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Excess Molar Volumes of Some Hydrogen-Bonded Complexes at 298.15 K and the Application of the ERAS Model

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Excess molar volumes V_m^E measured at 298.15 K are reported for single hydrogen bonded complexes involving propan-1-ol, di-*n*-propylamine, or propane-1-thiol + di-*n*-propyl ether, tri-*n*-propylamine, dipropyl sulfide, or heptan-4-one. Together with previously reported molar excess enthalpies (Letcher and Bricknell, 1996), the V_m^E data have been used in the application of the ERAS model to mixtures involving assumed single hydrogen bonds (O−H···O, O−H···N, OH···S, N−H···O, N−H···N, NH···S, SH···O, SH···N, and SH···S).

Introduction

Recently, we reported excess enthalpies for some mixtures involving single hydrogen bonds: OH···O, O−H···N, OH···S, N−H···O, N−H···N, NH···S, SH···O, SH···N, and SH···S (Letcher and Bricknell, 1996). Employing partial molar enthalpies at infinite dilution, we extended the technique of Van Ness *et al.* (1967) and Stokes *et al.* (1975) to approximate the strengths of the hydrogen-bonded interactions. In this work we describe the excess volumes for these same mixtures. The excess volumes together with the previously reported excess enthalpies have been used in applying the extended real associated solution (ERAS) model to the various hydrogen-bonded systems under consideration.

The ERAS model combines the real associated solution model (Kretschmer and Wiebe, 1954; Renon and Prausnitz, 1967; Kehiaian, 1968; Kehiaian and Treszczanowicz, 1968) with a free volume contribution using Flory's equation of state (Flory *et al.*, 1964). Developed to describe excess properties of binary (alkanol + alkane) mixtures (Heintz, 1985), the ERAS model has been extended to describe mixtures where one of the components shows only a weak self-association but a relatively strong cross-association (Funke *et al.*, 1989). The ERAS model has previously been applied to (alkanol + alkane) mixtures (Heintz, 1985; Bender and Heintz, 1993; Costas *et al.*, 1987), to (alkanol + amine) mixtures (Funke *et al.*, 1989; Reimann and Heintz, 1991), to (alkanol + alkene or alkyne) mixtures (Letcher *et al.*, 1995) and to (*n*-butylamine + ether) mixtures (Letcher and Goldon, 1996).

In this work, V_m^E's have been determined for propan-1-ol + di-*n*-propyl ether (OH···O), +tri-*n*-propylamine (OH···N), +di-*n*-propyl sulfide (OH···S), +heptan-4-one (OH···O), for di-*n*-propylamine + di-*n*-propyl ether (NH···O), +tri-*n*-propylamine (NH···N), +di-*n*-propyl sulfide (NH···S), +heptan-4-one (NH···O), and also for propane-1-thiol + di-*n*-propyl ether (SH···O), +tri-*n*-propylamine (SH···N), +di-*n*-propyl sulfide (SH···S), +heptan-4-one (SH···O).

Experimental Section

Propan-1-ol, di-*n*-propyl ether, di-*n*-propylamine, tri-*n*-propylamine, di-*n*-propyl sulfide, heptan-4-one, and propane-1-thiol were obtained from Janssen Chimica. GC−MS revealed that the purity was greater than 98.7 mass % in all liquids except propane-1-thiol (96 mass %). Propan-1-ol was dried with magnesium metal activated with iodine, using the method of Lund and Bjerrum as described by Letcher *et al.* (1990). Both amines were distilled and dried with molecular sieves (type 4A, ±3.2 mm beads from Saarchem). Di-*n*-propyl ether (99.7 mass %), di-*n*-propyl sulfide, and propane-1-thiol were used without further purification due to the high cost of these liquids. Solvents were degassed prior to actual measurements. The mole fraction of water in each of the liquids was determined by Karl Fischer titration to be less than 0.001.

