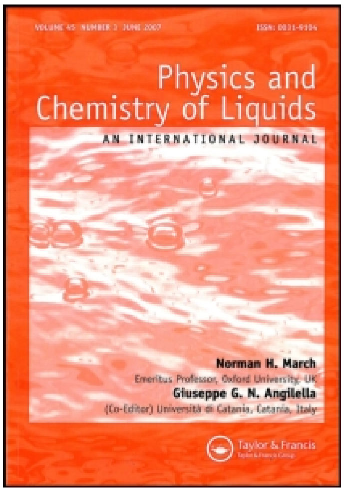

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Viscosities of Binary Mixtures Containing Non-polar Components

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Viscosities at 303.15 K have been measured for binary liquid mixtures of 1,1,2,2-tetrachloroethane ($C_2H_2Cl_4$) with *n*-hexane, *n*-heptane, *n*-octane and *n*-nonane. The viscosity data have been analysed in the light of absolute reaction rate and free volume theories of liquid viscosity. The values of η^E are negative over the entire composition range. Further, the study has been extended to evaluate interaction parameter, d. The values of both η^E and d indicate the existence of dispersion forces between unlike molecules.

Key Words: Viscosities, binary mixtures, non-polar components, absolute reaction rate, free volume.

1 INTRODUCTION

In continuation of our studies on the binary liquid mixtures of haloethanes,[1-3] we report here new viscosity data for mixtures of 1,1,2,2-tetrachloroethane with *n*-hexane, *n*-heptane, *n*-octane and *n*-nonane at 303.15 K. Further, the data have also been analysed in terms of Bloomfield and Dewan's theory[4] of liquid viscosity. Bloomfield and Dewan have obtained an equation for liquid viscosity by combining absolute reaction rate theory of Eyring[5] and free volume theory.[6-8] The analysis has been undertaken to know to what extent the theory can reproduce the viscosity data for binary liquid mixtures of components of varying complexity.

2 EXPERIMENTAL SECTION

Materials

All the materials were purified by the methods described by Reddick and Bunger.[9] 1,1,2,2-Tetrachloroethane (Riedel) was shaken with con-

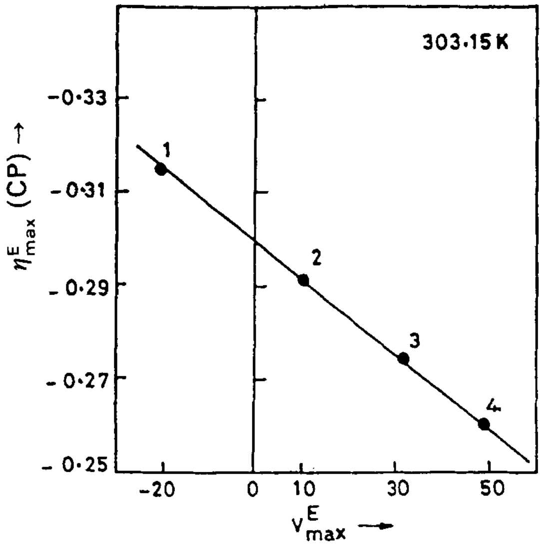

Figure 1 Plot of η^E_{max} vs. V^E_{max} for mixtures: 1. $C_2H_2Cl_4$-nC_6H_{14}, 2. $C_2H_2Cl_4$-nC_7H_{16}, 3. $C_2H_2Cl_4$-nC_8H_{18}, 4. $C_2H_2Cl_4$-nC_9H_{20}.

