Temperature Dependence of the Volumetric Properties of Binary Mixtures Containing Alcohols (1-Propanol, 1-Pentanol, 1-Heptanol) + Heptane

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Excess molar volumes of mixtures of heptane + 1-propanol, 1-pentanol, or 1-heptanol were determined from density measurements at 278.15, 288.15, 298.15, and 308.15 K. From these results $(\delta V^E/\delta T)_P$ and $(\delta H^E/\delta P)_T$ at 298.15 K were calculated. The results were compared with the values calculated using the Nitta–Chao theory of liquid mixtures.

Introduction

As a part of the studies on the properties of binary mixtures (a 1-alkanol + an alkane) (*1–3*), we report here the excess molar volumes of heptane + 1-propanol, 1-pentanol, and 1-heptanol at temperatures of 278.15, 288.15, 298.15, 308.15 K and atmospheric pressure. From these results, the values of V^E, $(\delta V^E/\delta T)_P$, and $(\delta H^E/\delta P)_T$ were determined and compared with those from the Nitta–Chao theory.

Experimental Section

Alcohols and heptane (better than 99.5 mol % pure) were obtained from Fluka. The chemicals were all partially degassed, dried over Fluka type 4Å molecular sieves, and otherwise used as supplied.

Densities of the pure liquids and mixtures were measured with a Kyoto Electronics densimeter. Using a Hetoterm PF-CBIIe thermostat, the vibrating-tube temperature was kept at better than ±0.005 K. The experimental technique has been previously described (*3, 4*). The compositions of the mixtures were determined by mass. The densities of the pure liquids agree closely with the literature values (*6–19*) as shown in Table 1. The accuracy of the measurements of the mole fractions in this instance was estimated at ±0.000 05, and that of the densities was ±0.000 01 g·cm⁻³.

Nitta–Chao Model

The Nitta–Chao model (Nitta et al. (*20*)) is based on the cell model, with the function of molecular cell partition being obtained by using the hard sphere state equation (Carnahan and Starling (*21*)). The equation of state expressed in reduced variables is

$$\tilde{p}\tilde{v}/\tilde{T} = 1 + \tilde{v}(4\tilde{v} - 2)/(\tilde{v} - 1)^3 - (1 + \kappa\tilde{v})\exp(\kappa/\tilde{v})/(\tilde{v}\tilde{T}) \qquad (1)$$

where κ is a constant whose value if 0.7. The reduced variables are defined by

$$\tilde{p} = pV^*/cNkT^* \qquad (2)$$

$$\tilde{v} = V/V^* \qquad (3)$$

$$\tilde{T} = cNkT/\tilde{Q}_e \qquad (4)$$

Table 1. Densities of the Pure Liquids

substance	T/K	ρ/(g·cm⁻³)		
		exptl	lit.	
1-propanol	278.15	0.815 41		
	288.15	0.807 60	0.807 49 (*5*) 0.807 7 (*12*)	0.807 71 (*18*)
	298.15	0.799 64	0.799 60 (*6*) 0.799 59 (*14*)	0.799 69 (*7*) 0.799 61 (*15*)
	308.15	0.791 58	0.791 6 (*12*) 0.791 48 (*19*)	0.791 62 (*18*)
1-pentanol	278.15	0.825 34		
	288.15	0.818 10		
	298.15	0.810 87	0.810 80 (*6*)	
	308.15	0.803 40		
1-heptanol	278.15	0.832 91		
	288.15	0.825 96		
	298.15	0.819 06	0.818 88 (*8*)	
	308.15	0.811 99		
heptane	278.15	0.696 18		
	288.15	0.687 89	0.687 9 (*13*)	
	298.15	0.679 51	0.679 53 (*9*) 0.679 56 (*10*)	0.679 46 (*5*) 0.679 55 (*11*)
	308.15	0.671 01	0.670 9 (*13*) 0.671 07 (*17*)	0.671 05 (*16*)

where c is the number of external degrees, N is the total number of molecules, k is the Boltzmann constant, T is the absolute temperature, p is the absolute pressure, V^* is the hard core volume, and

$$\tilde{Q}_e = \sum\sum N_{ij}E_{ij} \qquad (5)$$

For N_{ij}, the number of contacts, the quasi-chemical approximation is used.

