

other alcohol-water solutions studied, the excess Henry's constants of oxygen and nitrogen are approximately equal and are smaller than the values of carbon dioxide.

Regardless of the kinds of solute gases, the excess Henry's constants in alcohol-water solution do not converge to zero with temperature rising but increase in a negative direction.

Whether the observed excess Henry's constants could be fitted to a polynomial equation of the Redlich-Kister type or not was examined. However, the observed excess Henry's constants could not be expressed by a Redlich-Kister equation with four constants within experimental errors.

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#### Nomenclature

$f$  = fugacity, atm  
 $H$  = Henry's constant, atm  
 $L$  = Ostwald coefficient, —  
 $p$  = pressure, mm Hg  
 $R$  = gas constant, atm cc/mol K  
 $T$  = absolute temperature, K  
 $v_M$  = molar volume of solvent, cc/mol  
 $V$  = volume, cc  
 $x$  = mole fraction in liquid phase, —  
 $y$  = mole fraction in gas phase, —  
 $z$  = compressibility factor, —

$\gamma$  = activity coefficient, —  
 $\pi$  = total pressure, mm Hg

#### Superscripts

$E$  = excess quantity  
 $^{\circ}$  = pure component

#### Subscripts

im = impurity gas in solute gas  
 $R$  = solute gas  
 $R_{mix}$  = solute gas ( $R$ ) in mixed solvent  
 $s$  = solvent  
1 = alcohol  
2 = water

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## Viscosity of Ten Binary and One Ternary Mixtures

Marcel J. Mussche and Lucien A. Verhoeve<sup>1</sup>

Laboratory of Industrial Organic Chemistry and Chemical Engineering, Rijksuniversiteit, Krijgslaan, 271, B9000 Gent, Belgium

**The viscosity of 10 binary systems, including polar and nonpolar components, was determined at 20° and 25°C. The viscosity of the ternary system heptane-iso-octane-toluene was also determined at 25°C. Experimental data were correlated by means of the method of McAllister and that of Heric.**

The literature dealing with systematic studies of the viscosity of mixtures is rather limited. In this paper experimental data on a number of binary systems, including mixtures of strong polar components and a limited number of experimental data on the viscosity of the ternary system heptane-iso-octane(2,2,4-trimethylpentane)-toluene are published. The binary data have been correlated by means of the method of McAllister (3) and that of Heric (1). Both approaches apply to ternary systems. The extended equations contain the binary parameters of the related binary systems and one term containing a ternary parameter. The experimental ternary data have been correlated by this method. The ternary parameter has been

determined by a least-squares method applied to the differences of the experimental value and the computed value, taking into account all terms except the term containing the ternary parameter.

#### Experimental

The systems which are studied in this work are listed in Table I. The materials were purified by fractionation and dried afterward; the hydrocarbons were dried on sodium, and the other materials on molecular sieves. Methylcyclohexane contained some toluene. This toluene was first removed by sulfonation by means of a concentrated solution of sulfuric acid. The ethanol was first dehydrated by calcium oxide. The purity of the materials was checked by means of gas chromatographic analysis on two different columns: apiezon L on chromosorb P, 80-100 mesh and porapak Q, 80-100 mesh and by comparison of the value of the specific gravity and refractive index of the used materials with critically chosen values from the literature. Values are listed in Table II.

A Hoppler viscosimeter was used for determining the viscosities of the binary and ternary systems. The viscosimeter was calibrated against known viscosities of solu-

<sup>1</sup> To whom correspondence should be addressed.

tions of glycerin in water for the range  $\mu = 0.8973$  cp to  $\mu = 1.030$  cp. The specific gravity of the ball was determined by the conventional pycnometric method. The parameters of the apparatus were checked afterward by comparison of the measured value and the value from literature of the viscosity of pure heptane at 25°C  $\mu = 0.3967$ . The time of fall always exceeded 30 sec; the accuracy of the measurement of the time was 0.1 sec. Consequently, the error of the measured values of the viscosity may be estimated as less than 1%.

