and negative deviations from mole fraction additivity of the molar Gibbs free energies of activation for flow. The extent of the deviations in the systems increases somewhat in the order III > II > I, although the difference is not a gross one. Presumably the systems should be fairly typical of the extent of interaction to be expected in systems not possessing strong specific interactions such as acid-base or hydrogen bonding.

Viscosity results in the ternary subsystems showed that the ternary fitting term is of varying importance, ranging at equimolarity from about 2 to 40 cal. per mole. For the quaternary systems, Table II shows that the quaternary term in Equation 1 is significant only for system III. Only there is that term significantly greater than the typical standard error of 4 cal. per mole in the ternary subsystems to whose ternary constants the quaternary constants are related. System III is the only one in which at least one of the greater chain-lengthed components is not part of each ternary subsystem. It may, therefore, be argued that it is the perturbation by *n*-hexadecane of the carbon tetrachloride–benzene–hexane ternary subsystem that is responsible for the need of the quaternary constant in system III.

In the ternary subsystems, the ternary terms in Equation 1 for ΔV^E were generally less important than those for $\Delta^* G^E$. For five of those eleven systems the ternary term contributed at equimolarity essentially the same amount as the standard error in the system. Table II shows that there is also some difference in the significance of the quaternary constants for ΔV^E, paralleling the behavior of the quaternary terms for $\Delta^* G^E$.

Table I shows that in the binary and ternary subsystems, $\Delta^* G^E$ and ΔV^E are poorly correlated if it is assumed that free volume effects are dominant in governing viscosity behavior in these systems.

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NOMENCLATURE

A_{ij}, B_{ij}, C_{ij} = binary constants of Equation 1
A_{ijk} = ternary constant of Equation 1
A_{ijkl} = quaternary constant of Equation 1
$\Delta^* G$ = molar Gibbs free energy of activation of flow, cal. per mole
N = Avogadro number
R = gas constant, cal. per deg. mole
T = absolute temperature, ° K.
V = molar volume, ml. per mole
ΔV = molar volume of mixing, ml. per mole
X = mole fraction
h = Planck constant, erg sec.
η = dynamic viscosity, poises

Subscripts

i, j, k, l = component(s) associated with given property or symbol

Superscripts

E = excess
i = ideal

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Molar Excess Volumes of Binary Systems of Normal Alcohols at 25° C

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Volumes of mixing at 25° C were measured for the 10 binary systems formed from the components methanol, ethanol, propanol, hexanol, and decanol. The Flory theory of mixtures provides a useful semiquantitative correlation between the excess volumes and excess enthalpies of binary normal alcohol systems.

THE EXCESS VOLUMES of a number of binary normal alcohol systems, containing either butanol (BuOH) or octanol (OcOH) as one component, were reported in a previous publication (*8*). As an extension of this work the present paper describes the volume changes which occur when pairs of normal alcohols, selected from the list—methanol (MeOH), ethanol (EtOH), propanol (PrOH), hexanol (HxOH), and decanol (DeOH)—are mixed in varying proportions at 25° C.

EXPERIMENTAL

The component alcohols used for the present measurements were the same as employed in our previous volumetric and calorimetric studies of normal alcohol systems (*8–10*). Chromatographic analyses indicated that the purity of all the materials exceeded 99.8%.

Volumes of mixing were measured directly in a dilatometer which has been described in detail (*8*). Successive portions of one component liquid are added to a known amount of the other component (50 to 100 cc) confined over mercury at constant temperature and atmospheric

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Table I. Molar Excess Volumes at 25° C

(x_1 mole fraction of component with shorter hydrocarbon chain length, V^E cm^3 mole^{-1})

MeOH-EtOH	
x_1	V^E
0.0372	0.0012
0.0430	0.0015
0.0878	0.0027
0.0944	0.0029
0.1575	0.0043
0.1645	0.0043
0.2348	0.0058
0.2422	0.0059
0.3092	0.0071
0.3164	0.0069
0.3798	0.0078
0.3890	0.0078
0.4444	0.0084
0.4543	0.0082
0.5017	0.0085
0.5108	0.0083
0.5505	0.0086
0.5603	0.0084
0.5932	0.0085
0.5954	0.0093
0.6024	0.0082
0.6277	0.0084
0.6370	0.0090
0.6814	0.0088
0.7284	0.0081
0.7785	0.0073
0.8280	0.0062
0.8743	0.0050
0.9185	0.0035
0.9564	0.0021
0.9823	0.0009

