7 for the system ethanol + *n*-heptane.

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Volumetric Properties of Binary Mixtures. 2. Mixtures of *n*-Hexane with Ethanol and 1-Propanol

C. Ormanoudis, C. Dakos, and C. Panayiotou*

Department of Chemical Engineering and Chemical Process Engineering Research Institute, University of Thessaloniki, 540 06 Thessaloniki, Greece

In the second part of this series of papers we report experimental densities for the binary mixtures *n*-hexane + ethanol and *n*-hexane + 1-propanol. The pressure range at 298.15 K is from 1 to 340 bar. At atmospheric pressure the densities have been measured also at 288.15 and 308.15 K. The data have been used for calculating excess volumes, isothermal compressibilities, and thermal expansion coefficients. In addition ultrasound velocity measurements are reported that have been used for calculating isentropic compressibilities.

Introduction

Mixtures of 1-alkanols with *n*-alkanes have attracted particular attention in the thermodynamic literature. IUPAC has already organized five international workshops on the vapor–liquid equilibria and related properties of these systems. New theoretical approaches for data correlation and prediction in alkanol + alkane mixtures are based on equation-of-state theories, which are extended to account for hydrogen bonding and formation of association complexes (*1–3*). Volumetric properties of pure components and mixtures are of particular importance in the implementation of these new theoretical approaches. However, as it was pointed out in part 1 of this series of paper (*4*), the usefulness of volumetric properties is not confined to equation-of-state theories.

In the second part of this series of papers we report experimental densities at 298.15 K and in the pressure range from 1 to 340 bar for the mixtures of *n*-hexane with ethanol and 1-propanol. Densities at atmospheric pressure and at two other temperatures are also reported. In addition, ultrasound velocity measurements have been conducted, and the results have been used for calculating isentropic compressibilities.

Experimental Section

Materials. Pure ethanol and *n*-hexane used in this work were pro analysi grades from Merck while 1-propanol was a puriss. grade from Fluka. Their purity was determined by gas–liquid chromatography and was better than 99.8% for ethanol, better than 99.0% for *n*-hexane, and better than 99.5% for 1-propanol. Pure liquids have been used as received without any further purification. The mixtures were prepared by weight with precisions of 0.0001 g. 50 mL flasks with septum caps and magnetic stirring bars were used. The initial vapor space in the flask was less than 3 cm^3. Because of the small vapor space and the reproducibility of density measurements, no gas corrections were applied.

Density. The experimental setup for the density measurements was described previously (*4*). At atmospheric pressure the densities, ρ, have been measured in a vibrating tube densitometer, Model DMA 60/602 of Anton Paar. At higher pressures, a high-pressure density cell was used that consisted of a high-pressure density cell, Model DMA 512 of Anton Paar, a homemade compression cell, and a dead-weight tester, Model MTU600 of Metronex. No hysteresis was observed in the density measurements by increasing and then decreasing the external pressure. The temperature in the measuring cells was regulated through a Haake ultrathermostat and was kept constant to within 0.01 K, as measured by a precision digital thermometer, Model S1220 of Systemteknik. The estimated error in the density measurement at atmospheric pressure is 5×10^{-6} g/cm^3. The corresponding error with the high-pressure cell is 1×10^{-4} g/cm^3.

Ultrasonic Velocity. As previously reported (*4*), the ultrasound velocity was measured in sing-around equipment, Model RN-1A of DHN, at a resonance frequency of 4 MHz. The sound velocity, c, is related to the signal frequency, f, as follows:

$$\frac{1}{f} = \frac{L}{c} + \tau \qquad (1)$$

where L is the distance between the transducers and τ is the delay time of the impulse in the circuit. These are equipment constants.

Results and Discussion

The densities of the binary mixtures at each composition have been measured at 30 pressures between 1 and 340 bar. Selected data for 10 pressures are reported in Tables I and II. The complete sets of data are available upon request. In Figure 1 are compared our experimental data with literature data (*5*). As can be seen, our experimental data are in good agreement with literature values. The sets of data that have been used for calibrating our density cell are those of Kell and Whalley (*6*) for water and those of Machado and Street (*7*) for methanol. On the basis of the experimental densities, we may calculate the molar volume of mixing V^E (excess volume) at each pressure according to eq 2 of the previous paper in this

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* Author to whom correspondence should be addressed.

