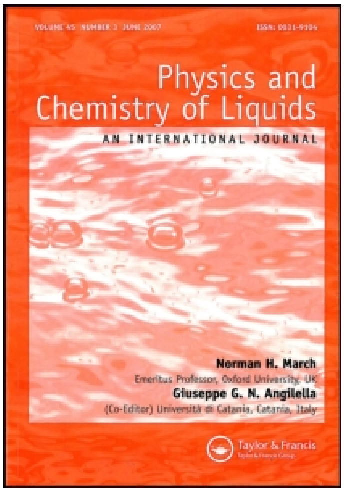

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Interaction Studies from Viscometric and Volumetric Behaviour of Binary Systems of Chlorinated Methanes with Normal Alkanols at 303.15 K

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INTERACTION STUDIES FROM VISCOMETRIC AND VOLUMETRIC BEHAVIOUR OF BINARY SYSTEMS OF CHLORINATED METHANES WITH NORMAL ALKANOLS AT 303.15 K

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Viscosities and densities have been measured for mixtures of chlorinated methanes mixing with normal alcohols at 303.15 K. The chlorinated methanes include carbon tetrachloride, chloroform and dichloromethane. The normal alcohols are methanol, ethanol, 1-proponal and 1-butanol. Excess viscosities η^E and molar excess volumes V^E were obtained together with the Grunberg-Nissan interaction parameter d and interaction energy for flow of activation W_{vis}.

The relation between the resulting η^E and V^E has been tested using existing equations. Interactions between molecules are discussed in detail. Specific interactions are not dominant or very weak and almost nonexistent between different components. A new assumption is proposed that interaction of C atom of chlorinated methanes with (C–C) backbone in ROH increases with decreasing number of Cl atoms in chlorinated methanes for screening the interaction.

KEY WORDS: Excess viscosity, molar excess volume, Grunberg-Nissan parameter.

INTRODUCTION

Vicosity is an important property of liquids. It has a close relation to many practical and theoretical problems, such as heat transfer, mass transfer, diffusion, biological membranes, orientation and reorientation of solutes in liquid media C brodening of chemical shifts in NMR), etc. Furthermore, viscosity has been regarded as an effective method to study molecular interactions in liquid mixtures. For example, the strength of interaction d, also called the Grunberg-Nissan parameter[1], and the interaction energy W_{vis}.[2] can be evaluated from viscosity values of binary systems. Binary viscosity data can also be used to test the validity of solution theories.

Alcohols are important solvents and structurally meaningful. They are regarded as being associated. Not only are chlorinated methanes widely used solvents, but also they are structurally typical with only one carbon atom for each molecule. We have selected the binary systems of carbon tetrachloride (CT), chloroform(CF) and dichloromethane (DCM) mixing with methanol (MeOH), ethanol (EtOH),

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1-propanol (1-PrOH) and 1-butanol (1-BuOH). Their viscosities were measured and also molar excess volumes were obtained. More detailed information on interactions can be gained by combining transport and thermodynamic properties. Meanwhile, the existing relationships between excess viscosities and molar excess volumes[3,4] can be checked.

To our knowledge, no complete and comprehensive work is available in the literature dealing with these systems[5-12]; at least, no excess viscosity and molar excess volume data for systems of dichloromethane mixing with the four alkanols were found except for the excess volume of dichloromethane and 1-butanol[6].

EXPERIMENTAL

Materials

A.R. grade anhydrous methanol and ethanol (both with purity better than 99.5%) were purified as follows. First, 100 ml methanol (or ethanol) was refluxed over 5 g magnesium pieces and 0.5 g iodine under the protection of anhydrous calcium chloride. After magnesium solved completely, another 0.5 g iodine was added into the distilling flask. Reflux continued for about 1 hour. Then 900 ml methanol (or ethanol) was poured into the flask. After half hour of reflux, 50 ml head fraction was discarded, so purified methanol (or ethanol) was collected uder the protection of anhydrous calcium chloride. 1-Propanol (Merck chemical reagent) and 1-butanol (A.R.) were refluxed over freshly ignited calcium oxide for 8 hours and distilled with 2 m high fractionating columns under the protection of anhydrous calcium chloride. Carbon tetracholoride (A.R.) was dried over anhydrous calcium chloride and distilled over phosphorous pentoxide. Chloroform (A.R.) was shaken several times with about half of its volume of distilled water, dried over anhydrous calcium chloride and then fractionally distilled. Dichloromethane (A.R.) was fractionally distilled over calcium oxide and the middle colourless fractions collected. The purities of the components can be further ascertained by measuring their densities and viscosities at 303.15 K and comparing them with available literature values[13-19]. It can be found from Table 1 that the results are satisfacting.

