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Excess Volumes and Viscosities of 1,4-Dioxane + Chlorinated Ethanes or + Chlorinated Ethenes at 303.15 K

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Excess volumes and viscosities at 303.15 K are reported for mixtures of 1,4-dioxane + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, + trichloroethene, and + tetrachloroethene. The results are interpreted in terms of molecular interactions between unlike molecules. Further, attempts are made to predict the viscosity values on the basis of the corresponding states approach and the Grunberg and Nissan treatment.

Introduction

In continuation of our studies on thermophysical properties of binary nonelectrolyte mixtures containing cyclic ethers as common components (*1–3*), we report here new experimental data on excess volume and viscosity for 1,4-dioxane + 1,2-dichloroethane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, + trichloroethene, and + tetrachloroethene over the entire range of composition at 303.15 K. This study is undertaken with a view to characterize intermolecular interactions between unlike molecules and also to examine the applicability of the corresponding states approach of Teja and Rice (*4*) and the Grunberg and Nissan theory (*5*) in predicting the viscosity of mixtures of 1,4-dioxane with chlorinated ethanes and ethenes.

Experimental Section

Materials. The chemicals used (AnalaR and LR Grade) in the present study were purified using the standard methods as described earlier (*6–7*). The middle fraction boiling within ±0.1 K was collected and used for the excess volume and viscosity measurements. The purities of the chemicals were checked by measuring densities and boiling points and comparing with those reported in the literature (*8*). The results are compared with literature values in Table 1.

Table 1. Properties of Pure Components

component	density[a]/(g·cm^{-3}) exp	density[a]/(g·cm^{-3}) lit. (*8*)	T_b/K exp	T_b/K lit. (*8*)
1,4-dioxane	1.022 34	1.022 30	374.55	374.44
1,2-dichloroethane	1.238 28	1.238 31	356.70	356.63
1,1,1-trichloroethane	1.320 92	1.320 96	347.00	347.15
1,1,2,2-tetrachloroethane	1.578 57	1.578 60	419.25	419.35
trichloroethene	1.451 34	1.451 40	360.40	360.34
tetrachloroethene	1.606 36	1.606 40	394.45	394.35

[a] At 303.15 K.

Apparatus. Excess volumes were determined directly using a single composition per loading type dilatometer described by Rao and Naidu (*9*). Four dilatometers with different capacities were used to cover the composition range. The measurements were made in a thermostat controlled to within ±0.01 K. The excess volumes are reproducible to ±0.003 cm^3·mol^{-1}. Viscosities were measured using a suspended level Ubbelohde viscometer. The viscometer was calibrated using distilled water. The viscometer constant, k, was calculated from the viscosity (η_w), density (ϱ_w), and flow time (t_w) of water using the relation $k = \eta_w/\varrho_w t_w$. An average of 10 measurements were taken, and the value of k did not differ more than ±0.005 m^2·s^{-2}. An electronic stopwatch capable of measuring time to ±0.01 s was used for the time measurement. Kinetic energy corrections were checked and found to be negligible. The estimated error in viscosity is ±0.0005 mPa·s. The performance of the viscometer was assessed by measuring viscosities of the pure components and comparing with the values reported in the literature.

Results and Discussion

Experimental values for the excess volumes and viscosities for mixtures of 1,4-dioxane with chlorinated ethanes and chlorinated ethenes at 303.15 K as a function of composition are given in Table 2. Excess volume data are fitted to an empirical equation of the form

$$V^E = x(1 - x)\{a_0 + a_1(1 - 2x) + a_2(1 - 2x)^2\} \qquad (1)$$

where a_0, a_1, and a_2 are adjustable parameters. The values of the parameters are obtained by the least-squares technique and are given in Table 3 along with the standard deviation of the fit, σ. The standard deviation of the fit is calculated from the equation

$$\sigma = [\sum\{V^E_{\text{exp}} - V^E_{\text{cal}}\}^2/(n - p)]^{1/2} \qquad (2)$$

where n is the number of results and p is the number of parameters used in eq 3.

On the basis of corresponding states treatment for mixture compressibility factors (*10, 11*), Teja and Rice (*4, 12*) proposed the following expression for liquid mixture viscosity:

$$\ln(\eta_m\zeta_m) = x \ln(\eta_1\zeta_1) + (1 - x) \ln(\eta_2\zeta_2) \qquad (3)$$

where $\zeta = (V_c)^{2/3}/(T_cM)^{1/2}$ and T_c, V_c, and M are critical temperature, critical volume, and molecular weight, respectively. The values of the critical temperature, critical

