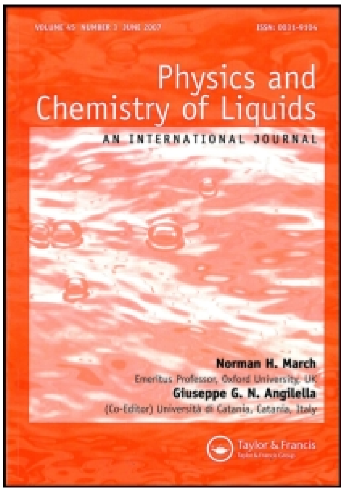

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Excess Molar Volumes of Aqueous Solutions of 1-Propanol, 2-Propanol, Allyl Alcohol and Propargyl Alcohol

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EXCESS MOLAR VOLUMES OF AQUEOUS SOLUTIONS OF 1-PROPANOL, 2-PROPANOL, ALLYL ALCOHOL AND PROPARGYL ALCOHOL

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Excess molar volumes, V^E, have been claculated from the density data of aqueous solutions of 1-propanol, 2-propanol, allyl alcohol and propargyl alcohol at temperatures ranging from 30°–50°C. The V^E values have been found to be negative at all temperatures. The volume contraction for saturated alcohols, both straight and branched chain, in aqueous media is accounted for mainly by the hydrophobic effect, while that for unsaturated alcohols is explained primarily by the formation of H-bond between the alcohol and water. The dV^E/dT values have been found to be positive for all alcohols. The temperature dependence of V^E is thought to be strongly influenced by the structural properties of water.

Keywords: Density; excess molar volume; unsaturated alcohol; hydrophobic effect

1. INTRODUCTION

Quite a number of papers on the volumetric properties of aqueous solutions of alcohols have recently been published [1–16]. A comprehensive review on physical properties of alcohol-water mixtures was earlier given by Franks and Ives [17]. Although substantial progress has been made towards understanding the nature

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of molecular interaction between alcohols and water, an acceptable model has yet to be developed that can account for the observed physical properties of aqueous alcohols over the whole concentration range. Reviewing the papers so far published, one can easily understand that water molecules interact with alcohol molecules in a very complex manner – the complexity, in particular, arises from the extreme sensitivity of water structure towards alcohols and vice-versa.

The work described in this paper is a part of our continuing studies on volumetric and viscometric properties of aqueous and non-aqueous alcohol systems. The primary objective of the present investigation is to examine the effect of branching and unsaturation of alcohols, mainly restricted to three carbon atoms, on the volumetric properties of aqueous alcohol solutions. The alcohols used are 1-propanol ($CH_3CH_2CH_2OH$), 2-propanol ($(CH_3)_2CHOH$), allyl alcohol ($CH_2{=}CHCH_2OH$) and propargyl alcohol ($CH{\equiv}CCH_2OH$). Since these alcohols are soluble in water in all proportions, they provide us an opportunity of studying the effects of branching and unsaturation of the alcohol chains. We report here the excess molar volumes, V^E, of aqueous solutions of these alcohols. For comparison, the excess molar volumes of aqueous *t*-butanol are also presented, the data of which have been collected from a published work [16]. Literature search reveals that as yet no works on aqueous solutions of allyl alcohol and propargyl alcohol are available.

2. EXPERIMENTAL SECTION

Alcohols used for experiment were procured from Aldrich. The quoted purities of these alcohols are as shown in parentheses: 1-propanol (99.7%), 2-propanol (99.9%), allyl alcohol (99+%), propargyl alcohol (99%). The alcohols were allowed to stand over molecular sieves (4A) for 2–3 weeks prior to their use. Before the density measurement, alcohols were distilled and water was redistilled. The densities of pure alcohols and water at different temperatures corresponded well with literature values. A specific gravity bottle of 25 ml capacity was used for measurement of density which was previously calibrated with the redistilled water. Weighing was made by an analytical balance with a sensitivity of ±0.1 mg. A thermostated water bath was used for measurements, the temperature of which was controlled to ±0.05°C. The average uncertainty in measurement of density is estimated as 1.5×10^{-4}g cm^{-3}.

