J. Chem. Eng. Data 1988, 33, 402–404

Shear Viscosities of Binary Mixtures of Polar Solutes Nitromethane, Nitroethane, and 2-Nitropropane with Nonpolar Aromatic Solvents Benzene, *p*-Xylene, and Mesitylene at 293.15 K

Raja R. Yadava,* Sarvanand S. Yadava,[†] and Vishwa N. Singh[‡]
Chemistry Department, Gorakhpur University, Gorakhpur 273 009, India

Viscosities of binary mixtures of polar solutes (viz., nitromethane, nitroethane, and 2-nitropropane) and nonpolar aromatic hydrocarbon solvents (viz., benzene, *p*-xylene, and mesitylene) of different molar concentrations have been measured at 293.15 K. The mixtures show a marked negative deviation in the case of benzene. The deviation gradually reduces in the case of *p*-xylene and mesitylene and becomes positive for the nitromethane–mesitylene system. The parameter *d* of the Grunberg–Nissan equation $\ln \eta_{12} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1X_2d$ has been calculated and found to have the order benzene < *p*-xylene < mesitylene for all the polar solutes. The behavior has been attributed to the dipole–induced dipole interactions and steric effects. The data have also been examined in the light of the Hind–McLaughlin–Ubbelohde and the Katti–Chaudhary equations. It has been found that the Hind–McLaughlin–Ubbelohde equation gives the most consistent values for the interaction parameter.

Introduction

Viscosity data of binary liquid mixtures have been employed (*1*, *2*) to yield information regarding the nature of molecular interactions in solution. However, there seems (*3*) to have been few studies on the interactions between polar nitroalkanes and nonpolar aromatic hydrocarbons. Therefore, it was thought worthwhile to study these mixtures, in continuation of our work (*4*–*6*) on molecular interactions in polar–nonpolar liquid mixtures.

Polar and nonpolar components of gradually differing dipole moment/polarizability and steric environments have been deliberately chosen for these studies so that information on the role of dipole–induced dipole forces and steric factors on these interactions may be obtained.

Experimental Section

The binary systems studied were nitromethane–benzene, nitromethane–*p*-xylene, nitromethane–mesitylene, nitroethane–benzene, nitroethane–*p*-xylene, nitroethane–mesitylene, 2-nitropropane–benzene, 2-nitropropane–*p*-xylene, and 2-nitropropane–mesitylene. Nitromethane (B.D.H., L.R.) was purified by the method described by Hammick et al. (*7*). Nitroethane (B.D.H., L.R.) was dried over anhydrous calcium chloride and distilled before use. 2-Nitropropane (E. Merck) was used after distillation. Benzene (Sarabhai Merck, spectroscopic grade) was used as such. *p*-Xylene (E. Merck) and mesitylene (E. Merck) were used after distillation. Purity of the chemicals used was checked by density measurements.

The dynamic viscosities η of liquids and liquid mixtures were measured at 293.15 ± 0.1 K as described elsewhere (*4*). The accuracy of the viscosity values was better than 0.001 cP. The densities of the liquid mixtures were measured with a pycnometer. Precautions were taken to avoid loss due to evaporation. The density values were correct to ±0.0001 g/mL.

Table I. Mole Fraction (X_2) of Nitromethane, Viscosity (η_{12}), Excess Viscosity (η^E), and Values of Parameters *d*, *C*, and *W* at 293.15 K for the Nitromethane–Benzene System

X_2	η_{12}, cP	η^E, cP	d	C	$W/10^{-3}$, kcal/mol
0.0000	0.645				
0.0919	0.627	–0.018	–0.34	0.54	-119.93
0.2238	0.606	–0.039	–0.36	0.53	-127.65
0.2978	0.597	–0.048	–0.37	0.53	-131.64
0.3994	0.587	–0.058	–0.39	0.52	-141.82
0.4940	0.582	–0.063	–0.41	0.52	-149.45
0.7053	0.585	–0.059	–0.47	0.50	-174.19
0.8004	0.595	–0.049	–0.50	0.49	-188.97
0.9073	0.620	–0.024	–0.45	0.50	-165.56
1.0000	0.644				

Table II. Mole Fraction (X_2) of Nitromethane, Viscosity (η_{12}), Excess Viscosity (η^E), and Values of Parameters *d*, *C*, and *W* at 293.15 K for the Nitromethane–*p*-Xylene System

