

Excess Volumes and Viscosities of Binary Mixtures of Organics

Maurizio Fermeglia* and Romano Lapasin

Istituto di Chimica Applicata e Industriale, University of Trieste, via Valerio 2, 34127 Trieste, Italy

Excess volumes and kinematic viscosities have been measured with a vibrating tube densimeter and an Ubbelohde viscometer for nine binary systems containing organic compounds. Excess volumes have been correlated by means of a polynomial expression and viscosities by means of the McAllister equation. The systems studied are 1-butanol/ethyl acetate; 1-butanol/*n*-butyl acetate; 1-butanol/*p*-xylene; ethylbenzene/2-ethoxyethanol; ethylbenzene/2-butanone; 1-butanol/ethylbenzene; toluene/ethylbenzene; *n*-butyl acetate/2-hexanone; and *n*-butyl acetate/*n*-amyl acetate. Investigations have been carried out at atmospheric pressure and 298.15 K.

Introduction

Mixing volume and viscosity effects are important from both a theoretical and a practical point of view: indeed, strong deviations from linearity are often encountered in liquid mixtures, even of similar nature.

In addition to the scientific interest, the knowledge of the mentioned phenomena is very useful for a number of practical applications in various fields; suffice it to mention here the field of paints, varnishes, and printing inks, where volume effects are involved in the conversion of formulations from a gravimetric into a volumetric base (solvent mixtures and polymer solutions for mill base and let down, evaluation of pigment volume concentration, volumetric yield in application, etc.). Different approaches have been suggested to the problem of predicting viscosity of mixtures. Among these the group contribution methods seem to be particularly promising. The development of a group contribution method requires that an adequate data base should be made available. The data base must consist of a sufficient number of systems containing all the chemical functional groups taken into account in the operating domain of the method.

The present work aims at contributing to the development of the above mentioned data base. The systems studied are 1-butanol/ethyl acetate; 1-butanol/*n*-butyl acetate; 1-butanol/*p*-xylene; ethylbenzene/2-ethoxyethanol; ethylbenzene/2-butanone; 1-butanol/ethylbenzene; toluene/ethylbenzene; *n*-butyl acetate/2-hexanone; and *n*-butyl acetate/*n*-amyl acetate; all the systems were measured at atmospheric pressure and 298.15 K.

Experimental Section

Materials. All the chemicals used in the present study were supplied by Fluka and were used as received. No further purification treatment was carried out. The stated purity of all the chemicals exceeded 99.0 mol %. Nitrogen and bidistilled water were used for the densimeter calibration and cyclohexane for the viscometer calibration. The purity of cyclohexane and water was higher than 99.9 mol %; that of nitrogen higher than 99.999 mol %. Densities and viscosities of the pure components at 298.15 K and atmospheric pressure were measured before preparing the mixtures and compared with literature values to check their purity (see Table I).

Mixture Preparation. All the solutions were prepared by using a Mettler balance (precision of 1×10^{-5} g) and air-tight

Table I. Comparison between Measured and Literature Data for Pure Components at 298.15 K

component	δ , g/cm ³		μ , m Pa s		ν , mm ² /s, this work
	this work	lit.	this work	lit.	
1-butanol	0.805 50	0.806 00	2.578		3.200
ethyl acetate	0.894 23	0.894 55	0.429	0.426	0.480
<i>n</i> -butyl acetate	0.875 99	0.876 36	0.678		0.774
<i>n</i> -amyl acetate	0.872 23	0.870 70	0.856	0.862	0.982
ethylbenzene	0.862 30	0.862 64	0.627	0.637	0.727
toluene	0.862 17	0.862 31	0.554	0.552	0.642
<i>p</i> -xylene	0.856 68	0.856 69	0.604	0.605	0.705
2-ethoxyethanol	0.959 97	0.960 24	1.541	1.600	1.605
2-butanone	0.799 93	0.799 70	0.380		0.475
2-hexanone	0.807 14		0.587		0.727

stoppered bottles. The more volatile component was directly poured into the bottle. The charged bottle was closed and weighed. The second component was injected into the bottle through the stopper by means of a syringe. This procedure hindered any vapor loss, contamination, and oxidation. Hence the possible error in the mole fraction is estimated to be lower than 3×10^{-5} .