The excess molar volume, V^E, was calculated by the following equation,

$$V^E = \frac{X_1M_1 + X_2M_2}{d} - \left(X_1\frac{M_1}{d_1} + X_2\frac{M_2}{d_2}\right) \tag{1}$$

where, d is the density of the mixture, M_1, M_2, X_1, X_2, d_1 and d_2 are the molecular weights, mole fractions and densities of components, the subscripts 1 and 2 denoting the values for water and alcohol, respectively. Each set of results covering the whole range of composition was fitted with a Redlich-Kister equation of the type,

$$Y^E = X_1X_2\sum_{i=0}^{n} A_i(2X_1 - 1)^i \tag{2}$$

Using $n=3$, at each temperature four different A_i values and a standard deviation, σ, were obtained through least squares method.

3. RESULTS AND DISCUSSION

Densities of aqueous solutions of 1-propanol, 2-propanol, allyl alcohol and propargyl alcohol have been shown in Table I. Excess molar volumes, V^E, have been calculated at 30°, 35°, 40°, 45° and 50°C by using Eq. (1) and the values are presented in Table I. The fitting coefficients A_i of Eq. (2) and the standard deviation, σ, for different systems are shown in Table II.

Figures 1–4 show the plots of excess molar volumes, V^E, of different systems as a function of the mole fraction of alcohols. Figures are drawn only at selective temperatures in order to avoid undesired clumsiness and overlapping of curves. On examination of these Figures, the following common features emerge: (i) excess molar volumes are negative for all systems over the whole range of composition. The negative values decrease with the increase of temperature, that is, dV^E/dT is positive, (ii) curves of all the systems

TABLE I Experimental densities, d (g cm^{-3}) and excess molar volumes, V^E (cm^3 mol^{-1}), of aqueous alcohol systems for different molar ratios at different temperatures

$t/°c$	30		35		40		45		50	
X_2	d	V^E	d	V^E	d	V^E	d	V^E	d	V^E
Water (X_1) + 1-propanol (X_2) system										
0.0000	0.9955	–	0.9939	–	0.9921	–	0.9901	–	0.9879	–
0.9000	0.9501	−0.4489	0.9468	−0.4317	0.9435	−0.4187	0.9400	−0.4030	0.9365	−0.3925
0.8000	0.9109	−0.5649	0.9072	−0.5462	0.9034	−0.5290	0.8996	−0.5127	0.8957	−0.4999
0.7000	0.8829	−0.6207	0.8790	−0.6017	0.8750	−0.5838	0.8709	−0.5615	0.8668	−0.5476
0.6000	0.8619	−0.6349	0.8579	−0.6155	0.8538	−0.5992	0.8495	−0.5704	0.8453	−0.5563
0.5000	0.8455	−0.6156	0.8413	−0.5903	0.8371	−0.5714	0.8327	−0.5380	0.8284	−0.5214
0.4000	0.8321	−0.5563	0.8279	−0.5331	0.8236	−0.5105	0.8193	−0.4831	0.8149	−0.4621
0.3000	0.8212	−0.4836	0.8169	−0.4552	0.8126	−0.4341	0.8083	−0.4069	0.8038	−0.3796
0.2000	0.8118	−0.3724	0.8075	−0.3444	0.8033	−0.3324	0.7989	−0.2970	0.7945	−0.2774
0.1000	0.8033	−0.2019	0.7992	−0.1912	0.7950	−0.1807	0.7907	−0.1525	0.7864	−0.1420
1.0000	0.7958	–	0.7918	–	0.7877	–	0.7837	–	0.7795	–
Water (X_1) + 2-propanol (X_2) system										
0.0000	0.9957	–	0.9940	–	0.9923	–	0.9902	–	0.9879	–
0.9000	0.9511	−0.6538	0.9476	−0.6384	0.9440	−0.6205	0.9405	−0.6158	0.9368	−0.6094
0.8000	0.9094	−0.8817	0.9054	−0.8642	0.9013	−0.8433	0.8971	−0.8331	0.8929	−0.8259
0.7000	0.8778	−0.9678	0.8736	−0.9508	0.8693	−0.9297	0.8649	−0.9118	0.8605	−0.9166
0.6000	0.8535	−0.9698	0.8492	−0.9539	0.8448	−0.9329	0.8402	−0.9228	0.8356	−0.9148
0.5000	0.8343	−0.9124	0.8299	−0.8949	0.8254	−0.8716	0.8209	−0.8722	0.8161	−0.8573
0.4000	0.8188	−0.8127	0.8143	−0.7914	0.8097	−0.7632	0.8050	−0.7556	0.8002	−0.7427
0.3000	0.8061	−0.6858	0.8016	−0.6659	0.7970	−0.6381	0.7923	−0.6334	0.7875	−0.6221
0.2000	0.7953	−0.5206	0.7907	−0.5032	0.7862	−0.4736	0.7814	−0.4627	0.7766	−0.4523
0.1000	0.7854	−0.2694	0.7810	−0.2591	0.7765	−0.2392	0.7718	−0.2381	0.7670	−0.2279
1.0000	0.7769	–	0.7726	–	0.7683	–	0.7636	–	0.7589	–

