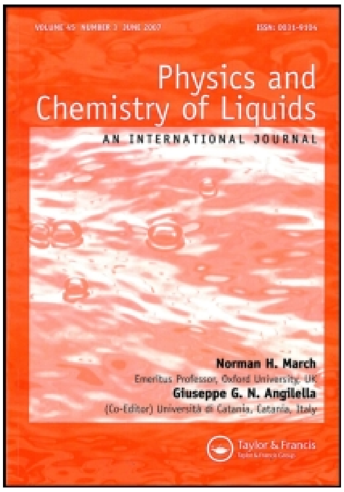

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Excess Volumes of 1-Alcohol Heptane Mixtures at 298.15 and 308.15 K-Application of An Association Model with Flory Interaction Term

N. V. Sastry[a]; M. K. Valand[a]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

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EXCESS VOLUMES OF 1-ALCOHOL +HEPTANE MIXTURES AT 298.15 AND 308.15K-APPLICATION OF AN ASSOCIATION MODEL WITH FLORY INTERACTION TERM

N. V. SASTRY* and M. K. VALAND

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar,
388 120, Gujarat, India

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The excess volumes of 1-pentanol+, 1-hexanol+, 1-heptanol+, 1-octanol+, 1-decanol+ and 1-dodecanol+heptane mixtures were evaluated at 298.15 and 308.15K from the density data. The excess volumes were found to decrease with the increase in the carbon chain length of alcohol molecules. The temperature coefficient for the excess volumes was also observed to show a decreasing trend from 1-pentanol+to 1-dodecanol+heptane mixtures. The excess volumes were also calculated by combining the individual physical and chemical contributions, evaluated by combining an association model with Flory's free volume theory. Reasonable agreement between the experimental and calculated excess volumes for all the mixtures at 298.15 and 308.15K was noted.

Keywords: Alcohol+heptane mixtures; association model; Flory theory

INTRODUCTION

The binary mixtures of alcohol+alkanes have been studied extensively and systematically in recent years. Benson and co-workers [1-5] reported excess volumes, speeds of sound and excess isentropic compressibilities for several primary alcohol+alkane binary mixtures with the variation in the alkyl chain length of both the components.

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*Corresponding author.

Treszczanowicz *et al.* [6] have reviewed in detail the existing literature data on the excess volumes of 1-alcohol + alkane mixtures and also recommended few data sets. Similarly the influence of alkyl chain length on the excess molar enthalpies and molar heat capacities for the similar mixtures was also reviewed by Roux *et al.* [7]. Most of the experimental data of excess volumes and molar excess enthalpies were collected at 298.15 K. Wagner and Heintz [8] and Heintz *et al.* [9] have measured the excess volumes of 1-alcohol + nonane and 1-alcohol + hexane mixtures at three different temperatures respectively. Attempts were also made by Heintz [10]; Liu *et al.* [11] and Treszczanowicz and Benson [12] to apply an association model and Flory's free volume theory for predicting the excess volumes of alcohol + alkane mixtures. Qualitative agreement between the predicted and experimental values was noted.

We are making systematic measurements of transport and dielectric properties 1-alcohol + alkane mixtures at different temperatures. We have recently reported the densities, speeds of sound, compressibilities, viscosities, dielectric constants and refractive indices for 1-heptanol + hexane and + heptane mixtures at 303.15 and 313.15 K [13] and similar properties for 1-propanol +, and 1-butanol + heptane mixtures at 298.15 and 308.15 K [14]. Viscosities of several normal alcohol + heptane mixtures at 298.15 and 308.15 K were also measured [15]. In continuation of our earlier work this paper presents the data on densities and excess volumes of six binary mixtures *viz.* 1-pentanol +, 1-hexanol +, 1-heptanol +, 1-octanol +, 1-decanol +, 1-dodecanol + heptane at 298.15 and 308.15 K. The excess volumes of these binary mixtures were also predicted by applying the Treszczanowicz and Benson [12] approach based on combination of an association model with the Flory interaction term. An attempt was also made to split the calculated physical contribution to the excess volumes into different terms *viz.* international, $V^E(\chi_{12})$, ν curvature, $V^E(\tilde{\nu})$ and $V^E(P^*)$. The resutls were used to explain the dominant molecular interactions in the alcohol + heptane mixtures.