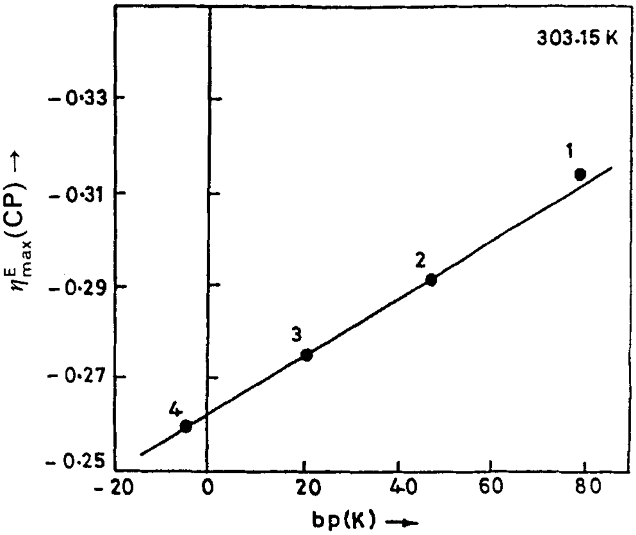

Figure 2 Plot of η^E_{max} vs. bp(K) for mixtures: 1. $C_2H_2Cl_4$-nC_6H_{14}, 2. $C_2H_2Cl_4$-nC_7H_{16}, 3. $C_2H_2Cl_4$-nC_8H_{18}, 4. $C_2H_2Cl_4$-nC_9H_{20}.

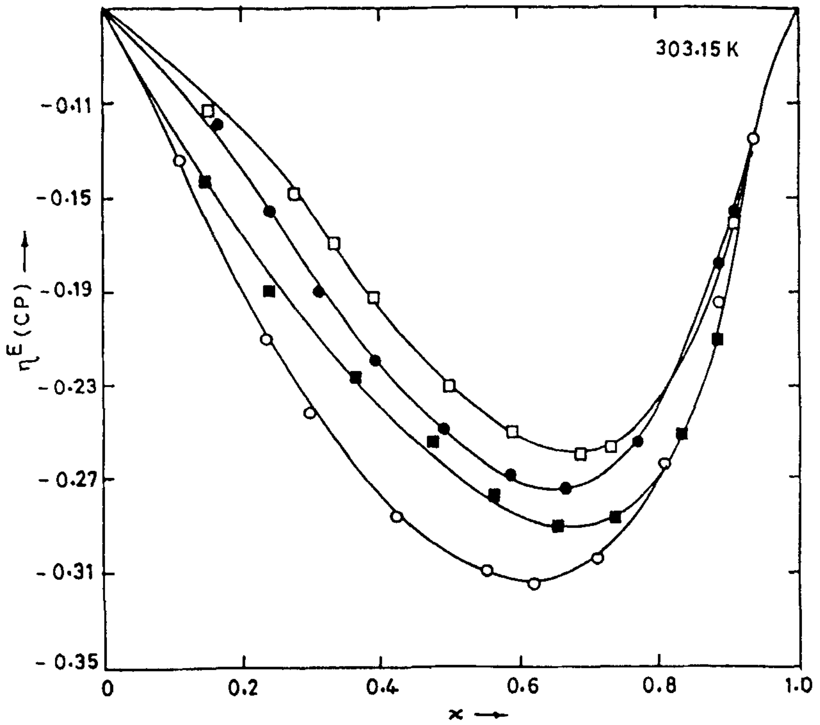

Figure 3 Plot of η^E vs. mole fraction of x of $C_2H_2Cl_4$: ○ $C_2H_2Cl_4$-nC_6H_{14}, ■ $C_2H_2Cl_4$-nC_7H_{16}, ● $C_2H_2Cl_4$-nC_8H_{18}, □ $C_2H_2Cl_4$-nC_9H_{20}.

Table 1 Densities and boiling points of the pure components.

