Partial Molal Volumes of Butyl Alcohols and of Related Compounds in Aqueous Solution

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The excess function of any thermodynamic quantities for liquid mixtures is symmetric in form with regards to the mole fraction of component, if the components are the " normal liquids " which consist of the spherical molecule with no specific interaction. However, this symmetry fails when the size and form of one component are different from those of another, or when a specific interaction plays an important role in intermolecular force. In the " associated solution ", this specific interaction which is attributed to the formation of hydrogen bonding is predominant, and the anomaly in the behavior of the excess function is often observed for a number of such systems[1].

The same is true for the excess volume (the volume change on mixing). For binary mixtures of the normal liquids the excess volume is generally small and nearly symmetric in form, and the interrelationships with other thermodynamic properties and parameters of the intermolecular force have been also investigated, both experimentally and theoretically, by many authors[2]. On the other hand, large negative excess volume is observed generally for the liquid mixtures containing water, alcohols or other associated liquids as one or both

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[1] J. A. Barker, *J. Chem. Phys.*, 20, 794, 1526 (1952); J. A. Barker and F. Smith, ibid., 22, 375 (1954).

[2] G. Scatchard, *Trans. Faraday Soc.*, 33, 160 (1937); J. H. Hildebrand and R. L. Scott, " Solubility of Non-Electrolytes ", 3rd. ed., Reinhold Publ. Corp., New York (1950), p. 138; I. Prigognie, " The Molecular Theory of Solution ", North-Holland Publ. Co., Amsterdam (1957), p. 176.

TABLE I. DENSITIES OF AQUEOUS SOLUTION OF BUTYL ALCOHOLS AT 20°C

Normal		Iso		Secondary		Tertiary	
Wt. %	Density	Wt. %	Density	Wt. %	Density	Wt. %	Density
1.2684	0.99623	1.3042	0.99610	1.2149	0.99621	1.3139	0.99593
1.9816	0.99514	2.0761	0.99495	1.8892	0.99522	2.3476	0.99425
2.7038	0.99405	2.7871	0.99395	2.7195	0.99400	3.7557	0.99199
3.2835	0.99321	3.2493	0.99319	3.4639	0.99299	4.7743	0.99052
4.0939	0.99211	3.4096	0.99308	4.3960	0.99173	6.2671	0.98843
4.8138	0.99114	4.1259	0.99206	4.9808	0.99102	7.4321	0.98689
5.5200	0.99016	4.4318	0.99154	5.7904	0.99005	8.3009	0.98578
5.6470	0.98993	4.9319	0.99091	7.0477	0.98848	9.4236	0.98432
6.0442	0.98950	5.2515	0.99050	8.3458	0.98678	10.132	0.98346
6.1640	0.98924	5.6818	0.98982	8.8445	0.98620	12.143	0.98098
6.5653	0.98878	5.9351	0.98946	9.6519	0.98517	13.662	0.97907
6.6262	0.98862	6.5070	0.98875	10.637	0.98396	14.612	0.97780
6.7731	0.98842	6.7836	0.98831	11.842	0.98239	15.529	0.97671
7.2231	0.98780	7.1135	0.98798	12.753	0.98119	16.159	0.97593
7.6415	0.98722	8.0334	0.98669	13.471	0.98019	17.943	0.97331
7.7671	0.98699	8.2184	0.98639	14.066	0.97932	19.425	0.97100
78.914	0.84872	83.448	0.83552	14.824	0.97802	21.328	0.96754
90.586	0.82837	85.353	0.83193	15.742	0.97668	24.536	0.96115
100.000	0.80973	88.757	0.82521	16.886	0.97467	30.483	0.94841
		90.703	0.82140	18.612	0.97211	39.115	0.92824
		94.613	0.81375	67.968	0.87176	49.449	0.90386
		95.391	0.81194	74.591	0.85869	58.386	0.88322
		100.000	0.80185	82.684	0.84231	69.937	0.85709
				88.435	0.83043	79.027	0.83481
				93.948	0.81901		
				100.000	0.80634		

components. The partial volumes of both components show complicated behavior with the variation in the composition of the component. The case of water-ethanol system, which has often been cited in many text-books of chemical thermodynamics, is a well-known example. At present, we have no clear understanding of this phenomenon, although a qualitative explanation[3] accounts for it as the disintegration of structure in water by the solute molecule which is capable of forming the hydrogen bonding with water.

It seems to be natural to expect an anomaly similar to the above for the case of aqueous solutions of alcohols other than ethanol and of other compounds having the hydroxyl group. In the present study, we obtained the dependence of partial molal volumes in water upon the composition for four isomers of butyl alcohol from the density measurement and compared them with that of other alcohols. For comparison's sake, the partial molal volume of ethylene glycol was also evaluated. In each case concerned, the general feature of partial volume vs. composition curve was the same as that for the case of ethanol in water.

