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EXCESS ENTHALPY AND EXCESS VOLUME OF CYCLOHEXANONE + TETRACHLOROETHENE *

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ABSTRACT

The excess enthalpy h^E and the excess volume v^E of the system cyclohexanone + tetrachloroethene have been measured. The values at equimolar composition are h^E (293.15 K) = 263 J mol^{-1}, v^E (293.15 K) = 0.113 and v^E (313.15 K) = 0.153 cm^3 mol^{-1}. The h^E value is found to be more positive than that of cyclohexanone + tetrachloromethane, as is usually found, and the v^E values obtained seen more viable than data in the literature, which show a very improbable temperature dependence.

INTRODUCTION

In the course of a systematic study of mixtures with ketones as one component, the system cyclohexanone + tetrachloroethene attracted interest for two reasons.

First, one may compare tetrachloromethane and tetrachloroethene as mixing partners. Both molecules are non-polar and interact essentially via four chlorine atoms; but whereas these four atoms form a very compact structure in tetrachloromethane, they are at the end of an elongated molecule in tetrachloroethene. The data available indicate that the excess functions are always more positive for tetrachloroethene systems than for tetrachloromethane systems, h^E and g^E by 100–400 J mol^{-1}, v^E by 0.1–0.3 cm^3 mol^{-1}.

The second reason for selecting this system was to check the literature data on v^E [1], which showed a very improbable temperature dependence. Such a result could not be reproduced by the present experiments.

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* Dedicated to Professor Edgar F. Westrum, Jr., in appreciation of his friendship extended to myself and my family over many years, and on the occasion of his 70th birthday.

** On leave from the University of Hanoi, S.R. Vietnam.

EXPERIMENTAL

Cyclohexanone (Merck, "rein") was dried with Na_2SO_4 and fractionally distilled; tetrachloroethene (Fluka AG, "for spectroscopy") was dried with $CaCl_2$ and also fractionally distilled. Analysis by GLC showed that purity of these compounds was better than 99.9%. Densities and molar volumes are given in Table 1. Excess volumes were calculated from densities, which were determined using a glass capillary vibrating tube densimeter (A. Paar, Austria) [2]; mixtures were prepared from degassed samples. Excess enthalpies were determined using a flow calorimeter of the Picker design (Setaram, France) in the discontinuous mode, in which the flow rate is controlled volumetrically and the mixture composition is controlled by passing the mixture through a vibrating tube densimeter [3].

RESULTS

Excess volumes

Direct experimental values are presented in Table 2 and 3, the Redlich–Kister correlations

$$v^{E} = x_2(1 - x_2)\sum A_i(2x_2 - 1)^i \qquad (1)$$

TABLE 1

Densities ρ and molar volumes v for cyclohexanone(1) and tetrachloroethene(2)

T (K)	ρ_1 (kg m^{-3})	v_1 (cm^3 mol^{-1})	ρ_2 (kg m^{-3})	v_2 (cm^3 mol^{-1})
293.15	946.509	103.693	1623.09	102.172
313.15	928.709	105.680	1589.99	104.299

TABLE 2

Densities ρ, excess volumes v^E and deviations from the Redlich–Kister correlation Δv^e (cf. Table 4) for cyclohexanone(1) + tetrachloroethene(2) at 293.15 K

x_2	ρ (kg m^{-3})	v^E (cm^3 mol^{-1})	Δv^E (cm^3 mol^{-1})
0.13042	1033.19	0.043	0.001
0.22446	1095.93	0.067	−0.002
0.32752	1164.87	0.092	0.000
0.39920	1212.97	0.105	0.001
0.50810	1286.36	0.113	0.000
0.61123	1356.16	0.115	0.000
0.81602	1495.82	0.088	0.000
0.92522	1571.06	0.048	0.000

TABLE 3

As Table 2, but at 313.15 K

x_2	ρ (kg m^{-3})	v^E (cm^3 mol^{-1})	Δv^E (cm^3 mol^{-1})
0.13042	1013.32	0.066	0.002
0.22446	1074.60	0.101	−0.002
0.32752	1141.94	0.130	−0.003
0.39920	1188.94	0.148	0.002
0.50810	1260.63	0.156	0.003
0.61123	1328.91	0.152	−0.001
0.81602	1465.30	0.123	−0.002
0.92522	1538.84	0.074	0.003

TABLE 4

The coefficients of the Redlich–Kister correlations (cf. eqn. (1)) for cyclohexanone(1) + tetrachloroethene(2)