Component	Density (ρ)/(g/cm^3)		Boiling point (°K)	
	Present work	Literature	Present work	Literature
Tetrachloroethane	1.57800	1.57860	419.85	419.35
Hexane	0.65064	0.65070	341.60	341.89
Heptane	0.67530	0.67538	371.80	371.58
Octane	0.69457	0.69450	398.65	398.82
Nonane	0.70998	0.70999	423.85	423.95

centrated sulphuric acid for 10 min. The operation was repeated until the acid developed no more colour. The chloroalkane was then washed with water, steam distilled, dried with potassium carbonate, and fractionally distilled. *n*-Hexane and *n*-heptane (BDH) were purified by shaking successively with concentrated sulphuric acid, water, potassium hydroxide and water and finally fractionating. *n*-Octane and *n*-nonane (Veb) were used without further purification. The purity of the samples was checked by comparing the measured densities and boiling points of the components with those reported in the literature.[10] The densities were determined with a bicapillary pycknometer described by Rao and Naidu.[11] The values are reproducible to $\pm 5 \times 10^{-5}$ g cm^{-3}. The data are given in Table 1.

Viscosities

Viscosity of liquids and liquid mixtures were determined by using Ostwald viscometers. The accuracy of the viscometer was checked by measuring the viscosities of pure benzene and cyclohexane. The results show very good agreement with those reported in the literature. Mixtures of various known compositions were prepared by weight. A constant volume of the mixture transferred in to the viscometer and then inserted in a water thermostat controlled at 303.15 ± 0.01 K. The time of flow of the liquid through capillary was determined. Viscosity was then obtained from density, flow time and constant of the viscometer using the relation.

$$\eta = K_v \rho t \tag{1}$$

where K_v is viscometer constant and ρ and t are the density and flow time respectively. Densities for pure components were determined experimentally. In case of mixtures densities were obtained from experimental excess volumes using the relation

$$\rho = \frac{xM_1 + (1 - x)M_2}{V + V^E} \tag{2}$$

where x stands for mole fraction of chloroethane, M_1 and M_2 are molecular weights of chloroethane and alkanes, respectively. V and V^E stand for the molar volume and excess molar volume respectively.

3 THEORETICAL ASPECTS

One of the simple additive relations[4] to predict the mixture viscosity from the properties of pure components, when the interactions between the components are neglected, is given by

$$\ln \eta = x \ln \eta_1 + (1 - x) \ln \eta_2 \tag{3}$$

where η_1 and η_2 are the viscosities of the pure components. Two major semiempirical theories which can be used to predict liquid viscosity are the absolute reaction rate theory of Eyring and co-workers and the free volume theory. Combining the absolute reaction rate and the free volume theories of liquid viscosity, Bloomfield and Dewan have obtained Eq. (4),

$$\begin{aligned} \ln \eta &= x \ln \eta_1 + (1 - x) \ln \eta_2 - \frac{\Delta H_m}{RT} + \frac{\Delta S^R}{R} \\ &\quad + \left(\frac{1}{\tilde{V} - 1} - \frac{x}{\tilde{V}_1 - 1} - \frac{1 - x}{\tilde{V}_2 - 1} \right) \\ &= \ln \eta_{\text{id}} + \ln \eta_H + \ln \eta_S + \ln \eta_V \end{aligned} \tag{4}$$

where ΔH_m is the enthalpy of mixing per mole of the solution, ΔS^R is the residual entropy per mole, R is the gas constant, T is the absolute temperature and $\tilde{V}_1$, $\tilde{V}_2$ and $\tilde{V}$ are the reduced volumes of component 1, component 2 and the mixture respectively. In order to estimate the contributions to the mixture viscosity from $\Delta H_m/RT$ and $\Delta S^R/R$ in Eq. (4), we use Flory's equations[12] for ΔH_m and ΔS^R, which can be written in the following form.

$$\begin{aligned} \frac{\Delta H_m}{RT} &= \frac{xC_1}{\tilde{T}_1} \left(\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}} \right) + \left(\frac{1 - x}{\tilde{T}_2} \right) C_2 \left(\frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}} \right) \\ &\quad + \frac{xC_1 \theta_2 X_{12}}{\tilde{V} \tilde{T}_1 P_1^*} \end{aligned} \tag{5}$$

$$\frac{\Delta S^R}{R} = -3xC_1 \ln \frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}^{1/3} - 1} - 3(1 - x) \ln \frac{\tilde{V}_2^{1/3} - 1}{\tilde{V}^{1/3} - 1} \tag{6}$$