Density Measurements. A digital densimeter (Anton Paar DMA 602H - DMA 60) was employed for the determination of the densities of the pure components and the binary mixtures. The density determination is based on the variation of the natural frequency of a tube oscillator filled with sample liquid with respect to the nitrogen. The measuring cell is embodied in its separate housing, complete with oscillator counter mass and thermostat connectors. The oscillator, or sample tube, made of borosilicate glass (Duran 50), is fused into a dual-wall glass cylinder thus allowing temperature control to be carried out by water circulating from a constant temperature bath. The operating conditions of the cell range from 93.15 to 423.25 K and extend up to 10 bar. The density determination is based on measuring the period of oscillation of the vibrating U-shaped sample tube, filled with the sample (liquid or gas). The following relationship between the density and the period of oscillation was used

$$\delta = A + B\Omega^2 \quad (1)$$

where A and B were determined by instrument calibration at 298.15 K with bidistilled water ($\delta_{\text{H}_2\text{O}} = 0.997\,047 \text{ g/cm}^3$) and nitrogen ($\delta_{\text{N}_2} = 0.001\,145\,6 \text{ g/cm}^3$). Water and nitrogen gas were chosen as calibrating fluids since they span a wide density range and can be obtained in high purity and their densities are known at a high precision level. Calibration was performed before each measurement at the same temperature and pressure conditions. All the measurements were carried out at atmospheric pressure. Pressure was measured by means of a mercury barometer. Density data for water and nitrogen were taken from ref 1 and 2. A time interval of 15 min was chosen to attain a satisfactory temperature constancy and oscillation period stability (fluctuations restricted to the sixth decimal digit). All the measurements were performed at 10 K period select switch. A Hetofrig constant-temperature bath circulator was used with a temperature control interval of ± 0.01 K. Temperature was detected with a digital precision thermometer (Anton Paar DT 100-20), calibrated against a platinum resistance thermometer (Rosemount Model 162 CE) and checked at the water triple point. The precision of the densities

Table II. Experimental Results for the 1-Butanol (1)/Ethyl Acetate (2) System at 298.15 K

x_1 , mole fracn	ν , mm ² /s	δ , g/cm ³	μ , m Pa s	V^E , cm ³ /mol
0.8918	2.136	0.814 88	1.741	0.0930
0.8010	1.617	0.822 83	1.331	0.1491
0.7033	1.252	0.831 29	1.041	0.2057
0.5952	0.997	0.840 67	0.838	0.2494
0.4809	0.812	0.850 66	0.691	0.2703
0.3724	0.696	0.860 33	0.599	0.2523
0.2522	0.594	0.871 15	0.517	0.2033
0.1338	0.531	0.881 86	0.468	0.1311

Table III. Experimental Results for the 1-Butanol (1)/*n*-Butyl Acetate (2) System at 298.15 K

x_1 , mole fracn	ν , mm ² /s	δ , g/cm ³	μ , m Pa s	V^E , cm ³ /mol
0.9172	2.392	0.813 35	1.946	0.0314
0.8330	1.888	0.820 68	1.549	0.0741
0.7567	1.588	0.826 84	1.313	0.1202
0.6606	1.337	0.834 41	1.116	0.1362
0.5578	1.146	0.841 77	0.965	0.1717
0.4456	0.985	0.849 47	0.837	0.1727
0.3115	0.899	0.857 96	0.771	0.1662
0.1678	0.822	0.866 55	0.712	0.1143