EXPERIMENTAL SECTION

1-Pentanol and 1-hexanol were of Riedel make and 1-heptanol and 1-dodecanol were Merck products. 1-Octanol and 1-decanol of Fluka purum grade were used. All the reagents were used as such without any purifications. Heptane was of SD fine chemicals and purified further by standard procedure [16]. The measured densities of all the pure components at both the temperatures were compared with the literature values and such a comparison is presented in Table I.

The binary mixtures of varying compositions were made by mass on a single pan Mettler balance in stoppered glass vials. The calculated mole fractions were accurate upto ±0.0001 units.

The densities of the pure and mixture components were measured by a precalibrated two stem pyknometer. The calibration of the pyknometer was made with triple distilled water. The measure densities have an accuracy of ±0.0001 units. The pyknometer was placed vertically in a thermostatic water bath maintained electronically at the measuring temperatures to an absolute precision of 0.01°C.

THEORY

Flory and co-workers [17, 18] have developed a statistical theory for the mixtures of nonpolar components differing in size and it has been successfully applied to correlate the excess thermodynamic functions of a number of binary mixtures. However in applying the Flory theory to predict the excess volumes of binary mixtures containing associating liquids such as alcohols, the contribution arising from the association ability of the alcohols to the over all change in the volume of mixing should be taken into account. Treszcznacowicz and Benson [12] have proposed the following two individual contributions to the excess

TABLE I Densities (ρ) of pure components at 298.15 and 308.15 K

	$\rho/g\ cm^{-3}$		$\rho/g\ cm^{-3}$	
	This work	*Lit.*	*This work*	*Lit.*
1-Pentanol	0.8107	0.81077 [24]	0.8034	0.8039 [25]
1-Hexanol	0.8160	0.8160 [26]	0.8083	–
1-Heptanol	0.8189	0.81942 [27]	0.8126	0.81228 [27]
1-Octanol	0.8212	0.8216 [28]	0.8146	0.8146 [28]
1-Decanol	0.8265	0.8263 [28]	0.8195	0.8194 [28]
1-Dodecanol	0.8281	0.82995 [27]	0.8217	0.8232 [27]
Heptane	0.6794	0.6794 [29]	0.6709	–

molar volumes of alcohol + alkane mixtures,

$$V^E = V_{\mathrm{chem}} + V_{\mathrm{phys}} \tag{1}$$

where V_{chem} is the chemical contribution and is viewed to arise from the association of alcohol molecules. The authors have evaluated the V_{chem} for a number of alcohol+alkane mixtures at 298.15 K by assuming an athermal association model of Mecke–Kempter by using the following expression,

$$V_{\mathrm{chem}} = \Delta\nu_H^{\circ} x_1 [\phi_1 \ln(1 + K^{(\phi)}) - \ln(1 + K^{(\phi)} \phi_1)] / K^{\phi} \phi_1 \tag{2}$$

where $K^{(\phi)}$ is the association constant and is related to the enthalpy and entropy of hydrogen bonding of alcohol functional group by following equation

$$K^{(\phi)} = \exp\{1 - [\Delta h_H^{\circ} - T(\Delta s_H^{\circ} - R \ln r_1)]/RT\} \tag{3}$$

and

$$r_1 = V_1^*/17.12 \tag{4}$$

The values of the association terms that are used in the evaluation of the association constant of 1-alcohols are, $\Delta\nu_H^{\circ} = -10\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$, $\Delta h_H^{\circ} = -24.4\,\mathrm{kJ\,mol}^{-1}$ and $\Delta s_H^{\circ} = -33.0\,\mathrm{J\,K}^{-1}$.