X_2	η_{12}, cP	η^E, cP	d	C	$W/10^{-3}$, kcal/mol
0.0000	0.648				
0.1151	0.632	–0.016	–0.24	0.57	23.32
0.1918	0.629	–0.018	–0.19	0.59	58.25
0.2724	0.628	–0.019	–0.15	0.60	82.40
0.4256	0.626	–0.020	–0.13	0.60	106.68
0.4810	0.625	–0.021	–0.13	0.60	111.65
0.6051	0.625	–0.021	–0.14	0.60	122.82
0.6915	0.626	–0.019	–0.14	0.60	129.85
0.7940	0.627	–0.018	–0.17	0.59	128.41
0.8837	0.632	–0.013	–0.19	0.59	129.40
1.000	0.644				

Table III. Mole Fraction (X_2) of Nitromethane, Viscosity (η_{12}), Excess Viscosity (η^E), and Values of Parameters *d*, *C*, and *W* at 293.15 K for the Nitromethane–Mesitylene System

X_2	η_{12}, cP	η^E, cP	d	C	$W/10^{-3}$, kcal/mol
0.0000	0.692				
0.1192	0.686	0.000	0.00	0.67	195.89
2.2065	0.683	0.001	0.01	0.67	211.09
0.3019	0.679	0.002	0.01	0.67	223.31
0.3858	0.679	0.003	0.02	0.68	247.48
0.4761	0.674	0.005	0.03	0.68	257.02
0.6061	0.671	0.008	0.05	0.68	290.24
0.7112	0.666	0.008	0.06	0.69	315.18
0.7985	0.657	0.003	0.03	0.68	320.42
0.8912	0.648	–0.001	–0.02	0.66	315.88
1.0000	0.644				

Values of the parameter *d* for each sample of all the mixtures were calculated by eq 1, first suggested by Grunberg and

$$\ln \eta_{12} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1X_2d \qquad (1)$$

Nissan (*8*), where η_1, η_2 and X_1, X_2 are the viscosities and mole fractions respectively of the components 1 and 2. η_{12} is the viscosity of the liquid mixture.

[†] Present address: Chemistry Department, Garhwal University Campus, Pauri (Garhwal), India.

[‡] Present address: M.M.M. Post-graduate College, Bhatpar Rani, Deoria (U.P.), India.

0021-9568/88/1733-0402$01.50/0

Table IV. Mole Fraction (X_2) of Nitroethane, Viscosity (η_{12}), Excess Viscosity (η^E), and Values of Parameters d, C, and W at 293.15 K for the Nitroethane-Benzene System

X_2	η_{12}, cP	η^E, cP	d	C	$W/10^{-3}$, kcal/mol
0.0000	0.645				
0.0901	0.628	-0.020	-0.38	0.54	-196.76
0.1956	0.611	-0.041	-0.41	0.53	-210.31
0.2856	0.602	-0.053	-0.41	0.53	-211.23
0.3897	0.595	-0.064	-0.43	0.53	-218.54
0.4893	0.594	-0.068	-0.43	0.53	-221.91
0.5827	0.597	-0.068	-0.45	0.52	-228.22
0.6952	0.608	-0.061	-0.45	0.52	-231.96
0.7869	0.622	-0.051	-0.47	0.51	-239.01
0.8790	0.644	-0.032	-0.45	0.51	-232.12
1.0000	0.680				

Table V. Mole Fraction (X_2) of Nitroethane, Viscosity (η_{12}), Excess Viscosity (η^E), and Values of Parameters d, C, and W at 293.15 K for the Nitroethane-p-Xylene System

X_2	η_{12}, cP	η^E, cP	d	C	$W/10^{-3}$, kcal/mol
0.0000	0.648				
0.0968	0.633	-0.018	-0.32	0.56	-105.64
0.1917	0.629	-0.025	-0.25	0.58	-65.41
0.3000	0.627	-0.031	-0.23	0.59	-49.09
0.4039	0.626	-0.035	-0.23	0.59	-45.42
0.4933	0.626	-0.038	-0.23	0.59	-47.93
0.6083	0.629	-0.039	-0.25	0.58	-52.52
0.6994	0.633	-0.037	-0.27	0.58	-61.89
0.7938	0.644	-0.029	-0.27	0.57	-58.46
0.9011	0.660	-0.017	-0.28	0.57	-60.54
1.0000	0.680				

