Viscosity in Three Quaternary Liquid Nonelectrolyte Systems

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Viscosities, densities, excess molar Gibbs free energies of activation for flow, and excess molar volumes are reported for mixtures of three quaternary nonelectrolyte systems at 25° C.: *n*-hexadecane–*n*-tetradecane–*n*-hexane–2-bromobutane, *n*-hexadecane–*n*-tetradecane–4-methylcyclohexanone–*n*-hexane, and *n*-hexadecane–carbon tetrachloride–benzene–*n*-hexane. The excess Gibbs free energies of activation for flow and the excess volumes are compared with values previously reported for the binary and ternary subsystems. A quaternary data-fitting term is necessary in only the third of the above systems. In the others, binary and ternary data-fitting terms from the subsystems fit the data well. For the three systems, there is a standard error of 3 cal. per mole and 0.02 to 0.05 ml. per mole for the respective molar properties.

VISCOMETRIC and volumetric behavior in 14 binary (*3*) and 11 ternary (*4*) nonelectrolyte systems has been described. The components varied in molecular size from 1 to 16 carbons, and some gross effects were evident. That work has now been extended to include three quaternary systems composed of the previous binary and ternary subsystems:

I. *n*-Hexadecane–*n*-tetradecane–*n*-hexane–2-bromobutane
II. *n*-Hexadecane–*n*-tetradecane–4-methylcyclohexanone–*n*-hexane
III. *n*-Hexadecane–carbon tetrachloride–benzene–*n*-hexane

The viscometric data include viscosity and excess Gibbs free energy of activation for flow. Volumetric data include density and excess volume of mixing. The molar properties of the quaternary systems are related to those of the binary and ternary subsystems (*3, 4*).

Quaternary studies are useful in testing the validity of terms introduced in ternary systems to account for the deviations of the extensive properties in the latter from the behavior in the binary subsystems. Reported measurements of viscosity in quaternary systems are rare. To the author's knowledge the previous literature contains no data on nonaqueous systems with this number of components.

EXPERIMENTAL

Equipment. A thermostatically controlled bath constant to ±0.01° C. was used. Bath temperature was monitored with a Beckman thermometer, set with a precision thermometer which had been calibrated against an NBS standardized thermometer. Times were measured with an electric stopclock calibrated against an electronic time standard. Weighings were made with a precision balance and certified balance weights. Density determination involved use of a cathetometer which indicated height to the nearest ±0.05 mm.

Densities were determined with Lipkin pycnometers constructed with precision glass capillary tubing of 1-mm. i.d. Total pycnometer volume was 3 ml. Pycnometers were calibrated with distilled water, with heights of liquid in the capillary arms measured then, as in determining unknown densities later, relative to a single etched mark on each arm.

Three Cannon-Fenske viscometers of different capillary diameters were used because of the tenfold range of viscosities of the components. The viscometers were calibrated with freshly obtained NBS oils. Agreement of experimental results with the different viscometers was established. Kinetic energy corrections were applied to viscosity data. Errors due to alignment and loading of viscometers were minimized by reproducible precautionary procedures.

In making determinations, both pycnometers and viscometers were maintained in the bath until at least two consecutive measurements of the liquid height in the capillaries or the flow time indicated that the sample had reached the temperature of the bath. As the ambient temperature was not far below bath temperature, time required for the mixtures to reach bath temperature was short, and evaporation of mixtures from either pycnometers or viscometers was experimentally negligible for even the most volatile mixtures.

Liquids were mixed in a modified glass syringe sealed by glass at the needle end. Again evaporation rates were negligible. Transfer of mixtures to viscometers and pycnometers was by overpressure through capillary tubing. The mixing syringe, transfer tubing, viscometers, and pycnometers were all provided with ball and socket joints to minimize evaporation effects accompanying transfer. Joints were treated with low boiling solvent after sample transfer to remove adhering amounts of high boiling components on those surfaces.

Replication of experimental measurements has not been routinely followed. Uncertainties in the properties presumably should be about the same as those reported for the binary subsystems (*3*): kinematic viscosity, ±0.10%; density, ±0.009%; excess volume, ±0.02 ml. per mole; excess Gibbs free energy of flow, ±0.7 cal. per mole.