Measurement

An Ubbelohde type glass capillary tube viscometer with a inner diameter of 0.39 mm was employed to measure the viscosities of the pure components and the mixtures. The temperature for the viscosity measurements was kept at 303.15±0.02 K with a stability of 0.002 K. The "kinetic term" in the viscosity equation could be neglected by selecting a proper capillary tube. So the viscosity η (cP) of one sample is related to its flow time t (second) and density ρ ($g\cdot cm^{-3}$) by the following formula

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

where A is the viscometer parameter. The viscometer was calibrated by measuring the flow times of deioned double-distilled water at 35, 30 and 35°C, because the A

Table 1 Density ρ (g·cm^{-3}) and viscosities η (cP) of pure component liquids at 303.15 K.

Component	ρ		η	
	Experimental	*Literature*	*Experimental*	*Literature*
Methanol	0.7822	0.7820	0.5058	0.514
Ethanol	0.7807	0.7807	0.9925	0.991
1-Propanol	0.7958	0.7956	1.7268	1.722
1-Butanol	0.8023	0.8019	2.2719	2.271
Carbon tetrachloride	1.5750	1.5748	0.8421	0.845
Chloroform	1.4705	1.4706	0.5137	0.514
Dichloromethane	1.3076	1.3077	0.3996	0.397

parameter is not influenced by temperatures in an appropriate temperature range. The viscosities and densities of pure water were obtained from the literature[20]. Flow time was obtained by a electric watch with a precision of 0.01 s. At least three flow times stablizing within 0.05 s were recorded for one sample and then the average value was used. Flow times could be reproduced at least to 0.05 s. The precision of the viscometer was further checked by measuring pure benzene, cyclohexane and carbon tetrachloromethane at 303.15 K. The results were satisfactory. The precision of the viscosity measurements can reach 0.0003 cP.

A Anton Paar DMA 45 densimeter was employed to measure density. The measuring temperature was stablized to ±0.01 K. The densimeter was calibrated by dry air and double-distilled water. The water's density used was 0.9957 g·cm^{-3} at 303.15 K. The densimeter can be read to 0.0001 g·cm^{-3}. Its real precision is better than $\pm 5\times 10^{-5}$ g·cm^{-3}. So molar excess volumes for mixing could be obtained with a precision which is generally better than 5×10^{-3} cm^3·mol^{-1}. The molar excess volume V^E(cm^3·mol^{-1}) is calculated from the equation

$$V^E = \frac{(x_1M_1 + x_2M_2)}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \tag{2}$$

where x_1 and x_2 are the molar fractions of component 1 and component 2 in a binary mixture; M_1 and M_2 are their molecular weights respectively; ρ, ρ_1 and ρ_2 are the densities of mixture, component 1 and component 2 respectively.

Binary mixtures were prepared by weighing in specially designed mixing-bottles, each with a capacity of about 80 ml. The bottle is similar to that used by Benson *et al*[21]. Thereby evaporation could be reduced to a minimum. All weighing with a precision of $\pm 1\times 10^{-4}$ g was corrected to vacuum.

RESULTS AND DISCUSSION

The experimentally obtained viscosities and densities for the mixtures are listed in Table 2. From these values, some meaningful quantities η^E, V^E, d and W_{vis} were

Table 2 Experimental values of density (ρ), viscosity (η) and the calculated excess viscosity (η^E), excess molar volume (V^E), Grunberg and Nissan parameter (d) and the interaction energy for the activation of flow W_{vis} for the systems of chlorinated methanes + alcohols at 303.15 K.