MeOH-PrOH	
x_1	V^E
0.0497	0.0072
0.1231	0.0171
0.2060	0.0275
0.2923	0.0366
0.3764	0.0436
0.4510	0.0483
0.5188	0.0509
0.5752	0.0517
0.6219	0.0514
0.6383	0.0504
0.6617	0.0504
0.6776	0.0493
0.7194	0.0470
0.7624	0.0436
0.8076	0.0386
0.8516	0.0326
0.8934	0.0253
0.9315	0.0173
0.9643	0.0098
0.9855	0.0041

MeOH-HxOH	
x_1	V^E
0.0643	0.0136
0.0914	0.0181
0.1732	0.0385
0.1920	0.0411
0.2876	0.0664
0.3091	0.0701
0.3958	0.0921
0.4207	0.0973
0.4908	0.1145
0.5138	0.1178
0.5699	0.1299
0.5841	0.1306
0.6345	0.1387
0.6489	0.1387
0.6847	0.1422
0.6997	0.1417
0.7256	0.1428
0.7392	0.1411
0.7522	0.1402
0.7580	0.1408
0.7710	0.1385
0.7824	0.1368
0.7845	0.1374
0.7964	0.1348
0.8135	0.1310
0.8463	0.1214
0.8778	0.1083
0.9075	0.0917
0.9139	0.0877
0.9347	0.0719
0.9400	0.0675
0.9585	0.0501
0.9629	0.0461
0.9798	0.0261
0.9808	0.0260
0.9929	0.0093
0.9931	0.0098

MeOH-DeOH	
x_1	V^E
0.0445	0.0110
0.1096	0.0312
0.1882	0.0582
0.2710	0.0892
0.3612	0.1248
0.3922	0.1366
0.4551	0.1604
0.4871	0.1732
0.5395	0.1902
0.5729	0.2027
0.6100	0.2115
0.6478	0.2232
0.6691	0.2255
0.6993	0.2322
0.7175	0.2322
0.7297	0.2328
0.7440	0.2344
0.7606	0.2339
0.7817	0.2335
0.7911	0.2319
0.8129	0.2287
0.8206	0.2265
0.8388	0.2216
0.8488	0.2173
0.8604	0.2126
0.8748	0.2043
0.8985	0.1875
0.9233	0.1634
0.9447	0.1350
0.9618	0.1049
0.9792	0.0650
0.9923	0.0266

EtOH-PrOH	
x_1	V^E
0.0361	0.0011
0.0787	0.0024
0.1508	0.0038
0.2130	0.0050
0.2748	0.0061
0.3382	0.0071
0.3967	0.0077
0.4507	0.0081
0.5009	0.0083
0.5285	0.0086
0.5440	0.0084
0.5666	0.0087
0.5817	0.0084
0.6084	0.0085
0.6544	0.0084
0.7046	0.0079
0.7587	0.0072
0.8066	0.0061
0.8590	0.0049
0.9073	0.0034
0.9503	0.0019
0.9788	0.0008

EtOH-HxOH	
x_1	V^E
0.0560	0.0035
0.1357	0.0092
0.2203	0.0152
0.3097	0.0222
0.3960	0.0288
0.4764	0.0346
0.5414	0.0387
0.5977	0.0412
0.6463	0.0428
0.6846	0.0427
0.6850	0.0433
0.7173	0.0434
0.7205	0.0425
0.7592	0.0417
0.7992	0.0396
0.8395	0.0368
0.8783	0.0318
0.9126	0.0259
0.9446	0.0184
0.9687	0.0114
0.9870	0.0051

EtOH-DeOH	
x_1	V^E
0.0667	0.0138
0.0791	0.0165
0.1658	0.0341
0.1949	0.0406
0.2787	0.0555
0.3242	0.0636
0.3895	0.0730
0.4388	0.0806
0.4845	0.0861
0.5366	0.0926
0.6166	0.0995
0.6769	0.1022
0.6782	0.1022
0.7128	0.1030
0.7254	0.1024
0.7507	0.1022
0.7626	0.1008
0.7900	0.0990
0.7922	0.0984
0.8308	0.0937
0.8701	0.0848
0.9065	0.0721
0.9401	0.0546
0.9689	0.0331
0.9884	0.0137