Table IV. Experimental Results for the 1-Butanol (1)/*p*-Xylene (2) System at 298.15 K

x_1 , mole fracn	ν , mm ² /s	δ , g/cm ³	μ , m Pa s	V^E , cm ³ /mol
0.7688	1.820	0.820 60	1.493	-0.0423
0.6932	1.546	0.824 88	1.275	-0.0327
0.5850	1.261	0.830 50	1.047	0.0008
0.5009	1.095	0.834 52	0.914	0.0396
0.3971	0.949	0.839 40	0.797	0.0623
0.2649	0.819	0.845 17	0.692	0.0966
0.1504	0.748	0.850 01	0.636	0.1014

Table V. Experimental Results for the Ethylbenzene (1)/2-Ethoxyethanol (2) System at 298.15 K

x_1 , mole fracn	ν , mm ² /s	δ , g/cm ³	μ , m Pa s	V^E , cm ³ /mol
0.8672	0.780	0.867 57	0.677	0.2112
0.7484	0.842	0.873 66	0.736	0.2490
0.6286	0.934	0.880 44	0.822	0.2467
0.5133	1.047	0.887 49	0.929	0.2240
0.4069	1.180	0.894 49	1.055	0.1840
0.2930	1.352	0.902 51	1.220	0.1289
0.1968	1.515	0.909 62	1.378	0.0845
0.0993	1.732	0.917 25	1.589	0.0333

measured is estimated to be better than 1×10^{-5} g/cm³.

Viscosity Measurements. Kinematic viscosities of the pure liquids and their mixtures were measured with a Schott measuring system, consisting of a basic control unit, a measuring stand, a constant-temperature bath and a calibrated Ubbelohde suspended level viscometer. Viscometer constants were controlled by using high-purity cyclohexane as standard fluid. Temperature fluctuations were limited to ± 0.01 K. Time measurements were made automatically using two light barriers across the viscometer and an electronic timer (Schott AVS 300) with a precision of ± 0.01 s. The Hagenbach correction was considered not necessary on account of long flow time obtained by a proper selection of the capillary. Consequently the precision of the kinematic viscosity data was estimated to be higher than 5×10^{-4} mm²/s.

Results and Correlation

Table I reports the comparison between the pure component densities and viscosities measured in this work and the literature data taken from ref 3 at 298.15 K and at atmospheric pressure; the agreement is satisfactory.

Table VI. Experimental Results for the Ethylbenzene (1)/2-Butanone (2) System at 298.15 K

x_1 , mole fracn	ν , mm ² /s	δ , g/cm ³	μ , m Pa s	V^E , cm ³ /mol
0.8394	0.686	0.855 22	0.846	-0.0803
0.7041	0.646	0.848 60	0.548	-0.1299
0.5818	0.613	0.841 95	0.516	-0.1498
0.4606	0.583	0.834 81	0.487	-0.1640
0.3470	0.555	0.827 34	0.459	-0.1446
0.2397	0.528	0.819 70	0.433	-0.1195
0.1608	0.511	0.813 63	0.416	-0.0898
0.0811	0.492	0.807 09	0.397	-0.0518

Table VII. Experimental Results for the 1-Butanol (1)/Ethylbenzene (2) System at 298.15 K

x_1 , mole fracn	ν , mm ² /s	δ , g/cm ³	μ , m Pa s	V^E , cm ³ /mol
0.9191	2.619	0.811 86	2.126	-0.0435
0.8339	2.148	0.817 68	1.756	-0.0269
0.7407	1.742	0.823 65	1.435	-0.0036
0.6392	1.426	0.829 72	1.183	0.0269
0.5335	1.195	0.835 64	0.999	0.0614
0.4235	1.009	0.841 44	0.849	0.0952
0.2901	0.867	0.848 16	0.735	0.1142
0.1608	0.780	0.854 41	0.666	0.1070