x	ρ ($g \cdot cm^{-3}$)	η (cP)	η^E (cP)	V^E ($cm^3 \cdot mol^{-1}$)	d	W_{vis} ($KJ \cdot mol^{-1}$)
XMeOH + (1 − X)CCl_4						
0.0396	1.5609	0.8187	−0.0101	0.038	−0.210	0.235
0.0862	1.5439	0.8054	−0.0077	0.056	−0.008	0.753
0.1437	1.5219	0.7973	0.0035	0.057	0.151	1.167
0.2352	1.4837	0.7930	0.0300	0.041	0.333	1.651
0.3077	1.4502	0.7919	0.0533	0.013	0.448	1.965
0.4129	1.3947	0.7852	0.0820	−0.015	0.580	2.339
0.5310	1.3205	0.7677	0.1042	−0.039	0.715	2.736
0.6187	1.2549	0.7443	0.1103	−0.048	0.814	3.031
0.6838	1.1992	0.7184	0.1063	−0.063	0.877	3.228
0.8240	1.0511	0.6435	0.0785	−0.068	1.042	3.734
0.8821	0.9751	0.6038	0.0584	−0.064	1.125	3.984
0.9292	0.9050	0.5669	0.0373	−0.046	1.185	4.172
0.9728	0.8322	0.5306	0.0157	−0.023	1.285	4.456
XEtOH + (1 − X)CCl_4						
0.0565	1.5462	0.8183	−0.0323	0.066	−0.712	−1.485
0.0932	1.5271	0.8112	−0.0449	0.090	−0.624	−1.264
0.1798	1.4806	0.8093	−0.0598	0.092	−0.470	−0.880
0.3120	1.4034	0.8313	−0.0577	0.047	−0.299	−0.449
0.4579	1.3069	0.8759	−0.0351	−0.018	−0.145	−0.055
0.5273	1.2560	0.8994	−0.0220	−0.050	−0.084	0.102
0.6028	1.1962	0.9240	−0.0088	−0.071	−0.026	0.252
0.6890	1.1218	0.9490	0.0033	−0.092	0.029	0.397
0.7868	1.0282	0.9740	0.0136	−0.103	0.097	0.571
0.8670	0.9430	0.9867	0.0142	−0.100	0.139	0.677
0.9134	0.8895	0.9917	0.0122	−0.075	0.170	0.757
0.9566	0.8368	0.9933	0.0073	−0.045	0.191	0.811
0.9724	0.8168	0.9934	0.0051	−0.034	0.203	0.835
XPrOH + (1 − X)CCl_4						
0.0615	1.5364	0.8319	−0.0646	0.064	−0.976	−2.354
0.0651	1.5341	0.8324	−0.0673	0.068	−0.958	−2.309
0.1059	1.5083	0.8333	−0.1025	0.084	−0.914	−2.203
0.2377	1.4225	0.8752	−0.1772	0.073	−0.729	−1.747
0.3576	1.3402	0.9546	−0.2039	0.022	−0.572	−1.358
0.4503	1.2733	1.0410	−0.1995	−0.032	−0.450	−1.055
0.5592	1.1904	1.1625	−0.1743	−0.089	−0.321	−0.736
0.6985	1.0767	1.3389	−0.1212	−0.134	−0.180	−0.387
0.7899	0.9968	1.4607	−0.0802	−0.126	−0.099	−0.187
0.8376	0.9534	1.5243	−0.0588	−0.115	−0.060	−0.089
0.8976	0.8970	1.6025	−0.0337	−0.088	−0.013	0.026
0.9626	0.8335	1.6824	−0.0113	−0.038	0.022	0.112
0.9633	0.8328	1.6838	−0.0105	−0.038	0.032	0.136
XBuOH + (1 − X)CCl_4						
0.0559	1.5331	0.8424	−0.0796	0.058	−1.044	−2.600
0.0570	1.5322	0.8423	−0.0813	0.064	−1.048	−2.607
0.1084	1.4941	0.8543	−0.1428	0.078	−0.964	−2.406
0.1137	1.4901	0.8560	−0.1487	0.083	−0.957	−2.388
0.1851	1.4370	0.8882	−0.2186	0.090	−0.865	−2.160
0.1887	1.4343	0.8907	−0.2212	0.091	−0.857	−2.140