The energy of the interaction is expressed by

$$E_{ij} = -(\epsilon_{ij}/\tilde{v})\exp(\kappa/\tilde{v}) - \sigma_{ij} \qquad (6)$$

ϵ_{ij} being the dispersive interaction energy parameter.

The chemical association energy σ_{ij} is temperature dependent and is given by

$$\frac{\sigma_{ij}}{T} = \frac{\sigma^\circ{}_{ij}}{T_0} + \sigma'{}_{ij}\left(\frac{1}{T} - \frac{1}{T_0}\right) \qquad (7)$$

where $\sigma^\circ{}_{ij}$ and $\sigma'{}_{ij}$ are characteristic parameters of this model.

The temperature dependence of the hard core volume of group i, $V^*{}_i$, is given by the empirical expression

$$V^*{}_i = V^*{}_{i0}\exp\left[a_i\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \qquad (8)$$

where $V^*{}_{i0}$ is the hard core volume at temperature T_0 (normally 298.15 K).

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Table 2. Characteristic Parameters for the Nitta et al. Model Calculated by Nitta et al. (*20*) and Fernández et al. (*1*)

group	$V^*_{i0}/(\mathrm{cm^3{\cdot}mol^{-1}})$	a_i/K	c_i	Q_i	$\epsilon_{ii}/(\mathrm{J{\cdot}mol^{-1}})$
$-CH_3$	13.46[a]	23.7[a]	0.338[a]	6.71[a]	2515[a]
$-CH_2$	10.25[a]	23.7[a]	0.093[a]	4.27[a]	2515[a]
-OH(O)	8.01[b]	10.0[b]	0.250[b]	3.62[a]	5893[b]
-OH(H)				1.00[b]	

$\epsilon_{ij}(\mathrm{CH_3,O})/(\mathrm{J{\cdot}mol^{-1}})$ $\epsilon_{ij}(\mathrm{CH_2,O})/(\mathrm{J{\cdot}mol^{-1}})$	$\sigma^\circ(\mathrm{O,O})/(\mathrm{J{\cdot}mol^{-1}})$	$\sigma'(\mathrm{O,O})/\mathrm{J{\cdot}mol^{-1}})$
3138[b]	13 263[b]	20 000[b]

[a] Nitta et al. (*20*). [b] Fernández et al. (*1*).

Both a_i and V^*_{i0} are characteristic parameters that are determined by fitting the theoretical equations to experimental data.

The expressions for the thermodynamic properties of both pure liquids and mixtures are derived by the standard methods of statistical thermodynamics.

Table 2 shows the characteristic parameters used.

Results and Discussion

The experimental excess molar volumes (V^E) (Tables 3–5) were calculated from the expression

$$V^E = xM_1(\rho^{-1} - \rho_1^{-1}) + (1-x)M_2(\rho^{-1} - \rho_2^{-1}) \qquad (9)$$

where M_1 and M_2 denote the molar masses, ρ_1 and ρ_2 denote the densities of the pure liquids, and x is the mole fraction of the alcohol.

The V^E values were fitted as a function of the molar fraction and temperature to a polynomial of the form

$$V^E/(\mathrm{cm^3{\cdot}mol^{-1}}) = x(1-x)\sum_{i=1}^{3}\sum_{j=1}^{3}A_{ij}x^{(i-1)/2}(T/\mathrm{K} - 298.15)^{j-1} \qquad (10)$$

The coefficients A_{ij} and standard deviations given in Table 6 were obtained by an optimization process which employed Marquardt's algorithm (*22*). Figure 1 shows the values found for experimental excess molar volumes together with the fitted curves $V^E(x,T)$.