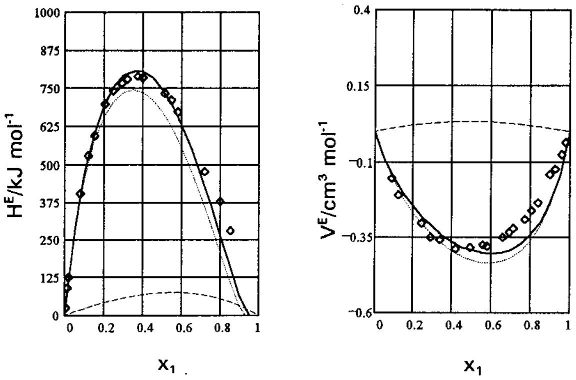

Figure 1. Excess enthalpy and excess volumes of (propan-1-ol (1) + di-*n*-propyl ether (2)) at 298 K: (◊) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

The excess molar volumes, V_m^E, accurate to 0.002 cm^3, were calculated from the densities (accurate to 1×10^{-4} g·cm^{-3}) and molar masses of the pure liquids and mixtures, measured using an Anton-Paar DMA 602 vibrating-tube densimeter, thermostated at the temperature (298.15 ± 0.01) K as previously reported (Letcher and Lucas, 1982).

Results

The V_m^E results are given in Table 1 together with the deviations Δ, calculated from the smoothing equation:

$$\Delta/(\mathrm{J\cdot mol^{-1}}) = V_m^E/(\mathrm{J\cdot mol^{-1}}) - x(1-x)\sum_{r=0}^{n} A_r(1-2x)^r \quad (1)$$

The coefficients A_r, determined by the method of least squares, are given in Table 2. ERAS model parameters used in this work relating to the pure substances are listed

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Table 1. Excess Molar Volumes V_m^E[x{C_3H_7OH, $(C_3H_7)_2NH$, or C_3H_7SH} + $(1 - x)${$(C_3H_7)_2O$, $(C_3H_7)_3N$, $(C_3H_7)_2S$, or $(C_3H_7)_2CO$}] and the Deviations Δ Calculated from Eq 1 and the Parameters of Table 2