Table 2 (*Contd.*)

x	ρ $(g \cdot cm^{-3})$	η (cP)	η^E (cP)	V^E $(cm^3 \cdot mol^{-1})$	d	W_{vis} $(KJ \cdot mol^{-1})$
0.2871	1.3608	0.9679	−0.2847	0.073	−0.712	−1.781
0.3823	1.2892	1.0763	−0.3124	0.034	−0.568	−1.423
0.4772	1.2171	1.2152	−0.3092	−0.011	−0.428	−1.077
0.5086	1.1931	1.2678	−0.3015	−0.029	−0.383	−0.964
0.6468	1.0860	1.5269	−0.2400	−0.078	−0.205	−0.522
0.6792	1.0606	1.5930	−0.2202	−0.087	−0.168	−0.430
0.7591	0.9974	1.7635	−0.1640	−0.094	−0.078	−0.206
0.8416	0.9314	1.9427	−0.1027	−0.088	0.005	−0.001
0.8807	0.8998	2.0263	−0.0750	−0.074	0.038	0.081
0.8930	0.8898	2.0535	−0.0654	−0.066	0.054	0.120
0.9516	0.8421	2.1763	−0.0264	−0.041	0.110	0.256
0.9563	0.8382	2.1857	−0.0237	0.032	0.112	0.266
XMeOH + (1 − X)$CHCl_3$						
0.0625	1.4482	0.5090	−0.0042	−0.005	−0.140	0.129
0.0947	1.4362	0.5084	−0.0046	−0.011	−0.104	0.226
0.1406	1.4185	0.5099	−0.0027	−0.026	−0.043	0.383
0.1830	1.4014	0.5138	0.0015	−0.042	0.020	0.550
0.2165	1.3874	0.5168	0.0048	−0.059	0.055	0.642
0.3004	1.3497	0.5296	0.0183	−0.091	0.167	0.937
0.3311	1.3350	0.5343	0.0232	−0.105	0.201	1.027
0.3671	1.3170	0.5424	0.0316	−0.118	0.258	1.179
0.3854	1.3075	0.5460	0.0353	−0.123	0.283	1.243
0.4503	1.2721	0.5601	0.0500	−0.144	0.378	1.494
0.5306	1.2239	0.5764	0.0669	−0.166	0.495	1.807
0.6150	1.1668	0.5904	0.0816	−0.169	0.628	2.161
0.6304	1.1555	0.5921	0.0834	−0.163	0.652	2.225
0.7056	1.0969	0.5975	0.0894	−0.152	0.780	2.568
0.7430	1.0649	0.5962	0.0884	−0.133	0.840	2.733
0.7810	1.0306	0.5924	0.0849	−0.122	0.904	2.905
0.8147	0.9982	0.5864	0.0791	−0.104	0.960	3.059
0.8944	0.9138	0.5613	0.0547	−0.054	1.085	3.408
0.9355	0.8655	0.5417	0.0354	−0.028	1.120	3.518
0.9610	0.8337	0.5281	0.0220	−0.013	1.135	3.573
XEtOH + (1 − X)$CHCl_3$						
0.0811	1.4281	0.5140	−0.0385	0.045	−0.709	−1.650
0.1571	1.3873	0.5247	−0.0642	0.050	−0.621	−1.435
0.2368	1.3432	0.5440	−0.0831	0.020	−0.546	−1.251
0.3342	1.2867	0.5774	−0.0963	−0.034	−0.464	−1.051
0.4545	1.2124	0.6351	−0.0962	−0.122	−0.352	−0.777
0.5514	1.1481	0.6970	−0.0807	−0.186	−0.234	−0.489
0.6372	1.0872	0.7617	−0.0571	−0.217	−0.111	−0.184
0.7644	0.9894	0.8683	−0.0114	−0.214	0.119	0.389
0.7943	0.9651	0.8927	−0.0013	−0.211	0.181	0.540
0.8607	0.9087	0.9412	0.0154	−0.163	0.323	0.896
0.9211	0.8550	0.9752	0.0205	−0.112	0.473	1.268
XPrOH + (1 − X)$CHCl_3$						
0.0590	1.4324	0.5225	−0.0628	0.052	−0.982	−2.441
0.1099	1.3996	0.5365	−0.1105	0.080	−0.918	−2.282
0.1428	1.3784	0.5488	−0.1381	0.092	−0.874	−2.174
0.1958	1.3443	0.5706	−0.1806	0.096	−0.840	−2.093
0.2432	1.3139	0.5949	−0.2138	0.081	−0.805	−2.008
0.3447	1.2483	0.6588	−0.2731	0.034	−0.749	−1.876

