Journal of Solution Chemistry, Vol. 17, No. 3", 1988

Partial Molar Volumes in Aqueous Mixtures of Nonelectrolytes. II. Isopropyl Alcohol

Masao Sakurai[1]

Received October 29,1987

Densities of isopropyl alcohol-water mixtures were measured over the entire mole fraction range at 5, 15, 25, 35 and 45°C. Apparent and partial molar volumes and partial molar expansibilities were derived for both components. The results were compared with those of a previous investigation of t-butyl alcohol-water mixtures.

KEY WORDS: Density; partial molar volume; partial molar expansibility; water; isopropyl alcohol.

1. INTRODUCTION

Although extensive data for alcohol-water systems are available,(1) there have been relatively few investigations of their thermal expansibilities and generally volumetric data for water in dilute solutions of alcohols are scarce. In Part I of this series(2) the partial molar volumes and expansibilities of *t*-butyl alcohol and water in their mixtures have been reported. As an extension of the study, the present paper describes density measurements for the mixtures of isopropyl alcohol (IPA) with water (W) over the entire mole fraction range at 10° intervals from 5 to 45°C.

2. EXPERIMENTAL

Isopropyl alcohol (Kanto, reagent) was further purified by fractional distillation and stored over molecular sieves (4A, Merck). The water content, determined by the Karl Fischer method, was less than 0.01%. The water was doubly distilled.

The solution density was determined with a vibrating tube densimeter (Anton Parr, DMA 60) operated in a phase locked loop mode

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[1] Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

using two measuring cells (DMA 601). Details of the apparatus and its calibration have been described elsewhere.(2,3) The temperatures of the cells were maintained within ±0.002°C by using a quartz temperature controller. All solutions were prepared by successive additions of a stock solution or a pure solute to a known quantity of solvent. The addition was carried out by weight in a mixing chamber connnected to the measuring cell with a teflon tube and a flow pump.

3. RESULTS AND DISCUSSION

Densities measured for wW + (1 - w)IPA mixtures are summarized in Table I, where w represents the weight fraction of water. The apparent molar volume $V_{\phi 2}$ of component 2 in a mixture of components 1 and 2 was calculated using the relation

$$V_{\phi 2} = X_1 M_1(\rho_1 - \rho)/X_2\rho_1\rho + M_2/\rho \tag{1}$$

where X and M are the mole fraction and molar mass and ρ is the density.

For very dilute solutions the variation of V_ϕ for both alcohol and water can be fitted with a linear equation

$$V_\phi = V^o + Am \tag{2}$$

where V^o is the limiting partial molar volume and m is the molality. The results for IPA in W and for W in IPA are plotted in Figs. 1 and 2, respectively, and the parameters of Eq. (2) are summarized in Table II. The value of V^o_{IPA} at 25°C is in good agreement with that from the literature: 71.89,(5) 71.93,(6) 71.95(7) and 71.79 cm^3-mol^{-1}.(8) No precise V^o_{W} data were available with which the present results could be compared. As is generally the case with other alcohol-water mixtures, (1,2,9) both V^o_{IPA} and V^o_{W} are smaller than the molar volume of the respective pure component.

The temperature dependence of V^o_{IPA} is shown in Fig. 3, including some values from the literature. It is apparent that the curve passes through a minimum at about 15°C; this is the same with the t-butyl alcohol(TBA)-water mixtures.(2) It is well known that for the systems of monofunctional nonelectrolytes in water, the limiting partial molar expansibility $E^o_2(= \partial V^o_2/\partial T)$ is smaller than molar expansibility of pure solute and sometimes has a negative value as observed in aqueous IPA or TBA solutions below 15°C. This has often been interpreted in terms of the structural changes of water by the hydrophobic groups of solutes, *i.e.*, hydrophobic hydration.(8,12-14)

