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VISCOSITIES AND DENSITIES OF BINARY LIQUID MIXTURES OF 2-BUTOXYETHANOL WITH ANILINE AND *N*-ALKYLANILINE

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ABSTRACT

Viscosities and densities of binary liquid mixtures containing 2-butoxyethanol as one component and aniline or *N*-alkylaniline as the other component have been measured over the whole composition range at five different temperatures. McAllister's approach correlates the viscosity data with a significantly high degree of accuracy for all these systems. From the experimental results, the excess volume, excess viscosity and excess molar free energy of activation of flow have been evaluated and the departure from ideal behaviour is explained on the basis of specific interactions between the components in these mixtures.

As a part of our studies on the thermodynamic properties of binary mixtures of aniline and substituted anilines, the excess volume and viscosity of binary mixtures of anilines with *o*-chlorophenol [1], *m*-cresol [2], acetonitrile [3] and 2,2,2,-trichloroethanol [4] have recently been reported. The results suggested that intermolecular interactions such as hydrogen bonding as well as geometrical effects affect the volume and viscosity behaviour of the mixture. It is generally known that viscosities of liquids and liquid mixtures are sensitive to factors affecting the liquid structure and thereby to various association equilibria [5,6]. Furthermore, the activation energy of viscous flow of hydrogen-bonded liquids contains contributions due to this association [7–9]. Thus the examination of the viscosity behaviour of binary mixtures of 2-butoxyethanol with anilines can be expected to yield valuable information on the type and strength of interactions between the components in these mixtures. In this work, the viscosities and densities of 2-butoxyethanol (BUT) with aniline (ANL), *N*-methylaniline (MEA), *N*,*N*-dimethylaniline (DMA), *N*-ethylaniline (EAN) and *N*,*N*-di-

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ethylaniline (DEA), and the thermodynamic functions derived from them are reported.

EXPERIMENTAL

The aniline and *N*-alkylanilines used were the same as in earlier studies [1–4]. 2-Butoxyethanol, an Aldrich product, was purified by distillation under reduced pressure and stored over molecular sieves.

Densities were measured with a digital density meter DMA 45 (Anton Parr, Austria) with an accuracy in the density measurement of ± 0.0001 g ml^{-1}. A Sodev temperature controller was used in the measurements of densities at different temperatures. Viscosities at different temperatures were measured using modified Ostwald or Cannon–Fenske viscometers and a viscosity bath (Koehler Instrumentation). The reproducibility in the viscosity measurements was within ± 0.005 cP. The observed densities and viscosities of the pure components at the various temperatures are in excellent agreement with the published values [10–12].

RESULTS AND DISCUSSION

The experimental values of viscosity and density for the five systems are listed in Tables 1–5.

The excess functions, V^E, η^E and $G^{\star E}$, were calculated from the experimental values using the following equations

$$V = (x_1 M_1 + x_2 M_2)/\rho \tag{1}$$

$$V^E = V - (x_1 V_1 + x_2 V_2) \tag{2}$$

$$\eta^E = \eta - (x_1 \eta_1 + x_2 \eta_2) \tag{3}$$

$$G^{\star E} = RT[\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \tag{4}$$

where ρ, η and V are the density, viscosity and molar volume of the mixture, M_1, M_2, V_1, V_2, η_1 and η_2 are molar masses, molar volumes and viscosities of the pure components 1 and 2 respectively. The excess quantities y^E were fitted to the Redlich–Kister equation [13]

$$y^E = x_1 x_2 \sum_{j=1}^{n} a_j (1 - 2x_1)^{j-1} \tag{5}$$

The values of the coefficients (a_j) of this equation, together with the standard deviation $\sigma(y^E)$ at 298 K are reported in Table 6. Figures 1–3 show the values of η^E, V^E and $G^{\star E}$ as a function of mole fraction of

