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Excess Molar Enthalpies and Excess Molar Volumes of Propionic Acid + Octane, + Cyclohexane, + 1,3,5-Trimethylbenzene, + Oxane, or + 1,4-Dioxane at 313.15 K

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Excess molar enthalpies and excess molar volumes of propionic acid + octane, + cyclohexane, + 1,3,5-trimethylbenzene, + oxane, and + 1,4-dioxane have been determined at 313.15 K and atmospheric pressure using an isothermal flow microcalorimeter and a digital vibrating density meter. Redlich−Kister polynomials were fitted to the experimental data, and smooth representations of the results are presented.

Introduction

The aim of this work is to study mixtures of propionic acid, a self-associated compound, with a variety or nonpolar and polar compounds.

Excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, of binary mixtures of propionic acid with octane, cyclohexane, 1,3,5-trimethylbenzene, oxane, and 1,4-dioxane have been determined: octane and cyclohexane interact with the acid through van der Vaals or London dispersion forces whereas the electron donor molecule of 1,3,5-trimethylbenzene gives rise to a charge-transfer complex with the electron acceptor C═O group of the acid. Finally oxane and 1,4-dioxane form chemical aggregates with acid through hydrogen bonding, the last compound capable of forming two complexes, owing to the presence of two hydrogen atoms (Prausnitz, 1969).

An attempt to interpret the excess properties of this paper by means of molecular theories, particularly the Lacombe−Sanchez model (1976), will be the goal of a future work.

Measurements were made at 313.15 K and atmospheric pressure. We are not aware of any previous investigations of the excess properties of these systems at this temperature: Lark and Palta (1980) and Wilhelm et al. (1982a,b) report some experimental values of binary mixtures containing propionic acid + cyclohexane, + oxane, and + 1,4-dioxane at different temperatures, lower than the temperatures of our experiments. We have repeated one measurement for each of the above mentioned mixtures, and our data are in agreement with those of the literature. Experimental values at $T = 298.15$ K in comparison with literature data are for the mixture propionic acid + oxane, at $x_1 = 0.58$, $H_m^E/(\mathrm{J \cdot mol^{-1}}) = -581.6$ (lit. value = −584.5 (Wilhelm et al., 1982a)), for the mixture propionic acid + 1,4-dioxane at $x_1 = 0.74$, $H_m^E/(\mathrm{J \cdot mol^{-1}}) = 131.1$ (lit. value = 130.0 (Wilhelm et al., 1984b)), and for the mixture propionic acid + cyclohexane at $x_1 = 0.56$, $V_m^E/(\mathrm{cm^3 \cdot mol^{-1}}) = 1.067$ (lit. value = 1.0553 (Lark and Palta, 1980)).

Experimental Section

Purity of Materials. Propionic acid (purity ≥ 99.5 mol %), octane (purity ≥99.5 mol %), and 1,3,5-trimethylbenzene (purity 99 mol %) were purchased from Fluka, while cyclohexane (99.9 mol %), oxane (anhydrous, 99 mol %), and 1,4-dioxane (99.9 mol %, HPLC grade) were Aldrich products. 1,3,5-Trimethylbenzene and oxane were fractionally distilled over Na wire in a 20 theoretical plates column (GLC purity > 99.9 mol % for both components). Other liquids, owing to their high-purity grade, were used as received. Before use, all components were stored in dark bottles over molecular sieves (Union Carbide Type 4A, 1/16-in. pellets) and degassed. The purities of the components were further ascertained by comparing their densities and refractive indices (Abbe refractometer, accuracy ±0.0001) as shown in Table 1.

Procedure. Calorimetric Measurements. The excess molar enthalpies, H_m^E, were determined with an LKB flow microcalorimeter (model 2107, LKB Produkter, Bromma, Sweden). Details of the equipment and its operation procedure have been described previously (Monk and Wadso, 1968; Francesconi and Comelli, 1986). Over most of the mole fraction range, the errors in H_m^E and in the mole fraction x_1 of propionic acid are estimated to be less than 0.5% and 5×10^{-4}, respectively.

