Whereas the boundary formation process used by Harris et al. was adequate for large concentration gradients (as in the Gouy method), a sharp boundary could not be formed in this way for small concentration gradients (as in the birefringence method), and this led to the design of the present cell. Its advantages are, as this study has shown, first the ability to work with both aqueous and organic systems, and second the ability to form sharp boundaries with small- and large-concentration gradients.

In addition, the larger reservoirs, coupled with two holes instead of one, enable a more efficient washing of the region above the boundary than the prototype used by Harris et al. (7).

Only one Gouy run has been carried out for the system benzene-carbon tetrachloride with the new cell, but it is believed that this cell will be used to its full potential if a concentration dependence study for a number of organic systems is done using Gouy and birefringence methods.

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Excess Enthalpies, Volumes, and Surface Tensions of Isomeric Butanol-*n*-decanol Mixtures

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Enthalpies of mixing, volumes of mixing, and surface tensions were measured for the three binary systems: isobutanol–*n*-decanol, *sec*-butanol–*n*-decanol, and *tert*-butanol–*n*-decanol. All determinations were carried out at 25°C, except for the calorimetric measurements on the system *tert*-butanol–*n*-decanol, which were made at 26°C. Correlation of the results by the theory of Flory combined with the principle of corresponding states was investigated.

Previous publications *(1, 8, 10)* from our laboratory have described investigations of the excess properties of the system *n*-butanol–*n*-decanol. These studies have been extended by measuring the excess enthalpies, excess volumes, and surface tensions of the binary systems formed by mixing isobutanol, *sec*-butanol, and *tert*-butanol with *n*-decanol.

Experimental

Isobutanol (2-methyl-1-propanol), *sec*-butanol (2-butanol), *tert*-butanol (2-methyl-2-propanol), and *n*-decanol were purified chromatographically *(9, 10)*. The purity of all samples used for the mixtures exceeded 99.8%.

Details of the experimental apparatus and procedures have been described previously *(5, 6, 8, 10)*. Except where indicated otherwise, all measurements were made at 25.00° ± 0.01°C.

Excess enthalpies for the systems isobutanol–*n*-decanol and *sec*-butanol–*n*-decanol were determined in the successive dilution calorimeter of Pope et al. *(10)*. The modified form of that calorimeter *(6)* (containing a cooling module) was used to study the system *tert*-butanol–*n*-decanol, and the measurements were made at 26.00° ± 0.01°C since it was difficult to operate the calorimeter at 25°C with *tert*-butanol as a supercooled liquid *(9)*. The error of the calorimetric measurements is believed to be less than 1%.

Volumes of mixing were measured directly in a dilatometer *(8)* using a successive dilution technique. The overall errors of the results for equimolar mixtures are estimated to be about 1%.

Surface tensions of the pure liquids and of their binary mixtures were determined by the maximum bubble pressure method *(5)*. The bubbler was calibrated frequently with research grade benzene (Phillips Petroleum Co.), assuming a surface tension of 28.20 dyn cm^{-1} for that material at 25°C. Values of the surface tension were generally reproducible within ±0.03 dyn cm^{-1}.

Results and Discussion

The experimental results for the molar excess enthalpy and molar excess volume are listed in Tables I and II. For each system, x_1 denotes the mole fraction of the butanol isomer. The observed surface tensions, along with values of the excess surface tension defined by the equation

$$\gamma^E = \gamma - x_1\gamma_1 - x_2\gamma_2 \qquad (1)$$

are summarized in Table III.

The method of least squares was used to fit the results for each of the excess functions with an equation of the form

$$X^E = x_1x_2 \sum_{j=1}^{n} c_j(x_2 - x_1)^{j-1} \qquad (2)$$

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Table I. Molar Excess Enthalpies

(*x_1 mole fraction of butanol isomer; H^E, J mol^{-1}*)