The specific gravity of the binary mixtures was measured by means of a pycnometer. The data have been

**Table I. Ratio of Molecular Weight and Molecular Radius of Binary Systems**

	$M_2/M_1$	$r_2/r_1$
Heptane(2)-methylcyclohexane(1)	1.02	1.051
Heptane(2)-toluene(1)	1.09	1.108
Iso-octane(2)-toluene(1)	1.24	1.145
Iso-octane(2)-benzene(1)	1.46	1.198
Ethanol(2)-methanol(1)	1.44	1.129
Dioxane(2)-benzene(1)	1.13	0.969
Methylethylketone(2)-ethanol(1)	1.56	1.152
Ethylacetate(2)-ethanol(1)	1.91	1.186
Benzene(2)-methylethylketone(1)	1.08	0.997
Iso-octane(2)-heptane(1)	1.14	1.033

**Table II. Physical Properties of Pure Materials**

	Viscosity, cS		Specific gravity, $d_{25}^4$		Refractive index, $n_{25}^D$	
	Exp	Lit (4)	Exp	Lit (4)	Exp	Lit (4)
Heptane	0.584	0.584	0.6795	0.67951	1.3852	1.38511
Methylcyclohexane	0.893	0.895	0.7651	0.76506	1.4206	1.42058
Iso-octane	0.687	0.694 <sup>a</sup>	0.6877	0.68781	1.3890	1.38898
Benzene	0.690	0.690	0.8737	0.8737	1.4980	1.49792
Toluene	0.641	0.638	0.8622	0.82291	1.4941	1.49413
1-4 Dioxane	1.175	1.167 <sup>a</sup>	1.0280	1.02797	1.4199	1.42025
Methanol	0.700	0.692	0.7871	0.78664	1.3265	1.32652
Ethanol	1.373	1.373	0.7851	0.78504	1.3593	1.35941
Methylethylketone	0.478	0.480 <sup>a</sup>	0.7997	0.7997	1.0576	1.05764
Ethylacetate	0.483	0.476	0.8946	0.89445	1.3698	1.36979

<sup>a</sup> Interpolated value.

**Table III. Specific Gravity of Binary Systems. Parameters of Relationships:  $d^4 = A + Bx + Cx^2 + Dx^3$  (x: Mole Fraction of Most Volatile Component)**

Systems	t, °C	Parameters				Standard error of estimate
		A	B	C	D	
Heptane-methylcyclohexane	20	0.7691	-0.09758	0.01212	0.00024	0.0004
	25	0.7656	-0.10360	0.02332	-0.00663	0.0009
Heptane-toluene	20	0.8657	-0.24990	0.7944	-0.11360	0.0009
	25	0.8615	-0.24129	0.06004	-0.0001	0.0008
Iso-octane-toluene	20	0.8668	-0.2778	0.14361	-0.04115	0.0006
	25	0.8618	-0.2723	0.13475	-0.03684	0.0009
Benzene-iso-octane	20	0.6917	0.10524	-0.00431	0.08624	0.00011
	25	0.6874	0.10461	-0.0030	0.08491	0.0005
Methanol-ethanol	20	0.7894	0.00161	0.00006	0.00020	0.0001
	25	0.7854	0.00224	-0.00303	0.00200	0.0001
Benzene-dioxane	20	1.03327	-0.1570	0.00306	-0.00017	0.0004
	25	1.02761	-0.1454	-0.00583	-0.00259	0.0011
Methylethylketone-ethanol	20	0.7892	0.3666	-0.2928	0.00828	0.0002
	25	0.7849	0.03190	-0.01985	0.00280	0.0002
Ethylacetate-ethanol	20	0.7893	0.17825	-0.09388	0.02718	0.0007
	25	0.7856	0.01722	-0.0922	0.0296	0.0008
Methylethylketone-benzene	20	0.8790	-0.07699	-0.00885	-0.00598	0.0003
	25	0.8739	-0.07392	-0.00020	0.0001	0.0003
Heptane-iso-octane	25	0.6878	-0.0079	0.00075	-0.00111	0.0001

correlated by a polynomial of the third degree. The parameters and the standard error of estimate of this correlation are listed in Table III.