The variation of V^o_{W} with temperature is shown in Fig. 4, along

Table I. Densities of Isopropyl Alcohol + Water

w	ρ/g-cm^{-3}	w	ρ/g-cm^{-3}	w	ρ/g-cm^{-3}	w	ρ/g-cm^{-3}
			5°C				
0	0.797258	0.16936	0.840721	0.63830	0.949132	0.95271	0.991958
0.001592	0.797751	0.20355	0.848848	0.64919	0.951626	0.96402	0.993678
0.003385	0.798312	0.23330	0.855855	0.67209	0.956342	0.972357	0.995022
0.005044	0.798826	0.26667	0.863696	0.69503	0.960824	0.975023	0.995462
0.007083	0.799449	0.29797	0.871045	0.71626	0.964681	0.977372	0.995856
0.008894	0.799997	0.32989	0.878498	0.73921	0.968424	0.979420	0.996204
0.010857	0.800584	0.36546	0.886794	0.75886	0.971221	0.981573	0.996576
0.012812	0.801165	0.40257	0.895446	0.77943	0.973725	0.983448	0.996902
0.014596	0.801689	0.43816	0.903739	0.79743	0.975625	0.985156	0.997202
0.016383	0.802210	0.47245	0.911690	0.81807	0.977579	0.987068	0.997542
0.018369	0.802784	0.50338	0.918842	0.83721	0.979289	0.988893	0.997872
0.020379	0.803361	0.53166	0.925587	0.85737	0.981096	0.990772	0.998217
0.03200	0.806597	0.53816	0.926816	0.87269	0.982526	0.992418	0.998521
0.04926	0.811183	0.55620	0.931175	0.88851	0.984089	0.993970	0.998810
0.06234	0.814548	0.57475	0.935115	0.90282	0.985610	0.995661	0.999130
0.07812	0.818535	0.57901	0.936325	0.91555	0.987062	0.996872	0.999360
0.09369	0.822403	0.60386	0.941844	0.93156	0.989042	0.998368	0.999648
0.11791	0.828348	0.60891	0.942731	0.94202	0.990442	1.0	0.999964[a]
0.14057	0.833834	0.62734	0.946947				
			15°C				
0	0.789127	0.13949	0.825062	0.61786	0.937376	0.95265	0.990970
0.001424	0.789557	0.16457	0.831115	0.64091	0.942472	0.96223	0.992476
0.003119	0.790067	0.18788	0.836703	0.66112	0.946847	0.971980	0.994081
0.004541	0.790490	0.21244	0.842551	0.68277	0.951407	0.974524	0.994509
0.006229	0.790990	0.24611	0.850554	0.70259	0.955428	0.976755	0.994887
0.007873	0.791471	0.27654	0.857752	0.72212	0.959213	0.979067	0.995286
0.009586	0.791969	0.30881	0.865377	0.74094	0.962638	0.981172	0.995651
0.011154	0.792423	0.34509	0.873916	0.76157	0.966107	0.982902	0.995954
0.012846	0.792908	0.37825	0.881717	0.78039	0.968980	0.984537	0.996242
0.014698	0.793435	0.41170	0.889568	0.80015	0.971704	0.986304	0.996558
0.016338	0.793899	0.44730	0.897856	0.81674	0.973813	0.987977	0.996858
0.018206	0.794423	0.48693	0.907161	0.83357	0.975834	0.989464	0.997128
0.020214	0.794984	0.52821	0.916759	0.85148	0.977921	0.991100	0.997428
0.02703	0.796841	0.52872	0.917049	0.86965	0.980033	0.992881	0.997756
0.04281	0.801024	0.55034	0.922046	0.88771	0.982181	0.994456	0.998048
0.05903	0.805206	0.56367	0.924941	0.90517	0.984351	0.995871	0.998313
0.07250	0.808614	0.57251	0.927130	0.92098	0.986423	0.997228	0.998570
0.09626	0.814517	0.59539	0.932329	0.93184	0.987915	0.998502	0.998813
0.11156	0.818271	0.59586	0.932287	0.94383	0.989643	1.0	0.999100[a]
			25°C				
0	0.780801	0.13072	0.814187	0.62174	0.930621	0.95308	0.988850
0.001758	0.781312	0.16069	0.821460	0.64469	0.935811	0.96450	0.990719
0.003602	0.781841	0.19678	0.830156	0.66767	0.940917	0.972571	0.992088
0.005393	0.782350	0.22754	0.837529	0.68993	0.945754	0.975101	0.992523
0.007070	0.782825	0.26171	0.845698	0.71023	0.950043	0.977519	0.992944
0.008887	0.783338	0.29554	0.853760	0.72916	0.953902	0.979769	0.993336
0.010888	0.783894	0.32652	0.861113	0.74895	0.957765	0.981864	0.993707
0.012622	0.784373	0.35961	0.868987	0.76740	0.961172	0.983740	0.994040

[a] Ref. 4.