	A_0	A_1	A_2	A_3
v^E (293.15 K) (cm^3 mol^{-1})	0.45304	0.11502	0.08749	0.11436
v^E (313.15 K) (cm^3 mol^{-1})	0.61397	0.06777	0.23019	0.31948
h^E (293.15 K) (J mol^{-1})	1050.6	689.21	548.09	647.73

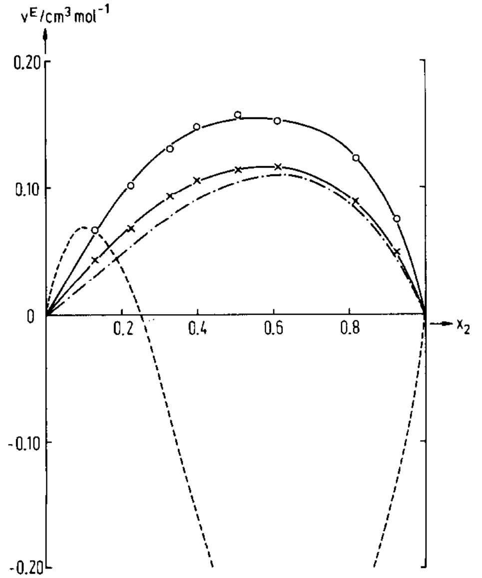

Fig. 1. Excess volume v^E of cyclohexane(1) + tetrachloroethene(2). × and ○, experimental points at 293.15 and 313.15 K, respectively; ———, corresponding Redlich–Kister correlations; — — — and ·—·—·, Redlich–Kister correlations of ref. 1 at 303.15 K and 313.15 K, respectively. The dashed curve has not been drawn in the middle portion as it runs off the scale.

TABLE 5

Excess enthalpies h^E and their deviations from the Redlich–Kister correlation Δh^E (cf. Table 4) of cyclohexanone(1) + tetrachloroethene(2) at 293.15 K

x_2	h^E (J mol^{-1})	Δh^E (J mol^{-1})
0.0543	16.1	−5.1
0.1077	52.5	1.1
0.1497	81.6	3.4
0.1930	109.7	3.1
0.2207	123.8	−0.7
0.2462	141.8	1.2
0.2830	160.3	−2.4
0.2940	167.9	−1.1
0.3382	192.5	−0.7
0.3597	198.2	−5.9
0.3971	224.0	2.2
0.4767	254.3	0.0
0.4998	269.0	6.4
0.5427	270.1	−6.4
0.5979	295.5	4.2
0.6514	302.9	1.4
0.6951	305.0	−0.5
0.7340	308.7	4.2
0.7906	285.2	−6.7
0.8256	274.5	−0.6
0.8517	254.1	−2.6
0.8861	218.3	−4.6
0.9185	183.6	4.5
0.9393	143.8	0.3
0.9737	84.7	14.5

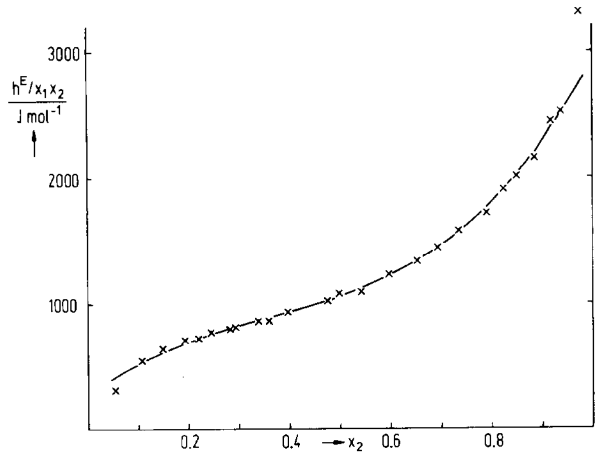

Fig. 2. Excess enthalpy, reduced by the product of mole fractions, of cyclohexane(1) + tetrachloroethene(2) at 293.15 K. ———, Redlich–Kister correlation.

where x_2 is the mole fraction of tetrachloroethene, are given in Table 4. Figure 1 shows the corresponding graph, where the full curves are the Redlich–Kister correlations; it also contains the curves given in the literature [1]. It may be seen that there is approximate agreement at 313.15 K, but complete disagreement at 303.15 K.

Excess enthalpies

Excess enthalpies are given in Table 5 and Fig. 2. The Redlich–Kister correlation is included in Table 4.