Table 2 Parameters of the pure components at 303.15 K

Component	$\alpha \times 10^3$ deg^{-1}	K_T T Pa^{-1}	$\tilde{V}$	V cm^3 mol^{-1}	V^* cm^3 mol^{-1}	P^* J cm^{-3}	T^* deg
Tetrachloroethane	0.998	792	1.251	106.37	85.03	597.8	5749.8
Hexane	1.404	1792	1.329	132.45	99.65	419.5	4445.0
Heptane	1.260	1526	1.303	148.39	113.88	425.0	4678.2
Octane	1.195	1374	1.290	164.46	127.47	438.8	4805.8
Nonane	1.062	1217	1.264	180.65	142.94	422.7	5101.0

Table 3 Values of experimental and calculated viscosities (cp) and the Parameter d for the various liquid mixtures at 303.15 K

x	η_{exptl}	η_{id}	η_H	η_S	η_V	η_G	$\eta_{\text{id}}\eta_H$	$\eta_{\text{id}}\eta_S$	$\eta_{\text{id}}\eta_G$	$\eta_{\text{id}}\eta_V$	$\eta_{\text{id}}\eta_H\eta_V$	$\eta_{\text{id}}\eta_H\eta_S\eta_V$	d
Tetrachloroethane + n — Hexane													
0.0000	0.309	—	—	—	—	—	—	—	—	—	—	—	—
0.1150	0.316	0.369	0.492	1.094	0.972	0.538	0.182	0.404	0.199	0.359	0.176	0.193	−1.53
0.2303	0.363	0.442	0.279	1.174	0.951	0.328	0.123	0.519	0.145	0.420	0.117	0.138	−1.11
0.2991	0.411	0.491	0.212	1.200	0.492	0.254	0.104	0.589	0.125	0.463	0.098	0.118	−0.85
0.4277	0.516	0.600	0.161	1.223	0.933	0.197	0.097	0.734	0.118	0.560	0.090	0.110	−0.62
0.5521	0.633	0.727	0.150	1.220	0.931	0.183	0.108	0.887	0.133	0.677	0.102	0.124	−0.56
0.6234	0.710	0.812	0.163	1.201	0.934	0.196	0.132	0.975	0.159	0.758	0.124	0.148	−0.57
0.7182	0.830	0.940	0.200	1.171	0.941	0.234	0.188	1.101	0.220	0.885	0.177	0.207	−0.62
0.8039	0.966	1.075	0.288	1.121	0.955	0.323	0.310	1.205	0.347	1.027	0.296	0.331	−0.68
0.8856	1.133	1.219	0.425	1.082	0.969	0.460	0.518	1.319	0.561	1.181	0.502	0.543	−0.72
0.9344	1.256	1.315	0.621	1.047	0.981	0.650	0.817	1.377	0.855	1.290	0.801	0.839	−0.75
1.0000	1.456	—	—	—	—	—	—	—	—	—	—	—	—
Tetrachloroethane + n-Heptane													
0.0000	0.393	—	—	—	—	—	—	—	—	—	—	—	—
0.1397	0.398	0.472	0.356	1.208	0.960	0.430	0.168	0.570	0.203	0.453	0.161	0.195	−1.42
0.2476	0.472	0.497	0.210	1.318	0.938	0.277	0.104	0.655	0.138	0.466	0.098	0.129	−0.27
0.3744	0.564	0.641	0.139	1.416	0.920	0.197	0.089	0.908	0.126	0.590	0.082	0.116	−0.55
0.4722	0.643	0.729	0.112	1.464	0.912	0.164	0.082	1.067	0.120	0.665	0.074	0.109	−0.56
0.5731	0.727	0.833	0.110	1.461	0.910	0.161	0.092	1.217	0.134	0.758	0.083	0.122	−0.56
0.6565	0.800	0.929	0.127	1.420	0.915	0.180	0.118	1.319	0.167	0.850	0.108	0.153	−0.66
0.7428	0.896	0.962	0.162	1.355	0.923	0.220	0.156	1.304	0.212	0.888	0.144	0.195	−0.18
0.8309	1.023	1.166	0.259	1.249	0.943	0.323	0.203	1.456	0.377	1.100	0.285	0.356	−0.93
0.9008	1.165	1.279	0.402	1.168	0.965	0.470	0.515	1.484	0.601	1.234	0.497	0.581	−1.04
0.9406	1.267	1.347	0.544	1.107	0.974	0.602	0.733	1.491	0.811	1.312	0.714	0.790	−1.10
1.0000	1.456	—	—	—	—	—	—	—	—	—	—	—	—