The performance of the apparatus was checked by measuring H_m^E of the well-investigated cyclohexane + hexane test mixture (Benson, 1974). Deviations between our data and those in the literature are less than 0.5% over the central range of the mole fraction of cyclohexane (the uncertainties in temperature control and in mole fraction are 0.01 K and 1.5×10^{-4}, respectively).

Volumetric Measurements. Solutions were prepared by mass using a Mettler balance (model AE 160) with a precision of $\pm 1 \times 10^{-4}$ g, taking precautions to prevent evaporation and following the same procedure used by other authors (Fermeglia and Lapasin, 1988). All measurements were corrected for buoyancy and for evaporation of components. The mean uncertainty of the mole fraction was estimated to be $\pm 2 \times 10^{-4}$. V_m^E values were calculated from the densities of the pure components and binary mixtures according to

$$V_m^E = (x_1 M_1 + x_2 M_2)/\rho - x_1 M_1/\rho_1 - x_2 M_2/\rho_2 \qquad (1)$$

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of component i, respectively.

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Table 1. Experimental Densities, ρ, at 298.15 and 313.15 K and Refractive Indices, n_D, at 298.15 K of Pure Components and Comparison with Literature Values

	ρ/(g·cm^{-3})				n_D	
	298.15 K		313.15 K		298.15 K	
component	exptl	lit.	exptl	lit.	explt	lit.
propionic acid	0.987 87	0.988 08[a]	0.971 74	0.972 20[b]	1.3844	1.3843
octane	0.698 48	0.698 62[a]	0.686 28	0.686 17[c]	1.3949	1.3050
cyclohexane	0.773 81	0.773 89[a]	0.759 53	0.759 54[c]	1.4237	1.4235
1,3,5-trimethylbenzene	0.861 10	0.861 11[b]	0.848 80	0.848 90[c]	1.4968	1.4968
oxane	0.879 09	0.878 8[d] 0.879 16[e]	0.863 98		1.4188	1.4186
1,4-dioxane	1.028 09	1.027 97[a] 1.027 92[e]	1.011 10	1.010 99[a]	1.4201	1.4202

[a] Riddick et al. (1986). [b] Dreisbach (1961). [c] Smith and Srivastava (1986). [d] Inglese (1989). [e] Inglese et al. (1983).

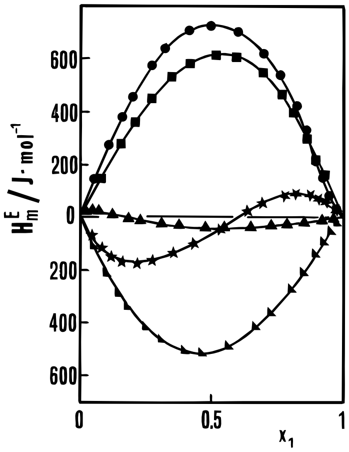

Figure 1. Dependence of the excess molar enthalpy H_m^E on the mole fraction x_1 at 313.15 K for binary mixtures containing propionic acid (1) + (■) octane (2), (●) cyclohexane (2), (▲) 1,3,5-trimethylbenzene (2), (filled right triangle) oxane (2), and (★) 1,4-dioxane (2): solid lines, calculated with eq 2.

Densities were determined using a digital vibrating density meter (Anton Paar, model 60/602, Graz, Austria) previously described by Fermeglia and Lapasin (1988), which operates on the basis of a linear relationship between the density ρ and the square of the resonance period τ of the vibrating tube (accuracy of the measured period 1×10^{-6} s). The temperature of the U-shaped tube was checked using a calibrated digital thermometer (Anton Paar, DT 100-40) with an accuracy of ±0.01 K while a Hetotherm bath circulator (Heto Type 01 DBT 623, Birkerød, Denmark) maintained the temperature constant to within ±0.005 K.

Freshly bidistilled and degassed water (Wagenbreth and Blanke, 1968) (ρ(298.15 K) = 0.997 047) and dry air (Kohlrausch, 1968) were used as standards for calibration of the apparatus before each series of measurements, and the calibrations were repeated periodically; fluctuations in τ did not exceed $\pm 1 \times 10^{-6}$ s.

The density measurements were reproducible to $\pm 1 \times 10^{-5}$ g·cm^{-3} corresponding to a mean uncertainty in the excess volume of $3 \cdot 10^{-3}$ cm^3·mol^{-1}.