Table 3. Excess Molar Volumes for *x* 1-Propanol + (1 − *x*) Heptane

	$V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$			
x	T = 278.15 K	T = 288.15 K	T = 298.15 K	T = 308.15 K
0.040 42	0.0743	0.0935	0.1240	0.1671
0.099 87	0.1521	0.1880	0.2312	0.2704
0.122 75	0.1773	0.1983	0.2376	0.2956
0.201 62	0.2110	0.2567	0.3148	0.3642
0.279 55	0.2282	0.2783	0.3290	0.3918
0.311 97	0.2255	0.2722	0.3316	0.3906
0.426 39	0.2272	0.2591	0.3178	0.3831
0.522 63	0.2020	0.2435	0.2881	0.3386
0.605 35	0.1668	0.1958	0.2407	0.2930
0.652 74	0.1635	0.1797	0.2117	0.2405
0.734 72	0.1271	0.1426	0.1656	0.1946
0.766 01	0.1264	0.1368	0.1614	0.1945
0.829 15	0.0985	0.1056	0.1206	0.1341
0.929 52	0.0355	0.0399	0.0462	0.0545

Table 4. Excess Molar Volumes for *x* 1-Pentanol + (1 − *x*) Heptane

	$V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$			
x	T = 278.15 K	T = 288.15 K	T = 298.15 K	T = 308.15 K
0.066 79	0.0348	0.0425	0.0830	0.1250
0.110 38	0.0789	0.0862	0.1075	0.1640
0.161 40	0.0979	0.1074	0.1354	0.1783
0.209 77	0.0959	0.1071	0.1411	0.1829
0.259 31	0.1105	0.1186	0.1377	0.1789
0.305 42	0.1176	0.1300	0.1349	0.1696
0.373 95	0.0985	0.1051	0.1146	0.1630
0.448 83	0.0579	0.0589	0.0871	0.1119
0.492 59	0.0473	0.0533	0.0760	0.1014
0.560 64	0.0288	0.0320	0.0445	0.0720
0.595 33	0.0191	0.0366	0.0422	0.0764
0.692 76	0.0063	0.0101	0.0120	0.0150
0.795 64	−0.0162	−0.0384	−0.0379	−0.0265
0.891 13	−0.0232	−0.0248	−0.0270	−0.0280
0.946 96	−0.0193	−0.0265	−0.0214	−0.0207

As far we know, excess molar volumes at 298.15 K have been measured (*7, 23*) before. The differences between the literature values and our results fitted with eq 10 were about 2.8% for 1-propanol + heptane and 1.2% for 1-pentanol + heptane.