Table I. Continued

w	ρ/g-cm^{-3}	w	ρ/g-cm^{-3}	w	ρ/g-cm^{-3}	w	ρ/g-cm^{-3}
0.014502	0.784891	0.40014	0.878609	0.78839	0.964795	0.985668	0.994386
0.016184	0.785352	0.43763	0.887492	0.80762	0.967873	0.987432	0.994703
0.018362	0.785945	0.48135	0.897812	0.82714	0.970797	0.989170	0.995020
0.020441	0.786510	0.52170	0.907308	0.84613	0.973494	0.990929	0.995344
0.03074	0.789214	0.55292	0.914730	0.86792	0.976500	0.992632	0.995658
0.04483	0.792857	0.55851	0.915915	0.88596	0.978976	0.994213	0.995954
0.05985	0.796682	0.57550	0.919986	0.90236	0.981261	0.995814	0.996252
0.07579	0.800672	0.59499	0.924384	0.91722	0.983385	0.997288	0.996529
0.09271	0.804868	0.59768	0.925112	0.93064	0.985367	0.998770	0.996811
0.11421	0.810154	0.61232	0.928358	0.94197	0.987094	1.0	0.997045[a]
35°C							
0	0.772198	0.11396	0.801123	0.62205	0.922926	0.94240	0.983905
0.001921	0.772732	0.14215	0.808018	0.64786	0.928902	0.95535	0.986054
0.003583	0.773189	0.17092	0.815013	0.67240	0.934507	0.96413	0.987549
0.005479	0.773708	0.20358	0.822924	0.69484	0.939542	0.972704	0.989039
0.007347	0.774215	0.23603	0.830749	0.71950	0.944945	0.975525	0.989536
0.009167	0.774705	0.26338	0.837332	0.74060	0.949421	0.977597	0.989902
0.011000	0.775200	0.30453	0.847227	0.76186	0.953760	0.980123	0.990353
0.012689	0.775652	0.34138	0.856064	0.77972	0.957251	0.982164	0.990721
0.014618	0.776168	0.37636	0.864449	0.79714	0.960498	0.983964	0.991045
0.016464	0.776657	0.41491	0.873677	0.81426	0.963538	0.986080	0.991430
0.018119	0.777096	0.44986	0.882031	0.82878	0.966004	0.988139	0.991808
0.020000	0.777591	0.49396	0.892555	0.84507	0.968663	0.990073	0.992162
0.021548	0.777998	0.53698	0.902795	0.85772	0.970669	0.992004	0.992521
0.03846	0.782360	0.55142	0.906309	0.87080	0.972704	0.993752	0.992848
0.05085	0.785494	0.57533	0.911966	0.88981	0.975635	0.995511	0.993177
0.06515	0.789079	0.57571	0.911962	0.90312	0.977690	0.996852	0.993431
0.07863	0.792424	0.59874	0.917477	0.91808	0.980024	0.998289	0.993703
0.09406	0.796235	0.61145	0.920359	0.93060	0.982006	1.0	0.994032[a]
45°C							
0	0.763288	0.15863	0.802730	0.64712	0.920896	0.96299	0.983398
0.002156	0.763855	0.18758	0.809794	0.67396	0.927190	0.96870	0.984414
0.004086	0.764362	0.22403	0.818673	0.70020	0.933255	0.972536	0.985103
0.006068	0.764881	0.25512	0.826224	0.72408	0.938668	0.975399	0.985619
0.007722	0.765311	0.29151	0.835052	0.75066	0.944534	0.977758	0.986049
0.009218	0.765703	0.32852	0.844013	0.77064	0.948794	0.980159	0.986488
0.010696	0.766086	0.36729	0.853418	0.79089	0.952957	0.982127	0.986849
0.012443	0.766540	0.40440	0.862407	0.81121	0.956961	0.984169	0.987226
0.014080	0.766963	0.44019	0.871064	0.82865	0.960248	0.985961	0.987557
0.015656	0.767370	0.48611	0.882174	0.84530	0.963272	0.987868	0.987911
0.017700	0.767896	0.52518	0.891698	0.85857	0.965607	0.989686	0.988252
0.020036	0.768496	0.52934	0.892617	0.87130	0.967802	0.991511	0.988592
0.03347	0.771898	0.54979	0.897632	0.88611	0.970318	0.993064	0.988886
0.04625	0.775104	0.56578	0.901398	0.89896	0.972476	0.994678	0.989193
0.06021	0.778577	0.57291	0.903191	0.91248	0.974738	0.996093	0.989462
0.07915	0.783247	0.59199	0.907687	0.92568	0.976964	0.997691	0.989769
0.09891	0.788106	0.59661	0.908877	0.93286	0.978167	0.998711	0.989964
0.12860	0.795396	0.62153	0.914828	0.94355	0.980000	1.0	0.990213[a]