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Table I. Experimental Densities ρ for the System Hexane (1) + Ethanol (2) at 298.15 K as a Function of Pressure P and Mole Fraction x_1 of Hexane

	ρ at various P/(g cm^{-3})									
x_1	1.01 bar	20.0 bar	39.9 bar	79.6 bar	119.4 bar	159.1 bar	198.9 bar	258.6 bar	298.3 bar	338.1 bar
0.0000	0.7852	0.7866	0.7884	0.7916	0.7948	0.7978	0.8008	0.8051	0.8079	0.8107
0.0499	0.7702	0.7719	0.7736	0.7769	0.7802	0.7833	0.7863	0.7907	0.7935	0.7963
0.1002	0.7573	0.7590	0.7608	0.7642	0.7675	0.7707	0.7738	0.7782	0.7811	0.7840
0.1496	0.7460	0.7477	0.7495	0.7530	0.7563	0.7595	0.7626	0.7671	0.7700	0.7729
0.2008	0.7355	0.7372	0.7391	0.7426	0.7460	0.7493	0.7525	0.7570	0.7600	0.7629
0.3020	0.7181	0.7199	0.7218	0.7254	0.7289	0.7322	0.7354	0.7401	0.7431	0.7460
0.4196	0.7017	0.7036	0.7055	0.7092	0.7127	0.7161	0.7194	0.7241	0.7271	0.7301
0.5485	0.6871	0.6890	0.6909	0.6947	0.6983	0.7018	0.7051	0.7099	0.7130	0.7160
0.5998	0.6821	0.6840	0.6860	0.6898	0.6934	0.6968	0.7002	0.7050	0.7081	0.7111
0.6992	0.6735	0.6754	0.6774	0.6812	0.6849	0.6884	0.6917	0.6965	0.6997	0.7027
0.8004	0.6661	0.6681	0.6700	0.6739	0.6775	0.6810	0.6843	0.6892	0.6923	0.6953
0.8973	0.6601	0.6620	0.6640	0.6678	0.6715	0.6750	0.6783	0.6832	0.6863	0.6893
0.9493	0.6573	0.6592	0.6612	0.6650	0.6686	0.6721	0.6755	0.6803	0.6834	0.6864
0.9666	0.6563	0.6582	0.6602	0.6640	0.6676	0.6711	0.6745	0.6793	0.6824	0.6855
1.0000	0.6549	0.6567	0.6587	0.6624	0.6661	0.6696	0.6730	0.6779	0.6810	0.6839

Table II. Experimental Densities ρ for the System Hexane (1) + 1-Propanol (2) at 298.15 K as a Function of Pressure P and Mole Fraction x_1 of Hexane

	ρ at various P/(g cm^{-3})									
x_1	1.01 bar	20.0 bar	39.9 bar	79.6 bar	119.4 bar	159.1 bar	198.9 bar	258.6 bar	298.3 bar	338.1 bar
0.0000	0.7996	0.8010	0.8025	0.8054	0.8082	0.8110	0.8137	0.8176	0.8202	0.8226
0.0996	0.7766	0.7781	0.7797	0.7827	0.7857	0.7885	0.7913	0.7954	0.7981	0.8007
0.3007	0.7368	0.7384	0.7401	0.7434	0.7466	0.7497	0.7528	0.7572	0.7600	0.7628
0.4087	0.7195	0.7212	0.7229	0.7263	0.7297	0.7329	0.7360	0.7405	0.7435	0.7463
0.5031	0.7060	0.7077	0.7095	0.7130	0.7164	0.7197	0.7229	0.7276	0.7305	0.7334
0.5999	0.6936	0.6954	0.6972	0.7008	0.7042	0.7076	0.7109	0.7155	0.7186	0.7215
0.7008	0.6819	0.6837	0.6856	0.6892	0.6927	0.6962	0.6995	0.7043	0.7074	0.7103
0.7984	0.6719	0.6737	0.6755	0.6792	0.6828	0.6863	0.6897	0.6945	0.6976	0.7005
0.8513	0.6669	0.6687	0.6706	0.6743	0.6779	0.6814	0.6848	0.6896	0.6927	0.6957
0.9316	0.6600	0.6619	0.6638	0.6675	0.6712	0.6747	0.6781	0.6829	0.6860	0.6890
1.0000	0.6549	0.6567	0.6587	0.6624	0.6661	0.6696	0.6730	0.6779	0.6810	0.6839