x	$V_m^E/cm^3\cdot mol^{-1}$	$10^3\Delta/cm^3\cdot mol^{-1}$	x	$V_m^E/cm^3\cdot mol^{-1}$	$10^3\Delta/cm^3\cdot mol^{-1}$	x	$V_m^E/cm^3\cdot mol^{-1}$	$10^3\Delta/cm^3\cdot mol^{-1}$
$xCH_3CH_2CH_2OH + (1 - x)(CH_3CH_2CH_2)_2O$								
0.0894	−0.1505	7.2	0.4923	−0.3846	1.1	0.8061	−0.2600	4.7
0.1203	−0.2080	−9.1	0.5565	−0.3764	3.8	0.8369	−0.2333	−2.3
0.2406	−0.3014	−9.2	0.5784	−0.3798	−3.5	0.9003	−0.1368	0.3
0.2908	−0.3485	8.7	0.6562	−0.3519	0.2	0.9250	−0.1197	3.2
0.3379	−0.3581	1.7	0.6927	−0.3311	4.0	0.9578	−0.0751	4.1
0.4138	−0.3792	0.3	0.7119	−0.3214	3.1	0.9794	−0.0361	2.4
0.4529	−0.3869	−2.5	0.7708	−0.2883	−3.4			
$xCH_3CH_2CH_2OH + (1 - x)(CH_3CH_2CH_2)_3N$								
0.1032	−0.3806	−5.9	0.5218	−0.8459	1.0	0.7881	−0.6393	11.1
0.2228	−0.6249	10.9	0.5748	−0.8568	16.2	0.8229	−0.5767	7.7
0.3079	−0.7604	14.8	0.6525	−0.8275	−2.1	0.9125	0.3747	−2.6
0.3982	−0.8044	9.9	0.7070	−0.7407	2.0	0.9397	−0.2461	7.6
$xCH_3CH_2CH_2OH + (1 - x)(CH_3CH_2CH_2)_2S$								
0.111	0.0772	−0.8	0.439	0.1090	−1.9	0.813	0.0577	0.7
0.215	0.1098	0.5	0.515	0.1036	0.4	0.836	0.0511	−0.7
0.271	0.1162	0.7	0.601	0.0936	1.1	0.902	0.0344	0.0
0.356	0.1164	0.1	0.652	0.0849	−0.5	0.926	0.0269	−0.1
0.430	0.1119	0.2	0.667	0.0830	−0.2			
$xCH_3CH_2CH_2OH + (1 - x)(CH_3CH_2CH_2)_2CO$								
0.127	0.0124	1.0	0.407	0.0141	−0.7	0.732	−0.0081	−0.4
0.185	0.0157	−0.1	0.510	0.0090	2.4	0.887	−0.0047	0.1
0.265	0.0176	−1.1	0.662	−0.0063	−1.2	0.939	−0.0016	0.8
$x(CH_3CH_2CH_2)_2NH + (1 - x)(CH_3CH_2CH_2)_2O$								
0.055	−0.0011	2.6	0.394	0.0182	−0.2	0.718	0.0148	2.5
0.155	−0.0023	−2.2	0.465	0.0201	−0.3	0.783	0.0126	9.4
0.236	0.0045	−2.4	0.531	0.0198	−0.7	0.801	0.0119	9.3
0.286	0.0149	3.5	0.624	0.0174	−0.8	0.882	0.0059	−1.4
0.381	0.0187	0.8	0.663	0.0168	0.0			
$x(CH_3CH_2CH_2)_2NH + (1 - x)(CH_3CH_2CH_2)_3N$								
0.038	0.0191	3.6	0.378	0.1377	−5.2	0.668	0.0818	8.0
0.075	0.0286	−3.6	0.426	0.1419	−3.2	0.755	0.0290	−2.0
0.130	0.0602	1.6	0.482	0.1422	1.9	0.802	0.0002	5.7
0.187	0.0811	−4.2	0.564	0.1184	−0.9	0.913	−0.0252	3.7
0.237	0.1097	3.3	0.593	0.1081	0.3	0.964	−0.0082	1.8
0.301	0.1333	5.4						
$x(CH_3CH_2CH_2)_2NH + (1 - x)(CH_3CH_2CH_2)_2S$								
0.069	−0.0056	−1.9	0.296	−0.0276	3.3	0.610	−0.0609	2.7
0.085	−0.0057	−1.1	0.349	−0.0374	4.0	0.807	−0.0139	−1.0
0.118	−0.0070	−0.4	0.400	−0.0561	−4.8	0.835	0.0030	0.6
0.139	−0.0095	−1.3	0.454	−0.0626	−2.7	0.877	0.0067	−0.7
0.195	−0.0120	2.2	0.522	−0.0683	−2.0	0.900	0.0054	−6.3
$x(CH_3CH_2CH_2)_2NH + (1 - x)(CH_3CH_2CH_2)_2CO$								
0.038	−0.0234	−5.5	0.291	−0.0321	−1.1	0.592	−0.0123	0.7
0.065	−0.0266	0.0	0.373	−0.0247	−1.3	0.794	−0.0097	−0.7
0.106	−0.0332	1.4	0.379	−0.0235	0.6	0.928	−0.0023	0.3
0.181	−0.0356	2.7	0.488	−0.0151	0.9			
$xCH_3CH_2CH_2SH + (1 - x)(CH_3CH_2CH_2)_2O$								
0.085	−0.0103	2.0	0.431	0.0154	−1.2	0.723	0.0162	−0.6
0.118	−0.0144	−1.6	0.559	0.0214	−0.2	0.839	0.0094	−0.1
0.171	−0.0119	−1.6	0.657	0.0211	1.2	0.915	0.0048	0.1
$xCH_3CH_2CH_2SH + (1 - x)(CH_3CH_2CH_2)_3N$								
0.127	0.1593	−2.3	0.538	0.4210	−7.5	0.891	0.1512	3.1
0.236	0.2908	4.9	0.618	0.4060	7.0	0.935	0.0861	−4.2
0.368	0.3860	−4.0	0.827	0.2180	−3.0	0.949	0.0800	8.7
$xCH_3CH_2CH_2SH + (1 - x)(CH_3CH_2CH_2)_2S$								
0.116	0.0037	−0.1	0.601	0.0158	0.0	0.868	0.0099	0.3
0.385	0.0127	0.5	0.688	0.0153	−0.1	0.933	0.0047	−0.7
0.501	0.0143	−0.5	0.770	0.0141	0.4			
$xCH_3CH_2CH_2SH + (1 - x)(CH_3CH_2CH_2)_2CO$								
0.054	0.0204	−0.3	0.343	0.1019	−0.6	0.687	0.1180	−2.0
0.131	0.0477	0.4	0.489	0.1230	−0.1	0.874	0.0722	2.0
0.228	0.0760	0.1	0.587	0.1285	1.8	0.902	0.0560	−1.5