PrOH-HxOH	
x_1	V^E
0.0482	0.0030
0.1028	0.0058
0.1751	0.0093
0.2561	0.0123
0.3329	0.0148
0.4073	0.0171
0.4736	0.0183
0.5298	0.0191
0.5792	0.0194
0.5882	0.0191
0.6205	0.0194
0.6242	0.0190
0.6565	0.0190
0.6634	0.0186
0.7050	0.0180
0.7488	0.0170
0.7943	0.0156
0.8403	0.0135
0.8830	0.0109
0.9226	0.0079
0.9561	0.0052
0.9838	0.0020

PrOH-DeOH	
x_1	V^E
0.0693	0.0227
0.2531	0.0628
0.3540	0.0773
0.4434	0.0857
0.5224	0.0895
0.5884	0.0901
0.6424	0.0882
0.6871	0.0854
0.7226	0.0820
0.7520	0.0784
0.7888	0.0717
0.8242	0.0650
0.8601	0.0567
0.8938	0.0469
0.9243	0.0363
0.9514	0.0250
0.9737	0.0147
0.9884	0.0069

HxOH-DeOH	
x_1	V^E
0.0429	0.0065
0.0468	0.0078
0.0945	0.0139
0.1042	0.0149
0.1641	0.0218
0.1818	0.0232
0.2411	0.0284
0.2654	0.0302
0.3146	0.0333
0.3810	0.0359
0.4475	0.0372
0.5048	0.0375
0.5548	0.0369
0.5723	0.0374
0.5975	0.0352
0.6338	0.0336
0.6489	0.0350
0.6930	0.0326
0.7393	0.0296
0.7877	0.0259
0.8365	0.0213
0.8811	0.0162
0.9231	0.0110
0.9587	0.0063
0.9823	0.0025

Table II. Coefficients for Least-Squares Fit of Results by Equation 1

(Units cm^3 mole^{-1})

System	c_1	c_2	c_3	c_4	c_5	c_6	$10^4\sigma_V$
MeOH-EtOH	0.0341	−0.0089	0.0100				2.2
MeOH-PrOH	0.2011	−0.0640	0.0167	−0.0077			1.7
MeOH-HxOH	0.4641	−0.4092	0.2032	−0.1799	0.144		7.2
MeOH-DeOH	0.7134	−0.7580	0.3395	0.0293	0.661	−0.911	17.2
EtOH-PrOH	0.0337	−0.0077	0.0031				1.3
EtOH-HxOH	0.1451	−0.1219	0.0424	−0.0434	0.052		2.7
EtOH-DeOH	0.3541	−0.2441	0.1602	−0.0556	0.186	−0.234	3.8
PrOH-HxOH	0.0749	−0.0249	0.0058	−0.0049	0.019		1.4
PrOH-DeOH	0.3559	−0.0791	0.0571	−0.0260	0.072		2.7
HxOH-DeOH	0.1500	0.0028	0.0148				4.5

pressure. At each stage, the volume change accompanying the dilution is obtained from the change in level of the mercury in a capillary tube. Three sizes (nominal i.d. 1.7, 1.0, and 0.5 mm) of Tru-bore tubing were used for the latter; selection of the capillary for a particular system was based on the magnitude of the volume change expected. The dilatometer was immersed in a water bath operated at 25.00 ± 0.01°C and controlled to ±0.001°C during a run. Estimates of the over-all error of the results for equimolar mixtures vary from about ±0.5% in cases where the molar excess volume is about 0.2 cm^3 mole^{-1} to ±5% where the excess volume is about 0.002 cm^3 mole^{-1}.

RESULTS

Table I contains the results for the molar excess volumes (V^E) of the 10 systems investigated. For each system x_1 represents the mole fraction of the component having the shorter hydrocarbon chain length. Values of the coefficients in the equation

$$V^E = x_1(1 - x_1) \sum_{q=1}^{n} c_q(1 - 2x_1)^{q-1} \tag{1}$$

which were determined to fit the results for each system by a least-squares procedure, are given in Table II. The last column of the table lists the standard error of the estimate associated with the use of Equation 1.