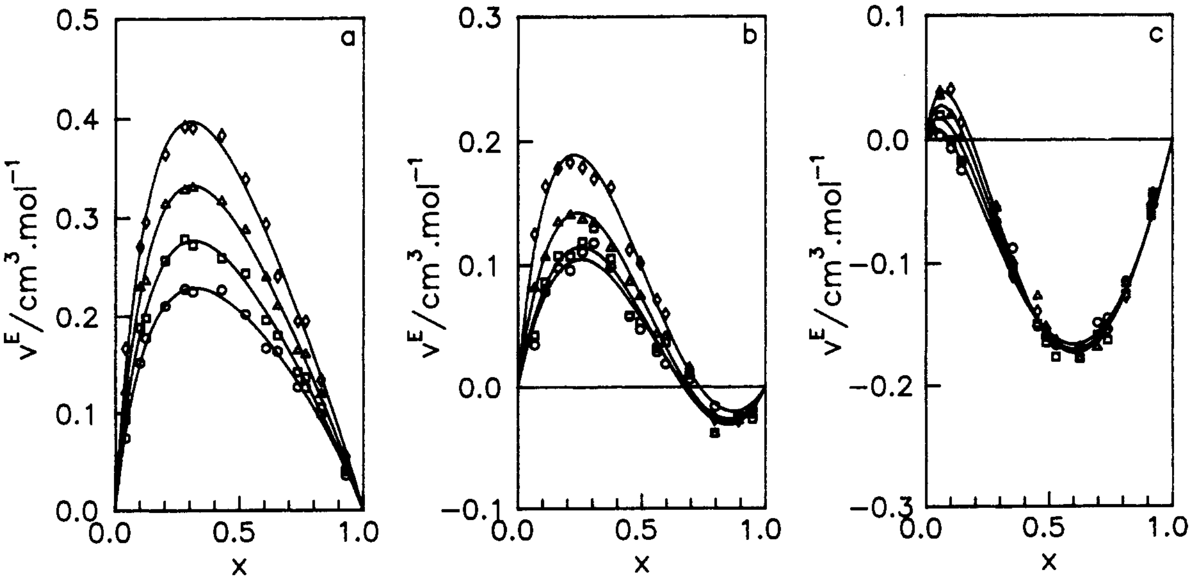

Figure 1. (a) Experimental excess molar volumes V^E for x 1-propanol + (1 − x) heptane at (○) 278.15 K, (□) 288.15 K, (△) 298.15 K, and (◇) 308.15 K. (b) Experimental excess molar volumes V^E for x 1-pentanol + (1 − x) heptane at (○) 278.15 K, (□) 288.15 K, (△) 298.15 K, and (◇) 308.15 K. (c) Experimental excess molar volumes V^E for x 1-heptanol + (1 − x) heptane at (○) 278.15 K, (□) 288.15 K, (△) 298.15 K, and (◇) 308.15 K.

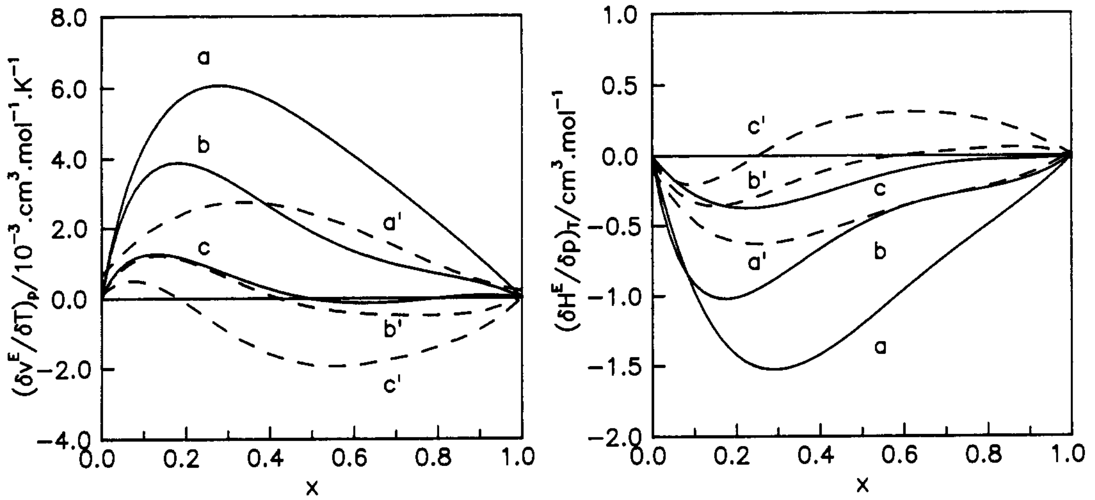

Figure 2. $(\partial V^E/\partial T)_P$ and $(\partial H^E/\partial P)_T$ for (a) x 1-propanol + $(1 - x)$ heptane, (b) x 1-pentanol + $(1 - x)$ heptane, and (c) x 1-heptanol + $(1 - x)$ heptane at 298.15 K: (—) derivation equation (10); (a′), (b′), (c′), (- - -) Nitta–Chao model.