Materials. Samples used in the present work were obtained from the same batches for which purification has been described (*3*). A tabulated comparison of the densities,

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Table I. Properties of

First-Named Component		Second-Named Component		Third-Named Component					
Volume fraction[a]	Mole fraction	Volume fraction[a]	Mole fraction	Volume fraction[a]	Mole fraction	Kinematic Viscosity, Cs.	Density, G. per Ml.	Δ^*G^E, Cal. per Mole	ΔV^E, Ml. per Mole
				n-Hexadecane–*n*-Tetradecane–*n*-Hexane–2-Bromobutane					
0.8590	0.7546	0.0506	0.0501	0.0452	0.0887	2.938	0.7869	106.1	−0.02
0.6854	0.5219	0.1091	0.0935	0.1041	0.1770	2.088	0.8066	171.5	0.01
0.4164	0.3130	0.3944	0.3337	0.0852	0.1431	1.982	0.8067	145.8	0.11
0.0939	0.0674	0.6981	0.5638	0.0992	0.1590	1.710	0.8042	126.4	0.09
0.5707	0.3966	0.1438	0.1125	0.1346	0.2090	1.679	0.8264	186.0	0.06
0.1245	0.0823	0.5764	0.4292	0.1451	0.2144	1.428	0.8220	149.9	0.10
0.3325	0.2166	0.3261	0.2392	0.1809	0.2632	1.386	0.8239	169.2	0.02
0.4437	0.2801	0.1712	0.1217	0.1934	0.2727	1.317	0.8390	184.7	0.05
0.1779	0.1089	0.4291	0.2958	0.1861	0.2545	1.201	0.8444	158.1	0.09
0.2547	0.1448	0.2660	0.1703	0.1842	0.2339	1.043	0.8883	160.5	0.18
0.3862	0.2282	0.1012	0.0673	0.4091	0.5401	1.032	0.7738	177.1	−0.30
0.2472	0.1432	0.2644	0.1724	0.2893	0.3743	1.029	0.8310	161.1	−0.05
0.2477	0.1412	0.2574	0.1652	0.2505	0.3190	1.010	0.8567	157.1	0.10
0.2903	0.1588	0.1785	0.1099	0.2004	0.2448	0.9564	0.9047	155.6	0.16
0.1750	0.0988	0.3092	0.1966	0.3059	0.3858	0.9552	0.8338	146.3	−0.03
0.1852	0.1011	0.2928	0.1799	0.1896	0.2312	0.9454	0.9053	145.8	0.20
0.0929	0.0534	0.3811	0.2467	0.4323	0.5551	0.9256	0.7633	138.5	−0.27
0.0922	0.0486	0.3797	0.2253	0.0914	0.1076	0.9111	0.9652	132.8	0.33
0.2567	0.1388	0.1759	0.1070	0.2866	0.3460	0.8924	0.8710	147.8	0.10
0.3289	0.1685	0.0852	0.0491	0.1056	0.1208	0.8812	0.9878	150.4	0.31
0.1674	0.0898	0.2690	0.1626	0.2693	0.3229	0.8779	0.8784	138.8	0.11
0.1677	0.0877	0.1850	0.1090	0.4502	0.5261	0.7665	0.8124	123.9	−0.07
0.1655	0.0813	0.1878	0.1038	0.1748	0.1917	0.7640	0.9749	120.2	0.26
0.1225	0.0554	0.1323	0.0674	0.1428	0.1443	0.6500	1.0422	90.7	0.22
0.1258	0.0625	0.1169	0.0654	0.6148	0.6820	0.6366	0.7680	88.0	−0.13
0.0833	0.0354	0.0954	0.0457	0.1045	0.0992	0.5743	1.1026	61.4	0.16
0.0834	0.0401	0.0843	0.0456	0.7380	0.7924	0.5655	0.7308	60.2	−0.12
0.0482	0.0226	0.0537	0.0283	0.8475	0.8855	0.5177	0.6974	39.5	−0.13
				n-Hexadecane–*n*-Tetradecane–4-Methylcyclohexanone–*n*-Hexane					
0.8450	0.7415	0.0545	0.0539	0.0566	0.1186	3.100	0.7726	59.8	0.16
0.6916	0.5415	0.1057	0.0931	0.0887	0.1659	2.407	0.7690	104.0	0.02
0.0572	0.0456	0.8289	0.7441	0.0603	0.1149	2.303	0.7643	40.2	0.03
0.3921	0.3004	0.4145	0.3576	0.0932	0.1705	2.237	0.7676	78.1	0.11
0.3887	0.2920	0.3961	0.3351	0.1021	0.1832	2.164	0.7678	85.4	0.06
0.5858	0.4280	0.1466	0.1206	0.1297	0.2264	2.140	0.7714	105.5	0.08
0.0906	0.0667	0.7037	0.5834	0.1003	0.1764	2.004	0.7654	63.9	0.00
0.3987	0.2374	0.1102	0.0740	0.3860	0.5490	1.907	0.8106	62.1	0.31
0.1486	0.1036	0.5767	0.4529	0.1438	0.2396	1.873	0.7698	69.1	0.04
0.4605	0.3071	0.1757	0.1319	0.1853	0.2951	1.820	0.7744	98.4	0.02
0.3042	0.1996	0.3273	0.2418	0.1822	0.2856	1.709	0.7716	86.6	0.00
0.3077	0.1831	0.1990	0.1333	0.3024	0.4298	1.609	0.7890	67.7	0.06
0.1793	0.1159	0.4448	0.3237	0.1755	0.2710	1.601	0.7679	78.3	−0.04
0.2674	0.1632	0.2754	0.1892	0.2576	0.3755	1.582	0.7811	68.5	0.02
0.1379	0.0693	0.1477	0.0835	0.5901	0.7078	1.575	0.8376	11.4	0.11

[a] Volume fraction = $X_iV_i/\Sigma X_iV_i$.

viscosities, and refractive indices of the purified components with literature values was included there.