in Table 3 (Funke *et al.*, 1989; Riddick *et al.*, 1986). The unknown cross term parameters K_{AB}, Δh^*_{AB}, Δv^*_{AB}, and X_{AB}, listed in Table 4, have been adjusted simultaneously to the experimental data of H_m^E and V_m^E using equations described elsewhere (Heintz, 1985; Bender and Heintz, 1993). The calculated density values of the pure components are recorded in Table 5.

Discussion

V_m^E's of (dipropyl ether + ethanol) and (dipropyl ether + butan-1-ol) have been measured by Iñarrea *et al.* (1988) at 298.15 K, where $V^E(x=0.5)$ was found to be (−0.29 and −0.51) $cm^3\cdot mol^{-1}$, respectively. Our $V^E(x=0.5)$ for (di-*n*-propyl ether + propan-1-ol) lies between these two values

Table 2. Parameters A_r and Standard Deviations σ for Representation of Molar Excess Volumes at 298.15 K by Eq 1

	A_0	A_1	A_2	A_3	$10^3\sigma$/ $cm^3 \cdot mol^{-1}$
xC_3H_7OH					
$+(1-x)(C_3H_7)_2O$	−1.542	−0.569	−0.413	−0.127	7
$+(1-x)(C_3H_7)_3N$	−3.384	0.186	−1.246	−0.050	15
$+(1-x)(C_3H_7)_2S$	0.419	0.219	0.279	0.066	1
$+(1-x)(C_3H_7)_2CO$	0.030	0.173	−0.007	−0.128	1
$x(C_3H_7)_2NH$					
$+(1-x)(C_3H_7)_2O$	0.083	0.001	−0.102	−0.107	2
$+(1-x)(C_3H_7)_3N$	0.549	0.400	−0.676	0.102	5
$+(1-x)(C_3H_7)_2S$	−0.260	0.157	0.461	−0.431	4
$+(1-x)(C_3H_7)_2CO$	−0.062	−0.079	−0.232	−0.199	2
xC_3H_7SH					
$+(1-x)(C_3H_7)_2O$	0.081	−0.071	−0.188	−0.088	2
$+(1-x)(C_3H_7)_3N$	1.707	−0.011	−0.374	−0.079	6
$+(1-x)(C_3H_7)_2S$	0.059	−0.034	0.003	0.005	0
$+(1-x)(C_3H_7)_2S$	0.496	−0.145	0.054	−0.006	1

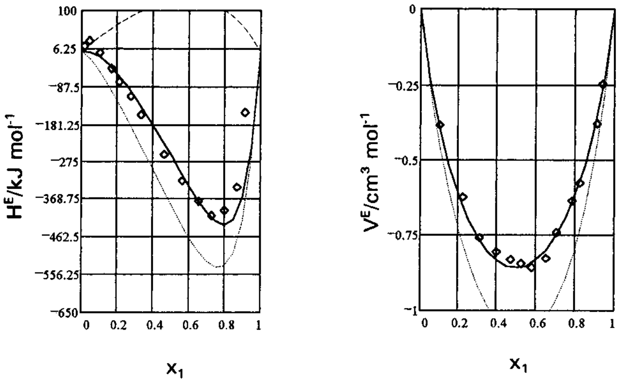

Figure 2. Excess enthalpy and excess volumes of (propan-1-ol (1) + tri-*n*-propylamine (2)) at 298 K; (◇) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