The V_{phys} term of Eq. (1) should take into account several effects *viz.* (i) the difference in free volumes of the individual pure components, which gives a negative contribution, (ii) the specific interactions between the binary component species *i.e.*, unimer and multimers of alcohol and the alkane molecules, resulting into a negative contribution, (iii) the differences in internal pressure, which may lead to a contribution of either type and finally (iv) the structural effects due to changes in order and packing. The Flory theory takes into account the first three effects and V_{phys} can be evaluated from it in the following manner; the reduced temperature, $\tilde{T}$ of the mixture is given by Flory as,

$$\tilde{T} = \left(\sum \phi_i P_i^* \tilde{T}_i\right) \Big/ \left\{\left(\sum \phi_i P_i^*\right) - (\phi_1 \theta_2 \chi_{12})\right\} \tag{5}$$

and since the reduced volume of the mixture can not be explicitly related to the reduced temperature the following relation can be derived by solving Flory's equation of state,

$$V_{\text{phys}} = \frac{[(x\,V^*)_1 + (x\,V^*)_2]\,[(\phi\tilde{v})_1 + (\phi\tilde{v})_2]^{7/3}\,(\tilde{T} - \tilde{T}^\circ)}{4/3 - [(\phi\tilde{v})_1 + (\phi\tilde{v})_2]^{1/3}} \tag{6}$$

The various terms that appear in Eqs. (5) and (6), $\tilde{v}_i$, $\tilde{T}_i$ and V_i^* are the reduced volume, reduced temperature and characteristic volume of the pure alcohol (1) and heptane (2) components and are obtained by following relations,

$$\tilde{v}_i{}^{1/3} - 1 = (1 + \alpha_{p.i}T)/\{3(1 + \alpha_{p.i}T)\} \tag{7}$$

$$T_i = (\tilde{v}_i^{1/3} - 1)/\tilde{v}_i^{4/3} \tag{8}$$

and

$$V_i^* = V_i/\tilde{v}_i \tag{9}$$

where the $\alpha_{p.i}$ is the isobaric thermal expansion coefficient and obtained from the pure densities at different temperatures. V_i is the molar volume of respective components. ϕ_1 and ϕ_2 are the segment fractions of 1-alcohol and heptane species and are defined by the relation,

$$\phi_2 = 1 - \phi_1 = x_2/(x_1 + x_2(V_1^*/V_2^*)) \tag{9a}$$

and θ_2 is the contact surface fraction for the heptane and is calculated as,

$$\theta_2 = (\phi_2/\phi_1\,(V_2^*/V_1^*)^{1/3} + \phi_2) \tag{10}$$

$P_i^* = \alpha_{p.i}T\tilde{v}_i^2/K_{T.i}$, is the characteristic pressure of the pure components, i and $K_{T.i}$ is the isothermal compressibility of respective components. All the calculated reduced and characteristic parameters along with the required physico-chemical data for the pure components at 298.15 and 308.15 K are given in Table II.

TABLE II Physico-chemical data and equation of state parameters of pure liquids at 298.15 and 308.15 K

	298.15 K						308.15 K					
	$\alpha \times 10^3$ K^{-1a}	V $cm^3\,mol^{-1}$	$\tilde{\nu}$	V^*	P^{*b} JCm^{-3}	$\tilde{T}$	$\alpha \times 10^3$ K^{-1a}	V $cm^3\,mol^{-1}$	$\tilde{\nu}$	V^*	P^{*b} JCm^{-3}	$\tilde{T}$
1-Pentanol	0.893	108.728	1.2253	88.736	453.1	0.05344	0.949	109.716	1.2439	88.203	484.3	0.05641
1-Hexanol	0.870	125.211	1.2204	102.598	460.3	0.05264	0.912	126.404	1.2359	102.277	487.5	0.05515
1-Heptanol	0.854	141.809	1.2170	116.523	463.2	0.05206	0.892	143.048	1.2314	116.167	490.2	0.05444
1-Octanol	0.827	158.578	1.2111	130.937	466.2	0.05107	0.878	159.863	1.2285	130.127	496.9	0.05397
1-Decanol	0.812	191.518	1.2078	158.568	478.6	0.05050	0.846	193.154	1.2215	158.129	502.3	0.05282
1-Dodecanol	0.800	225.009	1.2052	186.698	486.2	0.05001	0.841	226.762	1.2204	185.810	517.1	0.05264
Heptane	1.256	147.480	1.2979	113.630	431.9	0.06414	1.277	149.349	1.3098	114.024	430.0	0.06568

[a] Calculated from the density data at different temperatures.