RESULTS AND DISCUSSION

The experimental kinematic viscosities and densities of the mixtures are listed in Table I, as well as the excess molar volumes (ΔV^E) and the excess molar Gibbs free energies of activation for flow (Δ^*G^E). The excess molar volume is defined as $\Delta V^E = V - \Sigma X_iV_i$. The excess molar Gibbs free energy of activation of flow is defined as $\Delta^*G^E = RT\,[\ln \eta\ V - \Sigma X_i \ln \eta_i V_i]$ through combination of $\Delta^*G^i = \Sigma X_i \Delta^*G_i$ and (*1*) $\Delta^*G = RT \ln (\eta V/hN)$.

For quaternary systems Δ^*G^E values have been fitted to the equation

$$\Delta^*G^E = \sum_{\substack{i=1\\i<j}}^{n} X_iX_j\,[A_{ij} + B_{ij}X_i + C_{ij}X_i^2 + \ldots.] + \sum_{i=1}^{n}\sum_{\substack{j=1\\i<j<k}}^{n}\sum_{k=1}^{n} X_iX_jX_kA_{ijk} + X_iX_jX_kX_lA_{ijkl} \qquad (1)$$

The quaternary constants A_{ijkl} for Equation 1 are given in Table II, with the errors in fitting the data. The binary and ternary constants of Equation 1 have been reported (*4*). In each instance fitting has been with the aid of a digital computer, using weighted least-squares procedure (*2*). The adoption of a single constant for the quaternary term in Equation 1 was an arbitrary choice. Higher terms were not considered.

Densities have been included in the present work to relate kinematic and dynamic viscosities and to extend the comparison of volumetric and viscometric behavior noted in the subsystems (*3, 4*). In the quaternary systems the fitting equation between ΔV^E X_i, X_j, X_k, and X_l is precisely of the form of Equation 1 used above for Δ^*G^E. The same procedures for fitting were used for both of these excess properties. Table II includes the results for ΔV^E and the quaternary constants. As with Δ^*G^E, only one quaternary ΔV^E constant was considered in Equation 1.

A quaternary system involves interaction between six pairs of components. Each of the present systems contains a combination of binary subsystems showing both positive

Quaternary Mixtures at 25° C.

