Grade 99%	0.871963	0.87180 [9]
2-Propanone	Aldrich, Research Grade 99.9+%	0.785005	0.7844 [8]
2-Butanone	Aldrich, Research Grade 99.5+%	0.799905	0.7997 [8]
2-Pentanone	Fluka, Research Grade 99+%	0.801400	0.8015 [8]
2-Octanone	Aldrich, Research Grade 98%	0.814359	0.8143 [8]
2-Undecanone	Aldrich, Research Grade 99%	0.821704	0.8221 [10]

at 298.15 ± 0.01 K in a digital density meter (Anton Paar DMA 60/602) and are listed in Table 1, with values from the literature [8–10] for comparison. The density meter, described elsewhere [11], was thermostated by a Colora constant temperature bath circulator with a temperature control interval of ±0.01 K. The temperature was detected with a digital thermometer (Anton Paar DT 100-25) and the precision of the densities measured is estimated to be of the order of 1×10^{-6} g cm^{-3}.

CORRELATION OF THE CALORIMETRIC DATA

The experimental values of H^E are given in Table 2 and shown graphically in Figs. 1–3.

In all cases, x_1 denotes the mole fraction of toluene, *p*-xylene or pseudocumene in the mixture. The Redlich–Kister polynomial equation

$$H^E/x_1x_2 = \sum_{k=0}^{n-1} a_k(x_1 - x_2)^k \tag{1}$$

with n the number of the adjustable parameters a_k, was fitted to each set of data by the method of least-squares, with all points weighted equally; parameters a_k based on the lowest values of standard deviation

$$\sigma(H^E) = [\phi/(N - n)]^{0.5} \tag{2}$$

are listed in Table 3; ϕ is the objective function defined as

$$\phi = \sum_{k=1}^{N} \eta_k^2 \tag{3}$$

with N the number of experimental points, $\eta_k = H^E_{\text{calc}} - H^E$; H^E_{calc} has been determined from the right-hand side of eqn. (1).

The number of parameters of Table 3 corresponds to values of $\sigma(H^E)$ comparing with the mean uncertainty in the experimental H^E calculated following the procedure given in ref. 4.

Figure 4 shows the correlation between the values of H^E for $x_1 = 0.5$ and n_c, the number of carbon atoms in the linear methyl-alkyl ketones.

THE CELL MODEL

A thermodynamic description of the curves in Figs. 1–3 has been attempted on the basis of an extended cell model worked out by Prigogine et al. [12–14], Salsburg and Kirkwood [15] and Rowlinson [16, 17].

TABLE 2

Experimental molar excess enthalpies H^E of toluene, *p*-xylene or pseudocumene + methyl-*n*-alkyl ketone mixtures at 298.15 K

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
Toluene + 2-propanone					
0.0280	21.8	0.3158	200.9	0.7347	202.5
0.0545	40.9	0.4091	226.0	0.8060	165.6
0.1034	81.1	0.5095	243.8	0.8470	138.8
0.1875	134.8	0.5806	242.3	0.8925	104.0
0.2571	172.8	0.6750	221.9	0.9432	56.1
Toluene + 2-butanone					
0.0340	−1.0	0.3602	15.1	0.8352	64.0
0.0657	−1.8	0.4578	28.0	0.8711	57.6
0.1234	−1.7	0.5588	43.6	0.9102	46.3
0.1743	0.1	0.6281	53.9	0.9530	29.2
0.2196	2.2	0.7170	64.4	0.9643	23.5
0.2969	8.2	0.7716	66.4		
Toluene + 2-pentanone					
0.0773	−28.2	0.5014	−114.3	0.8009	−51.9
0.1436	−52.7	0.6014	−101.9	0.8578	−32.8
0.2510	−87.1	0.6679	−87.5	0.9235	−13.6
0.3346	−108.0	0.7511	−65.3	0.9602	−5.7
0.4014	−113.8				
Toluene + 2-octanone					
0.0578	−24.5	0.4242	−130.4	0.8155	−55.7
0.1093	−46.0	0.4955	−131.6	0.8551	−39.8
0.1971	−81.9	0.5956	−121.0	0.8984	−23.0
0.2692	−104.3	0.6884	−99.8	0.9465	−9.2
0.3293	−118.4	0.7466	−79.4	0.9725	−3.0
Toluene + 2-undecanone					
0.0748	−23.0	0.4923	−95.1	0.7950	−42.1
0.1391	−41.8	0.5639	−91.2	0.8533	−27.1
0.2443	−67.8	0.6598	−75.8	0.9209	−9.8
0.3266	−83.5	0.7442	−55.4	0.9588	−1.4
0.3927	−92.3				
p-*Xylene + 2-propanone*					
0.0474	64.5	0.3738	363.1	0.7817	280.9
0.0905	126.8	0.4725	387.3	0.8269	240.6
0.1660	216.3	0.5442	387.3	0.8775	184.6
0.2299	276.4	0.6417	365.6	0.9347	106.6
0.2847	315.6	0.7048	337.0	0.9502	84.1
p-*Xylene + 2-butanone*					
0.0572	17.1	0.3268	104.0	0.7444	149.2
0.1082	35.0	0.4214	126.8	0.8137	131.2
0.1540	50.1	0.5221	147.6	0.8535	113.1
0.1953	64.0	0.5929	156.6	0.8973	89.2
0.2669	85.9	0.6860	157.6	0.9459	53.5