TABLE 1

Density and viscosity data for 2-butoxyethanol–aniline

X [a]	ρ (g ml^{-1})					η (cP)				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.0000	1.0173	1.0131	1.0087	1.0045	1.0002	3.694	3.111	2.691	2.338	2.054
0.0995	1.0028	0.9987	0.9944	0.9900	0.9856	3.539	2.974	2.573	2.238	1.967
0.1968	0.9895	0.9852	0.9809	0.9765	0.9722	3.471	2.915	2.528	2.189	1.929
0.2548	0.9819	0.9775	0.9733	0.9689	0.9645	3.448	2.887	2.512	2.184	1.922
0.3024	0.9758	0.9714	0.9672	0.9629	0.9585	3.429	2.886	2.507	2.160	1.905
0.3953	0.9644	0.9598	0.9558	0.9513	0.9470	3.397	2.860	2.482	2.145	1.893
0.4355	0.9594	0.9548	0.9510	0.9463	0.9420	3.390	2.854	2.477	2.143	1.892
0.5146	0.9499	0.9455	0.9415	0.9369	0.9325	3.350	2.833	2.463	2.123	1.875
0.5909	0.9413	0.9369	0.9331	0.9284	0.9239	3.310	2.805	2.438	2.108	1.856
0.6936	0.9304	0.9255	0.9214	0.9172	0.9126	3.219	2.731	2.381	2.070	1.827
0.8002	0.9202	0.9142	0.9102	0.9061	0.9016	3.100	2.588	2.332	2.020	1.787
0.8933	0.9098	0.9064	0.9020	0.8953	0.8913	2.974	2.545	2.259	1.962	1.742
1.0000	0.8962	0.8920	0.8879	0.8836	0.8793	2.786	2.403	2.115	1.867	1.657

[a] Mole fraction of 2-butoxyethanol.

TABLE 2

Density and viscosity data for 2-butoxyethanol–*N*-methylaniline

X [a]	ρ (g ml^{-1})					η (cP)				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318K
0.0000	0.9816	0.9780	0.9740	0.9705	0.9663	1.963	1.717	1.538	1.386	1.251
0.0992	0.9723	0.9684	0.9642	0.9600	0.9558	2.010	1.756	1.567	1.398	1.256
0.2016	0.9629	0.9589	0.9548	0.9505	0.9466	2.089	1.811	1.613	1.433	1.302
0.3298	0.9517	0.9475	0.9433	0.9389	0.9349	2.213	1.918	1.699	1.502	1.352
0.4032	0.9454	0.9414	0.9370	0.9327	0.9286	2.314	1.999	1.753	1.550	1.444
0.4978	0.9372	0.9332	0.9292	0.9251	0.9210	2.425	2.094	1.836	1.619	1.495
0.6441	0.9254	0.9217	0.9177	0.9134	0.9092	2.589	2.232	1.951	1.718	1.576
0.7771	0.9162	0.9103	0.9066	0.9021	0.8983	2.709	2.319	2.049	1.792	1.661
0.8935	0.9083	0.9036	0.8990	0.8946	0.8897	2.788	2.395	2.111	1.851	1.696
1.0000	0.8962	0.8920	0.8879	0.8836	0.8793	2.786	2.403	2.115	1.867	1.657

[a] Mole fraction of 2-butoxyethanol.

TABLE 3

Density and viscosity data for 2-butoxyethanol–*N*,*N*-dimethylaniline

X [a]	ρ (g ml^{-1})					η (cP)				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.0000	0.9522	0.9478	0.9438	0.9397	0.9357	1.282	1.177	1.100	1.020	0.967
0.0991	0.9453	0.9409	0.9368	0.9312	0.9286	1.298	1.184	1.096	1.022	0.947
0.2007	0.9393	0.9352	0.9291	0.9248	0.9222	1.369	1.245	1.140	1.063	0.984
0.3163	0.9329	0.9288	0.9238	0.9195	0.9159	1.479	1.338	1.221	1.129	1.041
0.3988	0.9285	0.9244	0.9199	0.9156	0.9115	1.586	1.420	1.291	1.186	1.089
0.4955	0.9231	0.9190	0.9145	0.9095	0.9062	1.715	1.524	1.384	1.266	1.156
0.5977	0.9178	0.9137	0.9092	0.9045	0.9008	1.880	1.666	1.501	1.369	1.217
0.6989	0.9124	0.9081	0.9038	0.8995	0.8953	2.076	1.825	1.643	1.486	1.346
0.7971	0.9072	0.9028	0.8975	0.8938	0.8892	2.281	2.002	1.790	1.617	1.459
0.8968	0.9019	0.8981	0.8936	0.8896	0.8859	2.555	2.230	1.991	1.781	1.601
1.0000	0.8962	0.8920	0.8879	0.8836	0.8793	2.786	2.403	2.115	1.867	1.657

[a] Mole fraction of 2-butoxyethanol.