Isobutanol–*n*-decanol at 25° C		*sec*-Butanol–*n*-decanol at 25° C		*tert*-Butanol–*n*-decanol at 26° C	
x_1	H^E	x_1	H^E	x_1	H^E
0.0549	56.5	0.0520	41.9	0.0835	3.3
0.1158	115.0	0.1236	94.0	0.1681	6.5
0.2180	198.3	0.2117	149.2	0.2585	9.9
0.3229	261.1	0.3148	199.5	0.3524	13.4
0.4229	299.6	0.4059	230.5	0.4305	16.3
0.5179	315.4	0.4932	248.2	0.4993	18.7
0.5932	313.2	0.6337	248.2	0.5723	21.1
0.6544	300.5	0.6516	244.5	0.6194	22.2
0.7055	282.5	0.6872	237.3	0.6566	22.9
0.7198	275.5	0.7055	232.2	0.6935	23.1
0.7480	261.2	0.7356	221.3	0.6969	23.6
0.7715	248.3	0.7582	213.1	0.7264	23.3
0.8205	213.7	0.8098	186.9	0.7374	23.4
0.8652	174.3	0.8591	153.6	0.7798	22.7
0.9042	133.3	0.9019	117.2	0.8343	20.6
0.9399	89.3	0.9395	78.4	0.8811	17.5
0.9679	50.1	0.9676	44.3	0.9150	14.3
0.9857	22.8	0.9880	17.0	0.9429	10.6
				0.9684	6.5
				0.9847	3.4

Table II. Molar Excess Volumes at 25° C

(x_1 mole fraction of butanol isomer; V^E, cm^3 mol^{-1})

Isobutanol–*n*-decanol		*sec*-Butanol–*n*-decanol		*tert*-Butanol–*n*-decanol	
x_1	V^E	x_1	V^E	x_1	V^E
0.0456	0.0156	0.0333	0.0091	0.0768	−0.0042
0.0995	0.0310	0.0864	0.0262	0.1634	−0.0114
0.1676	0.0479	0.1503	0.0461	0.2525	−0.0229
0.2538	0.0635	0.2319	0.0669	0.3458	−0.0352
0.3442	0.0745	0.3157	0.0844	0.4289	−0.0471
0.4273	0.0800	0.3959	0.0972	0.5032	−0.0589
0.4968	0.0811	0.4682	0.1033	0.5647	−0.0689
0.5560	0.0795	0.5344	0.1060	0.6156	−0.0755
0.6054	0.0770	0.5889	0.1053	0.6420	−0.0803
0.6476	0.0734	0.6350	0.1030	0.6567	−0.0802
0.6810	0.0704	0.6651	0.1014	0.6734	−0.0812
0.7102	0.0663	0.6730	0.0996	0.7071	−0.0813
0.7682	0.0567	0.7032	0.0967	0.7456	−0.0806
0.8082	0.0502	0.7407	0.0907	0.7880	−0.0785
0.8472	0.0427	0.7815	0.0827	0.8327	−0.0729
0.8867	0.0354	0.8241	0.0722	0.8776	−0.0611
0.9252	0.0246	0.8628	0.0606	0.9196	−0.0453
0.9539	0.0163	0.8749	0.0560	0.9547	−0.0285
0.9748	0.0101	0.8993	0.0478	0.9806	−0.0134
0.9892	0.0050	0.9114	0.0426		
		0.9323	0.0342		
		0.9433	0.0285		
		0.9590	0.0217		
		0.9702	0.0157		
		0.9777	0.0125		
		0.9883	0.0062		
		0.9912	0.0051		

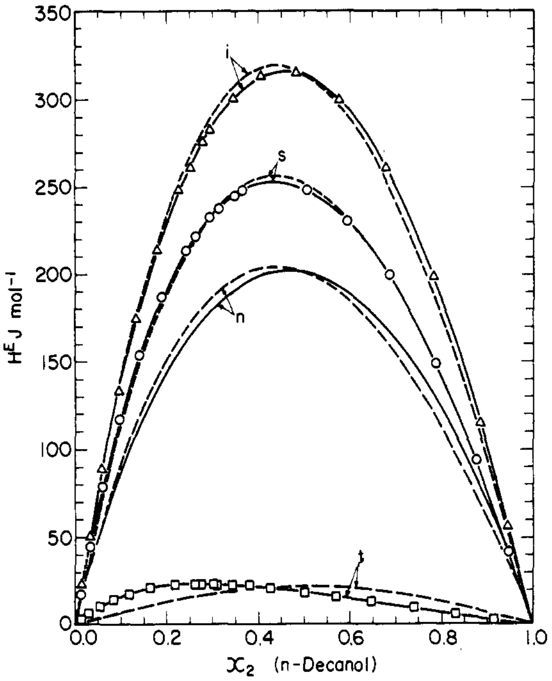

Figure 1. Molar excess enthalpies of isomeric butanol–*n*-decanol systems

Experimental results: △ isobutanol–*n*-decanol at 25°C; ○ *sec*-butanol–*n*-decanol at 25°C; □ *tert*-butanol–*n*-decanol at 26°C. Curves labeled *n*, *i*, *s*, and *t* refer to the different butanol isomers; solid curves are smoothed representations by Equation 2; broken curves were calculated from theory