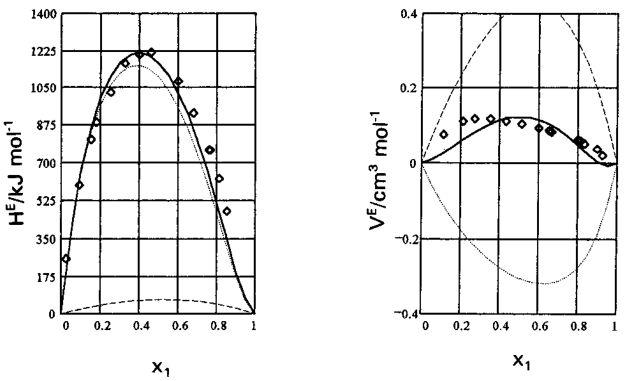

Figure 3. Excess enthalpy and excess volumes of (propan-1-ol (1) + di-*n*-propyl sulfide (2)) at 298 K: (◇) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

at −0.38 $cm^3 \cdot mol^{-1}$. V_m^E values for (propane-1-ol + tri-*n*-propylamine) are negative. V_m^E data for other (alcohol + amine) mixtures also exhibit strongly negative values (Funke *et al.*, 1989).

In this work, cross complex hydrogen bonding is assumed. In the ERAS model, Δh^*_{AB} is the hydrogen bonding energy, Δv_{AB} represents the molar volume effect due to hydrogen bond formation, and X_{AB} refers to intermolecular interactions characterizing physical van der Waals forces (Bender and Heintz, 1993). The strong negative experimentally observed V_m^E values, together with the previously reported negative H_m^E values Letcher and Bricknell, 1996) for the (propan-1-ol + tri-*n*-propylamine)

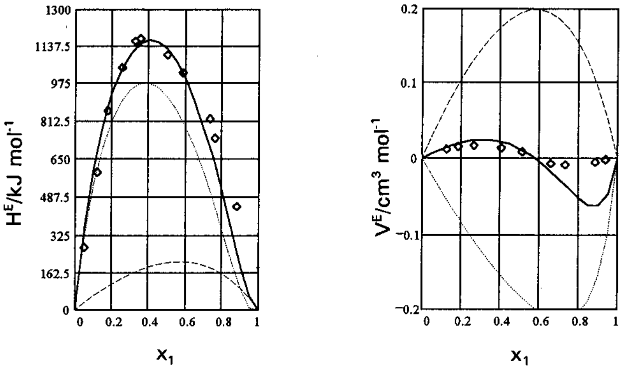

Figure 4. Excess enthalpy and excess volumes of (propan-1-ol (1) + heptan-4-one (2)) at 298 K: (◇) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

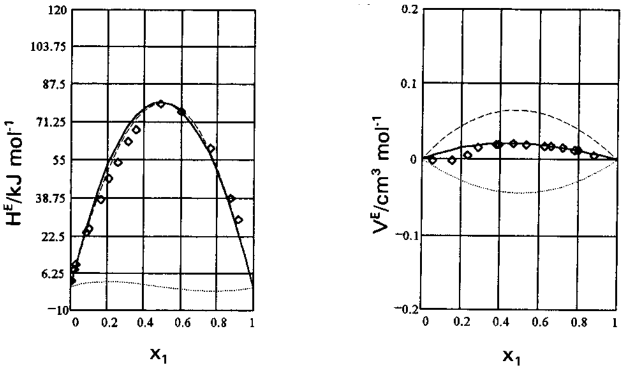

Figure 5. Excess enthalpy and excess volumes of (di-*n*-propylamine (1) + di-*n*-propyl ether (2)) at 298 K: (◇) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