Table VI. Mole Fraction (X_2) of Nitroethane, Viscosity (η_{12}), Excess Viscosity (η^E), and Values of Parameters d, C, and W at 293.15 K for Nitroethane-Mesitylene System

X_2	η_{12}, cP	η^E, cP	d	C	$W/10^{-3}$, kcal/mol
0.0000	0.692				
0.0912	0.690	-0.001	-0.02	0.68	92.63
0.1908	0.685	-0.005	-0.04	0.67	81.38
0.2974	0.680	-0.008	-0.06	0.67	78.71
0.3871	0.675	-0.012	-0.08	0.66	73.37
0.5179	0.669	-0.017	-0.10	0.65	68.81
0.6112	0.665	-0.020	-0.12	0.64	62.16
0.6912	0.665	-0.019	-0.13	0.64	63.68
0.7813	0.669	-0.014	-0.12	0.65	77.55
0.8874	0.671	-0.010	-0.15	0.63	67.73
1.0000	0.680				

Table VII. Mole Fraction (X_2) of 2-Nitropropane, Viscosity (η_{12}), Excess Viscosity (η^E), and Values of Parameters d, C, and W at 293.15 K for the 2-Nitropropane-Benzene System

X_2	η_{12}, cP	η^E, cP	d	C	$W/10^{-3}$, kcal/mol
0.0000	0.645				
0.0983	0.631	-0.026	-0.45	0.56	-242.86
0.2123	0.632	-0.050	-0.44	0.56	-241.53
0.2863	0.619	-0.063	-0.45	0.56	-245.60
0.4048	0.622	-0.074	-0.45	0.55	-244.58
0.5002	0.631	-0.077	-0.45	0.55	-241.94
0.5981	0.641	-0.079	-0.47	0.54	-254.98
0.7032	0.661	-0.073	-0.48	0.53	-261.98
0.7847	0.683	-0.061	-0.49	0.53	-265.52
0.9080	0.731	-0.028	-0.44	0.54	-239.85
1.0000	0.771				

Table VIII. Mole Fraction (X_2) of 2-Nitropropane, Viscosity (η_{12}), Excess Viscosity (η^E), and Values of Parameters d, C, and W at 293.15 K for the 2-Nitropropane-p-Xylene System

X_2	η_{12}, cP	η^E, cP	d	C	$W/10^{-3}$, kcal/mol
0.0000	0.648				
0.1052	0.640	-0.021	-0.33	0.60	-153.70
0.2079	0.636	-0.038	-0.33	0.60	-156.70
0.2945	0.638	-0.046	-0.32	0.60	-149.77
0.3973	0.644	-0.053	-0.31	0.60	-145.37
0.4976	0.651	-0.058	-0.33	0.59	-151.93
0.6039	0.664	-0.058	-0.34	0.59	-155.96
0.7089	0.678	-0.057	-0.38	0.57	-177.10
0.8008	0.699	-0.048	-0.40	0.56	-187.16
0.8925	0.727	-0.031	-0.42	0.55	-197.51

Table IX. Mole Fraction (X_2) of 2-Nitropropane, Viscosity (η_{12}), Excess Viscosity (η^E), and Values of Parameters d, C, and W at 293.15 K for the 2-Nitropropane-Mesitylene System

X_2	η_{12}, cP	η^E, cP	d	C	$W/10^{-3}$, kcal/mol
0.0000	0.692				
0.0955	0.691	-0.009	-0.14	0.68	-27.50
0.1983	0.691	-0.017	-0.14	0.68	-30.58
0.2294	0.690	-0.026	-0.17	0.67	-41.60
0.4005	0.691	-0.035	-0.19	0.66	-49.23
0.5048	0.696	-0.036	-0.20	0.66	-52.10
0.6007	0.701	-0.039	-0.22	0.65	-61.35
0.7022	0.708	-0.040	-0.25	0.64	-78.50
0.8014	0.717	-0.038	-0.32	0.61	-112.45
0.8980	0.738	-0.025	-0.36	0.60	-128.51
1.0000	0.771				