Water (X_1) + allyl alcohol (X_2) system

0.0000	0.9957	–	0.9941	–	0.9923	–	0.9903	–	0.9881	–
0.0995	0.9692	−0.4341	0.9662	−0.4241	0.9629	−0.4127	0.9598	−0.4093	0.9563	−0.3980
0.1993	0.9421	−0.5942	0.9386	−0.5831	0.9349	−0.5751	0.9310	−0.5617	0.9273	−0.5551
0.2986	0.9204	−0.6528	0.9167	−0.6444	0.9126	−0.6317	0.9087	−0.6287	0.9047	−0.6196
0.3999	0.9023	−0.6346	0.8984	−0.6258	0.8943	−0.6206	0.8899	−0.6048	0.8857	−0.5930
0.4999	0.8882	−0.5923	0.8842	−0.5849	0.8798	−0.5722	0.8756	−0.5711	0.8710	−0.5434
0.5998	0.8781	−0.6038	0.8740	−0.5964	0.8695	−0.5843	0.8648	−0.5617	0.8604	−0.5472
0.6957	0.8687	−0.5223	0.8642	−0.4932	0.8598	−0.4923	0.8551	−0.4718	0.8506	−0.4529
0.7951	0.8601	−0.4008	0.8557	−0.3820	0.8513	−0.3832	0.8466	−0.3645	0.8423	−0.3609
0.8956	0.8526	−0.2608	0.8482	−0.2438	0.8437	−0.2418	0.8395	−0.2625	0.8346	−0.2151
1.0000	0.8446	–	0.8404	–	0.8359	–	0.8314	–	0.8271	–