DISCUSSION

The most extensive comparison of CCl_4- and C_2Cl_4-mixtures has been done by Handa and Benson [4] on the basis of h^E with aromatic and alicyclic hydrocarbons. With the exception of the mixture with 1,3,5-trimethylbenzene (where $h^E_{0.5}$ of the C_2Cl_4-system was 41 J mol^{-1} more negative), h^E of the C_2Cl_4-systems was 95 to 382 J mol^{-1} more positive for the equimolar mixture, the difference being the same for mixtures with alicyclic hydrocarbons as with aromatic hydrocarbons. Handa and Benson explained this by suggesting that C_2Cl_4 acts as a weaker electron acceptor than CCl_4.

Though we believe that this phenomenon indeed contributes to the more positive excess properties, the results of Handa and Benson on alicyclic systems indicate that this is not the only factor. Another important point might be the effect of packing. Unfortunately, for the relatively complicated molecules we cannot provide a clear-cut theoretical explanation, but we can calculate the effect when in a simple mixture a large spherical molecule is elongated. Consider the mixture $CCl_4 + CS_2$ (modelled as 1CLJ + 2CLJ, 1CLJ and 2CLJ being abbreviations for one- or two-centre Lennard–Jones) and $C_2Cl_4 + CS_2$ (2CLJ + 2CLJ), and assume the unlike interaction to be given by the Lorentz–Berthelot rule. Then the equimolar excess properties of the C_2Cl_4-mixture are more positive by 601 J mol^{-1} for g^E, by 911 J mol^{-1} for h^E, and by 1.42 cm^3 mol^{-1} for v^E [5]. Similarly, we can calculate the effect when in an 1CLJ + 1CLJ mixture the larger molecule is elongated [6], e.g. for the same cohesive energy of both components ($\epsilon/k = 500$ K) and a size difference of 24% (with $\sigma_{12} = 4.64$ Å) we have for an elongation $L = 0.505$ $\Delta g^E = 262$ J mol^{-1}, $\Delta h^E = 614$ J mol^{-1}, $\Delta v^E = 0.02$ cm^3 mol^{-1}.

This effect can be understood by imagining that the groups within a molecule act more or less independently. A difference in size of two spherical molecules makes negative contributions to the excess properties. If the larger molecule is elongated, it consists then of two smaller groups. Therefore, the negative contributions due to size differences diminish. As the mixing partners of CCl_4 and C_2Cl_4 are not spherical molecules, one has to

TABLE 6

Data on excess properties of tetrahalogenide (CCl_4 and C_2Cl_4) systems in addition to those of Handa and Benson [4]

Mixing partner	Tetrahalogenide	
	CCl_4	C_2Cl_4
	$g^E_{0.5}$ (J mol^{-1})	
Carbon disulfide	172 [a]	296 [b]
Pyridine	330 [c]	505 [c]
	$h^E_{0.5}$ (J mol^{-1})	
Carbon disulfide	306 [d]	510 [b]
Cyclohexanone	−362 [e]	263 [f]
2-Propanone	161 [g]	865 [g]
1,1,2,2-Tetrachlorethane	581 [h]	639 [h]
	$v^E_{0.5}$ (cm^3 mol^{-1})	
Carbon disulfide	0.32 [a]	0.50 [b]
Cyclohexane	0.16 [i]	0.48 [i]
1,4-Dimethylbenzene	−0.01 [k]	0.03 [j]
Benzene	0.005 [l]	0.37 [j]
Toluene	−0.04 [k]	0.11 [j]

[a] Ref. 7 (298 K); [b] ref. 8 (298 K); [c] ref. 9 (313 K); [d] ref. 10 (298 K); [e] ref. 11 (298 K); [f] this work (293 K); [g] ref. 12 (298 K); [h] ref. 13 (303 K); [i] ref. 14 (298 K); [j] ref. 15 (303 K); [k] ref. 16 (298 K); [l] ref. 17 (298 K).

refer to an effective smaller group size. Thus the elongation effect occurs already when the mixing partner has about the same volume as the tetrahalogenides. It is interesting to note that the only reversal occurs with the very large and relatively compact molecule of 1,3,5-trimethylbenzene.

In real mixtures, this effect of packing is masked by additional contributions, which influence the numbers given above. A collection of literature data of CCl_4- and C_2Cl_4-systems (excluding those of Handa and Benson) is given in Table 6. It is seen that in ketones the difference between the electron-accepting power of the tetrahalogenides makes an additional contribution.

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