## Results and Discussion

The experimental data of the viscosity of the binary systems are listed in Table IV. The experimental data of the ternary system heptane-iso-octane-toluene are listed in Table V.

The binary data have been correlated by means of the cubic equation proposed by McAllister. The selection of the cubic equation is justified since for each system the ratio of the radii is small. These ratios are inserted in Table I and are computed as the cubic root of the molar volume at 25°C. In the case of ratios smaller than 1.5, McAllister showed that it may be expected that the cubic equation is suitable. In this case, the kinematic viscosity is given by the equation:

$$\ln \nu = x_1^3 \ln \nu_1 + 3 x_1^2 x_2 \ln \nu_{12} + 3 x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 + R \quad (1)$$

where

$$R = - \ln \left( x_1 + x_2 \frac{M_2}{M_1} \right) + 3 x_1^2 x_2 \ln \left( \frac{2}{3} + \frac{M_1}{3 M_2} \right) + 3 x_1 x_2^2 \ln \left( \frac{1}{3} + \frac{2 M_2}{3 M_1} \right) + x_2^3 \ln \left( \frac{M_2}{M_1} \right) \quad (2)$$

**Table IV. Viscosity of Binary Systems**

Mole fraction, $x_1$	Viscosity, cS		Mole fraction, $x_1$	Viscosity, cS	
	$t = 20^\circ\text{C}$	$t = 25^\circ\text{C}$		$t = 20^\circ\text{C}$	$t = 25^\circ\text{C}$
Heptane(2)-methylcyclohexane(1)			Dioxane(2)-benzene(1)		
0.0000	0.612	0.594	0.0000	1.376	1.175
0.1327	0.656	0.615	0.0950	1.294	1.117
0.2446	0.672	0.651	0.2950	1.136	0.998
0.2629	0.673	0.649	0.4890	1.000	0.897
0.3325	0.693	0.662	0.6890	0.790	0.791
0.4450	0.736	0.697	0.8940	0.788	0.715
0.5379	0.760	0.724	1.0000	0.736	0.690
0.6214	0.810	0.746	Methylethylketone(2)-ethanol(1)		
0.7579	0.858	0.803	0.0000	0.502	0.478
0.7572	0.855	0.806	0.0981	0.511	0.487
0.9622	0.935	0.881	0.1989	0.524	0.513
1.0000	0.954	0.893	0.2900	0.545	0.532
Heptane(2)-toluene(1)			0.4915	0.639	0.627
0.0000	0.612	0.584	0.5924	0.721	0.692
0.2213	0.604	0.576	0.6779	0.801	0.771
0.2781		0.569	0.7965	0.945	0.902
0.3198	0.607	0.570	0.8932	1.170	1.091
0.3686	0.608	0.571	1.0000	1.523	1.373
0.4987		0.581	Ethylacetate(2)-ethanol(1)		
0.6782		0.609	0.0000	0.510	0.483
0.6577	0.633	0.611	0.0366	0.512	0.485
0.8284		0.612	0.0513	0.521	0.493
0.9039		0.627	0.1441	0.531	0.500
0.9585		0.638	0.2337	0.562	0.527
0.9734	0.678	0.642	0.3508	0.584	0.546
0.9890		0.642	0.4664	0.632	0.583
1.0000	0.678	0.641	0.5770	0.697	0.644
Iso-octane(2)-toluene(1)			0.6752	0.779	0.713
0.0000	0.729	0.687	0.7970	0.946	0.862
0.0128	0.722	0.686	0.8766	1.124	1.007
0.0628	0.707	0.677	1.0000	1.523	1.373
0.1233	0.695	0.663	Benzene(2)-methylethylketone(1)		
0.2396	0.679	0.650	0.0000	0.736	0.690
0.3523	0.661	0.638	0.1424	0.685	0.643
0.4582	0.655	0.626	0.3070	0.631	0.596
0.5619	0.654	0.618	0.4361	0.597	0.559
0.6548	0.646	0.613	0.6088	0.560	0.532
0.7180	0.651	0.616	0.7739	0.533	0.510
0.8348	0.658	0.621	0.9139	0.513	0.486
0.9149	0.669	0.630	1.0000	0.502	0.478
0.9603	0.670	0.630	Iso-octane(2)-heptane(1)		
1.0000	0.678	0.641	0.0000		0.687
Iso-octane(2)-benzene(1)			0.2935		0.658
0.0000	0.726	0.687	0.1071		0.677
0.0234	0.719	0.675	0.1926		0.668
0.0708	0.701	0.667	0.3298		0.654
0.1495	0.686	0.651	0.4665		0.640
0.2508	0.670	0.629	0.5076		0.635
0.4002	0.641	0.617	0.5835		0.628
0.4986	0.634	0.610	0.7780		0.606
0.6009	0.624	0.608	0.8122		0.603
0.6992	0.630	0.599	1.0000		0.584
0.7912	0.637	0.600	Ethanol(2)-methanol(1)		
0.8651	0.665	0.611	0.0000	1.523	1.373
0.9407	0.693	0.630	0.1976	1.207	1.121
1.0000	0.736	0.690	0.4141	1.001	0.939
Ethanol(2)-methanol(1)			0.6625	0.875	0.815
0.0000	1.523	1.373	1.0000	0.755	0.700
0.1976	1.207	1.121			
0.4141	1.001	0.939			
0.6625	0.875	0.815			
1.0000	0.755	0.700			