Experimental

Purification of Materials.—*Normal*, *iso-*, *sec.-* and *tert.*-butyl alcohols and ethylene glycol were prepared as follows. The best grade available was dried over dehydrating agents and then fractionally distilled.

n-Butyl alcohol was at first treated with dilute sulphuric acid and sodium bisulphate solution for the removal of ketones and aldehydes, and then heated under reflux with a small amount of sodium hydroxide solution for the removal of esters. After the removal of alkali, the material was dried over calcium hydroxide, refluxed with calcium oxide, and then fractionally distilled a few times.

Isobutyl alcohol and *sec.*-butyl alcohol were boiled under reflux over calcium oxide for a few hours, and then fractionally distilled.

tert.-Butyl alcohol was dried over anhydrous potassium carbonate at 46°C for a long time, and then fractionally distilled.

Ethylene glycol was distilled under reduced pressure, and the middle fraction was dried over anhydrous sodium sulphate for a long time. The material was then redistilled.

Water was obtained by the repeated distillations of conductivity water.

All the sample liquid were stored in sealed glass containers and redistilled immediately before use. The densities of the sample liquids at 20°C were within 0.00005 g./cc. of the values given in literature.

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[3] For example, A. G. Mitchell and W. F. K. Wynne-Jones, *Discussion Faraday Soc.*, No. 15, 161 (1953).

Pycnometers.—The pycnometers used were of ordinary bicapillary type. Type A held slightly more than 25 cc. of liquid, while type B slightly less than 10 cc. The main body of the pycnometer was the usual flat-bottom type. The capillaries were calibrated with a travelling microscope by the conventional method of moving a small mercury column. In the middle of each capillary, a horizontal razor mark was applied and the volume of pycnometer with meniscus on this mark was obtained by the measurement with water.

Density Measurement.—The component liquids were mixed in a glass-stoppered weigh-bottle having a narrow mouthpiece. The mole fraction of the sample solution was determined from the weight of each component.

After being kept over night, the sample solution was transfused into the pycnometer by injection with a medical syringe until each of the two meniscus was near the horizontal mark on the capillary. The pycnometer was then placed into the thermostat at 20±0.005°C, and when complete thermal equilibrium was attained, the height difference between the meniscus and the mark was determined by means of a travelling microscope reading to ±0.01 mm.

Immediately after the volume determination, the apparent weights of the pycnometer and the sample solution were determined with an analytical balance. The values were converted into true weights by the cnventional procedure in which the buoyancy corrections were applied.

Thus, the densities of sample solutions were obtained with a precision of $\pm 2\times 10^{-5}$.

Results and Discussion

Densities.—The density data of butyl alcohol-water and ethylene glycol-water systems are summarized in two tables. Table I shows the densities of aqueous solution of four isomers of butyl alcohol, and Table II shows the densities of ethylene glycol-water system at 20°C. In all cases concerned, the densities of the solution can not be expressed by the conventional power series relation.

TABLE II. DENSITIES OF AQUEOUS SOLUTION OF ETHYLENE GLYCOL AT 20°C

Wt. %	Density	Wt. %	Density
1.5193	1.00013	30.440	1.03894
3.2341	1.00231	31.957	1.04095
5.7310	1.00554	36.540	1.04717
8.7395	1.00949	40.674	1.05276
9.3383	1.01019	41.410	1.05347
10.807	1.01215	51.737	1.06704
11.243	1.01277	58.341	1.07474
14.348	1.01693	71.378	1.08876
15.768	1.01879	80.617	1.09830
17.972	1.02182	87.942	1.10459
21.213	1.02621	94.169	1.10924
23.957	1.03001	100.000	1.11313
28.545	1.03628		

Volume of Mixing (Excess Volume).—Since the specific volumes of both components are known (except for *tert.*-butyl alcohol which has the melting point above 20°C), the volume of the mixing ΔV is easily calculated from the present data. It is a common characteristic that ΔV has large negative value in the whole range of composition and that there is an inflection point below the alcohol mole fraction of 0.1. Fig. 1. shows the general feature schematically.

Partial Volumes.—Partial specific (molal) volumes of alcohols V_2 are calculated from the density data directly by Eq. 1, or from the concentration dependence of apparent specific volume ϕ_2 by Eq. 2,

$$V_2=(1/d_{12})+(1-w_2)\frac{\partial(1/d_{12})}{\partial w_2} \tag{1}$$

$$V_2=\phi_2+w_2(1-w_2)\frac{\partial\phi_2}{\partial w_2} \tag{2}$$

where the apparent specific volume is defined as follows,

$$\phi_2=(1/d_1)-(d_{12}-d_1)/(d_{12}d_1w_2) \tag{3}$$

and d_{12} is the density of solution, d_1 is the density of water and w_2 is the weight fraction of alcohols.