Water (X_1) + propargyl alcohol (X_2) system

0.0000	0.9957	–	0.9941	–	0.9922	–	0.9902	–	0.9881	–
0.0996	0.9921	−0.2402	0.9883	−0.2135	0.9856	−0.2118	0.9824	−0.1990	0.9794	−0.1960
0.1656	0.9867	−0.3088	0.9822	−0.2727	0.9789	−0.2633	0.9757	−0.2581	0.9721	−0.2468
0.2997	0.9753	−0.3440	0.9705	−0.3103	0.9665	−0.2918	0.9626	−0.2757	0.9587	−0.2667
0.4004	0.9680	−0.3296	0.9628	−0.2888	0.9588	−0.2759	0.9548	−0.2615	0.9507	−0.2523
0.4990	0.9622	−0.3080	0.9580	−0.3124	0.9538	−0.2974	0.9496	−0.2798	0.9454	−0.2729
0.5992	0.9566	−0.2478	0.9522	−0.2526	0.9481	−0.2464	0.9438	−0.2280	0.9395	−0.2218
0.6997	0.9527	−0.2225	0.9484	−0.2410	0.9440	−0.2250	0.9397	−0.2100	0.9353	−0.2039
0.8007	0.9482	−0.1310	0.9439	−0.1583	0.9395	−0.1447	0.9351	−0.1276	0.9307	−0.1257
0.8986	0.9450	−0.0713	0.9407	−0.1073	0.9363	−0.0977	0.9319	−0.0826	0.9276	−0.0911
1.0000	0.9420	–	0.9370	–	0.9327	–	0.9285	–	0.9240	–

TABLE II Coefficients, A_i of Redlich-Kister equation (Eq. 2) and standard deviation, σ in cm^3 mol^{-1} of the systems

System	*Temperature* (°*C*)	A_0	A_1	A_2	A_3	σ
Water + 2-Propanol	30	−3.6170	−1.3577	−2.2110	−1.4890	0.01498
	35	−3.5455	−1.4025	−2.1036	−1.7214	0.01509
	40	−3.4526	−1.4656	−1.9261	−1.6509	0.01468
	45	−3.4249	−1.4090	−1.8520	−1.7316	0.01695
	50	−3.3870	−1.4922	−1.8147	−1.6179	0.01503
Water + 1-Propanol	30	−2.4094	−0.5397	−1.6241	−1.6486	0.01825
	35	−2.3174	−0.6252	−1.5014	−1.4792	0.01773
	40	−2.2395	−0.6602	−1.4366	−1.3663	0.01835
	45	−2.1280	−0.6735	−1.2832	−1.5220	0.01430
	50	−2.0553	−0.7671	−1.1979	−1.3731	0.01522
Water + Allyl alcohol	30	−2.4491	−0.5326	−2.0016	−1.2671	0.01820
	35	−2.4136	−0.6141	−1.8121	−1.2045	0.01995
	40	−2.3766	−0.5961	−1.8110	−1.1160	0.01770
	45	−2.3133	−0.7662	−1.8811	−1.6279	0.02096
	50	−2.2585	−0.7223	−1.7151	−0.9724	0.01688
Water + Propargyl alcohol	30	−1.1993	−0.6888	−0.7638	−0.8054	0.01058
	35	−1.1534	−0.3584	−0.8426	−0.7007	0.01717
	40	−1.0998	−0.3074	−0.7854	−0.8688	0.01594
	45	−1.0354	−0.3186	−0.7065	−0.9146	0.01533
	50	−0.9997	−0.3150	−0.7431	−0.7906	0.01699

at all temperatures are skewed towards the composition axis, (iii) the minima of the V^E vs. X_2 curves occur nearly at 0.3 mole fraction of alcohols.

To compare the above results, in Figure 5, plots of excess molar volumes against the mole fraction of *t*-butanol also are drawn with V^E estimated from *d* data of reference 16. Here, the negative values increase with the rise of temperature, that is, dV^E/dT is negative. The minima shift to higher alcohol concentrations with the increase of temperature.

The factors that are generally thought to be responsible for the contraction of volume on mixing are:

(i) Chemical interaction between component molecules.
(ii) Physical forces, such as, dipole – dipole interaction, dipole-induced dipole interaction, or van der Waals forces existing between component molecules.
(iii) Interstitial accommodation of molecules of one component into the structural network of molecules of the other component. Different but effectively a similar situation to this is envisaged