Table 2 (*Contd.*)

x	ρ $(g\cdot cm^{-3})$	η (cP)	$\cdot\eta^E$ (cP)	V^E $(cm^3\cdot mol^{-1})$	d	W_{vis} $(KJ\cdot mol^{-1})$
0.4974	1.1480	0.8026	−0.3145	−0.062	−0.627	−1.582
0.6171	1.0676	0.9716	−0.2907	−0.133	−0.469	−1.194
0.7318	0.9888	1.1847	−0.2167	−0.180	−0.263	−0.686
0.7983	0.9420	1.3246	−0.1575	−0.170	−0.128	−0.351
0.8606	0.8976	1.4601	−0.0976	−0.148	0.010	−0.008
0.9106	0.8615	1.5655	−0.0528	−0.114	0.127	0.280
0.9251	0.8510	1.5946	−0.0413	−0.105	0.161	0.362
0.9307	0.8468	1.6055	−0.0372	−0.089	0.173	0.398
0.9500	0.8327	1.6428	−0.0233	−0.070	0.226	0.528
			XBuOH + (1 − X)$CHCl_3$			
0.0563	1.4272	0.5315	−0.0812	0.047	−0.934	−2.306
0.0995	1.3946	0.5491	−0.1395	0.074	−0.907	−2.239
0.1395	1.3650	0.5709	−0.1881	0.086	−0.848	−2.094
0.1858	1.3312	0.6001	−0.2403	0.097	−0.798	−1.971
0.2305	1.2991	0.6329	−0.2861	0.098	−0.756	−1.866
0.2878	1.2588	0.6839	−0.3358	0.081	−0.691	−1.709
0.3010	1.2496	0.6958	−0.3471	0.077	−0.685	−1.694
0.3666	1.2043	0.7663	−0.3920	0.060	−0.625	−1.546
0.4891	1.1221	0.9373	−0.4363	−0.001	−0.503	−1.248
0.5662	1.0717	1.0762	−0.4330	−0.045	−0.416	−1.033
0.6718	1.0040	1.3139	−0.3810	−0.089	−0.271	−0.673
0.7659	0.9448	1.5737	−0.2866	−0.098	−0.107	−0.264
0.8333	0.9032	1.7800	−0.1988	−0.101	0.028	0.070
0.9010	0.8619	1.9922	−0.1056	−0.081	0.177	0.442
0.9386	0.8391	2.1066	−0.0573	−0.052	0.273	0.684
			XMeOH + (1 − X)CH_2Cl_2			
0.0752	1.2807	0.3905	−0.0171	0.063	−0.586	−1.206
0.1326	1.2598	0.3907	−0.0230	0.078	−0.468	−0.912
0.1509	1.2529	0.3917	−0.0239	0.085	−0.433	−0.825
0.2315	1.2221	0.3988	−0.0254	0.078	−0.318	−0.537
0.3029	1.1933	0.4078	−0.0240	0.062	−0.242	−0.346
0.3740	1.1627	0.4200	−0.0193	0.053	−0.164	−0.147
0.4070	1.1479	0.4262	−0.0166	0.047	−0.130	−0.062
0.5161	1.0957	0.4475	−0.0069	0.029	−0.034	0.187
0.6525	1.0222	0.4738	0.0049	0.026	0.073	0.468
0.7656	0.9535	0.4932	0.0123	0.019	0.167	0.716
0.8581	0.8911	0.5043	0.0136	0.012	0.250	0.934
0.9182	0.8470	0.5081	0.0110	0.011	0.317	1.113
0.9595	0.8150	0.5087	0.0072	0.008	0.393	1.312
0.9854	0.7942	0.5071	0.0029	0.003	0.418	1.378
			XEtOH + (1 − X)CH_2Cl_2			
0.0625	1.2756	0.3950	−0.0417	0.097	−1.168	−2.868
0.1074	1.2530	0.3980	−0.0653	0.137	−1.061	−2.607
0.1915	1.2110	0.4103	−0.1028	0.173	−0.955	−2.350
0.2935	1.1598	0.4387	−0.1349	0.186	−0.838	−2.064
0.4162	1.0979	0.4914	−0.1550	0.146	−0.707	−1.747
0.5331	1.0377	0.5595	−0.1562	0.096	−0.596	−1.476
0.6811	0.9594	0.6721	−0.1313	0.031	−0.459	−1.139
0.7823	0.9043	0.7670	−0.0964	−0.004	−0.350	−0.873
0.8482	0.8676	0.8337	−0.0688	−0.014	−0.282	−0.702
0.9067	0.8346	0.8949	−0.0423	−0.021	−0.220	−0.554
0.9571	0.8056	0.9476	−0.0195	−0.010	−0.177	−0.444