TABLE 2 (continued)

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
p-*Xylene* + 2-*pentanone*					
0.0674	−21.5	0.3663	−74.9	0.7762	−24.7
0.1263	−38.6	0.4644	−74.4	0.8388	−12.3
0.1782	−50.4	0.5655	−63.3	0.9123	−3.1
0.2242	−59.5	0.6343	−51.3	0.9542	−0.3
0.3025	−70.5	0.7223	−36.3		
p-*Xylene* + 2-*octanone*					
0.0503	−29.7	0.3884	−191.0	0.7921	−109.8
0.0957	−57.3	0.4585	−199.2	0.8358	−84.5
0.1747	−107.4	0.5595	−194.2	0.8840	−57.4
0.2410	−144.2	0.6558	−170.7	0.9384	−26.9
0.2975	−165.2	0.7176	−146.6	0.9682	−13.2
p-*Xylene* + 2-*undecanone*					
0.0651	−43.8	0.4554	−234.6	0.8338	−129.3
0.1223	−80.2	0.5272	−236.6	0.8702	−102.8
0.2180	−142.9	0.6258	−230.0	0.9094	−70.2
0.2949	−184.5	0.7150	−200.7	0.9525	−38.4
0.3579	−211.3	0.7698	−168.8		
Pseudocumene + 2-*propanone*					
0.0428	75.5	0.3493	417.4	0.7631	255.1
0.0821	136.2	0.4461	436.0	0.8111	214.4
0.1518	238.0	0.5177	423.2	0.8656	159.1
0.2116	306.7	0.6169	374.0	0.9280	86.7
0.2635	363.0	0.6822	324.4	0.9450	71.1
Pseudocumene + 2-*butanone*					
0.0546	43.3	0.3039	194.6	0.7237	208.3
0.0984	75.4	0.3957	228.4	0.7971	169.8
0.1407	102.6	0.4955	245.8	0.8871	103.8
0.1791	130.2	0.5670	249.0	0.9402	56.8
0.2466	168.6	0.6627	233.1		
Pseudocumene + 2-*pentanone*					
0.0610	−0.5	0.5392	−18.0	0.8618	−50.8
0.1150	−2.0	0.6093	−24.1	0.9034	−46.7
0.2063	−3.4	0.7005	−35.2	0.9258	−41.4
0.2805	−6.0	0.7572	−42.6	0.9493	−32.4
0.4381	−10.7	0.8239	−50.0	0.9615	−26.5
Pseudocumene + 2-*octanone*					
0.0454	−31.1	0.3635	−170.8	0.7741	−130.4
0.0869	−56.2	0.4323	−181.9	0.8207	−105.4
0.1599	−98.4	0.5332	−189.6	0.8727	−81.5
0.2221	−129.6	0.6315	−169.8	0.9320	−47.3
0.2757	−144.5	0.6956	−157.4	0.9648	−25.3
Pseudocumene + 2-*undecanone*					
0.0590	−46.8	0.4292	−243.9	0.8186	−162.3
0.1113	−83.3	0.5007	−253.3	0.8577	−131.0
0.2004	−146.2	0.6006	−249.6	0.9002	−101.2
0.2732	−188.5	0.6928	−225.3	0.9475	−58.3
0.3339	−215.4	0.7505	−200.7	0.9730	−32.2