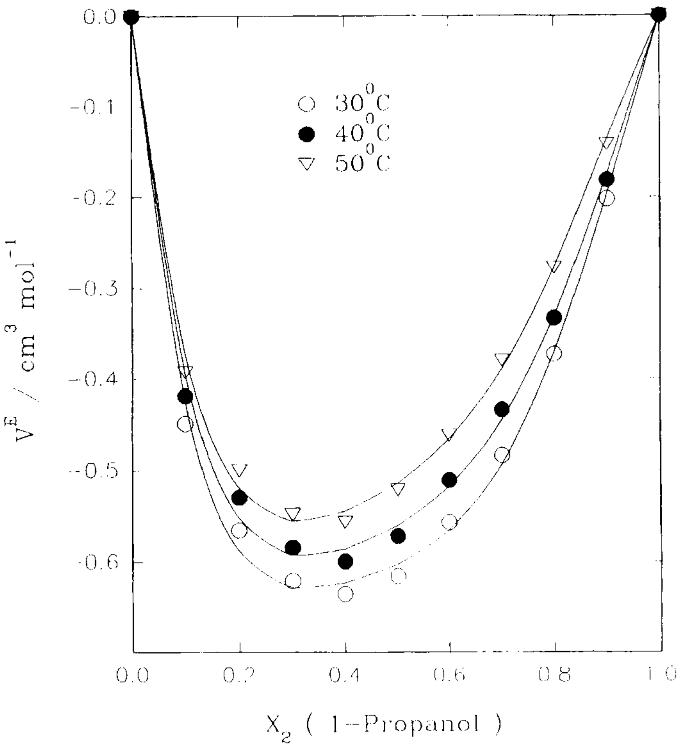

FIGURE 1 Plots of excess molar volume (V^E) against mole fractions of 1-propanol (X_2).

with aqueous alcohol systems, in which alcohol molecules are encaged by the highly structured water molecules. The phenomenon is called hydrophobic hydration.

(iv) Favourable geometric fitting of molecules.

(v) Size difference of molecules.

Likewise, the effects that cause volume expansion are:

(i) Dispersive forces – which occur in a system consisting of associated and non-polar components. The association of molecules takes place either through physical forces, like dipole – dipole type interaction or chemical forces, such as, H-bonding between homo-molecules.

(ii) Unfavourable geometric fitting of molecules.

(iii) Electrostatic repulsive forces.

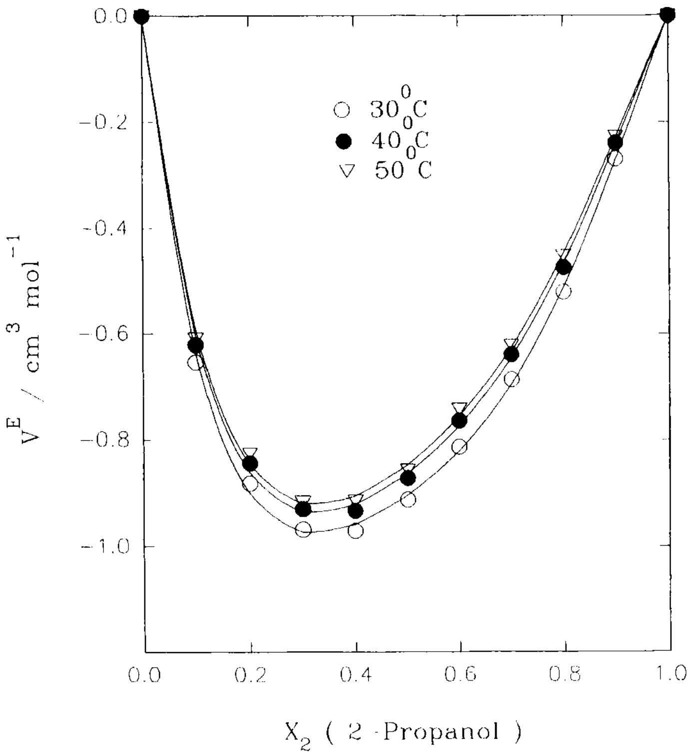

FIGURE 2 Plots of excess molar volume (V^E) against mole fractions of 2-propanol (X_2).

