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Thermodynamic Properties of Some Isomeric Butyl Alcohol Mixtures[1]

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Molar excess enthalpies and molar excess volumes are reported for binary mixtures of *n*-butyl alcohol with isobutyl alcohol, *sec*-butyl alcohol, and *t*-butyl alcohol. All of the measurements were carried out at 25°C except for the excess enthalpies of *n*-butyl alcohol–*t*-butyl alcohol which were determined at 26°C. Interpretation of the results in terms of a lattice model was investigated.

Measurements of the thermodynamic properties of binary mixtures of methanol with the four isomeric butyl alcohols were reported in previous publications.[3–5] Differences in the behaviour of these mixtures were attributed primarily to differences in hydrogen bonding. As an extension of our studies, we have measured the enthalpy and volume changes for the mixing of *n*-butyl alcohol with isobutyl alcohol (2-methyl-1-propanol), with *sec*-butyl alcohol (2-butanol) and with *t*-butyl alcohol (2-methyl-2-propanol).

Experimental

Details of the chromatographic purification of the isomeric butyl alcohols have been described.[5] Enthalpies and volumes of mixing were measured by successive dilution techniques, using a calorimeter[6] and dilatometer.[4] The uncertainties in the results for equimolar mixtures are estimated to be ± 0.5 J mol^{-1} for the molar excess enthalpies, and ± 0.0005 cm^3 mol^{-1} for the molar excess volumes.

Results

All of the measurements were carried out at 25.00 ± 0.01°C except for the determinations of the excess enthalpies of *n*-butyl alcohol–*t*-butyl alcohol mixtures. The latter were measured at 26.00 ± 0.01°C, since at 25°C

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3) A. E. Pope, H. D. Pflug, B. Dacre, and G. C. Benson, *Can. J. Chem.*, **45**, 2665 (1967).

4) H. D. Pflug and G. C. Benson, *ibid.*, **46**, 287 (1968).

5) J. Polák, S. Murakami, V. T. Lam, H. D. Pflug, and G. C. Benson, *ibid.*, **48**, 2457 (1970).

6) S. Murakami, and G. C. Benson, *J. Chem. Thermodyn.*, **1**, 559 (1969).

operation of the calorimeter was upset by the tendency of the *t*-butyl alcohol to solidify in the hypodermic needle. Results for the molar excess enthalpy H^E and the molar excess volume V^E are listed in Tables 1 and 2, respectively. In all cases, x_1 indicates the mole fraction of *n*-butyl alcohol. Graphs of the results are shown in Figs. 1 and 2, where it should be noted that scales differing by a factor of 10 have been used in plotting the excess functions for some of the systems.