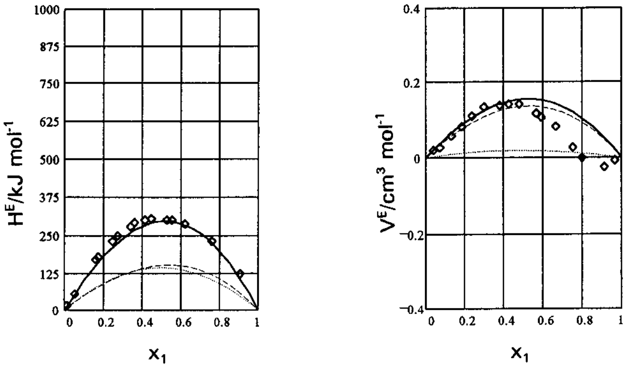

Figure 6. Excess enthalpy and excess volumes of (di-*n*-propylamine (1) + tri-*n*-propylamine (2)) at 298 K: (◇) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

Table 3. Thermodynamic Properties of the Pure Substances at 298 K

	K	$p^*/J \cdot cm^{-3}$	$V_{mol}/cm^3 \cdot mol^{-1}$	$V^*/cm^3 \cdot mol^{-1}$	$10^4\alpha/K^{-1}$	$10^{-4}\kappa/MPa^{-1}$	s/nm^{-1}	$\Delta h^*/kJ \cdot mol^{-1}$	$\Delta v^*/cm^3 \cdot mol^{-1}$
C_3H_7OH	197	414	75.2	61.1	10.2	10.1	14.9	−25.1	−5.6
$(C_3H_7)_2NH$	0.55	516	138.1	106.5	13.1	12.2	13.9	−7.5	−4.2
xC_3H_7SH	0.60	514	90.6	69.0	14.2	13.5	14.2	−6.8	−3.9
$(C_3H_7)_2O$	0	440	137.7	106.0	12.6	14.4	14.2	0	0
$(C_3H_7)_3N$	0	488	190.3	146.5	12.6	13.0	13.8	0	0
$(C_3H_7)_2S$	0	567	140.7	103.3	16.2	15.8	14.2	0	0
$(C_3H_7)_2CO$	0	491	139.8	112.4	9.8	9.2	14.1	0	0

Table 4. ERAS Model Parameters Characterizing Mixture Properties of Some Hydrogen-Bonded Systems

mixture	X_{AB}/ J·cm^{-3}	$-\Delta h^*_{AB}$/ kJ·mol^{-1}	$-\Delta v^*_{AB}$/ cm^3·mol^{-1}	K_{AB}
C_3H_7OH				
$+(C_3H_7)_2O$	6.0	18.6	7.0	60
$+(C_3H_7)_3N$	15.0	26.6	9.5	140
$+(C_3H_7)_2S$	6.7	14.8	6.4	45
$+(C_3H_7)_2CO$	17.0	18.0	6.1	75
$(C_3H_7)_2NH$				
$+(C_3H_7)_2O$	2.8	6.4	3.9	0.50
$+(C_3H_7)_3N$	4.7	5.5	4.1	0.52
$+(C_3H_7)_2S$	5.1	7.0	5.6	0.50
$+(C_3H_7)_2CO$	6.8	7.6	5.3	0.45
xC_3H_7SH				
$+(C_3H_7)_2O$	2.4	6.5	5.1	0.55
$+(C_3H_7)_3N$	5.5	4.5	2.7	0.37
$+(C_3H_7)_2S$	4.2	8.6	5.0	0.65
$+(C_3H_7)_2CO$	6.8	8.7	3.6	0.50

Table 5. Calculated (298 K) and Literature Densities of Pure Components

component	calc/g·cm^{-3}	lit.^{a}/g·cm^3 (temp/K)
propan-1-ol	0.7995	0.7796 (293)
propane-1-thiol	0.8358	0.8357 (298)
dipropylamine	0.7345	0.7384 (293)
dipropyl ether	0.7423	0.7360 (293)
tripropylamine	0.7524	0.753 (298)
dipropyl sulfide	0.8387	0.8385 (293)
heptan-4-one	0.8106	0.8174 (293)

[a] Weast, 1968.