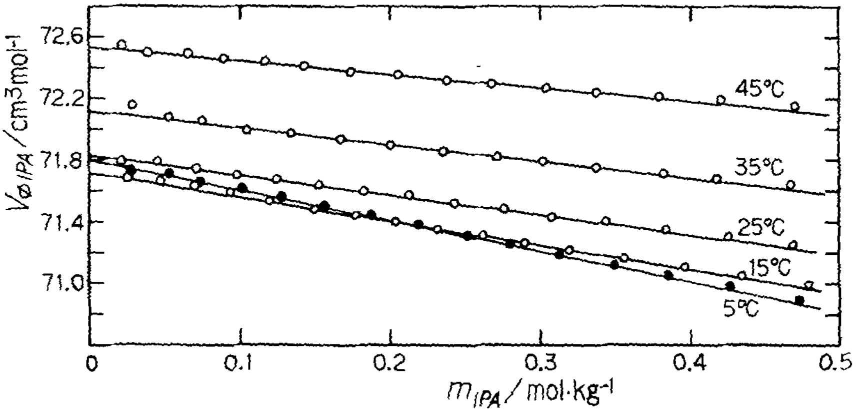

Fig. 1. Apparent molar volumes of isopropyl alcohol in dilute solutions of water.

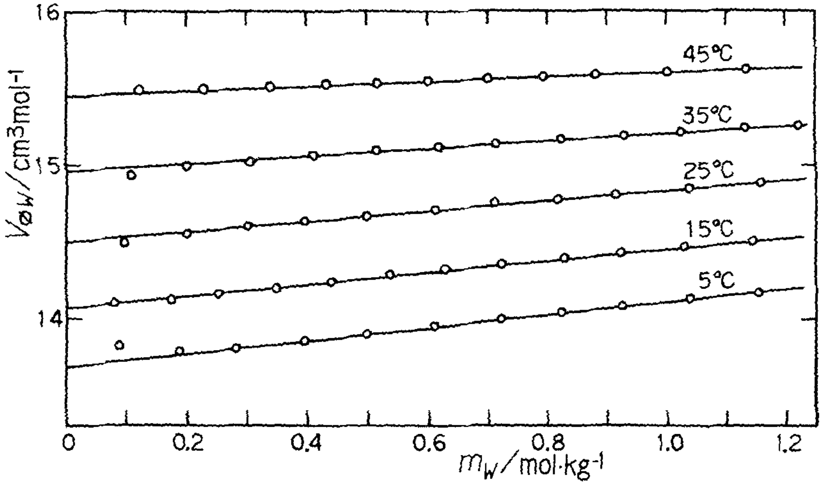

Fig. 2. Apparent molar volumes of water in dilute solutions of alcohol.

with the results for TBA,[(2)] *n*-propyl and *n*-buty alcohol solutions[(9)] for comparison. In contrast to TBA solution, V°_W in IPA increases monotonously with increasing temperature in a similar manner as those in most *n*-alcohols.[(9)] That is to say, the limiting partial molar expansibility of water in most alcohols is large compared to molar expansibility of pure water. This can be ascribed to the very low expansibility of pure water due to its temperature-sensitive open structure.