**Table V. Regression Coefficients of Correlation of Binary Viscosity Data**

System	Temp, °C	Heric's method		McAllister's method	
		$\beta_{12}'$	$\beta_{12}''$	$\nu_{12}$	$\nu_{21}$
Heptane(2)-methylcyclohexane(1)	20	-0.0425	-0.0651	0.828	0.684
	25	0.0884	-0.1218	0.670	0.752
Heptane(2)-toluene(1)	20	-0.1577	-0.0564	0.584	0.635
	25	-0.1829	-0.0963	0.538	0.612
Iso-octane(2)-toluene(1)	20	-0.3234	-0.0221	0.631	0.636
	25	-0.2451	0.0980	0.634	0.580
Iso-octane(2)-benzene(1)	20	-0.5394	-0.3018	0.533	0.656
	25	-0.5040	-0.3386	0.503	0.636
Ethanol(2)-methanol(1)	20	0.2390	-0.7385	0.861	0.957
	25	-0.3607	0.1922	0.806	0.901
Dioxane(2)-benzene(1)	20	-0.1755	-0.4073	0.751	1.190
	25	-0.0549	-0.1072	0.781	0.999
Methylethylketone(2)-ethanol(1)	20	-0.8992	0.3024	0.622	0.528
	25	-0.9391	0.2340	0.622	0.518
Ethylacetate(2)-ethanol(1)	20	-1.0346	0.3481	0.556	0.584
	25	-0.9485	0.7898	0.524	0.524
Benzene(2)-methylethylketone(1)	20	-0.1974	-0.0214	0.541	0.612
	25	-0.16350	0.0265	0.515	0.574
Iso-octane(2)-heptane(1)	25	0.0223	-0.0061	0.618	0.660

The term  $R$  may be straightforwardly computed from the composition of the mixture and the molecular weights of the components. Equation 1 contains two adjustable parameters  $\ln \nu_{12}$  and  $\ln \nu_{21}$ . They have been determined by a least-squares method and are listed in Table V. The binary data have also been correlated by means of the method of Heric (1):

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) + \delta_{12} \quad (3)$$

where

$$\delta_{12} = \alpha_{12} x_1 x_2 \quad (4)$$

$\delta_{12}$  is a deviation function, representing the departure from a noninteracting system, and  $\alpha_{12} = \alpha_{21}$  is the interaction parameter. This parameter was originally assumed to be independent of the concentration, but Heric (1) found a linear dependency of this parameter of the composition:

$$\alpha_{12} = \beta_{12}' + \beta_{12}'' (x_1 - x_2) \quad (5)$$

We also observed such a relationship and both binary parameters  $\beta_{12}'$  and  $\beta_{12}''$  have been determined, with a weighted linear least-squares method. The weight awarded to the data points was inversely proportional to the square of the probable error of the product  $x_1 x_2$ . The parameters are listed in Table V.