Table 2 (*Contd.*)

x	ρ ($g \cdot cm^{-3}$)	η (cP)	η^E (cP)	V^E ($cm^3 \cdot mol^{-1}$)	d	W_{vis} ($KJ \cdot mol^{-1}$)
			XPrOH$+(1-X)$CH$_2$Cl$_2$			
0.0434	1.2800	0.4010	−0.0562	0.100	−1.446	−3.521
0.0863	1.2539	0.4085	−0.1056	0.160	−1.322	−3.225
0.1371	1.2240	0.4230	−0.1586	0.206	−1.215	−2.967
0.1943	1.1914	0.4450	−0.2125	0.231	−1.129	−2.761
0.2863	1.1404	0.4936	−0.2860	0.263	−1.017	−2.486
0.3859	1.0876	0.5655	−0.3463	0.349	−0.918	−2.246
0.4983	1.0302	0.6748	−0.3861	0.212	−0.821	−2.011
0.5806	0.9896	0.7794	−0.3908	0.166	−0.746	−1.828
0.7402	0.9137	1.0588	−0.3232	0.061	−0.566	−1.388
0.8280	0.8732	1.2568	−0.2417	0.015	−0.463	−1.136
0.9016	0.8398	1.4472	−0.1490	−0.007	−0.368	−0.902
0.9459	0.8199	1.5700	−0.0850	−0.010	−0.313	−0.768
			XBuOH$+(1-X)$CH$_2$Cl$_2$			
0.0360	1.2804	0.4023	−0.0647	0.088	−1.609	−3.783
0.0601	1.2629	0.4082	−0.1039	0.135	−1.472	−3.446
0.1127	1.2266	0.4291	−0.1815	0.204	−1.246	−2.895
0.1672	1.1909	0.4596	−0.2530	0.259	−1.082	−2.491
0.3142	1.1037	0.5767	−0.4112	0.301	−0.832	−1.885
0.4391	1.0377	0.7209	−0.5008	0.272	−0.703	−1.577
0.5585	0.9803	0.9132	−0.5321	0.204	−0.585	−1.294
0.6635	0.9335	1.1430	−0.4989	0.143	−0.458	−0.984
0.7658	0.8909	1.4278	−0.4056	0.078	−0.320	−0.648
0.8429	0.8604	1.6837	−0.2941	0.044	−0.201	−0.352
0.9000	0.8387	1.8902	−0.1945	0.022	−0.113	−0.135
0.9566	0.8179	2.1047	−0.0859	0.002	−0.025	0.080

calculated

$$\eta^E = \eta - x_1\eta_1 - x_2\eta_2 \tag{3}$$

where η^E is excess viscosity for a mixture with component 1 of x_1 mole fraction and viscosity η_1 and component 2 of x_2 mole fraction and viscosity η_2, the viscosity of the mixture is η.

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2d \tag{4}$$

This equation is referred in the literature[1]; d, called parameter of strength of interaction, reflects the nonideality of the system. It is usually regarded as an approximate measurement of the strength of the interactions between both components[1,22-25]. One also has

$$\ln\eta V = x_1\ln\eta_1 V_1 + x_2\ln\eta_2 V_2 + x_1x_2W_{\text{vis}}/\text{RT}; \tag{5}$$

the so-called Katti and Chaudhri equation[2]. Here V, V_1 and V_2 are the molar volumes of the solution and the pure components respectively. The parameter W_{vis}

represents the interaction energy of activation. All calculated results are also displayed in Table 2.

The excess viscosities and molar excess volumes can be represented by one of the following polynomial equations

$$Y^E = X(1-X)\sum_{i=0}^{n} A_i(1-2X)^i \tag{6}$$

$$Y^E = X(1-X)\sum_{i=0}^{n} A_i X^{1/2} \tag{7}$$

where Y^E may be η^E or V^E, and A_i is parameter. The A_i's were obtained by least-square regression of experimental values. The results are presented in Table 3 with the standard deviation σ. Here, we should point out that only one of Eq. (6) and Eq. (7) can well represent some excess function of most binary mixtures existing; although Eq. (6), also called the Redllich-Kister equation, represents far more systems than does Eq. (7). We found that many authors only chose Eq. (6) no matter what the systems were[26].