Before each set of measurements, the apparatus was checked with the test mixture benzene + cyclohexane (Wilhelm, 1985), and results were in agreement with data in the literature, showing a discrepancy of less than 0.5% over the central range of the mole fraction of benzene.

Experimental Results and Data Treatment

The H_m^E and V_m^E data are reported as a function of the mole fraction of propionic acid in Tables 2 and 3 and graphically represented in Figures 1 and 2.

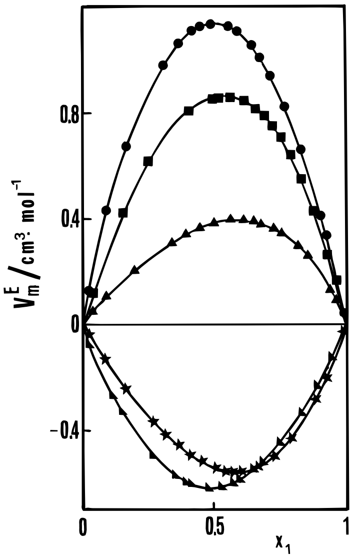

Figure 2. Dependence of the excess molar volume V_m^E on mole fraction x_1 of propionic acid (1) at 313.15 K in binary mixtures. Symbols are in the caption to Figure 1.

The experimental values were fitted to the Redlich–Kister equation

$$Q_m^E = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \tag{2}$$

where $Q_m^E = H_m^E$/(J·mol^{-1}) or V_m^E/(cm^3·mol^{-1}). The adjustable parameters a_k and standard deviations $\sigma(Q_m^E)$, the same as defined in a previous work (Francesconi and Comelli, 1994), were estimated by the unweighted least-squares method (Green and Margerison, 1977) and are also given in Tables 2 and 3.

The curves H_m^E and V_m^E as a function of x_1 can be interpreted, almost qualitatively, on the basis of the different interaction energies occurring between propionic acid and the second component.

In fact, mixtures of self-associated propionic acid with octane or cyclohexane show high positive values of H_m^E in agreement with the breaking of hydrogen bonding of acid dimers. In this case, only the interaction energy E_{11} contributes appreciably to the H_m^E (approximately, $H_m^E = E_{11} + E_{22} - 2E_{12}$ where E_{ij} is the interaction energy between molecules i and j).

Also V_m^E is positive owing to the prevalence of dimer bonds breaking on new bond formation between dissimilar molecules during mixing.

On the contrary 1,3,5-trimethylbenzene, oxane, and 1,4-dioxane (whose molecules interact with propionic acid) show lower values of both H_m^E and V_m^E. 1,4-Dioxane

Table 2. Experimental Excess Molar Enthalpies H_m^E, Adjustable Parameters a_k, and Standard Deviations $\sigma(H_m^E)$ According to Eq 2 for Binary Mixtures at 313.15 K