TABLE 4

Density and viscosity data for 2-butoxyethanol–*N*-ethylaniline

X [a]	ρ (g ml^{-1})					η (cP)				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.0000	0.9566	0.9528	0.9491	0.9448	0.9401	1.952	1.710	1.559	1.389	1.251
0.1017	0.9506	0.9466	0.9421	0.9379	0.9337	2.077	1.774	1.590	1.430	1.298
0.2027	0.9450	0.9408	0.9368	0.9324	0.9279	2.172	1.855	1.662	1.498	1.358
0.3026	0.9393	0.9350	0.9307	0.9266	0.9224	2.259	1.929	1.725	1.537	1.383
0.3980	0.9338	0.9292	0.9256	0.9211	0.9168	2.361	2.039	1.801	1.615	1.443
0.5004	0.9277	0.9238	0.9194	0.9151	0.9110	2.486	2.140	1.889	1.693	1.510
0.5947	0.9222	0.9183	0.9139	0.9095	0.9055	2.573	2.214	1.961	1.746	1.552
0.7010	0.9162	0.9118	0.9079	0.9040	0.8985	2.686	2.313	2.048	1.824	1.616
0.7971	0.9107	0.9060	0.9019	0.8973	0.8934	2.758	2.380	2.111	1.883	1.674
0.8933	0.9047	0.9006	0.8961	0.8916	0.8876	2.786	2.404	2.145	1.910	1.696
1.0000	0.8962	0.8920	0.8879	0.8836	0.8793	2.786	2.403	2.115	1.867	1.657

[a] Mole fraction of 2-butoxyethanol.

TABLE 5

Density and viscosity data for 2-butoxyethanol–*N*,*N*-diethylaniline

X [a]	ρ (g ml^{-1})					η (cP)				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.0000	0.9307	0.9261	0.9222	0.9182	0.9140	1.933	1.710	1.547	1.410	1.280
0.0979	0.9261	0.9219	0.9179	0.9132	0.9098	1.870	1.679	1.511	1.369	1.248
0.2008	0.9229	0.9186	0.9140	0.9094	0.9060	1.887	1.686	1.516	1.371	1.249
0.2890	0.9201	0.9156	0.9121	0.9071	0.9015	1.923	1.711	1.538	1.393	1.262
0.3526	0.9183	0.9140	0.9099	0.9047	0.9014	1.968	1.756	1.572	1.429	1.286
0.4964	0.9139	0.9091	0.9054	0.8997	0.8961	2.102	1.853	1.655	1.487	1.365
0.5968	0.9106	0.9052	0.9020	0.8958	0.8918	2.198	1.942	1.731	1.552	1.402
0.7021	0.9073	0.9009	0.8986	0.8928	0.8877	2.343	2.067	1.844	1.650	1.481
0.7940	0.9041	0.8993	0.8956	0.8914	0.8862	2.461	2.175	1.927	1.725	1.544
0.8979	0.9005	0.8949	0.8921	0.8871	0.8820	2.631	2.305	2.048	1.824	1.631
1.0000	0.8962	0.8920	0.8879	0.8836	0.8793	2.786	2.403	2.115	1.867	1.657

[a] Mole fraction of 2-butoxyethanol.

TABLE 6

Coefficients for the least-squares fit of results of eqn. (5) at 298 K

System	y^E	A_1	A_2	A_3	A_4	A_5	σ_X
ANL + BUT	η^E	0.478	−0.820	−0.552	−0.317		0.0033
	V^E	−2.716	0.854	−2.649	3.182		0.025
	G^{*E}	559.9	−638.4	−364.7	−161.4		3
MNA + BUT	η^E	0.200	−0.786	0.060			0.0072
	V^E	−0.967	0.056	−3.877	5.601		0.046
	G^{*E}	380.0	−721.1	−156.2			7
DMA + BUT	η^E	−1.235	0.072	−0.364	0.684	0.750	0.0081
	V^E	0.400	0.602	0.547	0.938		0.010
	G^{*E}	931.3	−358.6	−171.5	947.5		10
EAN + BUT	η^E	0.427	−0.611	0.416	0.438		0.0066
	V^E	−1.078	0.462	−1.500	2.240		0.0038
	G^{*E}	570.6	−506.5	356.6	530.4		7
DEA + BUT	η^E	−1.038	−0.291	−0.249	−0.383		0.0065
	V^E	0.857	0.831	0.981	2.036		0.017
	G^{*E}	926.3	−540.3	−352.9	−407.4		7