containing n adjustable coefficients. The minimum number of these needed to represent each set of results adequately was determined from the changes in the standard error of estimate

$$\sigma = [\Sigma(X_{\mathrm{obsd}}{}^E - X^E)^2/(n_{\mathrm{obsd}} - n)]^{1/2} \qquad (3)$$

for successively larger values of n. Values of the coefficients obtained from this analysis are given in Table IV along with the standard error of estimate associated with each representation. Plots of the experimental results and of their least-squares representations are shown in Figures 1–3, where curves for the system *n*-butanol–*n*-decanol (taken from ref. *1*, *8*, and *10*) are also included.

In Figure 1, the curves for H^E decrease in the order isobutanol > *sec*-butanol > *n*-butanol > *tert*-butanol. Apart from the position of the *n*-butanol curve, this order is the same as the order observed for methanol–isomeric butanol systems *(9)*, which [as noted previously *(9)*] correlates fairly well with the proton-accepting facility of the oxygen atoms in the butanol isomers. However, H^E is positive for all of the present systems (at the temperatures of our studies) and is generally greater than H^E for the corresponding methanol system. Thus, it appears that contributions to H^E from the formation of hydrogen bonds between unlike molecules are relatively of less importance than in the methanol systems.

The magnitudes of the volume changes for isomeric butanol–*n*-decanol systems are very similar to those for their methanol counterparts *(9)*. Most of the systems show expansions, but in both sets the values of V^E are predominantly negative for *tert*-butanol mixtures.

The excess surface tensions for all of the isomeric butanol–*n*-decanol systems are positive at 25°C. Similar behavior was observed for most of the binary alcohol systems studied previously *(1)*, but negative γ^E were reported for some methanol–isomeric butanol mixtures. In general, the magnitudes of γ^E for the present set of sys-

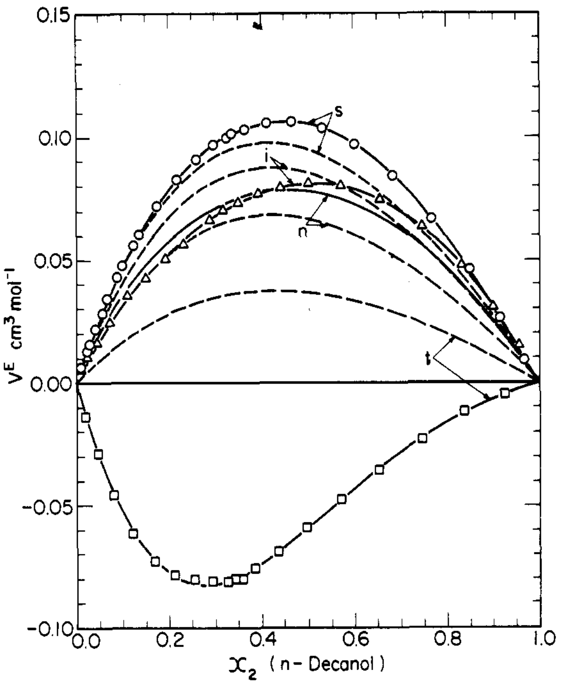

Figure 2. Molar excess volumes of isomeric butanol-*n*-decanol systems at 25°C

Experimental results: △ isobutanol-*n*-decanol; ○ *sec*-butanol-*n*-decanol; □ *tert*-butanol-*n*-decanol. Curves labeled *n*, *i*, *s*, and *t* refer to the different butanol isomers; solid curves are smoothed representations by Equation 2; broken curves were calculated from theory