As in the well-known example of ethanol-water system, characteristic behaviors of partial molal volume vs. composition curves are obtained with all systems investigated. Partial molal volume of alcohol decreases with increasing its mole fraction, reaches a minimum value and then increases gradualy to the molal volume. In the whole range of composition, it is always smaller than the molal volume V_2^0. Partial molal volume of water, on the other hand, increases slightly with increasing the alcohol mole fraction, reaches an indistinct maximum and then decreases gradually.

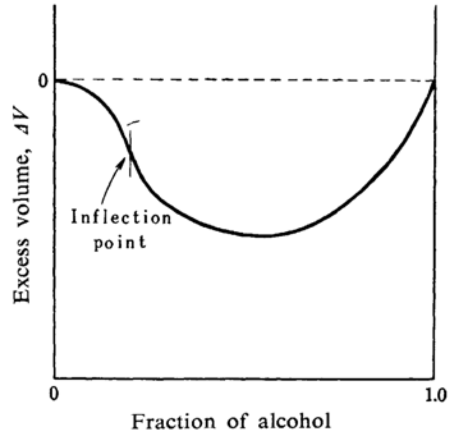
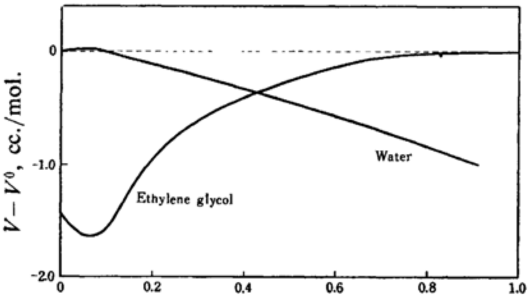


Fig. 1. Schematic diagram of excess function in alcohol-water systems.

The general feature just described above can well be understood by the case of ethylene glycol-water system given in Fig. 2.

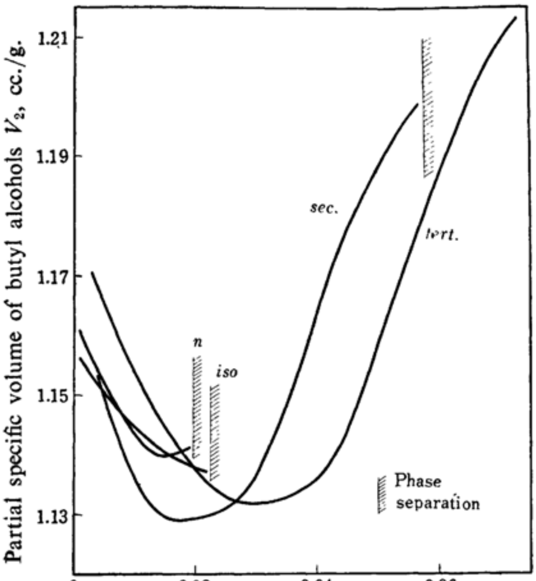
For the partial volumes of four isomers of butyl alcohol in water, the diagram is incomplete owing to the phase separation or high melting point. Fig. 3 shows the isomeric variation in the partial volumes of butyl alcohols in their low concentration region where the characteristic behavior is clearly observed.

For comparison's sake, the partial molal volumes of methanol, ethanol, propyl alcohols and glycerol in water are calculated and plotted in Fig. 4 together with the present data. The calculation is made with the ICT data[4]. In addition, an interesting temperature dependence, which is found in ethanol, is shown in Fig. 5.



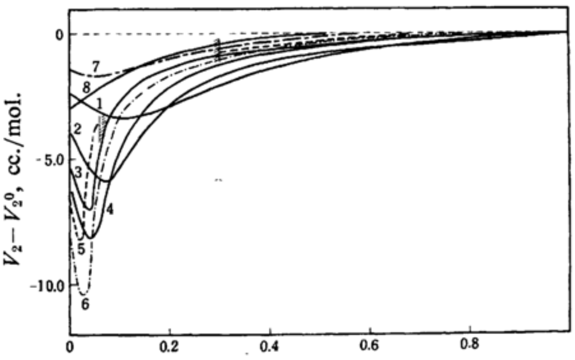
Mole fraction of ethylene glycol, x_2

Fig. 2. Partial molal volumes of ethylene glycol-water system at 20°C.



Mole fraction of butyl alcohol, x_2

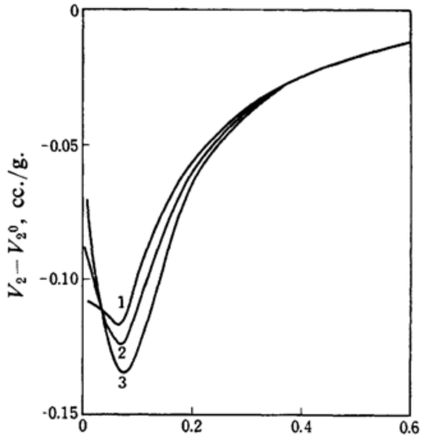
Fig. 3. Partial specific volume of butyl alcohols in water at their low concentration at 20°C.