The root-mean-square deviation of both methods is listed in Table VI. Comparison of these values shows that correlation by means of the method of McAllister gives better results, but that the difference of both methods is rather small. The agreement of the computed and experimental data is within 1-3% by the method of McAllister and seldom exceeds 4-5% by the method of Heric. This deviation is partially due to the random error of the experimental data, so that the lack of fit of the models is still smaller.

It is possible to extend the method of McAllister to ternary systems. Kallidas and Laddha (2) have derived the relation:

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + x_3^3 \ln \nu_3 + 3 x_1^2 x_2 \ln \nu_{12} + 3 x_1 x_2^2 \ln \nu_{13} + 3 x_2^2 x_1 \ln \nu_{21} + 3 x_2^2 x_3 \ln \nu_{23} + 3 x_3^2 x_1 \ln \nu_{31} + 3 x_3^2 x_2 \ln \nu_{32} + 6 x_1 x_2 x_3 \ln \nu_{123} + R \quad (6)$$

where

$$R = -\log(x_1 M_1 + x_2 M_2 + x_3 M_3) + x_1^3 \ln M_1 + x_2^3 \ln M_2 + x_3^3 \ln M_3 + 3 x_1^2 x_3 \ln [(2 M_1 + M_2)/3] + 3 x_1^2 x_3 \ln [(2 M_1 + M_3)/3] + 3 x_2^2 x_1 \ln [(2 M_2 + M_1)/3] + 3 x_2^2 x_3 \ln [(2 M_2 + M_3)/3] + 3 x_3^2 x_1 \ln [(2 M_3 + M_1)/3] + 3 x_3^2 x_2 \ln [(2 M_3 + M_2)/3] + 6 x_1 x_2 x_3 \ln [(M_1 + M_2 + M_3)/3] \quad (7)$$

All the terms of Equation 6 can be computed introducing the binary parameters except the term  $6 x_1 x_2 x_3 \ln \nu_{123}$  containing a ternary parameter. By neglecting this term, it is possible to predict the viscosity of a ternary system from the related binary systems. The prediction can be improved by determining the ternary parameter from a limited number of ternary data. This method has been applied to the experimental data of the system heptane-iso-octane-toluene. The ternary parameter was deter-

**Table VI. Root-Mean-Square Deviation of Experimental and Computed Data**

System	Temp, °C	McAllister's method, RMSD $\times 10^{-3}$	Heric's method, RMSD $\times 10^{-3}$
Heptane-methylcyclohexane	20	7.4	10.5
	25	12.4	12.5
Heptane-toluene	20	1.9	8.2
	25	6.0	18.5
Iso-octane-toluene	20	3.9	8.3
	25	2.9	3.9
Iso-octane-benzene	20	6.3	7.5
	25	13.8	21.7
Ethanol-methanol	20	24.1	30.7
	25	7.9	5.4
Dioxane-benzene	20	24.0	35.2
	25	7.5	16.2
Methylethylketone-ethanol	20	10.5	64.8
	25	8.6	8.3
Ethylacetate-ethanol	20	12.7	30.1
	25	11.0	29.0
Benzene-methylethylketone	20	2.5	15.0
	25	3.2	5.9
Iso-octane-heptane	25	0.8	0.7

**Table VII. Viscosity of Ternary System Heptane(1)-Iso-octane(2)-Toluene(3)**

Composition		Exptl viscosity, cS t, 25°C
x <sub>1</sub>	x <sub>2</sub>	
0.1780	0.0508	0.616
0.2999	0.0856	0.599
0.4721	0.1347	0.596
0.0702	0.0681	0.622
0.1982	0.1923	0.600
0.3622	0.3514	0.613
0.0411	0.0567	0.621
0.2031	0.2819	0.590
0.2174	0.3018	0.586
0.0822	0.1977	0.603
0.2668	0.6423	0.652
0.0296	0.0071	0.648
0.5717	0.3040	0.639
0.4787	0.2584	0.599
0.0809	0.0429	0.633
	Ternary parameter	RMSD
McAllister's method	0.450	10.210 <sup>-3</sup>
Heric's method	-0.089	10.710 <sup>-3</sup>

mined by a least-squares method applied to the difference of the experimental value and the value of the sum of all terms except the term containing the ternary parameter.