Tetrachloroethane + n − octane

0.0000	0.496	—	—	—	—	—	—	—	—	—	—	—	—
0.1642	0.536	0.592	0.247	1.104	0.967	0.273	0.146	0.656	0.162	0.572	0.141	0.156	−0.73
0.2409	0.562	0.643	0.146	1.120	0.957	0.164	0.094	0.720	0.105	0.615	0.190	0.101	−0.64
0.3162	0.610	0.697	0.100	1.139	0.949	0.114	0.070	0.794	0.079	0.661	0.66	0.075	−0.62
0.3944	0.655	0.759	0.075	1.132	0.944	0.085	0.057	0.859	0.065	0.716	0.054	0.061	−0.62
0.4996	0.725	0.850	0.064	1.105	0.943	0.071	0.054	0.939	0.060	0.802	0.051	0.057	−0.63
0.5896	0.794	0.936	0.068	1.085	0.945	0.074	0.064	1.016	0.069	0.885	0.060	0.065	−0.68
0.6696	0.864	1.020	0.082	1.069	0.950	0.088	0.084	1.090	0.090	0.369	0.079	0.085	−0.75
0.7658	0.976	1.131	0.133	1.033	0.961	0.137	0.150	1.168	0.155	1.087	0.145	0.149	−0.82
0.8847	2.												
	167	1.287	0.306	1.016	0.977	0.311	0.394	1.309	0.400	1.257	0.385	0.391	−0.96
0.9045	1.208	1.314	0.367	1.005	0.981	0.369	0.482	1.321	4.485	1.289	0.473	0.475	−0.97
1.0000	1.456	—	—	—	—	—	—	—	—	—	—	—	—

Tetrachloroethane + n-nonane

0.0000	0.639	—	—	—	—	—	—	—	—	—	—	—	—
0.1552	0.651	0.725	0.353	1.272	0.961	0.449	0.256	0.923	0.326	0.697	0.246	0.313	−083
0.2636	0.704	0.794	0.199	1.471	0.943	0.293	0.158	1.168	0.233	0.749	0.149	0.219	−0.62
0.3332	0.742	0.841	0.141	1.584	0.931	0.223	0.119	1.332	1.188	0.783	0.110	0.175	−.56
0.3926	0.770	0.882	0.115	1.677	0.923	0.193	0.101	1.479	0.170	0.814	0.094	0.157	−0.57
0.5196	0.836	0.980	0.089	1.768	0.912	0.157	0.087	1.733	0.154	0.894	0.080	0.171	−0.64
0.5976	0.879	1.045	0.090	1.754	0.911	0.158	0.094	1.833	0.165	0.952	0.086	0.150	−0.72
0.6903	0.943	1.129	0.110	1.659	0.918	0.182	0.124	1.873	0.205	1.036	0.114	0.189	−0.84
0.7468	0.991	1.182	0.132	1.582	0.924	0.209	0.156	1.870	0.247	1.092	0.144	0.228	−0.93
0.8858	1.163	1.326	0.330	1.278	0.956	0.422	0.438	1.695	0.560	1.268	0.418	0.535	−1.29
0.9204	1.235	1.363	0.445	1.195	0.968	0.532	0.607	1.623	0.725	1.019	0.587	0.702	−1.35
1.0000	1.456	—	—	—	—	—	—	—	—	—	—	—	—