Mole fraction of alcohols, x^2

Fig. 4. Partial molal volume of alcohols in water.

1 Methanol (15°C)
2 Ethanol (20°C)
3 *n*-Propyl alcohol (15°C)
4 Isopropyl alcohol (15°C)
5 *sec.*-Butyl alcohol (20°C)
6 *tert.*-Butyl alcohol (20°C)
7 Ethylene glycol (20°C)
8 Glycerol (15°C)



Mole fraction of ethanol, x_2

Fig. 5. Partial specific volume of ethanol in water at different temperatures.

1, 40°C; 2, 25°C; 3, 10°C;

Summary of Experimental Observations.— Partial volume behavior presented above may be summarized as in the following.

1) Partial volumes of alcohols take a minimum value at a definite point. The position of this minimum shifts systematically to the lower concentration of alcohol in the order of BuOH, PrOH, EtOH and MeOH, as is shown in Table III.

2) Depth of the minimum in $V_2-V_2^0$ depends on the kind of alcohol in a more

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[4] International Critical Table, Vol. III, p. 115~122.

TABLE III. MINIMUM POINT IN THE VALUE OF $V_2-V_2^0$

Compound		Minimum point at mole %	wt. %
Monohydric alcohol	CH_3OH	10.5	17.
	C_2H_5OH	7.0	16.
	n-C_3H_7OH	4.5	14.
	iso-C_3H_7OH	5.0	15.
	n-C_4H_9OH	1.5	6.
	iso-C_4H_9OH	>2.1	>8.
	$sec.$-C_4H_9OH	1.8	7.
	$tert.$-C_4H_9OH	3.0	11.
Dihydric alcohol	CH_2OH $\vert$ CH_2OH	6.0	16.
Trihydric alcohol	CH_2OH $\vert$ $CHOH$ $\vert$ CH_2OH	—	—

complicated manner than the above. The largest volume contraction is observed with *tert.*-butyl alcohol.

3) Volume contraction of polyhydric alcohols in water is generally smaller than that of monohydric alcohols. Moreover, it is of interest that the partial volume of ethylene glycol has a minimum value near the glycol mole fraction of 0.06, while that of glycerol has no minimum (Fig. 4).

4) Partial volume V_2 of ethanol at high dilution (below the alcohol mole fraction of 0.04) has a small temperature coefficient nearly half the value of ethanol itself. Thus, with the raise in temperature, a) the increase in the depth of $V_2-V_2^0$ at high dilution is observed, although b) the value at the minimum point decreases gradually.

Discussion.—Examination of all the experimental data available leads us to the conclusion that the partial volume behavior of mono- and dihydric alcohol-water system has a common characteristic. Qualitatively, the abrupt fold in the partial volume vs. composition curve would be interpreted[3] as the disintegration of the hydrogen-bonded structure in water by the increased strain due to the invading alcohol molecule with increasing fraction of the alcohol. It may be that there are two kinds of configuration of alcohol molecule in aqueous solution, one has a specific volume of alcohol itself, while the other has a small effective volume, and the fraction of the two may change with composition in a complicated manner in an alcohol-water system.

In this connection, it is of interest to examine the other properties of aqueous solution of alcohols. For example, ultrasonic absorption in aqueous solution of alcohol has a marked maximum in some definite composition[5]. But, this maximum in absorption does not always correspond to the minimum in partial volume, and moreover the former is found in aqueous solution of acetone which has smoothed partial volume vs. composition curve[6].

Another interesting result to be noted here is the partial volume behavior in dioxane-water system[7] in which a similar anomaly is observed. In this case, however, partial volume of water has a minimum point instead of a maximum as in alcoholic solutions, and the partial volume of dioxan has a maximum. It is an interesting fact that the role of the OH– group in alcohol molecules contrasts remarkably with that of ether bond –O– in the formation of intermolecular hydrogen bonding in aqueous solution.

In conclusion, all the available data seem to comprise only indirect evidences and it is obvious that more direct information about the inner structure of solutions is desirable for the elucidation of this phenomenon.

Summary

Partial molal volumes of four isomers of butyl alcohol and ethylene glycol in water are evaluated from the density measurement. They are compared with those of other monohydric alcohols and all the available data which have a common characteristic in the dependence upon the alcohol fraction are summarized.

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[5] O. Nomoto, *J. Phys. Soc. Japan*, **11**, 827 (1956); ibid., **12**, 300 (1957).

[6] V. S. Griffith, *J. Chem. Soc.*, **1953**, 860.

[7] G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).