DISCUSSION

The theory of Flory (*3*) has been useful in interpreting the results of measurements of the excess properties of a number of binary systems formed from molecular species which differ in size and shape (*1, 2, 4, 7*). Although in the development of the theory, hydrogen bonds and strong dipolar interactions were specifically excluded (*4*), we have found that a purely empirical application of the Flory formalism to binary normal alcohol systems provides an interesting correlation between the excess volumes and excess enthalpies of these hydrogen-bonded systems. In the remainder of this discussion, the Flory theory is reviewed briefly and its application to our results is described.

According to the Flory theory, a molecule consists of r segments (isometric portions), each having s intermolecular contact sites which can interact with neighboring sites. The molar volume, v, of a pure liquid is given by

$$\mathrm{v} = rv = \mathrm{v}^*\tilde{v} \tag{2}$$

where v is the volume of a mole of segments, v* is a characteristic (hard core) volume, and $\tilde{v}$ is the reduced volume. At temperature T, the value of $\tilde{v}$ can be calculated from the coefficient of thermal expansion α, using the expression

$$\tilde{v} = [(1 + \tfrac{1}{3}\alpha T)/(1 + \alpha T)]^3 \tag{3}$$

At zero pressure, the reduced volume and reduced temperature $\tilde{T}$ satisfy the equation of state

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{4}$$

Characteristic values of the temperature and pressure (T^* and p^*, respectively) can be obtained from the relations

$$T^* = T/\tilde{T} \tag{5}$$

and

$$p^* = (\alpha/\beta)T\tilde{v}^2 \tag{6}$$

where β is the isothermal compressibility.

It is assumed that Equation 4 is valid for mixtures as well as for the pure liquids. Flory has shown that the reduced temperature appropriate for a mixture of two species of molecules (indicated by subscripts 1 and 2) at mole fraction x_1 is

$$\tilde{T} = (\phi_1 p_1^* \tilde{T}_1 + \phi_2 p_2^* \tilde{T}_2)/(\phi_1 p_1^* + \phi_2 p_2^* - \phi_1\theta_2 X_{12}) \tag{7}$$

where ϕ_1 and ϕ_2 are segment fractions defined by

$$\phi_2 = 1 - \phi_1 = x_2/(x_2 + x_1 r_1/r_2) \tag{8}$$

and the site fraction θ_2 is defined by

$$\theta_2 = \phi_2/(\phi_2 + \phi_1 s_1/s_2) \tag{9}$$

In Equation 7, X_{12} is a constant which characterizes the difference in the energy of interaction between sites on neighboring molecules of different species, from the average of the interaction energies in the pure component liquids.

It is usual to treat X_{12} as an adjustable parameter and to determine its value by fitting the theoretical expression for the molar excess enthalpy

$$H^E_{\text{Flory}} = x_1 p_1^* \mathrm{v}_1^*(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + x_2 p_2^* \mathrm{v}_2^*(\tilde{v}_2^{-1} - \tilde{v}^{-1}) + x_1 \mathrm{v}_1^* \theta_2 X_{12} \tilde{v}^{-1} \tag{10}$$

to experimental results. Values of the molar excess volume can then be calculated from the formula

Table III. Properties of Pure Component Liquids at 25° C

	v,[a] Cm^3 Mole^{-1}	$10^3\alpha$,[b] Deg^{-1}	$10^6\beta$[c], Atm^{-1}	v*, Cm^3 Mole^{-1}	T^*, Deg K	p^*, J, Cm^{-3}
MeOH	40.73	1.185	126.4	31.71	4784	467.3
EtOH	58.68	1.083	116.5	46.41	5011	449.0
PrOH	75.16	0.981	102.5	60.43	5287	447.3
BuOH	91.96	0.937	94.5	74.48	5425	456.6
HxOH	125.26	0.852	84.3	102.96	5734	451.9
OcOH	158.42	0.818	78.9	131.02	5877	457.9
DeOH	191.43	0.804	73.9	158.72	5939	478.1

[a] Based on densities from (*10*). [b] Obtained from densities tabulated at various temperatures (*12*). [c] Adiabatic compressibilities derived from sound velocities (*11*) were converted to isothermal compressibilities using values of v and α indicated in columns 2 and 3, combined with heat capacities from the following sources: MeOH (*12*), EtOH (*12*), PrOH (*12*), BuOH (*6*), HxOH (*5*), OcOH (*5*), and DeOH (extrapolated from lower members of series).