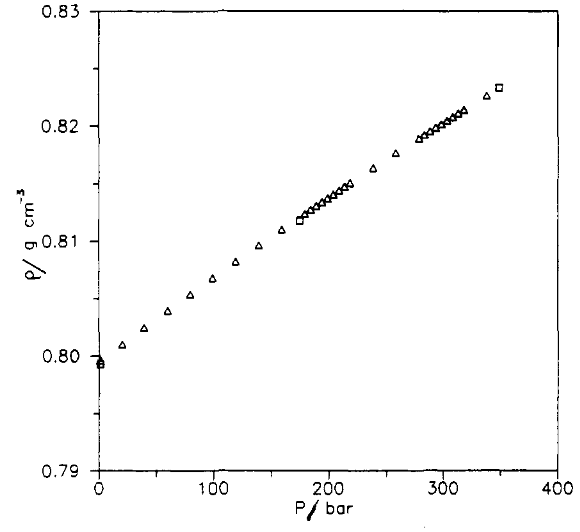

Figure 1. Experimental density ρ of pure 1-propanol at 298.15 K as a function of pressure P: □, Kubota et al. (*5*); Δ, this work.

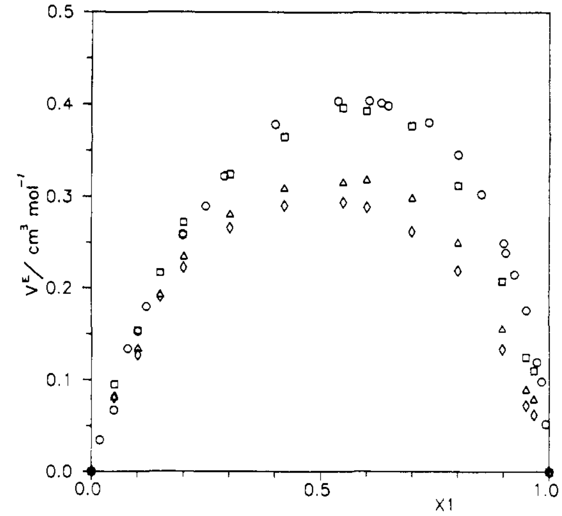

Figure 2. Excess molar volume V^E at 298.15 K for the system *n*-hexane (1) + ethanol (2) at various pressures P as a function of the mole fraction x_1 of hexane: ○, P = 1.01 bar with the DMA 602 cell; □, P = 1.01 bar with the DMA 512 cell; Δ, P = 198.9 bar; ◇, P = 338.1 bar.

issue. Excess volume is a very sensitive quantity and may be used for assessing the quality of the density measurements.

In Figures 2 and 3 are shown the excess volumes of the two binary systems at three representative pressures. The maximum excess volume is diminished with pressure in a similar way for both systems. However, the highly asymmetric character of the excess volume curves for the mixture of *n*-hexane with 1-propanol leads to a crossing of the curves in the side of the less compressible 1-propanol, as shown in Figure 3. S-shaped excess volume curves are quite common in 1-alkanol + *n*-alkane mixtures (*1*–*3*) at atmospheric pressure. The persistence of this S-shape with pressure is a subject of further investigation. In Figures 2 and 3 are also shown excess volumes at 1 atm measured with the low-pressure density cell, type DMA 602 of Anton Paar. As can be seen, the two sets of data measured with the two cells are in good agreement.

At each composition, the complete set of experimental densities (30 data points) has been used for the determination of the coefficients of the fourth-order polynomial

$$1/(\rho/(\mathrm{g\ cm^{-3}})) = \sum_{i=0}^{4} a_i (P/\mathrm{bar})^i \tag{2}$$

Coefficients a_i of eq 2, along with the standard deviation of fit, σ, are reported in Tables III and IV. Equation 2 has subsequently been used for the evaluation of the isothermal com-

Table III. Coefficients a_i in Equation 3 and Standard Deviation $\sigma(\rho)$ for the System Hexane (1) + Ethanol (2) at 298.15 K at Mole Fraction x_1 of Hexane