The parameter C_i for a component i is related to the characteristic pressure P_i^*, the characteristic temperature T_i^*, and the hard-core volume per mole V_i^* of component i as described earlier.[4,12] The characteristic parameters P_i^*, T_i^* and V_i^* and the reduced temperature $\tilde{T}_i$ and the reduced volume $\tilde{V}_i$ of the pure component i used in the calculations were obtained from the values of the molar volume V, thermal expansion coefficient α, and the isothermal compressibilities by using the methods described by Abe and Flory.[13] The data are given in Table 2. The parameter $\theta_2 X_{12}$ (characteristic of a system) used to calculate $\Delta H_m/RT$ from Eq. (5) at all concentrations for each system, was estimated from the reduced excess volumes $\tilde{V}^E$, by using the experimental values of the excess volumes and by employing the relations described by Abe and Flory. The values of $\tilde{V}$, the reduced volumes of mixtures, needed in Eqs (4–6) were also obtained from the relations of Abe and Flory by using the experimental data for excess volumes.

4 RESULTS AND DISCUSSION

Contributions of various terms involved in the Eq. (4) have been shown in columns 3–6 of Table 3, where as the values of the free energy contribution, defined by $\eta_G = \eta_H \eta_S$ are given in column 7. It is not clear that the contributions of all terms to mixture viscosity are equally important in Eq. (4). In the absence of this information, the various combinations of the calculated contributions from different terms to η, combining them multiplicatively in accordance with the additive logarithmic relation, are tabulated in columns 8–11 of Table 3. The absolute reaction rate theory, which takes into account free energy corrections to ideal mixture viscosity η_{id}, corresponds to the multiplicate term $\eta_{\mathrm{id}}\eta_G$, where as the free volume theory, which takes into account free volume corrections to the ideal mixture viscosity, corresponds to $\eta_{\mathrm{id}}\eta_V$. Further Macedo–Litovitz's theory[14] which accounts for enthalpic and free volume correlations to ideal mixture viscosity corresponds to $\eta_{\mathrm{id}}\eta_H\eta_V$, which is given in column 12 of the Table 3, whereas the values of the complete product $\eta_{\mathrm{id}}\eta_H\eta_S\eta_V$ are given in column 13. Table 3 shows that the experimental viscosities are best reproduced by the contribution of $\eta_{\mathrm{id}}\eta_V$ and the viscosities reproduced by other contributions are lesss satisfactory. The values of the quantity η^E, which refers to the deviations from the rectilinear dependence of viscosity of mixture on mole fraction, can be discussed from the viewpoint of intermolecular interactions.[15–16] The values of η^E are negative and fall in the order,

$$n\text{-hexane} > n\text{-heptane} > n\text{-octane} > n\text{-nonane}$$

The negative values of η^E may be attributed to the existence of dispersion and dipolar forces between unlike molecules.

According to Grungberg and Nissan[17] the viscosity η of a binary mixture can be expressed by Eq. (7)

$$\ln \eta = x \ln \eta_1 + (1 - x) \ln \eta_2 + x(1 - x)d \tag{7}$$

In Eq. (7), the parameter d has been regarded as a measure of the strength of the interaction between the components.[15–17] The values of d calculated for the various mixtures from Eq. (7) by using the viscosity data are given in the last column of Table 3. The values of d are negative over the entire composition range in all the mixtures. This suggests that the dispersion forces are predominant between the components. Further there exists a linear relationship between $\eta^E_{\max}$ and $V^E_{\max}$ and also between $\eta^E_{\max}$ and difference in boiling points of the components.

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