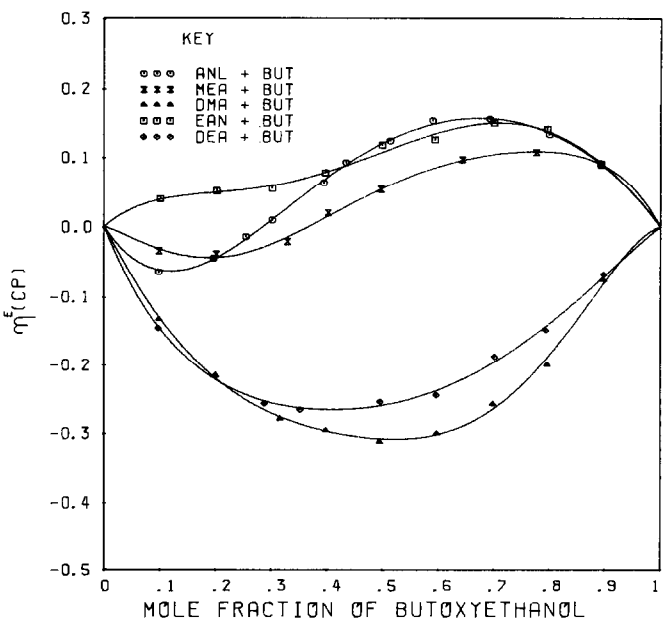

Fig. 1. Plot of excess viscosity versus mole fraction of 2-butoxyethanol at 298 K.

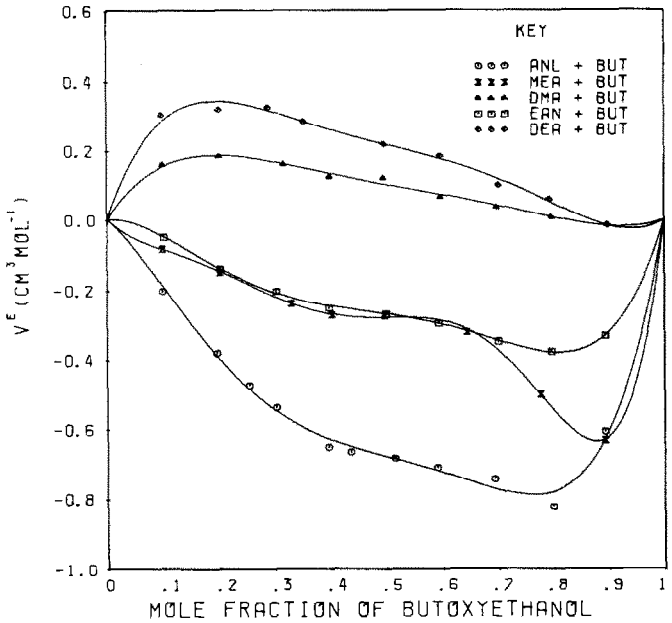

Fig. 2. Plot of excess volume versus mole fraction of 2-butoxyethanol at 298 K.