Table VIII. Experimental Results for the Toluene (1)/Ethylbenzene (2) System at 298.15 K

x_1 , mole fracn	ν , mm ² /s	δ , g/cm ³	μ , m Pa s	V^E , cm ³ /mol
0.9209	0.649	0.862 22	0.560	-0.0048
0.8024	0.659	0.862 28	0.568	-0.0104
0.6663	0.673	0.862 34	0.580	-0.0159
0.4784	0.687	0.862 37	0.592	-0.0171
0.3685	0.700	0.862 38	0.604	-0.0168
0.2529	0.714	0.862 38	0.616	-0.0151
0.1308	0.722	0.862 34	0.623	-0.0077

Table IX. Experimental Results for the *n*-Butyl Acetate (1)/2-Hexanone (2) System at 298.15 K

x_1 , mole fracn	ν , mm ² /s	δ , g/cm ³	μ , m Pa s	V^E , cm ³ /mol
0.8669	0.765	0.867 09	0.663	0.0380
0.7471	0.756	0.859 10	0.649	0.0500
0.6318	0.752	0.851 31	0.640	0.0586
0.5224	0.746	0.843 86	0.630	0.0588
0.4115	0.742	0.836 22	0.620	0.0555
0.3117	0.737	0.829 38	0.611	0.0330
0.1861	0.732	0.820 37	0.601	0.0443
0.1073	0.730	0.814 92	0.595	0.0092

Table X. Experimental Results for the *n*-Butyl Acetate (1)/*n*-Amyl Acetate (2) System at 298.15 K

x_1 , mole fracn	ν , mm ² /s	δ , g/cm ³	μ , m Pa s	V^E , cm ³ /mol
0.9088	0.793	0.875 46	0.694	0.0227
0.7859	0.817	0.874 95	0.715	0.0245
0.6578	0.844	0.874 45	0.738	0.0240
0.5285	0.870	0.873 95	0.760	0.0251
0.3941	0.901	0.873 47	0.787	0.0224
0.2559	0.928	0.872 98	0.810	0.0216
0.1115	0.956	0.872 56	0.834	0.0080

Tables II–X report the results of the measurements in terms of mole fractions for the systems investigated; the tables include kinematic viscosity data (ν) and density data (δ) (quantities directly measured), together with the dynamic viscosities (μ) and the excess volumes (V^E). According to ref 4, the excess volumes V^E were calculated by means of the equation

$$V^E = (x_1 M_1 + x_2 M_2) / \delta - x_1 M_1 / \delta_1 - x_2 M_2 / \delta_2 \quad (2)$$

where x_j are mole fractions and M_j and δ_j are molecular weight and densities of the pure component.

Table XI. Values of the Coefficients of the Correlation Equation and Standard Deviations for Excess Volumes and Kinematic Viscosities

system		correln eq coeff				σ_{V^E}, σ_ν
1-butanol/ethyl acetate	V^E	1.0513	-0.1408	-0.0321	0.0511	0.0053 ^a
	ν	0.8365	0.6404			0.0078 ^b
1-butanol/ <i>n</i> -butyl acetate	V^E	0.7030	-0.1013	-0.0503	-0.2721	0.0081 ^a
	ν	0.9480	0.9195			0.0172 ^b
1-butanol/ <i>p</i> -xylene	V^E	0.1246	-0.6621	0.1403	-0.3868	0.0063 ^a
	ν	1.3153	0.7504			0.0024 ^b
ethylbenzene/2-ethoxyethanol	V^E	0.8543	0.5965	0.5033	0.6481	0.0053 ^a
	ν	0.8295	1.2608			0.0038 ^b
ethylbenzene/2-butanone	V^E	-0.6363	0.0244	0.0073	0.0672	0.0035 ^a
	ν	0.6473	0.5551			0.0012 ^b
1-butanol/ethylbenzene	V^E	0.2120	-0.4717	-0.0700	-0.6927	0.0068 ^a
	ν	1.3723	0.7722			0.0057 ^b
toluene/ethylbenzene	V^E	-0.0722	0.0113	0.0078	-0.0153	0.0011 ^a
	ν	0.6663	0.7161			0.0024 ^b
<i>n</i> -butyl acetate/2-hexanone	V^E	0.2307	0.0012	0.0313	0.2159	0.0112 ^a
	ν	0.7499	0.7387			0.0010 ^b
<i>n</i> -butyl acetate/ <i>n</i> -amyl acetate	V^E	0.0937	-0.0339	0.1152	0.2333	0.0022 ^a
	ν	0.8449	0.9142			0.0013 ^b

^a Standard deviation for excess volume. ^b Standard deviation for excess kinematic viscosity.