[b] Calculated using the isothermal compressibilites from Ref. [27].

The term, χ_{12} that appear in Eq. (5) for the calculation of the reduced temperature of the mixture is usually estimated from the fit of excess enthalpies. But in the present model Treszczanowicz and Benson have proposed following relation for the evaluation of χ_{12} for any given pair of 1-alcohol + alkane as,

$$\chi_{12} = 1000\,(V_1^*)^{1/3}\,(V_2^*)^{-3/2}\,\{101.35\,(\alpha_{OH})^2 + 1.254\} \qquad (11)$$

where α_{OH} is the fraction of —OH type surface on an alcohol molecule and was related by the authors to the carbon number, n_C in the alcohol molecule as,

$$\alpha_{OH} = 8.04/\{21.71 + 10.23\,(n_C - 1)\} \qquad (12)$$

RESULTS

The densities and excess volumes, V^E for all the binary mixtures of 1-alcohol + heptane at 298.15 and 308.15 K are given in Table III. The excess volumes were calculated by the following relation,

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_{12}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \qquad (13)$$

where x, M and ρ are the mole fraction, molecular weight and density of pure 1-alcohol (1) and heptane (2) and mixture (12) components.

The V^E values are fitted to an equation of type,

$$V^E/(\mathrm{cm}^3\ \mathrm{mol}^{-1}) = x_1(1 - x_1) \sum a_j\, x_1^{(j-1)/2} \qquad (14)$$

where a_j are the coefficients and were evaluated from a multiple regression analysis based on least square method. The values of the coefficients along with the standard deviation, σ values are given in Table IV. The excess volumes of the binary mixtures at 298.15 and 308.15 K smoothed, by using Eq. (14) and using the coefficients from the Table V are graphically presented in Figures 1 and 2 respectively. The dashed lines in the Figures 1 and 2 represent the calculated excess volumes by combining the individual physical and chemical contributions, which were evaluated by the Eqs. (2) and (6). The details of the

TABLE III Density (ρ) and excess volume (V^E) for 1-alcohol + heptane binary mixtures at 298.15 and 308.15 K