TABLE 1. EXPERIMENTAL VALUES OF THE MOLAR EXCESS ENTHALPY OF SOME BINARY ISOMERIC BUTYL ALCOHOL SYSTEMS

n-Butyl alcohol–isobutyl alcohol at 25°C		*n*-Butyl alcohol–*sec*-butyl alcohol at 25°C		*n*-Butyl alcohol–*t*-butyl alcohol at 26°C	
x_1	H^E J mol^{-1}	x_1	H^E J mol^{-1}	x_1	H^E J mol^{-1}
0.0376	1.7	0.0341	−14.8	0.0272	−59.9
0.0382	1.7	0.0774	−31.6	0.0343	−74.0
0.0951	4.0	0.1266	−48.3	0.0649	−133.9
0.1000	4.2	0.1756	−62.7	0.0677	−138.8
0.1412	5.6	0.2933	−87.4	0.1046	−202.3
0.1421	5.7	0.3519	−94.8	0.1144	−217.2
0.1859	7.0	0.4005	−98.7	0.1482	−266.5
0.1948	7.3	0.4185	−99.1	0.1585	−279.1
0.2353	8.2	0.4186	−99.2	0.1993	−328.0
0.2401	8.3	0.4573	−99.7	0.2065	−335.3
0.2886	9.2	0.4576	−100.6	0.2485	−375.0
0.2909	9.5	0.4711	−100.1	0.2527	−378.1
0.3435	10.0	0.4738	−100.2	0.3043	−413.2
0.3451	10.4	0.5057	−100.2	0.3085	−416.1
0.3940	10.7	0.5185	−99.3	0.3550	−437.0
0.3956	10.9	0.5186	−99.5	0.3570	−437.4
0.4141	11.1	0.5218	−99.0	0.4104	−450.5
0.4425	11.0	0.5494	−98.1	0.4109	−449.9
0.4478	11.3	0.5644	−96.9	0.4636	−451.4
0.4559	11.1	0.5702	−96.0	0.4784	−450.8
0.4781	11.0	0.5752	−95.3	0.5159	−442.7
0.4879	11.1	0.6016	−94.3	0.5375	−437.5
0.4988	11.4	0.6218	−91.5	0.5631	−427.2
0.5235	11.4	0.6237	−90.8	0.6077	−406.5
0.5354	11.1	0.6768	−84.2	0.6108	−405.6
0.5356	11.0	0.6863	−82.1	0.6137	−403.8
0.5449	10.9	0.7262	−75.8	0.6619	−372.1
0.5799	10.9	0.7278	−75.3	0.7095	−334.1
0.5806	10.9	0.7399	−72.5	0.7590	−288.8
0.5923	10.4	0.7761	−65.8	0.8125	−233.9
0.5952	10.3	0.8014	−59.2	0.8603	−182.7
0.6316	10.3	0.8055	−58.3	0.9022	−131.6
0.6344	9.7	0.8196	−55.6	0.9396	−83.5
0.6833	9.3	0.8606	−44.1	0.9747	−35.8
0.7362	7.8	0.8649	−43.7		
0.7425	8.1	0.8860	−36.7		
0.7868	6.6	0.9084	−30.9		
0.8027	6.7	0.9349	−22.1		
0.8302	5.5	0.9488	−17.8		
0.8509	5.3	0.9675	−11.3		
0.8682	4.3				
0.9085	3.2				
0.9162	3.0				
0.9598	1.5				
0.9685	1.1				

TABLE 2. EXPERIMENTAL VALUES OF THE MOLAR EXCESS VOLUME OF SOME BINARY ISOMERIC BUTYL ALCOHOL SYSTEMS AT 25°C

n-Butyl alcohol–isobutyl alcohol		*n*-Butyl alcohol–*sec*-butyl alcohol		*n*-Butyl alcohol–*t*-butyl alcohol	
x_1	V^E cm^3 mol^{-1}	x_1	V^E cm^3 mol^{-1}	x_1	V^E cm^3 mol^{-1}
0.0419	0.0003	0.0275	0.0017	0.0481	−0.0662
0.0785	0.0015	0.0652	0.0024	0.0963	−0.1176
0.1030	0.0026	0.0705	0.0033	0.1496	−0.1581
0.1649	0.0029	0.1123	0.0046	0.2050	−0.1868
0.1656	0.0034	0.1233	0.0044	0.2640	−0.2043
0.2315	0.0044	0.1632	0.0047	0.3195	−0.2115
0.2445	0.0033	0.1810	0.0051	0.3747	−0.2116
0.2935	0.0043	0.2150	0.0055	0.4273	−0.2066
0.3178	0.0038	0.2392	0.0055	0.4706	−0.1992
0.3492	0.0043	0.2702	0.0057	0.5720	−0.1726
0.3800	0.0036	0.3308	0.0055	0.6090	−0.1601
0.3987	0.0041	0.4285	0.0046	0.6652	−0.1408
0.4351	0.0038	0.4626	0.0044	0.7244	−0.1191
0.4447	0.0042	0.4822	0.0048	0.7825	−0.0959
0.4818	0.0039	0.5023	0.0041	0.8412	−0.0713
0.4883	0.0039	0.5249	0.0044	0.8940	−0.0484
0.5220	0.0038	0.5495	0.0039	0.9453	−0.0253
0.5235	0.0038	0.5735	0.0040		
0.5986	0.0035	0.6000	0.0035		
0.6523	0.0033	0.6312	0.0034		
0.7085	0.0029	0.6547	0.0030		
0.7676	0.0025	0.6877	0.0029		
0.8261	0.0021	0.7163	0.0024		
0.8838	0.0017	0.7493	0.0022		
0.9308	0.0013	0.7788	0.0021		
0.9696	0.0004	0.7846	0.0016		
		0.8159	0.0015		
		0.8403	0.0013		
		0.8449	0.0013		
		0.8786	0.0013		
		0.9015	0.0006		
		0.9047	0.0007		
		0.9373	0.0005		
		0.9568	−0.0001		
		0.9573	−0.0001		
		0.9738	0.0001		