Table 6. Δh^*_{AB}, the Hydrogen Bonding Energy, and the Hydrogen Bond Interaction Energy, $\Delta H_{H\text{-bond}}$, Calculated from Partial Molar Enthalpies at Infinite Dilution^a

system	$\Delta H_{H\text{-bond}}$/kJ·mol^{-1}	Δh^*_{AB}/kJ·mol^{-1}
−OH···N	−23.21	−26.6
−OH···O	−20.02	−18.6
−OH···S	−19.91	−14.8
−OH···O=C	−23.51	−18.0
−NH···N	−1.33	−5.5
−NH···O	−2.84	−6.4
−NH···S	−4.11	−7.0
−NH···O=C	−7.61	−7.6
−SH···N	−1.71	−4.5
−SH···O	−3.20	−6.5
−SH···S	−4.72	−8.6
−SH···O=C	−7.30	−8.7

[a] −OH = propan-1-ol, N = tri-*n*-propylamine, −NH = di-*n*-propylamine, O = di-*n*-propyl ether, −SH = propanethiol, S = di-*n*-propyl sulfide, O=C = heptan-4-one.

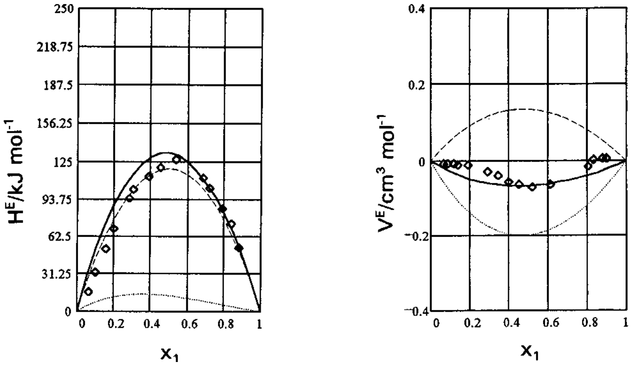

Figure 7. Excess enthalpy and excess volumes of (di-*n*-propylamine (1) + di-*n*-propyl sulfide (2)) at 298 K: (◊) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

mixture require values for Δh^*_{AB} and Δv^*_{AB} which are more negative than those obtained for propane-1-ol self-association (−25.1 kJ·mol^{-1} and −5.6 cm^3·mol^{-1}, respectively) (Renon and Prausnitz, 1967; Heintz, 1985). A Δh^*_{AB} value of −26.5 kJ·mol^{-1} and a Δv^*_{AB} value of −10.2 cm^3·mol^{-1} are obtained from the ERAS model.

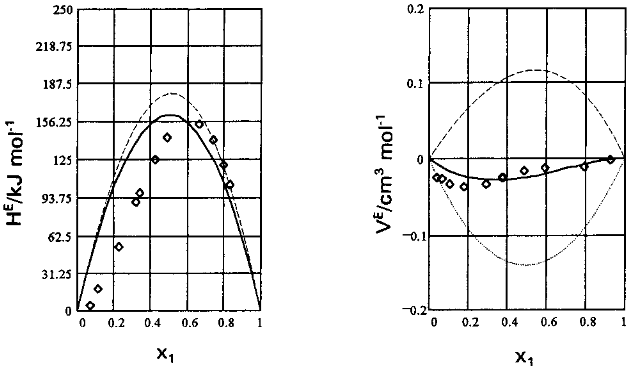

Figure 8. Excess enthalpy and excess volumes of (di-*n*-propylamine (1) + heptan-4-one (2)) at 298 K: (◊) experimental data; (—) ERAS model, (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

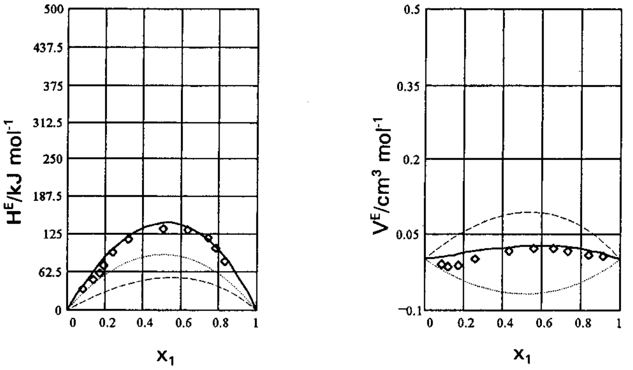

Figure 9. Excess enthalpy and excess volumes of (propane-1-thiol (1) + di-*n*-propyl ether (2)) at 298 K: (◊) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