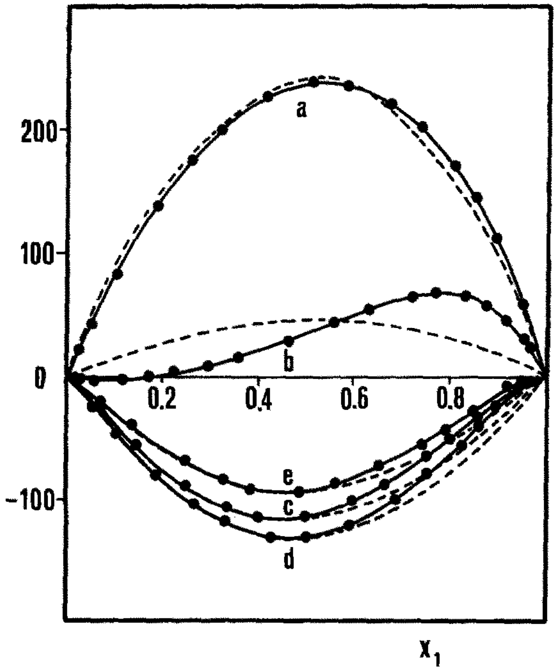

Fig. 1. Comparison between Redlich–Kister fit (——) and cell model (– – –) for H^E at 298.15 K for toluene: +2-propanone (a); +2-butanone (b); +2-pentanone (c); +2-octanone (d); +2-undecanone (e); (●) experimental points.

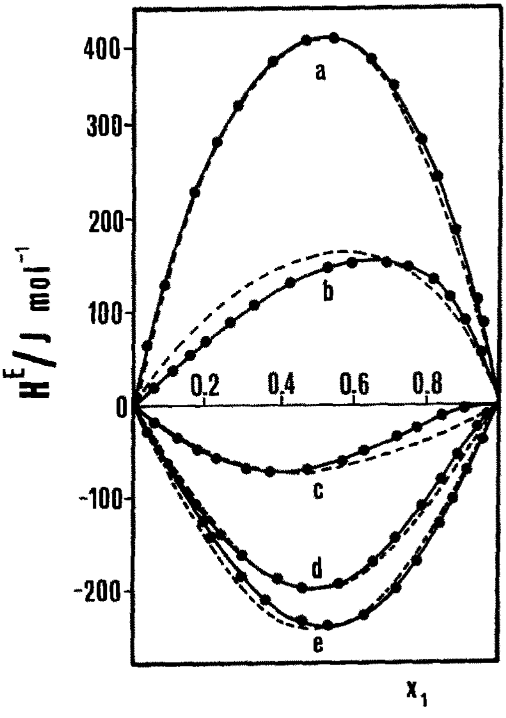

Fig. 2. Comparison between Redlich–Kister fit (——) and cell model (– – –) for H^E at 298.15 K for *p*-xylene: +2-propanone (a); +2-butanone (b); +2-pentanone (c); +2-octanone (d); +2-undecanone (e); (●) experimental points.

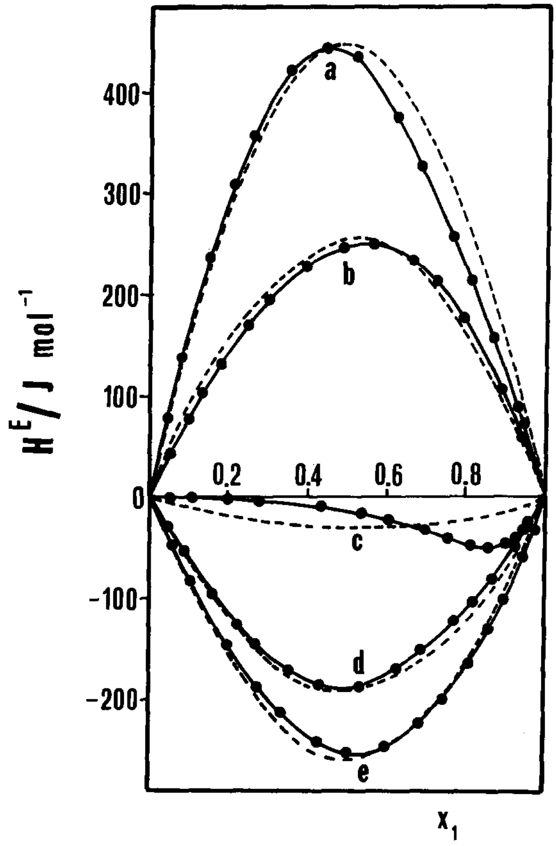

Fig. 3. Comparison between Redlich–Kister fit (——) and cell model (– – –) for H^E at 298.15 K for pseudocumene: +2-propanone (a); +2-butanone (b); +2-pentanone (c); +2-octanone (d); +2-undecanone (e); (●) experimental points.