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Table 2. Excess Volumes V^E and Viscosities η for 1,4-Dioxane + Chlorinated Hydrocarbons at 303.15 K

x	V^E/(cm^3·mol^{-1})	η/(mPa·s)	x	V^E/(cm^3·mol^{-1})	η/(mPa·s)
x 1,4-Dioxane + (1 − x) 1,2-Dichloroethane					
0.0000	0.000	0.7295	0.5670	0.195	0.8832
0.0462	0.030	0.7468	0.6362	0.188	0.9068
0.1984	0.110	0.7909	0.7673	0.154	0.9595
0.2786	0.136	0.8101	0.8428	0.118	0.9960
0.3663	0.173	0.8307	0.9185	0.060	1.0369
0.4515	0.189	0.8512	1.0000	0.000	1.0863
x 1,4-Dioxane + (1 − x) 1,1,1-Trichloroethane					
0.0000	0.000	0.7243	0.5168	−0.230	0.9291
0.0725	−0.032	0.7541	0.6428	−0.215	0.9700
0.1135	−0.063	0.7710	0.7459	−0.177	1.0015
0.2041	−0.120	0.8089	0.8153	−0.137	1.0229
0.3360	−0.194	0.8625	0.9277	−0.061	1.0595
0.4193	−0.221	0.8943	1.0000	0.000	1.0863
x 1,4-Dioxane + (1 − x) 1,1,2,2-Tetrachloroethane					
0.0000	0.000	1.4554	0.5705	−0.274	1.2867
0.0869	−0.127	1.4406	0.6587	−0.221	1.2448
0.1835	−0.237	1.4189	0.7613	−0.156	1.1976
0.2833	−0.304	1.3925	0.8189	−0.108	1.1692
0.3491	−0.315	1.3721	0.9080	−0.049	1.1276
0.4610	−0.320	1.3314	1.0000	0.000	1.0863
x 1,4-Dioxane + (1 − x) Trichloroethene					
0.0000	0.000	0.5230	0.5728	0.016	0.8370
0.0577	−0.019	0.5863	0.6186	0.029	0.8515
0.1189	−0.035	0.6434	0.7841	0.057	0.9264
0.2890	−0.048	0.7496	0.8920	0.044	0.9979
0.3696	−0.037	0.7787	0.9513	0.025	1.0446
0.4012	−0.030	0.7885	1.0000	0.000	1.0863
x 1,4-Dioxane + (1 − x) Tetrachloroethene					
0.0000	0.000	0.7976	0.5332	0.312	0.9725
0.0711	0.084	0.8321	0.6532	0.292	0.9982
0.1527	0.160	0.8661	0.7921	0.220	1.0298
0.2465	0.231	0.8991	0.8937	0.123	1.0553
0.3656	0.290	0.9331	0.9581	0.053	1.0735
0.4126	0.301	0.9447	1.0000	0.000	1.0863

Table 3. Values of the Parameters of Eq 1 and the Standard Deviation of the Fit (σ) for 1,4-Dioxane + Chlorinated Hydrocarbons at 303.15 K

chlorinated hydrocarbon	a_0/(cm^3·mol^{-1})	a_1/(cm^3·mol^{-1})	a_2/(cm^3·mol^{-1})	σ/(cm^3·mol^{-1})
1,2-dichloroethane	0.776	0.116	−0.020	0.005
1,1,1-trichloroethane	−0.931	−0.185	0.310	0.005
1,1,2,2-tetrachloroethane	−1.227	0.642	0.191	0.004
trichloroethene	−0.022	0.512	0.138	0.003
tetrachloroethene	1.225	0.046	0.142	0.005

Table 4. Absolute Deviation of Calculated Viscosity Values from Experimental Results for 1,4-Dioxane + Chlorinated Hydrocarbons at 303.15 K