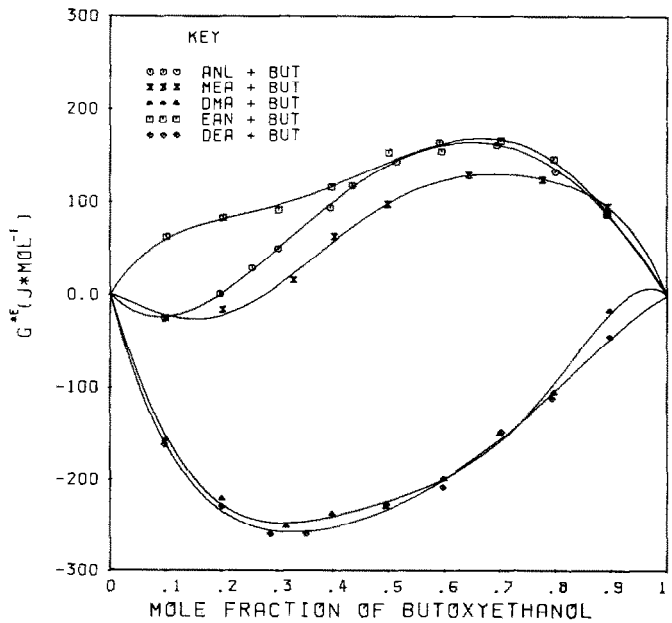

Fig. 3. Plot of excess free energy of activation of flow versus mole fraction of 2-butoxyethanol at 298 K.

2-butoxyethanol. The continuous curves were generated with the aid of the coefficients of eqn. (5).

Viscosity data for the liquid mixtures were also analysed in terms of McAllister's equation [14]

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln\left[x_1 + \frac{x_2 M_2}{M_1}\right] + 3x_1^2 x_2 \ln\left[\frac{2}{3} + \frac{M_2}{3M_1}\right] + 3x_1 x_2^2 \ln\left[\frac{1}{3} + \frac{2M_2}{3M_1}\right] + x_2^3 \ln\left[\frac{M_1}{M_2}\right] \quad (6)$$

In eqn. (6), ν_1, ν_2 and ν refer to the kinematic viscosities of the pure components 1, 2 and the mixture respectively. The interaction parameters ν_{12} and ν_{21} were determined by the least-squares method as described by Reid et al. [15]. As our data extended over a wide temperature range, the temperature functionality for the interaction parameters was obtained by the assumption of an Andrade's form [14]

$$\nu_{12} = A_{12} \exp \frac{(B_{12})}{T}$$

$$\nu_{21} = A_{21} \exp \frac{(B_{21})}{T} \quad (7)$$

Table 7 shows the values of A and B for the various systems of the current study. In a comparison of the experimentally determined data with the values obtained by McAllister's method, the average error was found to be less than 1.0%. The selection of a cubic equation (McAllister) is justified as in all the systems the ratio of the radius is smaller than 1.5.

Examination of Fig. 1 shows that the values of η^E become negative when 2-butoxyethanol is added to dimethyl- and diethylanilines and exhibited a minimum for these systems. According to Fort and Moore [16], the values of η^E are negative for systems of different sizes in which dispersion forces are

TABLE 7

Andrade coefficients for the temperature functionality of McAllister constants for binary mixtures

System	ν_{12}		ν_{21}	
	A_{12}	B_{12}	A_{21}	B_{12}
ANL + BUT	3.50×10^{-4}	2725.1	4.70×10^{-4}	2678.7
MNA + BUT	7.90×10^{-4}	2363.8	2.22×10^{-3}	2149.7
EAN + BUT	7.70×10^{-3}	2392.7	2.45×10^{-3}	2126.7
DMA + BUT	3.65×10^{-4}	1779.2	7.57×10^{-3}	1696.4
DEA + BUT	2.82×10^{-3}	1939.2	4.91×10^{-3}	1866.8

dominant. In the case of *N*-methyl- and ethylanilines, η^E values become slightly negative initially and positive at higher concentrations of 2-butoxyethanol. The η^E values for the ANL–BUT system are slightly positive in the entire composition range of the mixture. The observed behaviour of the system can be explained on the basis of the difference in sizes as well as the ability to form weak hydrogen bonding of the type O–H $\cdots$ N or N–H $\cdots$ O. Positive values of V^E in the case of DEA + BUT and DMA + BUT could be attributed to a looser liquid structure which may be due to the break-up of the hydrogen bonds in the pure components [17]. The negative V^E values for BUT mixtures with ANL, MEA and EAN could be attributed to the strong effect these components have on each other's structure [18]. The positive $G^{\star E}$ values can be seen in binary systems as an indication of the strength of the interaction between molecules [19,20]. From the values of excess functions, one can conclude that the strength of specific interactions varies in the order ANL + BUT > MEA + BUT > EAN + BUT > DMA + BUT > DEA + BUT.

The specific interactions between 2-butoxyethanol and the anilines are mainly due to dispersion forces due to different sizes and weak hydrogen bonding of the type N–H $\cdots$ O and O–H $\cdots$ N.

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