The theoretical expression for H^E given by this model and reported in ref. 14 is

$$H^E = x_1x_2E_{11}z[-1.44\theta + 10.76(RT/zE_{11})^2 \times(-2\theta - \delta^2 + 4\,\delta\theta x_2 + 4x_1x_2\theta^2)] \tag{4}$$

where z is the number of nearest neighbors in the quasi-lattice model

$$\delta = (E_{22} - E_{11})/E_{11} \tag{5}$$

$$\theta = [E_{12} - (E_{11} + E_{22})/2]/E_{11} \tag{6}$$

E_{kk} = intermolecular energy between identical molecules kk and E_{12} = intermolecular energy between dissimilar molecules.

Equation (4) has been applied to other binary systems [18, 19] and good agreement between calculated and experimental H^E values has been obtained. Calculation of H^E by eqn. (4) for the mixtures in this paper has

TABLE 3

Redlich–Kister constants a_k and standard deviation σ of the molar excess enthalpy according to eqn. (1)

Mixture	a_0 (J mol^{-1})	a_1 (J mol^{-1})	a_2 (J mol^{-1})	a_3 (J mol^{-1})	a_4 (J mol^{-1})	σ (J mol^{-1})
Toluene						
+2-propanone	969.2	137.3				1.6
+2-butanone	137.6	313.5	206.2	74.1		0.4
+2-pentanone	−463.1	114.8	229.1			1.3
+2-octanone	−534.2	69.4	264.8	109.4		1.5
+2-undecanone	−382.3	46.0	215.7	117.8		1.1
p-Xylene						
+2-propanone	1564.2	108.4	105.7			2.9
+2-butanone	580.3	373.7	126.1			1.3
+2-pentanone	−284.2	183.6	136.7			0.6
+2-octanone	−809.5	84.0	312.4			2.0
+2-undecanone	−963.8	−95.9	229.8			2.4
Pseudocumene						
+2-propanone	1701.4	−504.2	−181.4	311.4		3.0
+2-butanone	992.8	126.3	−81.4			2.0
+2-pentanone	−58.0	−127.2	−239.0	−295.5	−140.0	0.5
+2-octanone	−739.8	−7.7				2.0
+2-undecanone	−1005.5	−150.5				2.6

been carried out following the procedure outlined in ref. 18. Essentially, θ is adjusted so that the experimental $H^E(x_1 = 0.5)$ equals the value calculated by the righthand side of eqn. (4). E_{11} and E_{22} are evaluated from the heats of vaporization of the pure components. No relevant difference has been achieved by giving z values from 8 to 12.

RESULTS AND DISCUSSION

As can be seen from Figs. 1–3, the cell model gives a good description of the calorimetric data of the present paper except for the mixtures toluene–butanone, *p*-xylene–pentanone and pseudocumene–pentanone, which show markedly asymmetric curves. Equation (6) may be used to obtain values of E_{12} which may be compared with the arithmetic mean E_m and the geometric mean E_g of the interaction energies E_{11} and E_{22}.

The binary mixtures of toluene, *p*-xylene or pseudocumene with the three longer-chained ketones have E_{12} values very close to E_m and consistently display negative H^E values, in agreement with the limiting case $E_{12} = E_m$ treated in ref. 14.

The mixture toluene–butanone gives $E_{12} \approx E_g$, in agreement with positive H^E [14]; the other mixtures showing positive H^E have E_{12} in the range $E_g \leqslant E_{12} \leqslant E_m$.