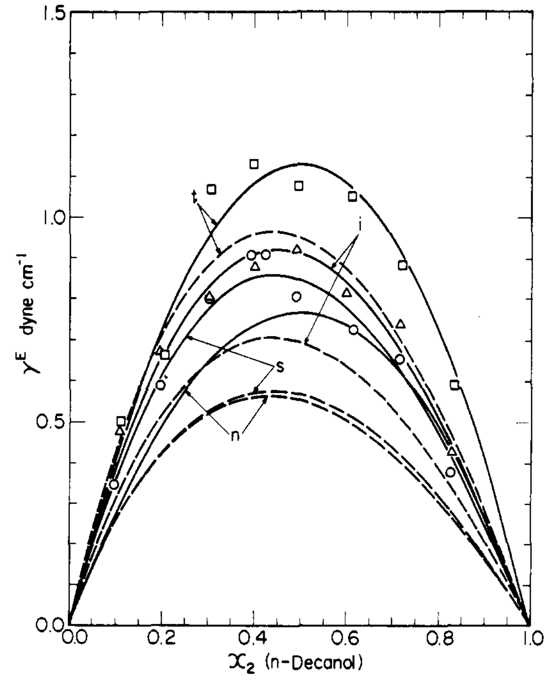

Figure 3. Excess surface tensions of isomeric butanol-*n*-decanol systems at 25°C

Experimental results: △ isobutanol-*n*-decanol; ○ *sec*-butanol-*n*-decanol; □ *tert*-butanol-*n*-decanol. Curves labeled *n*, *i*, *s*, and *t* refer to the different butanol isomers; solid curves are smoothed representations by Equation 2; broken curves were calculated from theory

tems tend to be larger than for the corresponding methanol set, and the relative order of the γ^E curves is inverted. Thus the difference between the two sets is most noticeable for the *tert*-butanol systems for which the values of γ^E have the largest magnitudes but differ in sign.

Correlation of results. Previous calculations *(2)* have shown that useful estimates of the excess volumes of binary *n*-alcohol systems can be derived from their excess enthalpies through an empirical application of the Flory theory of mixtures *(3)*, despite the fact that the original development of the theory specifically excluded hydrogen bonds and strong dipolar interactions *(4)*. The Flory theory has also been used in conjunction with the reduced surface tension equation of Patterson and Rastogi *(7)* to calculate the excess surface tensions of alcohol mixtures *(1)*. Although this treatment was less successful in correlating the excess functions of methanol-*sec*-butanol and methanol-*tert*-butanol mixtures than in the case of binary *n*-alcohol mixtures, an investigation of its application to the present systems appeared worthwhile.

The formulas needed for this treatment have been outlined several times *(2, 5)* and will not be repeated here. Characteristic pressures, volumes, and temperatures (p^*, V^*, T^*) for the butanol isomers and *n*-decanol were taken from ref. *1*. The ratio of the molecular surface areas of contact (s_{12}) for each system was calculated from the characteristic volumes on the assumption that the molecules were approximately spherical. Flory's energy parameter, X_{12}, was selected to give a least-squares fit of the theoretical formula for H^E to the smoothed experimental results; in doing this for *tert*-butanol-*n*-decanol the 1° temperature deviation (from 25°C) of the results for H^E was neglected. The values adopted for s_{12} and X_{12} are listed in Table V. Using these values, the broken curves for H^E, V^E, and γ^E in Figures 1-3 were calculated from the theoretical formulas. Standard

Table III. Surface Tensions and Excess Surface Tensions at 25° C
(x_1 mole fraction of butanol isomer; γ and γ^E, dyn cm^{-1})

Isobutanol-*n*-decanol			*sec*-Butanol-*n*-decanol			*tert*-Butanol-*n*-decanol		
x_1	γ	γ^E	x_1	γ	γ^E	x_1	γ	γ^E
0.0000	28.30	0.00	0.0000	28.30	0.00	0.0000	28.30	0.00
0.1724	27.72	0.43	0.1659	27.80	0.38	0.1664	27.53	0.59
0.2834	27.38	0.74	0.2775	27.48	0.65	0.2782	26.91	0.89
0.4003	26.77	0.82	0.3785	27.02	0.72	0.3883	26.17	1.05
0.5080	26.25	0.92	0.5032	26.43	0.80	0.5041	25.25	1.08
0.5985	25.67	0.88	0.5711	26.18	0.90	0.6006	24.51	1.13
0.6984	25.01	0.80	0.6036	26.00	0.90	0.6932	23.69	1.07
0.7995	24.28	0.66	0.6959	25.40	0.79	0.7946	22.46	0.66
0.8929	23.54	0.48	0.7958	24.66	0.58	0.8875	21.54	0.50
1.0000	22.44	0.00	0.8947	23.90	0.34	1.0000	20.11	0.00
			1.0000	23.00	0.00			