The negative excess molar volume of the systems under study is a manifestation of predominance of contractive effects over the expansive effects. In view of the present state of our knowledge about the structure and related properties of water and alcohol molecules, one can easily visualise that factors, such as dipole–dipole interaction, chemical interaction between water and alcohol through H-bonding, size difference between alcohol and water molecules etc. – all are potential causes for volume contraction in aqueous alcohol systems. Whereas, factors causing volume expansion as mentioned above are of little or no significance for these systems. Contractive forces thus far outweigh the expansive forces, resulting in negative excess volumes as observed experimentally.

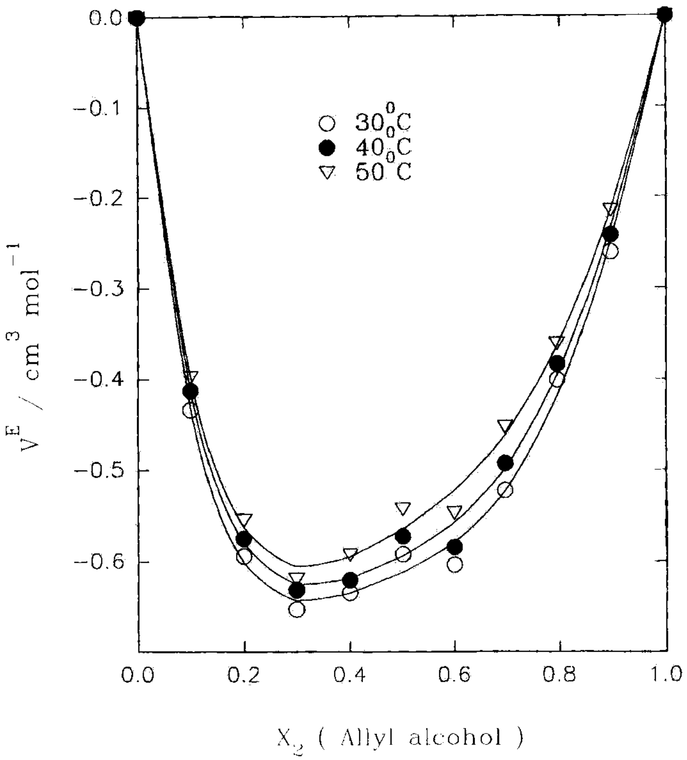

FIGURE 3 Plots of excess molar volume (V^E) against mole fractions of allyl alcohol (X_2).

Perhaps the most satisfactory way of rationalising the observed results, at least of the saturated alcohols, is to postulate that the introduction of apolar molecules or apolar residues on otherwise polar molecules (alcohols in the present study) into water leads to a reduction of mobility of neighbouring molecules. In other words, the hydrocarbon parts of alcohols induce a quasi-crystallisation or a solid-like structure of water, which is now called the hydrophobic hydration [18]. It is commonly believed that the phenomenon of hydrophobic hydration leads to the formation of the so-called cages made up of highly structured water molecules, and alcohol molecules are held in the cavities formed by these cages. As a result, a significant loss of volume takes place. This is regarded to be the single most important factor leading to volume contraction, i.e., the negative excess molar