x_1	a_0	$a_1/10^{-3}$	$a_2/10^{-7}$	$a_3/10^{-10}$	$a_4/10^{-13}$	$\sigma(\rho)/(10^{-5}$ g cm$^{-3})$
0.0000	1.273 797	−0.137 39	0.682 93	−0.562 54	0.487 31	2
0.0499	1.298 46	−0.149 35	0.902 30	−0.841 37	0.570 10	3
0.1002	1.320 588	−0.158 14	0.979 09	−0.846 99	0.426 46	3
0.1496	1.340 726	−0.166 27	1.037 65	−0.637 61		3
0.2008	1.359 865	−0.175 85	1.260 30	−1.270 62	0.711 61	3
0.3020	1.392 757	−0.189 14	1.368 45	−1.029 25		3
0.4196	1.425 309	−0.203 35	1.556 25	−1.210 12		3
0.5485	1.455 626	−0.214 12	1.356 87		−1.539 64	3
0.5998	1.466 209	−0.217 17	1.366 95		−1.635 29	3
0.6992	1.484 948	−0.226 12	1.636 02	−0.875 82	−0.569 67	3
0.8004	1.501 441	−0.232 27	1.797 02	−1.356 75		3
0.8973	1.515 191	−0.237 39	1.853 97	−1.391 30		3
0.9493	1.521 719	−0.238 82	1.863 37	−1.414 81		3
0.9666	1.523 984	−0.239 59	1.879 25	−1.440 91		3
1.0000	1.527 240	−0.231 58	1.330 80	−0.845 53	0.925 51	2

Table IV. Coefficients a_i in Equation 3 and Standard Deviation $\sigma(\rho)$ for the System Hexane (1) + 1-Propanol (2) at 298.15 K at Mole Fraction x_1 of Hexane

x_1	a_0	$a_1/10^{-3}$	$a_2/10^{-7}$	$a_3/10^{-10}$	$a_4/10^{-13}$	$\sigma(\rho)/(10^{-5}$ g cm$^{-3})$
0.0000	1.250 687	−0.114 64	0.085 89	1.262 23	−1.664 18	2
0.0996	1.287 732	−0.130 98	0.519 21		−0.345 74	3
0.3007	1.357 346	−0.158 06	0.633 46		−0.127 44	3
0.4087	1.389 981	−0.171 31	0.694 84			3
0.5031	1.416 536	−0.180 91	0.508 14	1.147 20	−1.547 92	3
0.5999	1.441 947	−0.194 52	0.894 31		−0.261 99	3
0.7008	1.466 618	−0.202 82	0.786 47	0.227 80		3
0.7984	1.488 658	−0.213 86	0.978 60			3
0.8513	1.499 765	−0.218 50	1.020 35		−1.387 025	3
0.9316	1.515 300	−0.225 58	1.171 44	−0.434 54	0.482 058	3
1.0000	1.527 240	−0.231 58	1.330 80	−0.845 53	0.925 51	2

Table V. Experimental Sound Velocities c and Calculated Isentropic Compressibilities β_S, Equation 5, for the System Hexane (1) + Ethanol (2) at 298.15 K and Atmospheric Pressure as a Function of the Mole Fraction x_1 of Hexane

x_1	$c/$ (m s^{-1})	$\beta_S/$ (10^{-9} Pa^{-1})	x_1	$c/$ (m s^{-1})	$\beta_S/$ (10^{-9} Pa^{-1})
0.0000	1142.4	0.9757	0.6989	1065.6	1.3075
0.0999	1114.6	1.0625	0.7989	1066.6	1.3198
0.2989	1085.0	1.1824	0.8996	1069.5	1.3250
0.3968	1077.7	1.2221	0.9498	1071.6	1.3253
0.4995	1072.1	1.2567	1.0000	1076.6	1.3174

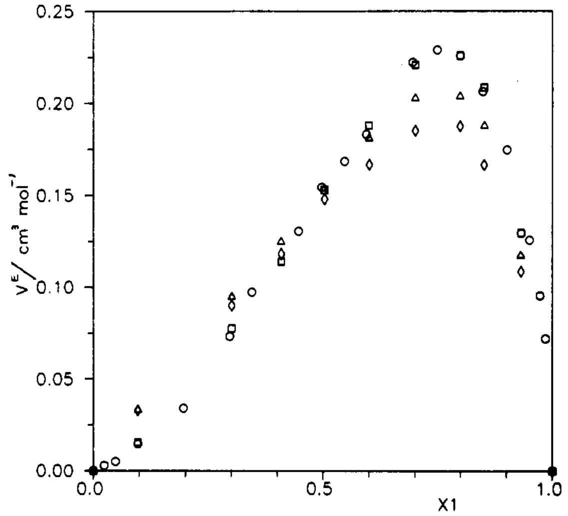

Figure 3. Excess molar volume V^E for the system n-hexane (1) + 1-propanol (2) at 298.15 K at various pressures P as a function of the mole fraction x_1 of hexane: ○, P = 1.01 bar with the DMA 602 cell; □, P = 1.01 bar with the DMA 512 cell; △, P = 198.9 bar; ◊, P = 338.1 bar.