The partial molar volumes of isopropyl alcohol V_{IPA} and water V_W were evaluated at each of the five temperatures over the whole composi-

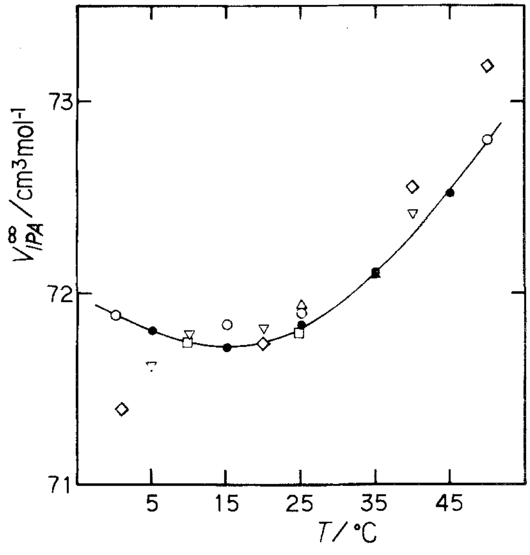

Fig. 3. Limiting partial molar volumes of isopropyl alcohol in water. •, present results; O, Alexander and Hill;(5) □, Roux *et al.*;(8) <>, Friedman and Scheraga;(10) Δ, Hoiland and Vikingstad;(6) ∇, Høiland.(11)

Table II. Partial Molar Volumes for IPA - W Mixtures

T(°C)	V^{o}_{IPA} ^{a}	A_{IPA} ^{b}	V^{o}_{W} ^{a}	A_{W} ^{b}
x5	71.80	-1.96	13.69	0.42
15	71.71	-1.54	14.08	0.38
25	71.83	-1.30	14.51	0.32
35	72.11	-1.06	14.97	0.24
45	72.52	-0.87	15.45	0.15

^{a} cm^{-3}-mol^{-1}. ^{b} cm^{-3}-kg-mol^{-2}

tion range by using the relation

$$V_2 = V_{\phi 2} + X_1 X_2(\partial V_{\phi 2}/\partial X_2) \qquad (3)$$

The $(\partial V_{\phi 2}/\partial X_2)$ values were calculated by a local fitting procedure(15) in which five consecutive values of $V_{\phi 2}$ were represented by a quadratic equation in a certain mole fraction range. Furthermore, the partial molar expansibilities $E_2 = (\partial V_2/\partial T)$ of both the components were evaluated from V_2 at each mole fraction and temperature. The results for V_2 and E_2 at 25°C are shown in Fig. 5. The sharp V_{IPA} minimum and E_{IPA} max-

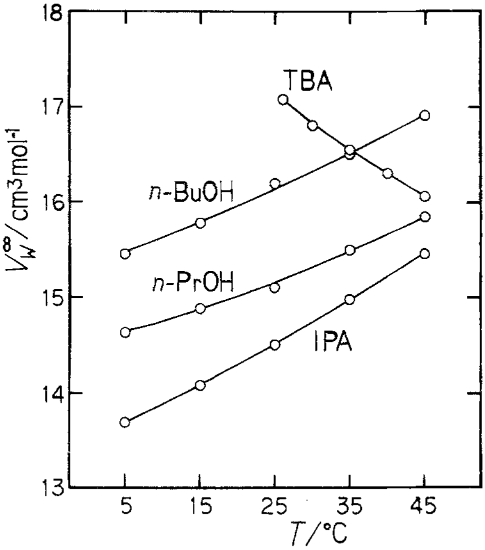

Fig. 4. Limiting partial molar volumes of water in isopropyl alcohol, *n*-propyl alcohol,$^{(9)}$ *n*-butyl alcohol$^{(9)}$ and *t*-butyl alcohol.$^{(2)}$

imum in the water-rich region are typical of many aqueous nonelectrolyte solutions. The trends with the temperature are shown in more detail in Figs. 6 and 7.