The method of least squares was used to fit the results with equations of the type

$$X^E = x_1(1-x_1)\sum_{j=1}^{n} c_j(1-2x_1)^{j-1} \qquad (1)$$

where X^E is either H^E or V^E. The minimum number of coefficients required to represent the results adequately was determined by examining the statistical significance of the improvement in the fit with the increase in the number of coefficients. The values obtained for the coefficients c_j are summerized in Table 3, along with the standard error of estimate σ associated with each representation. The curves in Figs. 1 and 2 were calculated from Eq. (1) using these values for the coefficients.

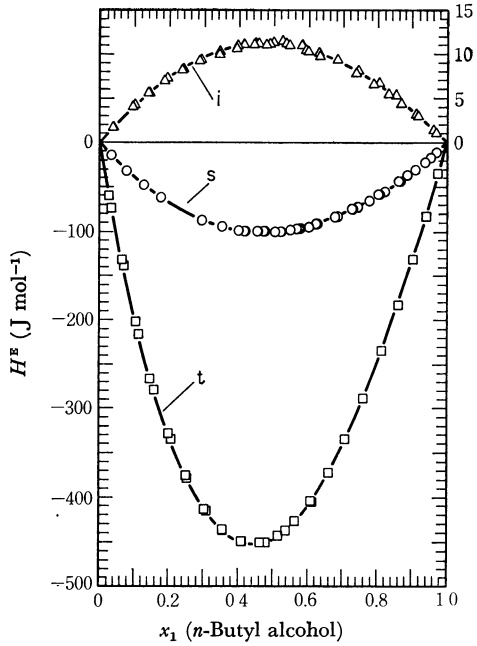

Fig. 1. Molar excess enthalpies of *n*-butyl alcohol–isomeric butyl alcohol mixtures. Experimental results; △: *n*-butyl alcohol–isobutyl alcohol at 25°C; ○: *n*-butyl alcohol–*sec*-butyl alcohol at 25°C; □: *n*-butyl alcohol–*t*-butyl alcohol at 26°C. Curves are least-squares representations of experimental results by Eq. (1). Labels *i*, *s*, and *t* indicate the three isomeric butyl alcohols used as second components. Ordinate scale at right is for mixtures containing isobutyl alcohol and ordinate scale at left is for those containing *s*-butyl alcohol or *t*-butyl alcohol.

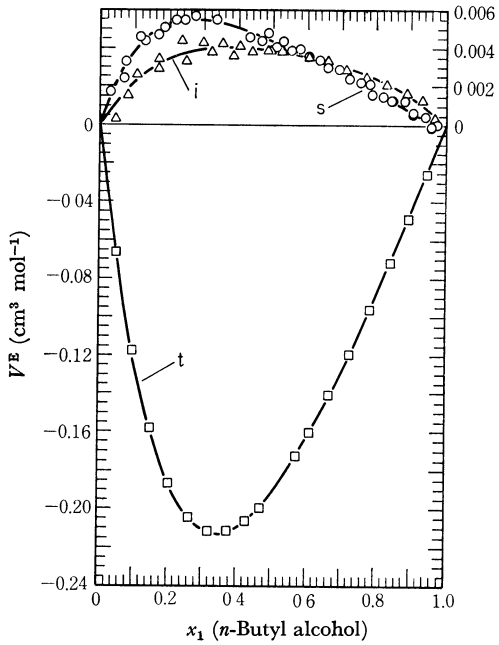

Fig. 2. Molar excess volumes of *n*-butyl alcohol–isomeric butyl alcohol mixtures at 25°C. Experimental results; △: *n*-butyl alcohol–isobutyl alcohol; ○: *n*-butyl alcohol–*sec*-butyl alcohol; □: *n*-butyl alcohol–*t*-butyl alcohol. Curves are least-squares representations of experimental results by Eq. (1). Labels *i*, *s*, and *t* indicate the three isomeric butanols used as second components. Ordinate scale at right is for mixtures containing isobutyl alcohol or *sec*-butyl alcohol, and ordinate scale at left is for those containing *t*-butyl alcohol.