x_1	ρ g/cm^3		V^E cm^3/mol		x_1	ρ g/cm^3		V^E cm^3/mol	
	298.15	308.15	298.15	308.15		298.15	308.15	298.15	308.15
	1-*pentanol* + *heptane*					1-*hexanol* + *heptane*			
0.0652	0.6854	0.6769	0.0891	0.0993	0.0567	0.6857	0.6771	0.0709	0.0987
0.1304	0.6919	0.6834	0.1174	0.1367	0.1134	0.6924	0.6838	0.0797	0.1119
0.2489	0.7045	0.6961	0.1329	0.1485	0.2217	0.7057	0.6972	0.0610	0.0809
0.3595	0.7172	0.7088	0.1172	0.1494	0.3279	0.7192	0.7108	0.0407	0.0508
0.4654	0.7302	0.7220	0.0935	0.1060	0.4307	0.7328	0.7245	0.0046	0.0068
0.5682	0.7438	0.7356	0.0429	0.0738	0.5294	0.7463	0.7382	−0.0308	−0.0530
0.6617	0.7569	0.7488	0.0005	0.0375	0.6292	0.7604	0.7523	−0.0647	−0.0717
0.7552	0.7707	0.7629	−0.0153	−0.0103	0.7248	0.7743	0.7663	−0.0869	−0.0954
0.8805	0.7905	0.7829	−0.0306	−0.0236	0.8643	0.7951	0.7873	−0.0676	−0.0823
0.9606	0.8039	0.7965	−0.0164	−0.0149	0.9526	0.8086	0.8010	−0.0254	−0.0524
	1-*heptanol* + *heptane*					1-*octanol* + *heptane*			
0.0508	0.6860	0.6774	0.0496	0.0662	0.0448	0.6861	0.6780	0.0232	−0.0510
0.1004	0.6929	0.6842	0.0057	0.0365	0.0922	0.6934	0.6854	−0.0084	−0.0898
0.2012	0.7068	0.6984	−0.0390	−0.0854	0.1826	0.7072	0.6993	−0.0711	−0.1449
0.3013	0.7210	0.7127	−0.1056	−0.1840	0.2780	0.7215	0.7139	−0.1214	−0.2261
0.4001	0.7347	0.7265	−0.1529	−0.2600	0.3705	0.7352	0.7277	−0.1736	−0.2653
0.4992	0.7486	0.7404	−0.1754	−0.2890	0.4690	0.7495	0.7422	−0.2096	−0.3047
0.5981	0.7626	0.7543	−0.2012	−0.3008	0.5664	0.7633	0.7563	−0.2158	−0.3325
0.6990	0.7768	0.7685	−0.1906	-0.2942	0.6697	0.7777	0.7709	−0.2170	−0.3301
0.8500	0.7979	0.7892	−0.1108	−0.1443	0.7784	0.7925	0.7857	−0.1939	−0.2586
0.9456	0.8115	0.8025	−0.0825	−0.0646	0.8336	0.7998	0.7930	−0.1573	−0.1966
					0.8844	0.8064	0.7997	−0.1110	−0.1464
					0.9381	0.8134	0.8067	−0.0774	−0.0876
	1-*decanol* + *heptane*					1-*dodecanol* + *heptane*			
0.0386	0.6867	0.6785	−0.0023	−0.0059	0.0343	0.6872	0.6790	−0.0341	−0.0859
0.0772	0.6941	0.6859	−0.0620	−0.1095	0.0687	0.6950	0.6871	−0.1225	−0.2276
0.1584	0.7090	0.7010	−0.1543	−0.2250	0.1389	0.7098	0.7021	−0.2301	−0.3495
0.2472	0.7245	0.7167	−0.2458	−0.3360	0.2173	0.7252	0.7176	−0.3524	−0.4591
0.3368	0.7392	0.7316	−0.2947	−0.4018	0.2965	0.7394	0.7320	−0.4159	−0.5309
0.4264	0.7532	0.7456	−0.3414	−0.4195	0.3920	0.7550	0.7479	−0.4387	−0.5773
0.5326	0.7688	0.7613	−0.3603	−0.4245	0.4898	0.7696	0.7627	−0.4415	−0.5795
0.6364	0.7830	0.7759	−0.3238	−0.4413	0.5941	0.7839	0.7772	−0.4427	−0.5777
0.7498	0.7976	0.7909	−0.2684	−0.4357	0.7213	0.7967	0.7932	−0.3450	−0.5408
0.8055	0.8044	0.7977	−0.2191	−0.3655	0.7853	0.8066	0.8001	−0.2834	−0.4752
0.8688	0.8119	0.8052	−0.1656	−0.2879	0.8475	0.8132	0.8071	−0.2065	−0.3670
0.9331	0.8192	0.8125	−0.0913	−0.1885	0.9227	0.8208	0.8146	−0.1174	−0.2129

physical basis of their evaluations is already described in the earlier section. It can be seen from the figures that the calculated excess volumes are in reasonable agreement with the experimental values both at 298.15 and 308.15 K for all the mixtures. An increase in the temperature in general is found to decrease the excess volumes in all the mixtures over the whole mole fraction range. The temperature