Table X. Dipole Moment (μ_{gas}) of the Polar Solutes in the Gas Phase and Polarizabilities (α) of the Nonpolar Solvents along the Sixfold Symmetry Axis

polar solute	μ_{gas}, D	nonpolar solvent	$\alpha/10^{30}$, m^3
nitromethane	3.46	benzene	7.33
nitroethane	3.65	p-xylene	10.75
2-nitropropane	3.73	mesitylene	12.47

Results and Discussion

Values of the viscosity η_{12}, excess viscosity $\eta^E = \eta_{12} - X_1\eta_1 - X_2\eta_2$, and the parameter d as a function of the composition for all the systems studied are reported in Tables I–IX.

A perusal of the Tables I–III for the polar solute nitromethane shows that there is an appreciable negative deviation from the rectilinear dependence of viscosity on mole fractions for the mixtures containing benzene as the nonpolar component. The negative deviation is significantly reduced in the case of p-xylene while mesitylene mixtures show a small positive deviation. Nitroethane and 2-nitropropane (vide Tables IV–IX) also show negative deviations with benzene, p-xylene, and mesitylene, the deviations being in the order benzene > p-xylene > mesitylene.

It is evident that most of the liquid mixtures become more fluid in comparision to the pure components, indicating reduced forces between unlike molecules. It may be recalled that the neat polar solutes have a tendency for self-association which is likely to gradually disappear on dilution with the nonpolar solvent.

It is apparent from the data in tables that for any of the polar solutes viscosity for eqimolar mixtures has the order mesitylene > p-xylene > benzene. In this connection it may be pointed out that the three aromatic hydrocarbons have polarizabilities in the same order given in Table X (*9*). Similarly it is also evident from the data for any of the nonpolar aromatic solvents that viscosity for equimolar mixtures for different polar solutes is in the order 2-nitropropane > nitroethane > nitromethane, which is also the order of their dipole moments given in Table X (*10*). This behavior emphasizes the importance of dipole-induced-dipole interactions between unlike molecules of the liquid mixtures. However, the dipole-induced-dipole interactions perhaps do not exclusively govern the behavior of such liquid mixtures. An abnormal order of viscosity value for the equimolar mixture of nitromethane and nitroethane with mesitylene seems to be a counterbalance of steric effects due to the presence of methyl substituents and molecular size.

As is evident from Tables I-IX, values of the parameter d are negative for all the systems except for the nitromethane-mesitylene system which has a small positive value for most of the mixtures. For all the polar solutes, d values increase, i.e., become less negative, as one goes from benzene to mesitylene, indicating a stronger interaction as a result of methyl subtitution in the benzene ring. This behavior is in accordance with the progressive enhancement in the polarizability of the aromatic hydrocarbons on gradual methyl substitution.

Irving has rigorously analyzed (*3*) the suitability of different equations proposed for the viscosity of liquid mixtures and found the Grunberg-Nissan equation to have the highest goodness factor for polar-nonpolar liquid mixtures. Other attempts have also been made to describe the viscosity of binary liquid mixtures in terms of those of the components and a parameter attributed to the interaction between them. Hind, McLaughlin, and Ubbelohde (*11*) suggested that

$$\eta_{12} = X_1^2\eta_1 + X_2^2\eta_2 + 2X_1X_2C \qquad (2)$$

Katti and Chaudhary (*12*), using the Eyring concept of viscosity, obtained the expression

$$\ln \eta_{12}V_{12} = X_1 \ln \eta_1V_1 + X_2 \ln \eta_2V_2 + X_1X_2/(W/RT) \qquad (3)$$

where V_1 and V_2 are the molar volumes of the two components. $V_{12} = (X_1M_1 + X_2M_2)/\rho_{12}$, where ρ_{12} is the density of the mixture and M_1 and M_2 are the molecular weights of the components; W is the interaction energy term.

Data obtained from the present studies have been analyzed for these models and values of the parameters C and W are also given in Tables I-IX along with d. A perusal of the tables shows that the parameter C calculated by eq (2) shows the smallest variation over the whole composition range for any of the systems. Values of C for different aromatics for all the three polar solutes rise with the polarizability of the aromatic hydrocarbon, indicating a stronger dipole-induced-dipole interaction. Not only this, C values for an aromatic solvent with the different polar solutes are not that anomalous as is the case with corresponding d values.