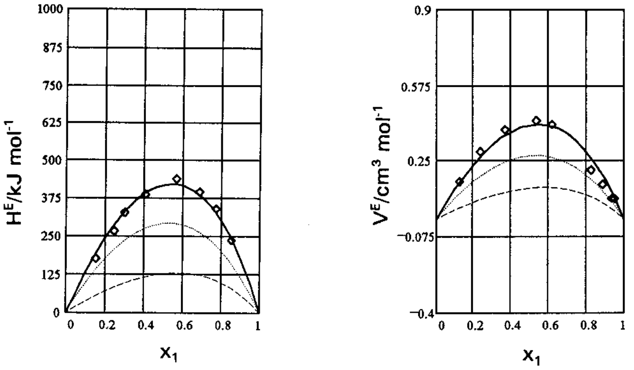

Figure 10. Excess enthalpy and excess volumes of (propane-1-thiol (1) + tri-*n*-propylamine (2)) at 298 K: (◊) experimental data; (—) ERAS model, (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

Δh^*_{AB} is compared in Table 6 with hydrogen bond interaction energies reported previously (Letcher and Bricknell, 1996) using partial molar enthalpies at infinite dilution. The order of the hydrogen bond strengths (OH···N > O > S, NH, or SH···S > O > N) is the same using both techniques, the values varying somewhat. This fact supports the assertion in a previous publication (Letcher and Bricknell, 1996) that in liquid mixtures where the proton donor shows a relatively weak self-association, the available surface area of the proton acceptor is the dominant factor in determining the relative strengths of hydrogen bonding.

The ERAS model also gives a graphical depiction of the physical and chemical contributions to the H^E_m and V^E_m

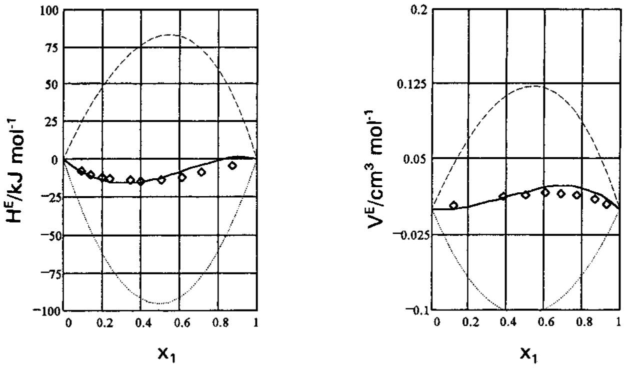

Figure 11. Excess enthalpy and excess volumes of (propane-1-thiol (1) + di-*n*-propyl sulfide (2)) at 298 K: (◇) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

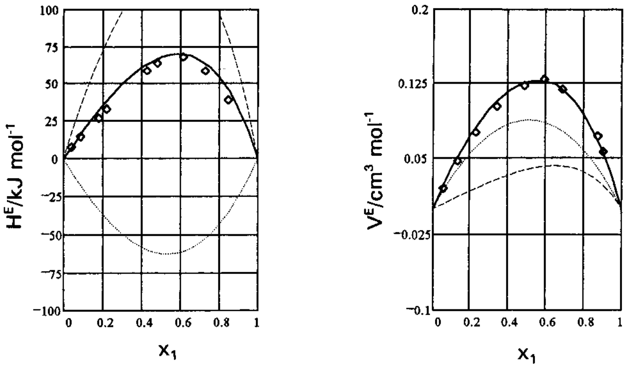

Figure 12. Excess enthalpy and excess volumes of (propane-1-thiol (1) + heptan-4-one (2)) at 298 K: (◇) experimental data; (—) ERAS model; (···) chemical contribution to ERAS; (- - -) physical contribution to ERAS.

data (see Figures 1−12). This data has a strong chemical bias in the systems involving propan-1-ol, while a greater physical contribution is manifest in the weaker heteroassociated systems involving dipropylamine and propane-1-thiol.

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