TABLE IV Coefficients of Eq. (14) for the least square representation of excess volumes along with the standard deviation, σ for the 1-alcohol + heptane mixtures at 298.15 and 308.15 K

	298.15 K					308.15 K				
heptane +	a_1	a_2	a_3	a_4	σ	a_1	a_2	a_3	a_4	σ
1-pentanol	2.0663	−2.7087	0.2138	–	0.004	2.2600	−2.8158	0.1786	–	0.004
1-hexanol	2.2513	−4.6929	1.8424	–	0.003	2.9095	−5.5688	1.6994	–	0.011
1-heptanol	4.6186	−23.119	34.805	−17.929	0.001	4.9564	−20.696	22.790	−8.277	0.001
1-octanol	2.6393	−13.702	19.042	−9.3711	0.002	−2.155	6.8233	−12.317	6.1986	0.001
1-decanol	2.0722	−15.291	22.043	−10.397	0.001	3.9772	−31.629	55.449	−31.267	0.001
1-dodecanol	0.8724	−15.319	25.084	−12.407	0.001	−1.6128	−11.216	26.516	−17.173	0.001

TABLE V Calculated and experimental equimolar excess volumes of 1-alcohol + heptane mixtures at 298.15 K

heptane +	χ_{12} [a] $J cm^{-3}$	V^E_{chem} $cm^3\ mol^{-1}$	V^E_{phys} $cm^3\ mol^{-1}$	$V^E(\chi_{12})$ $cm^3\ mol^{-1}$	$V^E(\tilde{v})$ $cm^3\ mol^{-1}$	$V^E(P^*)$ $cm^3\ mol^{-1}$	δV^E [b] $cm^3 mol^{-1}$
1-pentanol	10.771	0.130	−0.031	0.261	−0.196	−0.087	−0.009
1-hexanol	9.621	0.126	−0.110	0.229	−0.242	−0.108	−0.010
1-heptanol	9.350	0.123	−0.203	0.234	−0.280	−0.163	0.006
1-octanol	8.414	0.121	−0.316	0.219	−0.340	−0.201	0.006
1-decanol	7.867	0.116	−0.472	0.219	−0.395	−0.303	0.007
1-dodecanol	7.633	0.110	−0.614	0.224	−0.441	−0.382	−0.015

[a] Calculated from Treszcznacowicz and Benson model.

[b] $\delta V^E = V^E_{\text{phys}} - (V^E(\chi_{12}) + V^E(\tilde{v}) + V^E(P^*))$.

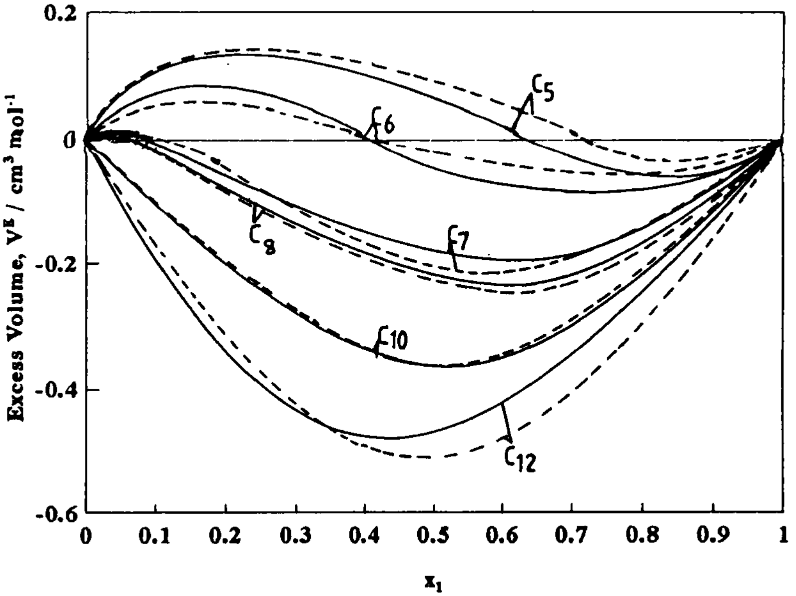

FIGURE 1 Excess Volumes, V^E for binary mixtures of 1-alcohol + heptane at 298.15 K vs. mole fraction of 1-alcohol: (——) smoothed experimental results by Eq. (14) using coefficients from Table IV; (– –) calculated from the Treszcznacowicz and Benson model. Curves are labeled with the no. of carbon atoms of 1-alcohol component.