First-Named Component		Second-Named Component		Third-Named Component					
Volume fraction[a]	Mole fraction	Volume fraction[a]	Mole fraction	Volume fraction[a]	Mole fraction	Kinematic Viscosity, Cs.	Density, G. per Ml.	Δ^*G^E, Cal. per Mole	ΔV^E, Ml. per Mole
n-Hexadecane–*n*-Tetradecane–4-Methylcyclohexanone–*n*-Hexane (*contd.*)									
0.1944	0.1040	0.1775	0.1069	0.4684	0.5983	1.547	0.8160	26.9	0.11
0.2729	0.1699	0.2877	0.2017	0.1789	0.2661	1.455	0.7638	90.5	−0.22
0.2836	0.1661	0.1983	0.1307	0.2790	0.3903	1.454	0.7807	65.4	−0.06
0.2439	0.1445	0.2541	0.1694	0.2416	0.3417	1.412	0.7726	74.8	−0.11
0.1759	0.0995	0.2614	0.1664	0.2672	0.3608	1.268	0.7722	53.2	−0.13
0.1821	0.1066	0.2962	0.1953	0.1761	0.2463	1.218	0.7536	87.7	−0.22
0.1884	0.1019	0.1802	0.1097	0.3059	0.3952	1.202	0.7752	48.2	−0.16
0.1684	0.0887	0.1611	0.0955	0.3304	0.4156	1.149	0.7773	34.3	−0.18
0.0928	0.0550	0.4041	0.2698	0.0934	0.1323	1.105	0.7338	110.7	−0.35
0.0905	0.0439	0.1109	0.0606	0.3982	0.4615	0.9839	0.7810	−10.3	−0.27
0.1827	0.0989	0.1697	0.1034	0.1740	0.2249	0.9609	0.7402	67.8	−0.31
0.0927	0.0446	0.0920	0.0498	0.3972	0.4563	0.9558	0.7791	−13.6	−0.28
0.1429	0.0741	0.1335	0.0779	0.1299	0.1608	0.7963	0.7208	62.7	−0.35
0.0889	0.0434	0.0827	0.0455	0.0992	0.1158	0.6424	0.7010	35.1	−0.29
n-Hexadecane–Carbon Tetrachloride–Benzene–*n*-Hexane									
0.7871	0.5779	0.0645	0.1432	0.0460	0.1108	2.149	0.8153	182.0	0.20
0.6720	0.4270	0.0899	0.1728	0.0928	0.1939	1.619	0.8348	193.8	0.39
0.4223	0.2048	0.1961	0.2877	0.1849	0.2946	0.9703	0.9233	129.3	0.50
0.3766	0.1718	0.4005	0.5529	0.1002	0.1503	0.9262	1.0886	125.7	0.50
0.3592	0.1567	0.1019	0.1345	0.4000	0.5734	0.9032	0.8742	101.7	0.66
0.3800	0.1941	0.1200	0.1855	0.0931	0.1562	0.8639	0.8305	122.5	0.09
0.2994	0.1296	0.3044	0.3986	0.1952	0.2776	0.7830	1.0114	79.1	0.48
0.2748	0.1153	0.2811	0.3568	0.2532	0.3490	0.7622	0.9995	70.6	0.47
0.2925	0.1318	0.1981	0.2700	0.1806	0.2672	0.7479	0.9100	72.1	0.34
0.2463	0.1030	0.2257	0.2856	0.2691	0.3697	0.7156	0.9486	53.1	0.45
0.2489	0.1045	0.1813	0.2304	0.2953	0.4075	0.7144	0.9133	48.7	0.47
0.2484	0.1059	0.2832	0.3654	0.1841	0.2579	0.7018	0.9841	52.6	0.39
0.1391	0.0499	0.1436	0.1559	0.5818	0.6857	0.6768	0.9281	16.1	0.42
0.1088	0.0376	0.0925	0.0967	0.6885	0.7809	0.6736	0.9008	5.5	0.37
0.1716	0.0648	0.1835	0.2098	0.4562	0.5662	0.6711	0.9411	19.8	0.47
0.1710	0.0662	0.4581	0.5369	0.1862	0.2370	0.6476	1.1377	29.7	0.35
0.0472	0.0154	0.0681	0.0674	0.7873	0.8460	0.6457	0.8937	−14.4	0.23
0.1774	0.0709	0.2800	0.3385	0.2534	0.3326	0.6307	0.9880	16.7	0.38
0.1648	0.0653	0.1872	0.2243	0.3290	0.4281	0.6224	0.9165	6.2	0.43
0.1208	0.0449	0.5998	0.6744	0.1248	0.1523	0.6072	1.2508	12.8	0.24
0.0828	0.0289	0.3847	0.4056	0.4119	0.4717	0.6060	1.1090	−0.7	0.28
0.1670	0.0673	0.3344	0.4077	0.1799	0.2382	0.6059	1.0215	9.4	0.34
0.1631	0.0687	0.2012	0.2565	0.1729	0.2394	0.5876	0.8967	9.6	0.28
0.0783	0.0280	0.6957	0.7538	0.0995	0.1170	0.5812	1.3300	1.2	0.17
0.1255	0.0530	0.1604	0.2047	0.1556	0.2157	0.5458	0.8511	−5.6	0.21
0.0807	0.0307	0.0898	0.1033	0.4036	0.5043	0.5450	0.8314	−45.8	0.62
0.1012	0.0397	0.3965	0.4704	0.1210	0.1559	0.5365	1.0594	−20.4	0.24
0.0922	0.0399	0.1146	0.1499	0.0962	0.1367	0.5107	0.7921	−7.2	0.18
0.0564	0.0245	0.0744	0.0979	0.0726	0.1038	0.4833	0.7460	−12.7	0.13

Table II. Excess Gibbs Free Energy of Activation for Flow and Excess Volume at 25° C.

	Free Energy			Volume		
	Quaternary constant, A_{ijkl}, Eq. 1	Error, Cal. per Mole		Quaternary constant, A_{ijkl}, Eq. 1	Error, Ml. per Mole	
		Stand.[a]	Max.		Stand.[a]	Max.
n-Hexadecane– *n*-tetradecane– *n*-hexane– 2-bromobutane	1042	3.4	7.6	−8.4	0.03	0.10
n-Hexadecane– *n*-tetradecane– 4-methylcyclohexanone– *n*-hexane	−490	3.3	7.0	−2.3	0.02	0.08
n-Hexadecane– carbon tetrachloride– benzene– *n*-hexane	−1824	2.6	6.2	−24.1	0.05	0.17

[a] $\{\Sigma[\text{exptl.} - \text{calcd.}]^2/\text{number of observations}\}^{1/2}$.

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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