Figures 1–3 show positive values of H^E for the binary mixtures of toluene, *p*-xylene or pseudocumene with acetone and butanone. The other mixtures have negative H^E. *p*-Xylene and pseudocumene in mixtures with ketones display a trend towards less positive H^E values as a function of

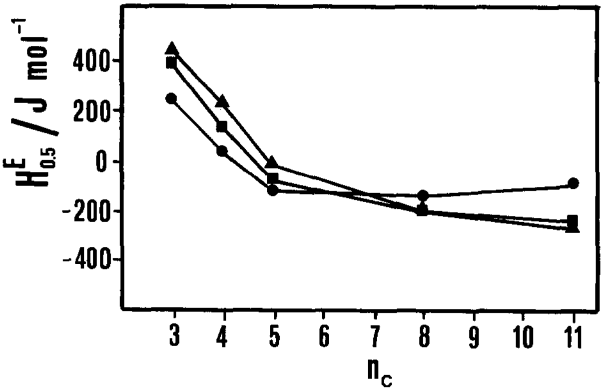

Fig. 4. Values of $H^E_{0.5} = H^E(x_1 = 0.5)$ at 298.15 K as a function of n_c for the binary mixtures of methyl-n-alkyl ketones: +toluene (●); +p-xylene (■); +pseudocumene (▲).

increased ketone chain length. This behavior is probably due to the fact that increasing the chain length of the ketone induces more polarization to the C=O group, giving rise to a stronger interaction with the electrons of the aromatic ring. This produces a larger value of E_{12} and a smaller value of H^E, which is approximately proportional to $E_{11} + E_{22} - 2E_{12}$.

However, the mixture toluene–undecanone contradicts this behavior, because this curve shows values of H^E more positive than pentanone and octanone. Here the Patterson effect [20] seems to overcome the inductive effect of chain length.

The same conclusions can better be seen in Fig. 4, showing values of $H^E(x_1 = 0.5)$ as a function of the number n_c of C atoms in ketones.

Similar results have been observed for other binary mixtures containing methyl-alkly ketones, e.g. with halothane [1] or 1-methylnaphthalene [3] as the second component, (although the mixtures with halothane show curves overlapping and intersecting each other, with consequent difficulty in drawing conclusions).

The mixtures cyclohexane + 2-propanone, +2-butanone, +2-pentanone and, +2-hexanone [21] also show an analogous trend.

Our next work will consider the determination of excess volumes V^E for the same mixtures as this paper, and the calculation of V^E by means of the cell model leading to eqn. (4).

REFERENCES

1 R. Francesconi, F. Comelli and H.V. Kehiaian, J. Chem. Eng. Data, 36 (1991) 479.
2 F. Comelli, Chim. Ind. (Milan), 73 (1991) 269.
3 F. Comelli, Chim. Ind. (Milan), 74 (1992) 243.
4 R. Francesconi and F. Comelli, J. Chem. Eng. Data, 31 (1986) 250.
5 P. Monk and I. Wadso, Acta Chem. Scand., 22 (1968) 1842.
6 G.C. Benson, Int. Data Ser., Sel. Data Mixtures, Ser A, (1987) 935.

7 R.R. Collerson, J.F. Counsell, R. Handley, J.F. Martin and C.H.S. Sprake, J. Chem. Soc., (1965) 3697.
8 J.A. Riddik, W.B. Bunger and T.K. Sakano, Organic Solvents, Wiley–Interscience, New York, 1986.
9 R. Dreisbach, Physical Properties of Chemical Compounds, American Chemical Society, New York, 1955.
10 B.D. Smith and R. Srivastava, Thermodynamic Data for Pure Compounds, Part A, Elsevier, Amsterdam, 1986.
11 M. Fermeglia and R. Lapasin, J. Chem. Eng. Data, 33 (1988) 415.
12 I. Prigogine and G. Garikian, Physica, 16 (1950) 239.
13 I. Prigogine and V. Mathot, J. Chem. Phys., 20 (1952) 49.
14 I. Prigogine, The Molecular Theory of Solutions, North-Holland, Amsterdam, 1957.
15 Z.W. Salsburg and J.K. Kirkwood, J. Chem. Phys., 20 (1952) 1538.
16 J.S. Rowlinson, Proc. R. Soc. London, 214 (1952) 192.
17 J.S. Rowlinson, J. Chem. Phys., 20 (1952) 337.
18 F. Comelli, Chim. Ind. (Milan), 72 (1990) 695.
19 F. Comelli and R. Francesconi, J. Chem. Eng. Data, 36 (1991) 32.
20 D. Patterson, Pure Appl. Chem., 47 (1976) 305.
21 B. Marongiu, Int. Data Ser., Sel. Data Mixtures, Ser. A, (1987) 1.