W values obtained by eq 3 show almost the same, rather worse, variation over the whole composition range as d. Of course, W values for all the three polar solutes are in the order mesitylene > *p*-xylene > benzene, which is also the order of their polarizabilities. W values for any of the aromatic solvents with the polar solutes have again the same anomalous order as exhibited by the corresponding d values. In fact, one could say that the parameters d and W exhibit almost similar behavior which is not unlikely in view of logarithmic nature of both the equations. However, the Hind-McLaughlin-Ubbelohde equation seems to be the most suitable one for the viscosity data of binary mixtures of the type studied.

It may be pointed out that equations with single disposable constants, which may be regarded as interaction parameters, are simple to apply. Values of the constants may be calculated for each composition and, from the scatter of the values for the mixtures of different compositions in a series, suitability of the different equations can be compared. Inferences can be drawn regarding the extent of interaction from the values of the constant. In the case of equations containing a power series with more than one constants the viscosity data can be represented to within their scatter by taking an appropriate number of terms, which is little more than an exercise in curve fitting.

Registry No. Nitromethane, 75-52-5; nitroethane, 79-24-3; 2-nitropropane, 79-46-9; benzene, 71-43-2; *p*-xylene, 106-42-3; mesitylene, 108-67-8.

Literature Cited

(1) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1966**, *62*, 142.
(2) Nigam, R. K.; Mahl, B. S. *Indian J. Chem.* **1971**, *9*, 1255.
(3) Irving, J. B. *NEL Report* **1977**, No. 631.
(4) Yadava, R. R.; Yadava, S. S. *Indian J. Chem.* **1981**, *20A*, 221.
(5) Yadava, R. R.; Singh, V. N. *Indian J. Chem.* **1982**, *21A*, 17.
(6) Yadava, R. R.; Yadava, S. S. *J. Chem. Eng. Data* **1987**, *32*, 54-56.
(7) Hammick, D. L.; Norris, A.; Sutton, L. E. *J. Chem. Soc.* **1938**, 1755.
(8) Grunberg, L.; Nissan, A. H. *Nature (London)* **1949**, *164*, 799.
(9) Le Fevre, C. G.; Le Fevre, R. J. W. *Rev. Pure Appl. Chem.* **1955**, *5*, 261.
(10) Weast, R. C. *Handbook of Chemistry and Physics*; Chemical Rubber Co.: Cleveland, OH, 1971; p E-52.
(11) Hind, R. K.; McLaughlin, E.; Ubbelohde, A. R. *Trans. Faraday Soc.* **1960**, *56*, 328.
(12) Katti, P. K.; Chaudhary, M. *J. Chem. Eng. Data* **1964**, *9*, 442.

Received for review November 3, 1986. Revised August 12, 1987. Accepted March 23, 1988. V.N.S. is grateful to the U.G.C., New Delhi, for the award of a teacher fellowship during the course of the present investigation.

Densities and Viscosities of Propionic Acid in Benzene, Methylbenzene, Ethylbenzene, and Propylbenzene

M. C. S. Subha and S. Brahmaji Rao*

Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003, India

The densities and the viscosities at 308.15 K were determined for the systems propionic acid (PA) + benzene (B), + methylbenzene (MB), + ethylbenzene (EB), and + propylbenzene (PB). The excess viscosities and excess molar volumes were calculated from the experimental results. The excess molar volumes show a slight consistent trend toward more positive values as the length of the hydrocarbon side chain of the benzene ring increases. The results suggest the presence of specific interactions.

As part of our studies on physicochemical properties of binary liquid mixtures with carboxylic acids (*1-3*) (carboxylic acid as the main component), we have obtained the excess molar volumes and excess viscosities from the measured densities and the viscosities of the following binary liquid mixtures: propionic acid (PA) + benzene (B), + methylbenzene (MB), + ethylbenzene (EB), and + propylbenzene (PB) at 308.15 K and under atmospheric pressure. The results are communicated here.

Experimental Section

Densities were measured with a 18-mL bicapillary pycnometer having a capillary diameter of 0.85 mm. The pycnometer was calibrated by using double distilled water (density 994.06 kg m^{-3} at 308.15 K). All weighings were done on a Mettler

0021-9568/88/1733-0404$01.50/0