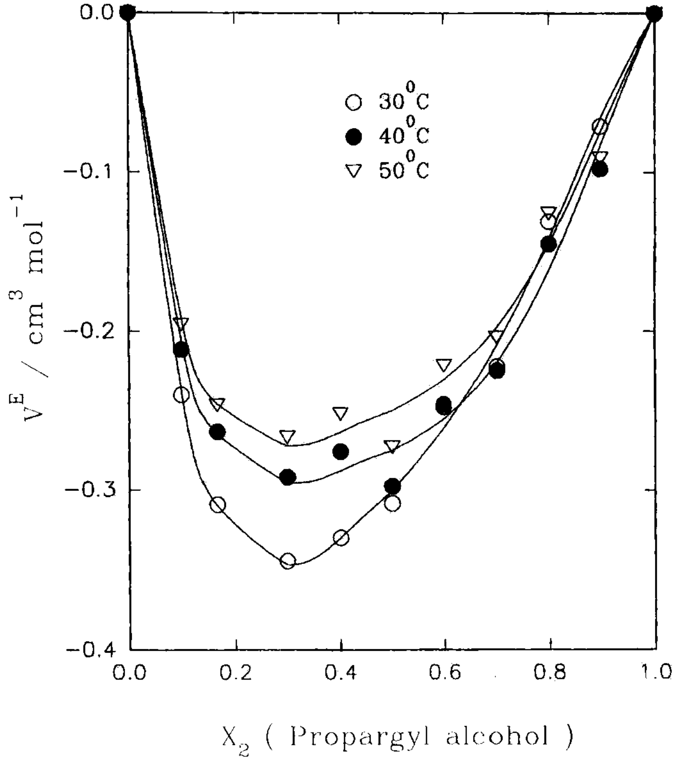

FIGURE 4 Plots of excess molar volume (V^E) against mole fractions of propargyl alcohol (X_2).

volume. The hydrophilic hydration, perhaps to be attached more appropriately to unsaturated alcohols, is assumed to be much less effective as a contractive factor than the hydrophobic hydration.

While the hydrophobic effect is considered by far the most important factor for the reduction of volume for aqueous saturated alcohols, the effect is thought to be lessened as the alcohol chains become increasingly unsaturated, and in turn, the hydrophilic effect becomes more important than the hydrophobic effect. Thus, of the two unsaturated alcohols, allyl alcohol and propargyl alcohol, having double and triple bonds, respectively, the latter should show less hydrophobicity than the former. This idea is fully in consistence with the data of standard thermodynamic transfer functions of some hydrocarbons from organic solvents to water [18–20].

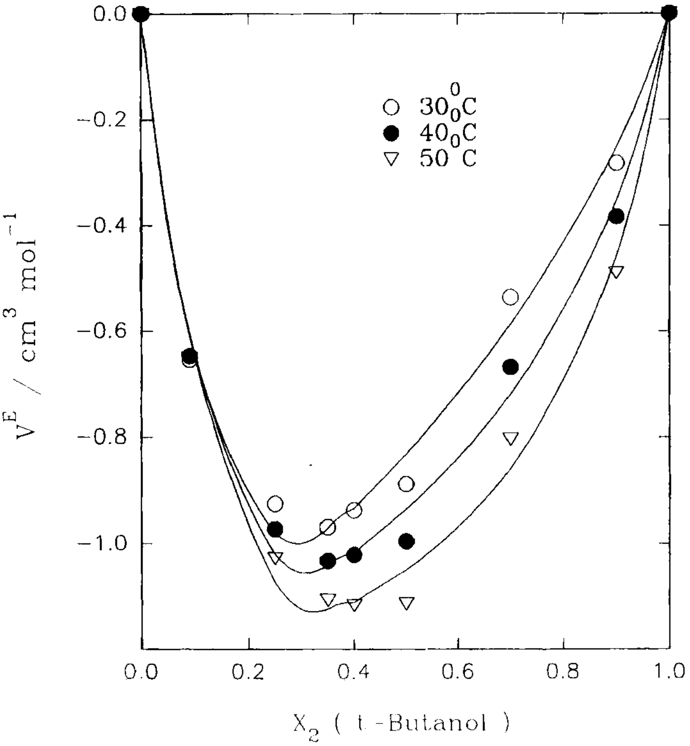

FIGURE 5 Plots of excess molar volume (V^E) against mole fractions of *t*-butanol (X_2). The values were calculated from the density data of ref. 16.