TABLE 3. COEFFICIENTS FOR LEAST SQUARES FIT OF RESULTS BY EQ. (1)[a)]

System	X^E	Coefficient				Std. error. σ
		c_1	c_2	c_3	c_4	
n-Butyl alcohol–isobutyl alcohol	H^E	44.68	4.44	−3.60		0.17
	V^E	0.01542	0.00574	0.00770		0.00032
n-Butyl alcohol–*sec*-butyl alcohol	H^E	−339.75	−47.06	−7.68		0.34
	V^E	0.01741	0.01448	0.01286	0.01251	0.00023
n-Butyl alcohol–*t*-butyl alcohol	H^E	−1787.28	−400.40	−52.46	−36.96	0.79
	V^E	−0.76783	−0.47710	−0.24097	−0.06597	0.00038

a) Units: H^E, J mol^{-1}; V^E, cm^3 mol^{-1}

Discussion

There is a fairly close similarity between Figs. 1 and 2, and graphs presented previously[5)] for the excess enthalpies and volumes of methanol-isomeric butyl alcohol systems. In general the signs of the excess functions are the same for systems of the two sets with a common second component. However, the greater similarity in size of the component molecules in the present systems leads to smaller magnitudes for the excess functions than those observed for the methanol systems. Thus it appears that the qualitative discussion[5)] of the role of hydrogen bonding in determining the excess properties of methanol–isomeric butyl alcohol mixtures is also valid for the present systems.

The generalized quasi-lattice theory of Barker[7,8)] should be well suited for analysing the excess properties of mixtures in which association by hydrogen bonding occurs, since it deals explicitly with the specific interactions between different parts of the component molecules. It is customary to adjust the parameters characterizing these interactions to fit the theoretical values of the excess energy and/or free energy to the experimental results. In developing a Barker type of model for binary mixtures of butanol isomers, we found it useful also to consider the results reported earlier for methanol–isomeric butyl alcohol mixtures.[5)]

The mixing process treated by Barker is one in which the volume for each molecule remains constant. However, it is useful to compare the theoretical values with experimental results measured essentially at constant pressure and corrected to constant total volume. In the case of the free energy, this correction is negligible and values of A_V^E, the molar excess Helmholtz free energy at constant volume are identified with values

7) J. A. Barker, *J. Chem. Phys.*, **20**, 1526 (1952).
8) J. A. Barker and F. Smith, *ibid.*, **22**, 375 (1954).

of G^E, the molar excess Gibbs free energy at constant pressure. The difference between U_V^E, the molar excess energy at constant volume, and H^E, the molar excess enthalpy at constant pressure, is more significant and can be estimated from the relation

$$H^E - U_V^E \approx TV^E(\alpha_1\phi_1+\alpha_2\phi_2)/(\kappa_1\phi_1+\kappa_2\phi_2) \quad (2)$$

where ϕ_i is the volume fraction of component i in the mixture, and α_i and κ_i are respectively the coefficients of expansion and isothermal compressibility for pure i. The curves for A_V^E and U_V^E at 25°C (Figs. 3—5) were obtained from the smoothed representations of the experimental results for G^E, H^E, and V^E. In calculating U_V^E, the values of α and κ listed in Table 4 were used. These values were derived previously[9] from density, velocity of sound, and heat capacity data. The one degree temperature deviation (from 25°C) of the *n*-butyl alcohol–*t*-butyl alcohol results for H^E was neglected.