Table IV. Application of Flory Theory to Binary Normal Alcohol Systems at 25° C

System	X_{12}, J Cm^{-3}	$\sigma_H(X_{12})$, J Mole^{-1}	H^E (0.5), J Mole^{-1} Theory	H^E (0.5), J Mole^{-1} Expt.	V^E (0.5), Cm^3 Mole^{-1} Theory	V^E (0.5), Cm^3 Mole^{-1} Expt.
MeOH-EtOH	0.556	0.3	4.5	4.5	0.0066	0.0085
MeOH-PrOH	8.58	2.1	82.6	82.1	0.0648	0.0503
MeOH-BuOH	14.26	6.5	144.8	142.4	0.0909	0.0738
MeOH-HxOH	22.73	19.1	245.2	236.1	0.1321	0.1160
MeOH-OcOH	31.12	25.9	352.7	337.6	0.1665	0.1563
MeOH-DeOH	35.64	32.2	418.1	397.4	0.1418	0.1783
EtOH-PrOH	1.57	0.4	19.5	19.2	0.0096	0.0084
EtOH-BuOH	3.67	1.6	48.6	48.1	0.0140	0.0121
EtOH-HxOH	8.96	4.4	128.3	126.4	0.0396	0.0363
EtOH-OcOH	14.61	7.1	222.8	217.5	0.0659	0.0599
EtOH-DeOH	19.35	9.9	309.3	301.0	0.0574	0.0885
PrOH-BuOH	0.343	0.1	5.5	5.4	–0.0009	–0.0019
PrOH-HxOH	3.54	0.7	62.2	61.5	0.0197	0.0187
PrOH-OcOH	8.16	1.9	154.3	153.5	0.0543	0.0513
PrOH-DeOH	12.68	6.4	252.5	252.1	0.0668	0.0890
BuOH-HxOH	1.35	0.3	27.3	27.0	0.0133	0.0115
BuOH-OcOH	4.72	2.2	104.3	103.8	0.0466	0.0413
BuOH-DeOH	8.59	6.6	201.2	201.3	0.0667	0.0778
HxOH-OcOH	0.930	0.6	26.3	26.0	0.0119	0.0098
HxOH-DeOH	3.19	2.3	95.8	95.6	0.0362	0.0375
OcOH-DeOH	0.635	0.3	22.7	22.4	0.0085	0.0075

$$V^E_{\text{Flory}} = (x_1\text{v}_1^* + x_2\text{v}_2^*)(\tilde{v} - \phi_1\tilde{v}_1 - \phi_2\tilde{v}_2) \tag{11}$$

Alternatively, X_{12} could be determined by fitting Equation 11 to experimental results for the molar excess volume and then Equation 10 could be used to calculate the molar excess enthalpy. However, the determination of X_{12} from enthalpy results is a more logical procedure and generally leads to better agreement between theoretical and experimental values (*1, 2*).

The equations outlined above were applied to the set of 21 binary alcohol systems which can be formed from the components MeOH, EtOH, PrOH, BuOH, HxOH, OcOH, and DeOH. Values of v, α, and β for these liquids at 25° C are given in Table III, along with results of calculations of the characteristic volume, temperature, and pressure.

In treating mixtures, the relations

$$r_1/r_2 = \text{v}_1^*/\text{v}_2^* \tag{12}$$

and

$$s_1/s_2 = (\text{v}_2^*/\text{v}_1^*)^{1/3} \tag{13}$$

were used. The first of these assumes that the same hard core volume is valid for segments of each molecular species. The second relation was suggested by Abe and Flory (*1*) for small molecules which were approximately spherical, and has been adopted as part of the formalism of the present treatment. A value of the interaction parameter X_{12} was selected for each system to minimize the integral

$$\sigma_H^2(X_{12}) = \int_0^1 [H^E_{\text{Exptl}} - H^E_{\text{Flory}}(X_{12})]^2 dx_1 \tag{14}$$

where the experimental molar excess enthalpies H^E_{Exptl} were represented by a form analogous to Equation 1 with values of the coefficients taken from (*9*) and (*10*). Theoretical estimates of the molar excess enthalpy and volume for an equimolar mixture were then computed from Equations 10 and 11. The results of these calculations are summarized in Table IV, where equimolar "experimental" values of H^E (*9, 10*) and of V^E [from the present work and (*8*)] are given for comparison.