coefficients, $(\partial V^E/\partial T)_{0.5}$ were found to be 0.0025, 0.004, −0.011, −0.011, −0.011 and −0.016 for the binary mixtures of heptane with 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-decanol and 1-dodecanol respectively. Such a decreasing trend in the $(\partial V^E/\partial T)_{0.5}$ with the increase in the carbon chain length of the 1-alcohols was also noted for

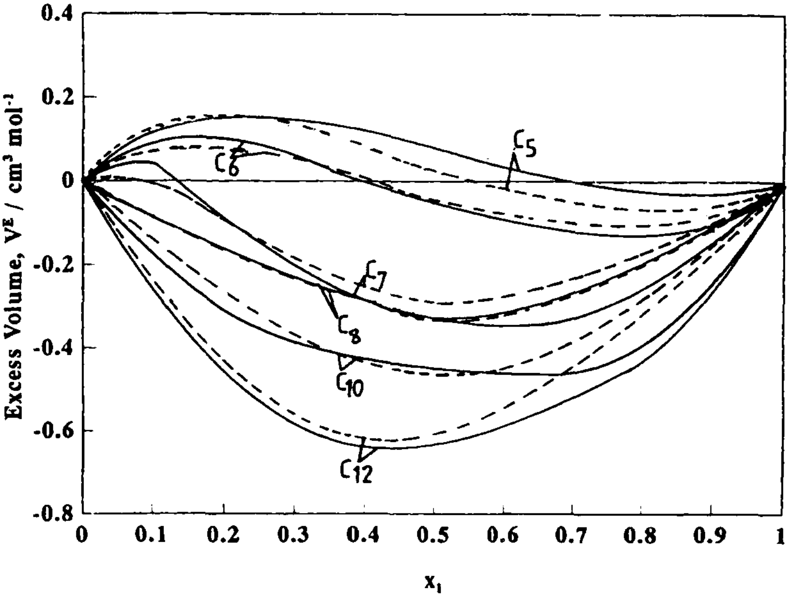

FIGURE 2 Excess Volumes, V^E for binary mixtures of 1-alcohol + heptane at 308.15 K vs. mole fraction of 1-alcohol: (——) smoothed experimental results by Eq. (14) using coefficients from Table IV; (– –) calculated from the Treszcznacowicz and Benson model. Curves are labeled with the no. of carbon atoms of 1-alcohol component.

several binary mixtures of 1-alcohol + hexane and 1-alcohol + nonane by Treszczanowicz and Treszczanowicz [19].

DISCUSSION

The trend in the dependence of excess volumes on the alcohol mole fraction as presented in Figures 1 and 2 is typical and follows the same pattern both in the magnitude and the nature as observed previously for the similar mixtures at 298.15 K by Treszczanowicz and Benson [10]. The curves were found to show sigmoidal nature with initial positive regions followed by negative lobes for the 1-pentanol +, 1-hexanol + heptane mixtures at both the temperatures. The negative regions were found to extend to a wider mole fraction range with the increase in the carbon chain length from 1-hexanol to 1-heptanol and to 1-octanol. The excess volumes however were found to be negative over the whole mole fraction range in case of 1-decanol+, 1-dodecanol+heptane mixtures. Benson and coworkers [1–5] have given an excellent qualitative treatment of V^E and K_S^E functions at 298.15 K for several alcohol+alkane mixtures, covering the very dilute, rich and intermediate alcohol mole fraction ranges and as well as variation in the chain length of both the components. The authors have attributed the rupturing of the hydrogen bonding in alcohol molecules by unlike alkane species, change in mutual orientation of pure alkane molecules (this is especially true for higher alkanes $> c_7$) and the dipole–dipole interactions between the dissociated unimer and associated multimer alcohol molecules as the main contributors to the initial positive V^E values in very dilute alcohol regions. It is however envisaged that the interstitial accommodation of alkane molecules into the branched multimer alcohol structures and the accompanying free volume changes upon mixing are the chief factors responsible for the negative excess volumes in alcohol rich regions. The balance of these chemical, physical and structural factors one over the other are thus expected in the intermediate mole fraction range.