x	$\lvert\eta_{exp} - \eta_{eq\ 3}\rvert$/(mPa·s)	$\lvert\eta_{exp} - \eta_{eq\ 9}\rvert$/(mPa·s)	x	$\lvert\eta_{exp} - \eta_{eq\ 3}\rvert$/(mPa·s)	$\lvert\eta_{exp} - \eta_{eq\ 9}\rvert$/(mPa·s)
x 1,4-Dioxane + (1 − x) 1,2-Dichloroethane					
0.0000	0.0002	0.0000	0.5670	0.0040	0.0045
0.0462	0.0073	0.0077	0.6362	0.0066	0.0073
0.1984	0.0158	0.0164	0.7673	0.0088	0.0097
0.2786	0.0140	0.0144	0.8428	0.0076	0.0083
0.3663	0.0096	0.0098	0.9185	0.0049	0.0053
0.4515	0.0037	0.0036	1.0000	0.0003	0.0000
x 1,4-Dioxane + (1 − x) 1,1,1-Trichloroethane					
0.0000	0.0003	0.0000	0.5168	0.0011	0.0003
0.0725	0.0012	0.0002	0.6428	0.0079	0.0049
0.1135	0.0019	0.0003	0.7459	0.0127	0.0086
0.2041	0.0047	0.0015	0.8153	0.0138	0.0095
0.3360	0.0041	0.0025	0.9277	0.0096	0.0068
0.4193	0.0025	0.0018	1.0000	0.0003	0.0000
x 1,4-Dioxane + (1 − x) 1,1,2,2-Tetrachloroethane					
0.0000	0.0007	0.0000	0.5705	0.0003	0.0009
0.0869	0.0007	0.0012	0.6587	0.0050	0.0004
0.1835	0.0014	0.0016	0.7613	0.0060	0.0062
0.2833	0.0028	0.0027	0.8189	0.0070	0.0074
0.3491	0.0031	0.0028	0.9080	0.0056	0.0053
0.4610	0.0016	0.0011	1.0000	0.0003	0.0000
x 1,4-Dioxane + (1 − x) Trichloroethene					
0.0000	0.0001	0.0000	0.5728	0.0295	0.0219
0.0577	0.0375	0.0313	0.6186	0.0465	0.0342
0.1189	0.0696	0.0537	0.7841	0.0763	0.0524
0.2890	0.0744	0.0602	0.8920	0.0571	0.0370
0.3696	0.0518	0.0411	0.9513	0.0308	0.0192
0.4012	0.0406	0.0319	1.0000	0.0003	0.0000
x 1,4-Dioxane + (1 − x) Tetrachloroethene					
0.0000	0.0004	0.0000	0.5332	0.0020	0.0021
0.0711	0.0079	0.0090	0.6532	0.0091	0.0100
0.1527	0.0128	0.0143	0.7921	0.0120	0.0133
0.2465	0.0136	0.0152	0.8937	0.0095	0.0079
0.3656	0.0088	0.0099	0.9581	0.0048	0.0050
0.4126	0.0058	0.0066	1.0000	0.0003	0.0000

Table 5. Values of the Interaction Parameters (ϵ_{12} and d_{12}) and Average Absolute Deviation (AAD) at 303.15 K for 1,4-Dioxane + Chlorinated Hydrocarbons

chlorinated hydrocarbon	ϵ_{12}	d_{12}	AAD (eq 3)	AAD (eq 9)
1,2-dichloroethane	0.992	−0.120	0.0082	0.0087
1,1,1-trichloroethane	1.022	0.160	0.0060	0.0036
1,1,2,2-tetrachloroethane	0.989	0.181	0.0034	0.0030
trichloroethene	1.053	0.316	0.0514	0.0328
tetrachloroethene	0.989	0.143	0.0045	0.0088

volume, and molar mass of the mixtures are evaluated using the equations (*10, 11*)

$$V_{m,c} = x^2V_{1,c} + (1-x)^2V_{2,c} + 2x(1-x)V_{12,c} \quad (4)$$

$$T_{m,c} = [x^2T_{1,c}V_{1,c} + (1-x)^2T_{2,c}V_{2,c} + 2x(1-x)T_{12,c}V_{12,c}]/V_{m,c} \quad (5)$$

$$M_m = xM_1 + (1-x)M_2 \quad (6)$$

$$V_{12,c} = [\{(V_{1,c})^{1/3} + (V_{2,c})^{1/3}\}/2]^3 \quad (7)$$

$$T_{12,c}V_{12,c} = \epsilon_{12}(T_{1,c}T_{2,c}V_{1,c}V_{2,c})^{1/2} \quad (8)$$

where ϵ_{12} is an interaction parameter on the order of unity which was obtained from the viscosity at x = 0.5.

According to Grunberg and Nissan (*5*), the viscosity for the mixture is given by

$$\ln \eta = x \ln \eta_1 + (1-x) \ln \eta_2 + x(1-x)d_{12} \quad (9)$$

where d_{12} is an interaction parameter which is a function of the chemical nature of the components and temperature. d_{12}, obtained from a fit of eq 9 to the viscosity at x = 0.5, is used to compute the viscosities over the entire composition range. The absolute deviations of the calculated values of viscosity from the experimental results are given in Table 4. The values of ϵ_{12} and d_{12} are shown in Table 5 along with the average absolute deviation (AAD). AAD is calculated using the equation

$$\text{AAD} = \sum[|\eta_{exp} - \eta_{cal}|/\eta_{exp}]/n \quad (10)$$

where n represents the number of experimental points excluding the end points.

The excess volumes are positive in mixtures of 1,4-dioxane with 1,2-dichloroethane and tetrachloroethene and negative in the systems 1,4-dioxane + 1,1,1-trichloroethane and + 1,1,2,2-tetrachloroethane. An inversion in sign of V^E is observed from negative to positive in the trichloroethene system. Deviations in viscosity are positive in mixtures of 1,4-dioxane with 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and tetrachloroethene. An inversion in sign of the deviation in viscosity is observed in 1,4-dioxane + 1,2-dichloroethane and trichloroethene systems.

A comparison of the data included in Table 4 indicates that the viscosities of these mixtures can be adequately represented by the corresponding states method and by the Grunberg and Nissan relation.

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