It is clear from Table IV that significant deviations between theoretical and experimental values of the excess enthalpy occur for systems having large differences in chain length. These deviations may be due in part to the use of Equation 13 and to uncertainties in the values of the properties of the pure component liquids. However it is also probable that the failures to obtain closer fits of the experimental enthalpies reflect a more fundamental weakness of the present treatment which essentially assumes that sites of specific interactions associated with different parts of a molecule can be averaged over the molecule and that a single energy parameter can be used to describe the interactions of unlike molecules in a mixture. Despite these failings, the present treatment yields values of the molar excess volume which are in semiquantitative agreement with the experimental results. Thus it appears that the Flory theory may be of use in estimating excess volumes from excess enthalpy results for other mixtures involving hydrogen-bonded molecules.

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NOMENCLATURE

$c_1, c_2, \ldots, c_q$ = coefficients in representation of molar excess volumes by Equation 1
H^E = molar excess enthalpy
n = number of coefficients in Equation 1
p = pressure
r = number of segments per molecule
s = number of contact sites per segment
T = absolute temperature
v = molar volume
v = volume of a mole of segments
V^E = molar excess volume
x = mole fraction
X_{12} = interaction energy parameter in Flory theory

Greek Letters

α = coefficient of thermal expansion
β = adiabatic compressibility
ϕ = segment fraction

$\sigma_H(X_{12})$ = standard deviation between theoretical and experimental molar excess enthalpies
σ_V = standard error of estimate for representation of molar excess volume results by Equation 1
θ = site fraction

Subscripts

1 = component of binary mixture with shorter hydrocarbon chain
2 = component of binary mixture with longer hydrocarbon chain

Superscripts

* = characteristic values of p, v, and T
$\tilde{}$ = reduced values of v and T

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Vapor-Liquid Equilibria of the Quinary System Hexane, Methylcyclopentane, Cyclohexane, Benzene, and Toluene

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Vapor-liquid equilibria were determined for the quinary system of hexane, methylcyclopentane, cyclohexane, benzene, and toluene at 760 mm of mercury. Ten data points were run for this system. Six additional points were taken on the five possible quaternaries. Nine of the required sets of binary equilibria were obtained from the literature, and the methylcyclopentane-cyclohexane data were experimentally determined by the authors. The Wilson equation was used to predict the experimental values; agreement was excellent.

BATCH FRACTIONATION to separate benzene and cyclohexane azeotrope indicated that the presence of the other three components enhanced the separation. Recent investigations (*6, 8, 16*) wherein accurate multicomponent polar and hydrogen-bonding data have been experimentally determined, have given opportunity to compare the capability of various two-parameter equations to predict highly nonideal multicomponent vapor-liquid equilibria data from binary data. A modified form of the Wilson (*17*) equation assuming ideal vapor mixtures and requiring only binary equilibrium and pure component data served this purpose satisfactorily. Because multicomponent data for different types of systems are not abundant, this investigation was initiated to determine experimental quinary data for a multitype hydrocarbon mixture. In addition, it was desirable to learn the capability of the equation to predict equilibrium data for multicomponent hydrocarbon mixtures at atmospheric pressure from binary data.

EXPERIMENTAL

Materials. The hexane and methylcyclopentane were Phillips pure grade (99 mole % minimum). The cyclohexane was obtained from the Phillips Petroleum Co. as the 99.5 weight % minimum purity grade. The benzene was certified ACS reagent grade solvent from the Fisher Scientific Co., which had been further purified by distillation by Hudson (*8*). The toluene was obtained from the Monsanto Co. Analysis by a GC-2A gas chromatograph indicated that the toluene and benzene exceeded 99.9 mole % purity, and these components were not further purified. The hex-

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