The method of Heric can also be extended to ternary systems:

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_3 \ln \nu_3 + x_1 \ln M_1 + x_2 \ln M_2 + x_3 \ln M_3 - \ln (x_1 M_1 + x_2 M_2 + x_3 M_3) + \delta_{123} \quad (8)$$

where:

$$\delta_{123} = x_1 x_2 [\beta_{12}' + \beta_{12}''(x_1 - x_2)] + x_1 x_3 [\beta_{13}' + \beta_{13}''(x_1 - x_3)] + x_2 x_3 [\beta_{23}' + \beta_{23}''(x_2 - x_3)] + \alpha_{123} x_1 x_2 x_3 \quad (9)$$

The ternary parameter  $\alpha_{123}$  was computed by means of the same method as used for the computation of the ternary parameter of the equation of Kallidas and Laddha, but in this method by awarding a weight to the data points that was inversely proportional to the square of the probable error of the product  $x_1 x_2 x_3$ .

The ternary parameters and the root-mean-square deviation of the computed and experimental data are inserted in Table VII. The root-mean-square deviation of both methods is almost equal. The prediction by means of both methods was within 1-2%.

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#### Nomenclature

- $M_i$  = molecular weight of component  $i$
- $r_i$  = molecular radius of component  $i$
- $x_i$  = mole fractions of component  $i$
- $\alpha_{ij}, \alpha_{ijk}$  = binary, ternary interaction parameter
- $\beta_{ij}', \beta_{ij}''$  = binary parameters correlating the interaction parameter to the composition
- $\delta_{ij}, \delta_{ijk}$  = deviation from noninteraction in a mixture
- $\mu$  = viscosity, cp
- $\nu_i$  = kinematic viscosity of component  $i$ , cS
- $\nu_{ij}, \nu_{ijk}$  = binary, ternary parameter of the equation of McAllister

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## Solubility and Solvate Formation of Lithium Perchlorate in Lower Nitriles

Reginald P. T. Tomkins<sup>1</sup> and Peter J. Turner

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y. 12181

Solubility data for LiClO<sub>4</sub> in acetonitrile and propionitrile are determined by use of cooling curve methods adapted for nonaqueous solvents. Partial phase diagrams for these systems are presented. A distinct dystectic corresponding to the compound LiClO<sub>4</sub>·4MeCN is obtained in the acetonitrile system with a less pronounced dystectic appearing in the propionitrile system. Results are discussed in terms of ion-solvent interactions.

The stoichiometry of solid adducts between electrolytes and solvents in which they are readily soluble can often be used as a guide to likely coordination patterns of the ions in solution. These patterns can then be used in

<sup>1</sup> To whom correspondence should be addressed.

formulating models of electrolyte solutions (1), although caution is necessary in exercising such analogies.

In this paper, phase diagrams are presented showing the stoichiometry and thermodynamics of the systems LiClO<sub>4</sub>-MeCN and LiClO<sub>4</sub>-EtCN in the nitrile-rich composition range.

#### Experimental

The purification procedures for lithium perchlorate, acetonitrile, and propionitrile have been described elsewhere (2).

Phase diagrams were recorded by use of the cooling method. The system LiClO<sub>4</sub>-MeCN was examined with an apparatus which consists essentially of a Pyrex test tube with a  $\frac{3}{8}$  24/40 ground joint as container, and a  $\frac{1}{2}$ -in. Teflon-coated magnetic stirring bar. Several indentations