Table IV. Coefficients for Least-Squares Fit of Results by Equation 2

System	Function	c_1	c_2	c_3	c_4	σ
Isobutanol–*n*-decanol	H^E, J mol^{-1}	1255.58	−190.97	105.13	−108.71	0.37
	V^E, cm^3 mol^{-1}	0.3231	0.0225	0.0332	−0.0361	0.0008
	γ^E, dyn cm^{-1}	3.646	−0.740			0.045
sec-Butanol–*n*-decanol	H^E, J mol^{-1}	993.90	−223.69	148.48	−99.46	0.41
	V^E, cm^3 mol^{-1}	0.4214	−0.0820	0.0188	−0.0520	0.0005
	γ^E, dyn cm^{-1}	3.393	−0.725			0.044
tert-Butanol–*n*-decanol	H^E, J mol^{-1}	74.73	−65.64	53.08	−28.11	0.17
	V^E; cm^3 mol^{-1}	−0.2376	0.3223	−0.1491		0.0009
	γ^E, dyn cm^{-1}	4.521				0.061

Table V. Comparison of Calculated and Experimental Values of Excess Functions at 25°C System

	n-Butanol–*n*-decanol	Isobutanol–*n*-decanol	*sec*-Butanol–*n*-decanol	*tert*-Butanol–*n*-decanol
Flory parameters				
s_{12}	1.287	1.283	1.289	1.300
X_{12}, J cm^{-3}	8.59	13.25	10.89	3.71
H^E, J mol^{-1}				
Std dev[a]	6.6	6.2	2.8	6.1
Calcd at $x_1 = 0.5$	201.2	314.1	251.6	21.9
Expt at $x_1 = 0.5$	201.3[b]	313.9	248.5	18.7[c]
V^E, cm^3 mol^{-1}				
Std dev[a]	0.0088	0.0089	0.0074	0.0780
Calcd at $x_1 = 0.5$	0.0667	0.0854	0.0948	0.0364
Expt at $x_1 = 0.5$	0.0778[d]	0.0808	0.1053	−0.0594
γ^E, dyn cm^{-1}				
Std dev[a]	0.16[e]	0.15	0.20	0.14
Calcd at $x_1 = 0.5$	0.55	0.70	0.57	0.95
Expt at $x_1 = 0.5$	0.77[e]	0.91	0.85	1.13

[a] Std dev of $X^E = [\int_0^1 (X^E{}_{\text{calcd}} - X^E{}_{\text{expt}})^2 dx_1]^{-1/2}$. [b] Ref. *10.* [c] At 26°C. [d] Ref. *8.* [e] Ref *1.*

deviations between the calculated and smoothed experimental curves are included in Table V along with a comparison of calculated and experimental results for equimolar mixtures.

It can be seen from Figures 1–3 and Table V that the theoretical treatment provides a better correlation of the excess properties of the isomeric butanol–*n*-decanol systems than was found previously for the methanol–isomeric butanol systems *(1)*. Again, the treatment is least satisfactory for the *tert*-butanol system. In particular, the fit of H^E (achieved by adjusting X_{12}) is poorest for *tert*-butanol–*n*-decanol and, although the curves predicted for V^E fall in the observed relative order over most of the concentration range, the values of V^E estimated for *tert*-butanol–*n*-decanol have the wrong sign.

The excess surface tensions are underestimated for all of the present systems but the deviations are relatively small. Bearing in mind that no surface properties of the mixtures or of the component liquids were used in their calculation, the estimates of γ^E appear to be fairly satisfactory. It must be pointed out however, that the corresponding estimates of γ for the mixtures would be too large by several dyn cm^{-1} since estimates for the pure liquids were in error by that amount *(1)*.

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Nomenclature

$c_1, c_2 \cdots c_j$ = coefficients in representation of excess properties by Equation 2
H^E = molar excess enthalpy, J mol^{-1}
n = number of coefficients in Equation 2
p^* = characteristic pressure in Flory theory
s_{12} = ratio of molecular surface areas of contact, approximated by $(V_2^*/V_1^*)^{1/3}$
T^* = characteristic temperature in Flory theory
V^E = molar excess volume, cm^3 mol^{-1}
V^* = characteristic molar volume in Flory theory
X^E = typical excess property
x_i = mole fraction of component i
X_{12} = interaction energy parameter in Flory theory

Greek Letters

γ = surface tension, dyn cm^{-1}
γ^E = excess surface tension defined by Equation 1
γ_i = surface tension of pure component i
σ = standard error of estimate defined by Equation 3

Subscripts

1 = first component of mixture, one of the isomeric butanols
2 = second component of mixture, *n*-decanol

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