Table 4. Values of the coefficient of thermal expansion α, and the isothermal compressibility κ for the component liquids at 25°C

Component	$10^3\alpha$ K^{-1}	$10^6\kappa$ atm^{-1}
Methanol	1.185	126.4
n-Butyl alcohol	0.937	94.5
Isobutyl alcohol	0.948	102.6
sec-Butyl alcohol	0.988	98.2
t-Butyl alcohol	1.344	126.1

Our model for binary alcohol mixtures assumes that an alcohol molecule of species i, containing m carbon atoms, occupies $r_i=m+1$ sites of a lattice with coordination number equal to four. Three different types of contact areas are recognized on the surface of the moledule: hydrocarbon denoted by I, hydroxyl oxygen by O, and hydroxyl hydrogen by H. A subscript (1) or (2) is added to these symbols when it is necessary to indicate that the contact is on a molecule of the first or second component in the mixture. The number of contact points of type a on a molecule of species i is denoted by Q_i^a. The values of Q_i^a were chosen to satisfy the condition

$$\sum_a Q_i^a = zr_i + z$$

Q^I was assigned values of 3 and 9 for methanol and the isomeric butyl alcohols respectively; values of $Q^O=2$ and $Q^H=1$ were adopted for all of the alcohols.

Table 5. Simplified scheme for interchange parameters U_{ij}^{ab} and A_{ij}^{ab}

Bond	U_{ij}^{ab}	A_{ij}^{ab}
$I_{(1)}$—$O_{(1)}$, $I_{(1)}$—$H_{(1)}$, $I_{(2)}$—$O_{(2)}$, $I_{(2)}$—$H_{(2)}$	0	0
$O_{(1)}$—$H_{(1)}$	U_1	A_1
$O_{(2)}$—$H_{(2)}$	U_2	A_1
$I_{(1)}$—$I_{(2)}$, $I_{(1)}$—$O_{(2)}$, $I_{(1)}$—$H_{(2)}$, $O_{(1)}$—$I_{(2)}$, $O_{(1)}$—$O_{(2)}$, $H_{(1)}$—$I_{(2)}$, $H_{(1)}$—$H_{(2)}$	U_3	A_3
$O_{(1)}$—$H_{(2)}$	U_1+U_3	A_1+A_3
$H_{(1)}$—$O_{(2)}$	U_2+U_3	A_2+A_3

Normally, 15 interchange energies U_{ij}^{ab} and 15 interchange free energies A_{ij}^{ab} would be needed to describe the interaction between all possible pairs of contacts of type a on species i and type b on species j. However, differences in the behaviour of the systems under consideration seem to be attributable primarily to differences in the proton accepting facility of the oxygen atoms attached to primary, secondary, and tertiary carbon atoms. We have therefore attempted to describe the interactions by three energy parameters and three free energy parameters according to the scheme shown in Table 5. This scheme singles out the four hydrogen bonds for special consideration, and divides them into two classes according to the host molecule of the oxygen atom involved. In addition it assumes that a nonspecific van der Waals interaction occurs between contacts on unlike molecules.

Detailed equations for the calculation of A_V^E and U_V^E can be found in Barker's original publications,[7,8] examples of their application to particular cases being also available.[8,10] The presentation here is limited to outlining the course of the calculations leading to the final selection of the interchange energies and free energies summarized in Table 6. The use of these parameters in the formulas of Barker leads to the results represented by the points in Figs. 3—5.

The methanol-isomeric butyl alcohol mixtures were considered first since experimental results for both A_V^E and U_V^E were available. In methanol–*n*-butyl alcohol and methanol–isobutyl alcohol mixtures, all of the oxygen atoms are attached to primary carbons. For these mixtures, A_1 and A_2 were set equal to -11420 J mol^{-1} and U_1 and U_2 to -28200 J mol^{-1}, where the numerical values are the same as those used by Barker and Smith[8]

Table 6. Values of interchange parameters for methanol–isomeric butyl alcohol mixtures and *n*-butyl alcohol–isomeric butyl alcohol mixtures

Component 1	Component 2	Interchange parameters J mol^{-1}					
		U_1	A_1	U_2	A_2	U_3	A_3
Methanol	*n*-Butyl alcohol	−28200	−11420	−28200	−11420	50	50
Methanol	Isobulyl alcohol						
Methanol	*sec*-Butyl alcohol	−28200	−11420	−30700	−14320	50	50
Methanol	*t*-Butyl alcohol	−28200	−11420	−32730	−15420	50	50
n-Butyl alcohol	Isobulyl allcoho	−28200	−11420	−28200	−11420	3.3	3.3
n-Butyl alcohol	*sec*-Butyl alcohol	−28200	−11420	−29180	−12800	3.3	3.3
n-Butyl alcohol	*t*-Butyl alcohol	−28200	−11420	−30960	−13650	3.3	3.3

9) G. C. Benson and V. T. Lam, *J. Colloid Interfac. Sci.*, **38**, 294 (1972).