The only available literatue viscosity data suitable for comparison with ours are for systems of chloroform with methanol, ethanol and 1-propanol[12]. Even in the literature, only scarce experimental points can be employed for comparison. For mixtures containing methanol, our viscosity values are in good agreement with the literature values at the two end compositions; in the middle region, ours are apparently lower than those in the literature. For mixtures containing ethanol, ours are in excellent agreement with the literature values. For a mixture including 1-propanol, the agreement is excellent except for a point at chloroform's molar fraction 0.2987 with an especially large difference. For other systems excess viscosity values were not found at 303.15 K, even at other temperatures. Our experimental molar excess volumes are in good agreement with Singh's[5] for a mixture of chloroform and methanol. For the system of chloroform and ethanol, the agreement is fair. For a mixture of chloroform and 1-propanol, our results are in good agreement with Singh's below 0.2 molar fraction of 1-propanol: then ours become much more negative. For a system of dichloromethane and 1-butanol, our molar excess volumes, being a little more positive, are in good agreement with Pardo's[6].

There have been few studies on the relation of excess viscosity to molar excess volume. We are mainly interested in Singh's recent investigations[3,4]. Based on topological investigations, two equations had been obtained by Singh:

$$\eta^E = KV^E \tag{8}$$

$$\eta^E = K_1(x_2 - x_1) + K_2 V^E \tag{9}$$

where K, K_1, and K_2 are parameters, x_1 is the molar fraction of component which is associated in pure state. Equation (8) generally fits for binary system with none of the two components being associated in pure states. Evidently, Eq. (8) could not

Table 3 Values of parameters in Eq. (5) or (6) and the standard deviation, $\sigma(Y^E)$ at 303.15K.

	A_0	A_1	A_2	A_3	A_4	$\sigma(V^E)$ ($cm^3 \cdot mol^{-1}$)	$\sigma(\eta^E)$ (cP)	*equation* (*used*)
(1 − X)CT +								
XMeOH	−0.6338	2.0499	−0.8279				0.0005	7
	−0.145	0.337	0.253	0.751		0.003		6
XEtOH	−0.8552	1.0546					0.0004	7
	−0.149	0.750	0.290	0.723		0.002		6
XPrOH	−0.7606	−0.4478	0.0510				0.0004	6
	1.859	−2.969				0.002		7
XBuOH	−1.2161	−0.5097	0.2134				0.0006	6
	1.726	−2.587				0.003		7
(1 − X)CF +								
XMeOH*	0.4264	1.4128	−3.3753	1.4328			0.0004	7
	0.243	−3.619	3.370			0.002		7
XEtOH	−0.3605	−0.3096	0.3445	−0.2327			0.0004	6
	−0.607	1.263	0.225			0.003		6
XPrOH	−1.2576	0.0278	0.5477	−0.4734			0.0003	6
	−0.255	1.377				0.003		6
XBuOH	−1.7501	0.1594	0.4334	−0.6062	0.2562		0.0004	6
	−0.028	1.042				0.003		6
(1 − X) DCM +								
XMeOH	−0.0348	−0.1723	−0.0115	−0.0867			0.0004	6
	1.981	−4.588	2.803			0.003		7
XEtOH	−0.6295	−0.0507	0.0463	−0.0989			0.0005	6
	2.296	−2.622				0.003		7
XPrOH	−1.5458	0.3678	0.0533	−0.2425			0.0003	6
	3.904	−9.330	11.861	−6.798		0.003		7
XBuOH	−2.0988	0.5283	0.1663	−0.4932			0.0004	6
	3.114	−3.060				0.003		7

*In this system, X is taken over by $(1-X)$ for least-square regression by Eq. (6).

represent our systems. We chose Eq. (9) for testing. First we transformed Eq. (9), because η^E is more accurate than V^E in this paper and generally so:

$$\frac{V^E}{(1-2x)} = -K_1 + \frac{(1/K_2)\eta^E}{(1-2x)}. \tag{10}$$

If Eq. (10) functions well, $V^E/(1-2x)$ should be linearly related to the term $\eta^E/(1-2x)$. We found the results were not satisfactory. It seems as if these types of system should not fit Eq. (10).