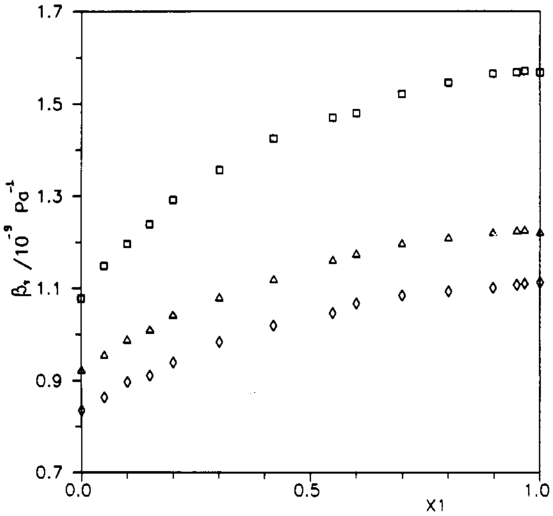

Figure 4. Isothermal compressibility β_T for the system n-hexane (1) + ethanol (2) at 298.15 K at various pressures P as a function of the mole fraction x_1 of hexane. □, P = 1.01 bar; △, P = 198.9 bar; ◊, P = 338.1 bar.

Table VI. Experimental Sound Velocities c and Calculated Isentropic Compressibilities β_S, Equation 5, for the System Hexane (1) + 1-Propanol (2) at 298.15 K and Atmospheric Pressure as a Function of the Mole Fraction x_1 of Hexane

x_1	$c/$ (m s^{-1})	$\beta_S/$ (10^{-9} Pa^{-1})	x_1	$c/$ (m s^{-1})	$\beta_S/$ (10^{-9} Pa^{-1})
0.0000	1205.3	0.8609	0.4994	1104.7	1.1598
0.1010	1175.2	0.9333	0.6997	1085.9	1.2435
0.2027	1151.2	0.9988	0.7977	1077.9	1.2810
0.2995	1131.0	1.0606	0.8998	1074.0	1.3088
0.3996	1115.1	1.1157	1.0000	1076.6	1.3174

pressibilities, β_T, of the mixtures given by eq 4 of the previous paper in this issue.

In Figures 4 and 5 are shown isothermal compressibility data for the two systems at three representative pressures. As can be seen in both, the isothermal compressibility is larger than the additively calculated value, the difference decreasing with increasing pressure. β_T itself is also diminished significantly as the pressure increases.

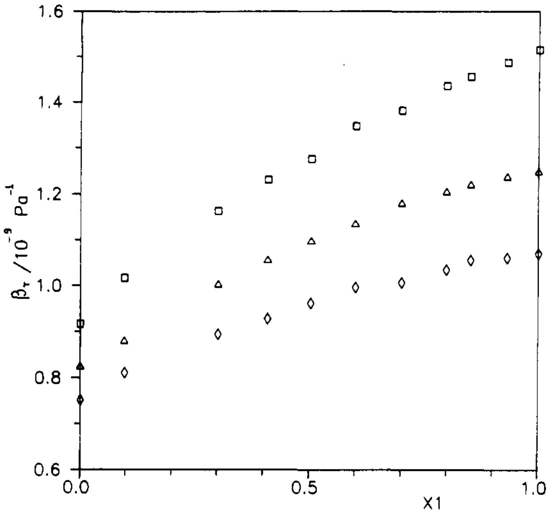

Figure 5. Isothermal compressibility β_T for the system *n*-hexane (1) + 1-propanol (2) at 298.15 K at various pressures *P* as a function of the mole fraction x_1 of hexane. Symbols as in Figure 4.

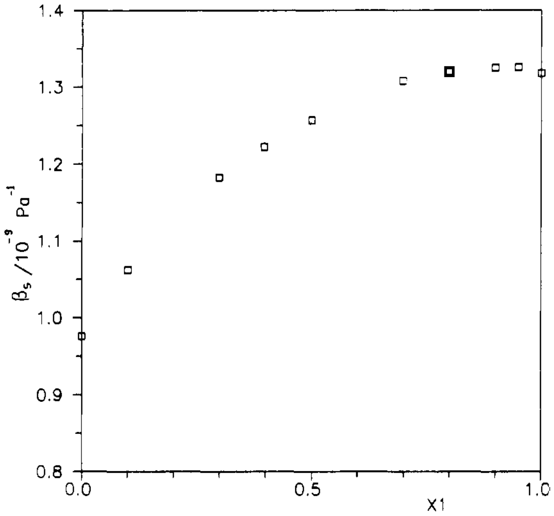

Figure 6. Isentropic compressibility β_S for the system *n*-hexane (1) + ethanol (2) at 298.15 K at atmospheric pressure as a function of the mole fraction x_1 of hexane.