10) G. C. Benson, S. Murakami, and D. E. G. Jones, *J. Chem. Thermodyn.*, **3**, 719 (1971).

for the hydrogen bonds in acetone–ethanol mixtures. The nonspecific interaction was assumed to be the same between methanol and any of the butyl alcohol molecules. It was further assumed that $U_3=A_3$; this also is in line with the findings for acetone–ethanol. Quite clearly these assumtions foregothe possibility of distinguishing theoretically between methanol–*n*-butyl alcohol and methanol–isobutyl alcohol mixtures. The experimental values of U_V^E for both sets of mixtures are very similar and a value of 50 J mol^{-1} for U_3 provides a fairly good representation of either. It can be seen from Fig. 3 that the points calculated for A_V^E reach a maximum falling between the peaks of the two experimental curves. Better individual fits of A_V^E were obtained by adjusting A_3 separately for each system, but even in that case it was not possible to reproduce the negative values of A_V^E observed experimentally. In both methanol–*sec*-butyl alcohol and methanol–*t*-butyl alcohol mixtures, A_2 and U_2 can be expected to differ from A_1 and U_1 since the configurations around the oxygen atoms are different. Values of A_2 and U_2 were obtained by successively adjusting them to make the theoretical results for A_V^E and U_V^E approximate the experimental observations.

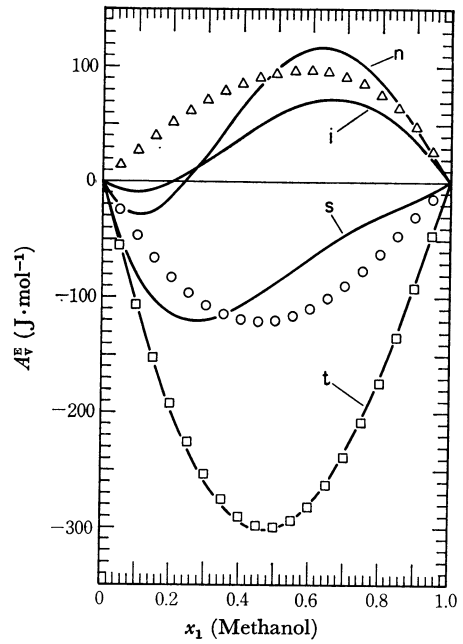

Fig. 3. Comparison of theoretical and experimental excess free energies at constant volume for methanol–isomeric butyl alcohol mixtures at 25°C. Points calculated from Barker theory; △: methanol–*n*-butyl alcohol and methanol–isobutyl alcohol; ○: methanol–*sec*-butyl alcohol; □: metanol–*t*-butyl alcohol. Curves represent the smoothed experimental results. Labels *n*, *i*, *s*, and *t* indicate the four isomeric butyl alcohols used as second components.

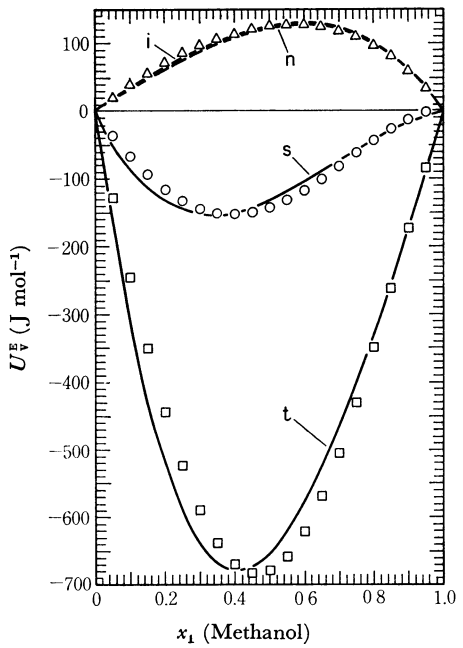

Fig. 4. Comparison of theoretical and experimental excess energies at constant volume for methanol–isomeric butyl alcohol mixtures at 25°C. Significances of points curves and labels are the same as in Fig. 3.