x_1	$H_m^E/(J\cdot mol^{-1})$	x_1	$H_m^E/(J\cdot mol^{-1})$
Propionic Acid (1) + Octane (2)			
0.0834	150	0.5928	612
0.1539	272	0.6859	545
0.2144	358	0.7661	460
0.2668	435	0.8137	390
0.3531	528	0.8676	299
0.4212	579	0.8973	237
0.5219	612	0.9291	170
$a_0 = 2430.1$; $a_1 = 364.6$; $a_3 = -217.0$; $\sigma(H_m^E)/(J\cdot mol^{-1}) = 2.4$			
Propionic Acid (1) + Cyclohexane (2)			
0.0571	141	0.6856	616
0.1080	275	0.7440	538
0.1537	382	0.8134	411
0.1950	467	0.8532	324
0.2665	574	0.8971	212
0.3264	645	0.9208	150
0.4209	705	0.9458	82
0.4921	714	0.9721	43
0.5924	697		
$a_0 = 2855.1$; $a_1 = 0$; $a_2 = 680.7$; $a_3 = -558.8$; $a_4 = -1689.3$; $\sigma(H_m^E)/(J\cdot mol^{-1}) = 4.9$			
Propionic Acid (1) + 1,3,5-Trimethylbenzene (2)			
0.0444	23	0.4815	−34
0.0548	24	0.5532	−36
0.0718	25	0.6500	−34
0.1340	14	0.7359	−27
0.1884	−1	0.7879	−24
0.2364	−12	0.8479	−18
0.3171	−22	0.9176	−12
0.3824	−30	0.9571	−8
$a_0 = -138.0$; $a_1 = -60.9$; $a_2 = 0$; $a_3 = 129.1$; $a_4 = 439.6$; $a_5 = -648.0$; $\sigma(H_m^E)/(J\cdot mol^{-1}) = 0.7$			
Propionic Acid (1) + Oxane (2)			
0.0528	−110	0.6675	−424
0.1003	−211	0.7280	−364
0.1433	−284	0.8006	−271
0.1823	−340	0.8426	−209
0.2507	−421	0.8893	−140
0.3085	−467	0.9146	−96
0.4009	−505	0.9414	−53
0.4715	−512	0.9698	−25
0.5723	−490		
$a_0 = -2032.5$; $a_1 = 325.0$; $a_2 = -207.5$; $a_3 = 434.5$; $a_4 = 880.9$; $\sigma(H_m^E)/(J\cdot mol^{-1}) = 3.1$			
Propionic Acid (1) + 1,4-Dioxane (2)			
0.0455	−76	0.6317	24
0.0870	−123	0.6957	55
0.1250	−147	0.7742	86
0.1600	−163	0.8205	91
0.2222	−170	0.8728	85
0.2759	−164	0.9014	73
0.3636	−133	0.9321	57
0.4325	−100	0.9648	34
0.5334	−43		
$a_0 = -248.3$; $a_1 = 1252.4$; $a_2 = 144.3$; $a_3 = 283.5$; $a_4 = -393.4$; $\sigma(H_m^E)/(J\cdot mol^{-1}) = 1.8$			

Table 3. Experimental Excess Molar Volumes V_m^E, Adjustable Parameters a_k and Standard Deviations $\sigma(V_m^E)$ According to Eq 2 for Binary Mixtures at 313.15 K