Table 5. Excess Molar Volumes for x 1-Heptanol + $(1 - x)$ Heptane

	V^E/cm^3·mol^{-1})			
x	T = 278.15 K	T = 288.15 K	T = 298.15 K	T = 308.15 K
0.018 70	0.0107	0.0101	0.0099	0.0073
0.056 67	0.0032	0.0198	0.0365	0.0382
0.101 58	−0.0067	−0.0008	0.0209	0.0407
0.142 57	−0.0245	−0.0172	0.0027	0.0139
0.282 45	−0.0665	−0.0692	−0.0542	−0.0548
0.350 14	−0.0878	−0.1051	−0.0976	−0.1103
0.451 08	−0.1513	−0.1495	−0.1254	−0.1387
0.485 90	−0.1599	−0.1650	−0.1509	−0.1566
0.527 33	−0.1669	−0.1768	−0.1646	−0.1642
0.624 41	−0.1689	−0.1779	−0.1770	−0.1695
0.696 74	−0.1486	−0.1588	−0.1681	−0.1612
0.738 51	−0.1447	−0.1630	−0.1513	−0.1549
0.813 16	−0.1147	−0.1250	−0.1155	−0.1267
0.914 42	−0.0545	−0.0613	−0.0502	−0.0610
0.920 91	−0.0526	−0.0433	−0.0421	−0.0468

Table 6. Coefficients A_{ij} of Equation 10 and Standard Deviations s

	A_{ij}		
	$j = 1$	$j = 2$	$j = 3$
	x 1-Propanol + $(1 - x)$ Heptane (s = 0.0071)		
$i = 1$	2.9133	0.0410	0.00111
$i = 2$	−4.5981	−0.0318	−0.00271
$i = 3$	2.3189	−0.0105	0.00019
	x 1-Pentanol + $(1 - x)$ Heptane (s = 0.0092)		
$i = 1$	1.0480	−0.0169	0.002 57
$i = 2$	−0.5228	0.0622	−0.006 17
$i = 3$	−0.9118	−0.0550	0.003 99
	x 1-Heptanol + $(1 - x)$ Heptane (s = 0.0094)		
$i = 1$	0.7422	0.0400	−0.000 04
$i = 2$	−2.8102	−0.1016	0.000 09
$i = 3$	1.2358	0.0608	0.000 02

When the alcohol chain length increases, the excess volume at $x = 0.5$ decreases, eventually becoming negative.

$(\delta V^E/\delta T)_P$ and $(\delta H^E/\delta P)_T = V^E - (1/T)(\delta V^E/\delta T)_P$ values (Figure 2) were computed by analytical derivation of eq 10 at 298.15 K for each mixture.

V^E values at $x = 0.5$ as a function of the temperature are given in Figure 3. An almost linear decrease in V^E with an increase in the alcohol chain length is observed. The values obtained for $(\delta V^E/\delta T)_P$, shown in Figure 2, are positive for all systems, and decrease as the alcohol chain length increases. $(\delta H^E/\delta P)_T$ at 298.15 K is negative at all concentrations.

The results were compared with those of the Nitta–Chao theory using the parameters for both alkane–alkane and alkane–alcohol interactions given in Table 2. The latter have been calculated by Fernández et al. (*1*). The results obtained reproduce the variation of V^E with the temperature. V^E values decrease with an increase in the length of the alcohol chain. For the parameters $(\delta V^E/\delta T)_P$ and $(\delta H^E/\delta P)_T$ the calculated values show the same tendency as the experimental results (Figures 2 and 3).

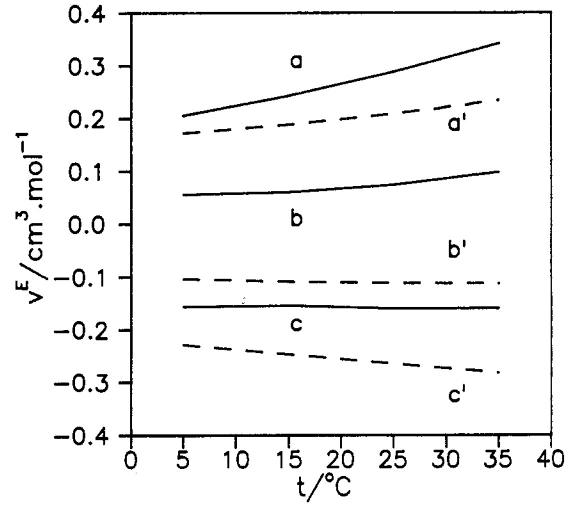

Figure 3. V^E (x = 0.5) for (a) propanol + heptane, (b) 1-pentanol + heptane, and (c) 1-heptanol + heptane against t: (—) values from eq 10; (a′), (b′), (c′), (- - -) Nitta–Chao model.

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