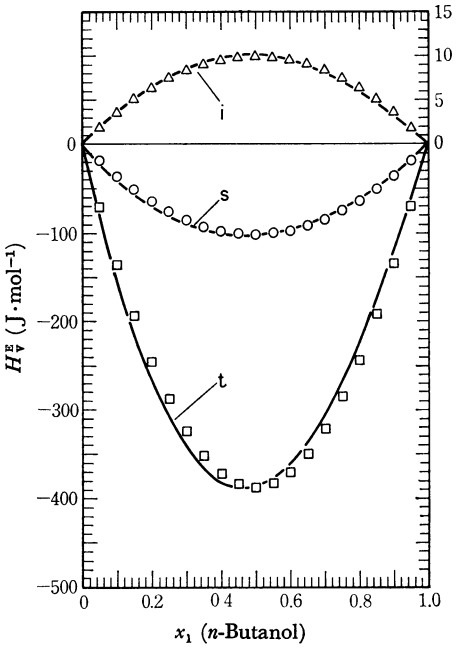

Fig. 5. Comparison of theoretical and experimental excess energies at constant volume for *n*-butyl alcohol–isomeric butyl alcohol mixtures at 25°C. Points calculated from Barker theory; △: *n*-butyl alcohol–isobutyl alcohol; ○: *n*-butyl alcohol–*s*-butyl alcohol; □: *n*-butyl alcohol–*t*-butyl alcohol. Curves represent the smoothed experimental results. Labels *i*, *s*, and *t* indicate the three isomeric butyl alcohols used as second components. Ordinate scale at right is for mixtures containing isobutyl alcohol, and ordinate scale at left is for those containing *sec*-butyl alcohol or *t*-butyl alcohol.

Calculations for *n*-butyl alcohol–isomeric butyl alcohol mixtures followed as closely as possible the treatment described for the methanol systems. However, since experimental results for A_V^E were not available it was further assumed that the bond interchange entropy terms

$$TS_{ij}^{ab} = U_{ij}^{ab} - A_{ij}^{ab} \qquad (4)$$

were the same as in the corresponding methanol systems. Fitting the U_V^E results for *n*-butyl alcohol–isobutyl alcohol led to a value of 3.3 J mol^{-1} for the nonspecific interchange energy between *n*-butyl alcohol and its isomers. Values of U_2 for the hydrogen bonds at secondary

and tertiary OH groups were then obtained by adjusting the calculations to fit U_V^E for mixtures of *n*-butyl alcohol with *sec*-butyl alcohol and *t*-butyl alcohol.

It should be noted that the calculations for methanol mixtures give values for the parameters characterizing the hydrogen bonds at secondary and tertiary OH groups which differ by five to ten percent from those resulting from the calculations for *n*-butyl alcohol mixtures. If the values of A_2 and U_2 obtained from the methanol mixtures are used to estimate U_V^E for mixtures of *n*-butyl alcohol with *sec*-butyl alcohol and *t*-butyl alcohol, the results have the correct sign but are three to five times larger in magnitude than observed experimentally. Thus it appears that estimates of U_V^E are fairly sensitive to the values of the interchange parameters used to describe the hydrogen bonds.

In summary, the Barker model described above reproduces the thermodynamic behavior of *n*-butyl alcohol–isomeric butyl alcohol mixtures fairly satisfactorily. Although it is doubtful that the absolute values of the bond interchange parameters are meaningful, the general features of these values are reasonable. In particular, the nonspecific interactions are very small compared to the hydrogen bonding, and furthermore the nonspecific interaction between the isomeric butyl alcohol is smaller than that between methanol and the butanols. Finally, the relative order of the values for the hydrogen bonds agrees with experimental evidence indicating that the proton accepting facility of the oxygen atoms in the present alcohols increases in the order primary<secondary<tertiary.[11]

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11) W. Gerrard and E. D. Macklen, *Chem. Rev.*, **59**, 1105 (1959)