x_1	$\rho/(g\cdot cm^{-3})$	$V_m^E/(cm^3\cdot mol^{-1})$	x_1	$\rho/(g\cdot mol^{-3})$	$V_m^E/(cm^3\cdot mol^{-1})$
Propionic Acid (1) + Octane (2)					
0.0382	0.690 90	0.114	0.6880	0.823 54	0.781
0.1550	0.706 49	0.415	0.7194	0.834 34	0.743
0.2576	0.722 34	0.610	0.7525	0.846 38	0.702
0.4130	0.751 19	0.801	0.7937	0.862 65	0.629
0.4992	0.770 38	0.846	0.8363	0.880 98	0.544
0.5252	0.776 73	0.850	0.8840	0.903 77	0.423
0.5608	0.785 84	0.849	0.9358	0.931 57	0.260
0.6158	0.801 10	0.834	0.9631	0.947 85	0.156
0.6551	0.812 97	0.805	0.9920	0.966 33	0.036
$a_0 = 3.3769$; $a_1 = 0.4930$; $a_2 = 0.4162$; $a_3 = 0.2490$; $\sigma(V_m^E)/(cm^3\cdot mol^{-1}) = 0.0022$					
Propionic Acid (1) + Cyclohexane (2)					
0.0257	0.762 45	0.126	0.5891	0.854 49	1.102
0.0991	0.771 36	0.432	0.6412	0.866 3	1.051
0.1693	0.780 68	0.666	0.673	0.873 89	1.011
0.3107	0.801 89	0.983	0.7165	0.884 60	0.938
0.3760	0.812 87	1.065	0.7726	0.899 39	0.820
0.4285	0.822 24	1.109	0.8307	0.915 85	0.663
0.4573	0.827 68	1.117	0.9059	0.939 05	0.409
0.4944	0.834 81	1.130	0.9247	0.945 28	0.334
0.5553	0.847 22	1.121	0.9924	0.968 93	0.036
$a_0 = 4.5229$; $a_1 = 0.0521$; $a_2 = 0.4624$; $a_3 = -0.1463$; $\sigma(V_m^E)/(cm^3\cdot mol^{-1}) = 0.0018$					
Propionic Acid (1) + 1,3,5-Trimethylbenzene (2)					
0.0390	0.851 15	0.045	0.6504	0.906 78	0.387
0.0956	0.854 76	0.105	0.6807	0.910 95	0.379
0.2007	0.862 09	0.202	0.7281	0.917 86	0.361
0.3474	0.873 90	0.310	0.7542	0.921 93	0.346
0.3961	0.878 34	0.336	0.8219	0.933 35	0.292
0.4527	0.883 81	0.363	0.8564	0.939 76	0.254
0.5089	0.889 70	0.380	0.9383	0.956 79	0.133
0.5695	0.896 58	0.391	0.9578	0.961 28	0.094
0.6164	0.902 34	0.391			
$a_0 = 1.5105$; $a_1 = 0.5462$; $a_2 = 0.2663$; $a_3 = 0.0832$; $\sigma(V_m^E)/(cm^3\cdot mol^{-1}) = 0.0012$					
Propionic Acid (1) + Oxane (2)					
0.0296	0.867 01	−0.074	0.5723	0.924 27	−0.602
0.1213	0.876 45	−0.270	0.5992	0.927 21	−0.591
0.1581	0.880 22	−0.331	0.6530	0.933 08	−0.555
0.2762	0.892 61	−0.501	0.6856	0.936 66	−0.528
0.3615	0.901 59	−0.571	0.7538	0.944 20	−0.453
0.3952	0.905 22	−0.595	0.8324	0.952 90	−0.337
0.4229	0.908 18	−0.606	0.8888	0.959 25	−0.239
0.4820	0.914 53	−0.618	0.9452	0.965 61	−0.125
0.5345	0.920 17	−0.613			
$a_0 = -2.4697$; $a_1 = 0.0608$; $\sigma(V_m^E)/(cm^3\cdot mol^{-1}) = 0.0016$					
Propionic Acid (1) + 1,4-Dioxane (2)					
0.0237	1.010 74	−0.039	0.5396	0.998 03	−0.556
0.0864	1.009 72	−0.139	0.5697	0.996 89	−0.560
0.1655	1.008 25	−0.251	0.6037	0.995 53	−0.558
0.2699	1.006 00	−0.377	0.6632	0.992 95	−0.542
0.3194	1.004 79	−0.427	0.7335	0.989 56	−0.500
0.3544	1.003 87	−0.459	0.7945	0.986 22	−0.436
0.4090	1.002 32	−0.499	0.8857	0.980 47	−0.288
0.4445	1.001 25	−0.521	0.9233	0.977 85	−0.210
0.4992	0.999 46	−0.546	0.9877	0.972 73	−0.031
$a_0 = -2.1831$; $a_1 = -0.6850$; $a_2 = -0.2244$; $\sigma(V_m^E)/(cm^3\cdot mol^{-1}) = 0.0018$					

displays in mixtures with propionic acid a peculiar behavior which can be observed in aqueous mixtures, that is, a sign inversion in the H_m^E vs x_1 curve (Rowlinson, 1959). It must be remarked that the mixture propionic acid + 1,4-dioxane at 298.15 K does not show a sign inversion in H_m^E (Wilhelm, 1982b), which implies a strong temperature dependence of H_m^E. This behavior was also observed for other nonaqueous systems, for instance 2-methylpropyl ethanoate + 1,4-dimethylbenzene (Gmehling and Meents, 1992) and cycloheptane + cyclohexane (Marsh, 1977), which however show S-shaped H_m^E vs x_1 curves at the lower temperature. More difficult to explain is the difference between oxane and 1,4-dioxane.

Indeed, the diether 1,4-dioxane should interact more strongly with propionic acid and give rise to values of H_m^E and V_m^E more negative than the ones of the monoether oxane, as could be inferred by the results obtained by McGlashan and Rastogi (1958) for the mixture chloroform + *p*-dioxane, reported by Prausnitz (1969).

This trend has been pointed out also by Wilhelm et al. (1982a,b) and is discussed in the paper of Kalali et al. (1990).

In a coming paper, an attempt will be made to interpret the above results on the basis of the Lacombe−Sanchez theory, in a modified version allowing for the presence of self-association of the propionic acid and considering this compound as a binary mixture of monomers and dimers.

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