As has been observed for aqueous TBA solutions,$^{(2)}$ both extrema are more pronounced and shift to higher concentrations as the temperature is lowered. It is worth noting that the mole fraction of the two extrema differ significantly from each other. The well-known characteristics of volumetric properties in water-rich regions, represented typically by aqueous IPA or TBA solutions, have generally been interpreted in terms of hydrophobic hydration.$^{(1)}$ However, it should be noted that the exact nature of the hydrophobic hydration has remained obscure; consequently the volume change accompanying the hydrophobic hydration is still open to question.$^{(2)}$

On the other hand, the volumetric behavior of water in the IPA-rich regions is quite different from that of TBA-W mixture. In the IPA case, V_W increases and E_W decrease monotonously as the mole fraction of water increases. In contrast to this behavior, in TBA solutions, V_W passes through a minimum at about $X_W = 0.2$ and E_W increases with increasing X_W. At present we cannot offer any reasonable explanation for the difference in concentration dependence of V_W or E_W in IPA and in TBA solutions, along with the difference in the temperature dependence of the limiting partial molar volume illustrated in Fig. 4.

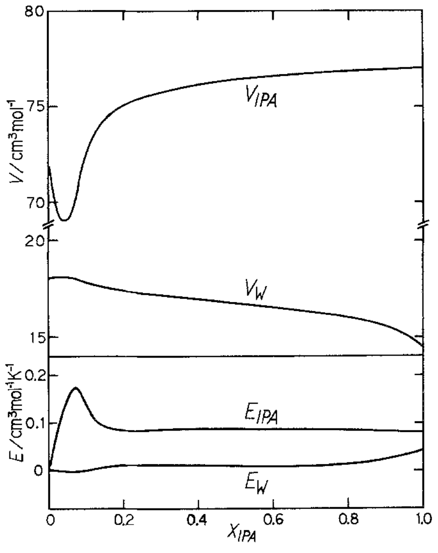

Fig. 5. Partial molar volumes and expansibilities of isopropyl alcohol and water.

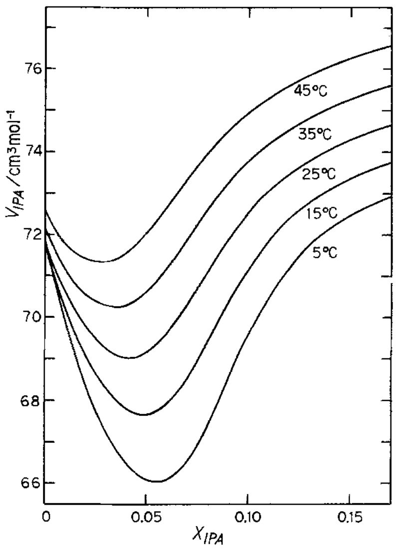

Fig. 6. Partial molar volumes of isopropyl alcohol in the water-rich regions.

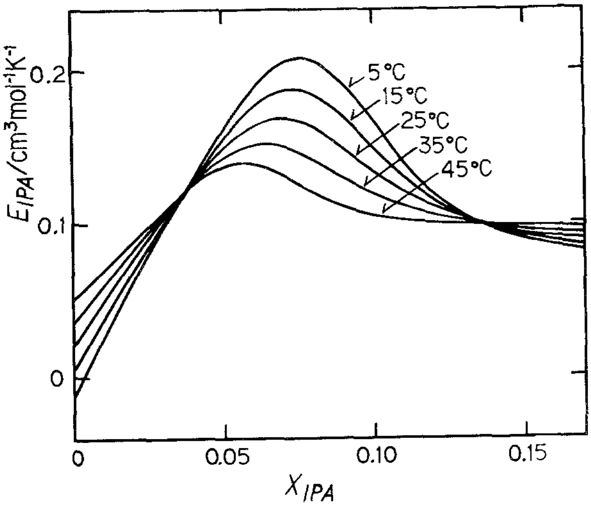

Fig. 7. Partial molar expansibilities of isopropyl alcohol in the water-rich regions.

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