To describe the composition dependence of the excess volumes the following equation was used (5)

$$V_{\text{calcd}}^E = x_1 x_2 \sum_{j=0}^3 a_j (x_1 - x_2)^j \quad (3)$$

and the composition dependence of the kinematic viscosity was expressed by the McAllister equation (6).

The data reduction was separately performed on ν and V^E data by means of a least-squares method, minimizing an objective function made up by the sum of the squares of the absolute differences between the experimental and the calculated values. The experimental test indicated that no appreciable difference can be detected within each data set as regards the standard deviations for the single data points. Accordingly the same weight has been assigned to all the data points in the minimizing procedure.

The coefficients a_j (eq 3) and ν_j (McAllister equation) obtained are listed in Table XI along with the standard deviations σ_{V^E} and σ_ν for each system. The standard deviations were calculated with the following equations (5)

$$\sigma_{V^E} = \left[\sum (V_{\text{calcd}}^E - V_{\text{exptl}}^E)^2 / (N - n) \right]^{1/2} \quad (4)$$

$$\sigma_\nu = \left[\sum (\nu_{\text{calcd}} - \nu_{\text{exptl}})^2 / (N - n) \right]^{1/2} \quad (5)$$

where N is the number of data points for each system and n is the number of parameters.

Discussion

Viscometric Behavior. For all the systems containing 1-butanol the deviations of the mixture kinematic viscosity from the linearity are marked and can be ascribed to the different molecular structure of the components. In the case of the system ethylbenzene/2-ethoxyethanol the deviation from the linearity is limited.

For all the other systems the deviations are small or almost negligible. It is pointed out that among the systems investigated the deviation from linearity is associated with the presence of the -OH group in the mixture.

The McAllister correlation equation gives excellent results for all the systems investigated ($\sigma_\nu < 0.007$) except for the system 1-butanol/*n*-butyl acetate where a limited scattering of data was detected.

Volumetric Behavior. The systems 1-butanol/ethyl acetate, ethylbenzene/2-ethoxyethanol, and ethylbenzene/2-butanone show strong deviations from the ideal volumetric behavior; only slight deviations from ideality are found for toluene/ethylbenzene

and *n*-butyl acetate/2-hexanone systems.

For all the above-mentioned systems the V^E sign does not change in the whole concentration range; on the other hand, a similar pattern of V^E versus x (sign inversion) is shown for the system 1-butanol/*p*-xylene and 1-butanol/ethylbenzene.

The results obtained from the correlation equation (eq 3) are quite satisfactory for all the systems investigated ($\sigma_{V^E} < 0.008$) with the only exception of the *n*-butyl acetate/2-hexanone system.

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Glossary

A, B	instrument constants, eq 1
a	coefficients in eq 3
M	molecular weight
N	number of experimental data points
n	number of parameters
V^E	excess volume, cm ³ /mol
x	mole fraction

Greek Letters

ν	kinematic viscosity, mm ² /s = cSt
ν_j	coefficients in the McAllister equation
μ	dynamic viscosity, m Pa s = cP
δ	density, g/cm ³
Ω	period of oscillation
σ_ν	kinematic viscosity standard deviation
σ_{V^E}	excess volumes standard deviation

Registry No. 1-Butanol, 71-36-3; ethyl acetate, 141-78-6; *n*-butyl acetate, 123-86-4; ethyl benzene, 100-41-4; 2-ethoxy ethanol, 110-80-5; 2-butanone, 78-93-3; toluene, 108-88-3; 2-hexanone, 591-78-6; *n*-amyl acetate, 628-63-7.

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