Primary ultrasound velocity measurements are reported in Tables V and VI, along with the isentropic compressibilities calculated by

$$\beta_S = \frac{1}{\rho c^2} \tag{3}$$

From classical thermodynamics β_S is related to β_T according to the equation

$$\beta_S = \beta_T - \frac{VT\alpha^2}{C_P} \tag{4}$$

where C_P is the molar heat capacity at constant pressure, V is the molar volume of the system, and α is the cubic expansion coefficient. As indicated by eq 4, $\beta_S \leq \beta_T$ always. Figures 4 and 6 are in conformity with this thermodynamic requirement.

In Tables VII and VIII are reported experimental densities at atmospheric pressure and for temperatures different from 298.15 K. These data (at three temperatures) are not sufficient for an accurate estimation of the cubic expansion coefficient of the liquids. They may, however, be used for an approximate estimation of it by the equation

$$\alpha = -\rho\left(\frac{\Delta\rho}{\Delta T}\right)_P \tag{5}$$

Table VII. Experimental Densities ρ for the System Hexane (1) + Ethanol (2) at Temperature *T* and Atmospheric Pressure as a Function of the Mole Fraction x_1 of Hexane

	ρ/(g cm^{-3})			ρ/(g cm^{-3})	
x_1	T = 288.15 K	T = 308.15 K	x_1	T = 288.15 K	T = 308.15 K
0.0000	0.7937	0.7764	0.6989	0.6827	0.6641
0.1000	0.7661	0.7486	0.7989	0.6752	0.6567
0.2989	0.7274	0.7093	0.8996	0.6689	0.6504
0.3968	0.7137	0.6953	0.9498	0.6662	0.6478
0.4995	0.7014	0.6828	1.0000	0.6639	0.6459

Table VIII. Experimental Densities ρ for the System Hexane (1) + 1-Propanol (2) at Temperature *T* and Atmospheric Pressure as a Function of the Mole Fraction x_1 of Hexane

	ρ/(g cm^{-3})			ρ/(g cm^{-3})	
x_1	T = 288.15 K	T = 308.15 K	x_1	T = 288.15 K	T = 308.15 K
0.0000	0.8077	0.7916	0.4994	0.7153	0.6973
0.1010	0.7840	0.7673	0.6997	0.6911	0.6727
0.2027	0.7634	0.7465	0.7977	0.6812	0.6627
0.2996	0.7455	0.7282	0.8998	0.6717	0.6533
0.3996	0.7299	0.7124	1.0000	0.6639	0.6459

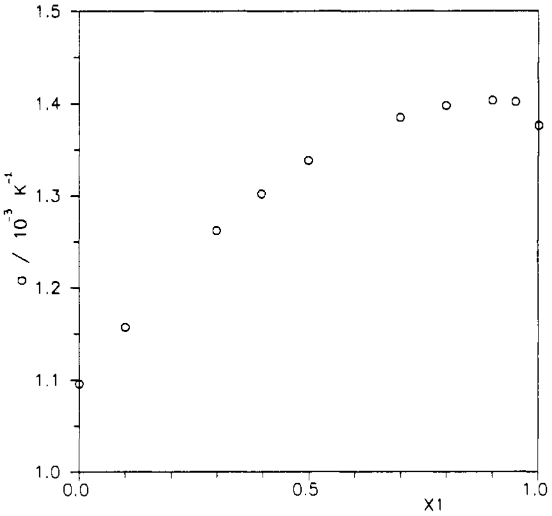

Figure 7. Cubic expansion coefficient α for the system *n*-hexane (1) + ethanol (2) at 298.15 K and atmospheric pressure as a function of the mole fraction x_1 of hexane.

The density data of the above tables are first fitted to Redlich–Kister polynomials for the necessary interpolations. Thermal expansion coefficients from such calculations are shown in Figure 7 for the system ethanol + *n*-hexane.

The present data when coupled with relevant calorimetric data for C_P may lead to an estimation of C_V since

$$C_V = C_P\frac{\beta_S}{\beta_T} \tag{6}$$

When C_P data are available, eq 4 may be used as a consistency test of the experimental data for α, β_S, β_T, and C_P.

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