The preference of one factor over the others is observed to be dependent on the chain length of both the components. Positive excess volumes (in lower chain alcohol+higher chain alkane mixtures) and negative excess volumes (in higher chain alcohol+lower chain alkane mixtures) are reported by Benson *et al.* [1, 3, 4]. The corresponding excess isentropic compressibilities conforming to the trend in the excess volumes for the similar mixtures were also reported by the same group.

However the excess enthalpies as derived from the microcalorimetric measurements for several mixtures of alcohol+heptane [20, 21] were reported to be always endothermic in nature in the overall mole fraction range with the variation in the magnitude with the change in the alcohol chain length. These studies concluded that the breaking up of hydrogen bonds in the self associated alcohol structures by unlike alkane molecules seems to be the dominant factor that contribute to the positive excess enthalpies. It is also further suggested that the proportion of broken alcohol structures is very high in alcohol deficient regions and the proportion of unbroken structures is maximum in alcohol rich regions.

Thus our results on the variation of V^E with the mole fraction of 1-alcohol as presented in Figures 1 and 2 in which an initial positive trend in the lower 1-pentanol, hexanol, 1-heptanol and 1-octanol mole fractions followed by negative lobes at higher alcohol proportions conform to the above arguments. The negative excess volumes over the whole mole fraction of 1-decanol + , and 1-dodecanol + heptane mixtures suggest that the effects due to the interstitial accommodation of heptane molecules into multimer alcohol species and the fee volume change upon mixing are predominant in the higher alcohol + heptane mixtures.

An attempt is also made to split the observed V^E_{phys} into different terms *viz.* interactional, $V^E(\chi_{12})$, $\tilde{\nu}$ curvature, $V^E(\tilde{\nu})$ and $V^E(P^*)$. This treatment is popularly known as Prigogine–Flory–Patterson (PFP) theory. The appropriate relations that were used for the evaluation of the individual terms and their significance are the same as described by Patterson and Delmas [22] and Letcher and Baxter [23]. The characteristic parameters and other physico-chemical data of the pure components needed for evaluation are taken from Table II. The individual contributions as derived from PFP treatment at equimolar fractions for all the mixtures at 298.15 K are presented in Table V. An inspection of the data presented in the Table V reveals interesting observations. The closeness between the calculated excess volumes from PFP treatment and the physical contribution to the excess volume, V^E_{phys} not only suggest that PFP theory can reasonably be applied to the excess volumes of 1-alcohol + alkane mixtures once the contribution due to the association ability of alcohol species is isolated from the over all value, but also justifies the physical basis of separation of chemical and physical contributions to the excess volumes of these mixtures by Treszczanowicz and Benson approach. The $V^E(\chi_{12})$ values were found to be close with each other for all the alcohol + heptane mixtures, while $V^E(\tilde{\nu})$ was found to become more negative with the increase in the carbon chain length of the alcohol molecules. Both the $V^E(\tilde{\nu})$ and $V^E(P^*)$ were found to be in sign agreement with the V^E_{phys} for all the binary mixtures. The sum of the $V^E(\tilde{\nu})$ and $V^E(P^*)$ was found to be more negative than the V^E_{phys} value but the positive contribution of $V^E(\chi_{12})$ seems to balance the over estimations due to the combined contributions of free volume change and P^* effects. These observations suggest that all the three factors contribute importantly to the excess volumes of 1-alcohol + heptane mixtures.

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