For the aqueous 1-propanol and 2-propanol, dV^E/dT is found to be positive, i.e. the rise of temperature is accompanied by reduction in volume contraction. This can readily be understood by the fact that the cages formed around alcohol molecules are unstable thermally. So these cages are destroyed by the temperature increase, and the alcohol molecules lodged inside them are exposed, resulting in an expansion of volume. This idea applies well to systems consisting of saturated alcohols, for which hydrophobic hydration is dominant. However, the formation of H-bond between water and the unsaturated alcohols, which is considered to be a major cause of volume contraction, is disrupted by the rise of temperature, resulting in an expansive effect on volume. This effect also applies to saturated alcohols, but to a much

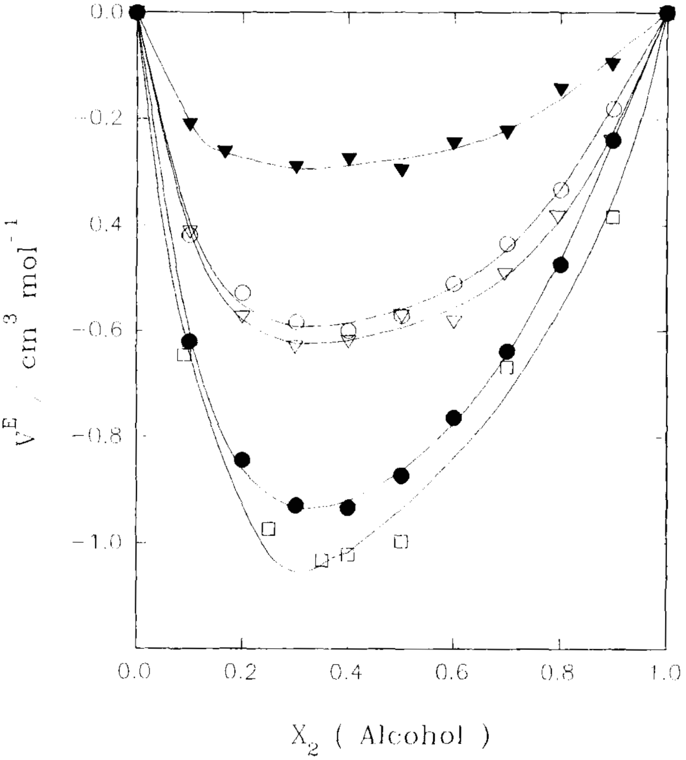

FIGURE 6 Plots of excess molar volume, V^E vs. mole fractions of different alcohols (X_2) at 40°C. The points for water + *t*-butanol system were obtained from the density data of ref. 16. ▼-Propargyl alcohol; ▽-Allyl alcohol; ○-1-Propanol; ●-2-Propanol; ☐-*t*-Butanol.

lesser extent. Likewise, the hydrophobic effect is of less importance for unsaturated alcohols.

From their recent studies on hydrophobic interactions in the aqueous solutions of alkane-1,2-diols, Andini [21] showed that, hydrophobic capacity of hydrocarbon groups varies in the order: $CH_3 > CH_2 > CH$. Therefore, assuming that the double bonded alcohol, allyl alcohol, is more effective than the triple bonded alcohol, propargyl alcohol, towards hydrophobicity, it is possible to predict that, V^E is to be in the order: *t*-butanol > 2-propanol > 1-propanol > allyl alcohol > propargyl alcohol. Experimentally, the order is found to be *t*-butanol > 2-propanol > allyl alcohol $\gtrsim$ 1-propanol > propargyl alcohol (Fig. 6), which is in fair agreement with the predicted order.

It is also interesting to note that the temperature derivative of the limiting partial molar volumes of water, $dV_W{}^o/dT$, as found for aqueous solutions of 1-propanol and 2-propanol, has the same positive sign as dV^E/dT for these alcohols. Whereas, both $dV_W{}^o/dT$ and dV^E/dT for *t*-butanol have negative signs [5]. This leads one to believe that the volumetric properties of these aqueous systems are primarily governed by the structural characteristics of water molecules, which appear to be highly sensitive to alcohols, their concentrations and the solution temperature.

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