Figures are presented below to show the relations of η^E's or V^E's to molar fractions. Figure 1 is for systems containing carbon tetrachloride; Figure 2 for systems including chloroform and Figure 3 for systems including dichloromethane.

It can be seen from (a) in Figure 1 that η^E becomes more and more negative rapidly with increasing carbon chain length of alcohols. S-shaped curves are formed for systems containing methanol and ethanol. This may suggest that at least two opposing factors dominate the excess viscosities. It is commonly admitted that alcohols are self-associated through hydrogen bonds, which usually causes negative excess viscosity when being ruptured in the process of mixing with unlike

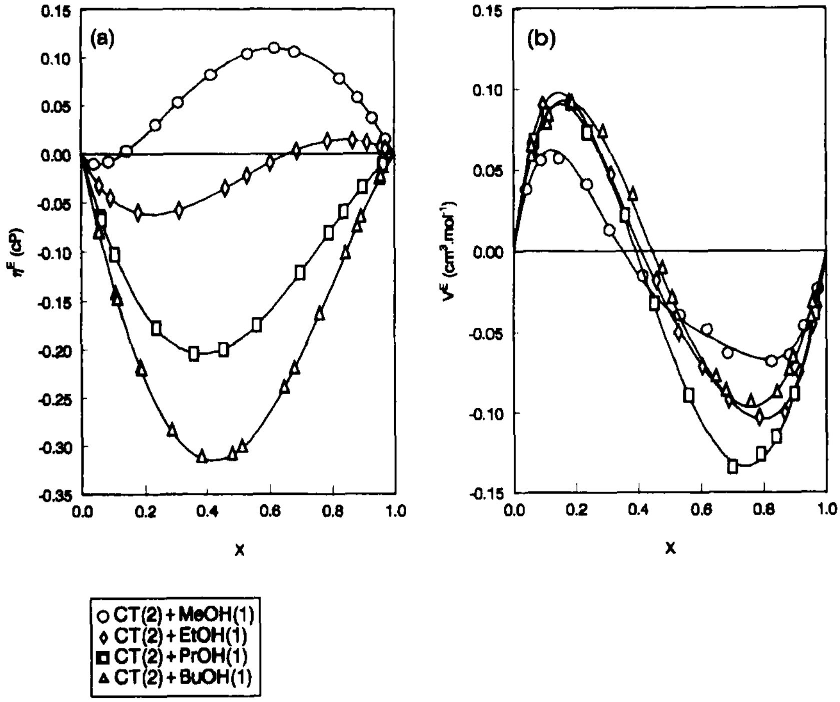

Figure 1 Excess viscosity and molar excess volume at 303.15 K for mixture of $(1-X)$ CT + XMeOH; + XEtOH; X1 − PrOH; X1 − BuOH.

components. When much less alcohols dissolve into CCl_4, the O—H···O—H bond is broken. So the excess viscosity may become negative. Another factor is the interaction between ROH and CCl_4. With positive η^E in a wide region for MeOH—CCl_4 system, it is supposed that the interaction of MeOH—CCl_4 is much stronger than that of CCl_4—CCl_4, but less weak than that of MeOH—MeOH. Similarly, interaction of EtOH—CCl_4 is less strong than that of CCl_4—CCl_4 and relatively much weaker than that of EtOH—EtOH. The interaction of ROH (PrOH or BuOH) with each other is much stronger than both that of ROH—CCl_4 and that of CCl_4—CCl_4. All the preceding suppositions may also be supported by the positions of the minimum for EtOH, PrOH and BuOH and that of the maximum for MeOH. Now attention will be focused on V^E curves in (b). All the four curves are S-shaped and also basically symmetric about $x = 0.5$ except that the system formed by MeOH shows an obviously different behaviour from the others. According to the traditional viewpoint, the volumetric expansion can be mainly attributed to the breaking-up of H—bonds of alcohols. The volumetric contraction may be explained by assuming that molecules of CCl_4 settle down in the H—bonding networks of alcohols, which is usually called interstitial accommodation. The conclusions from the analysis of V^E do not contradict those from η^E and both conform satisfactorily. We can conclude

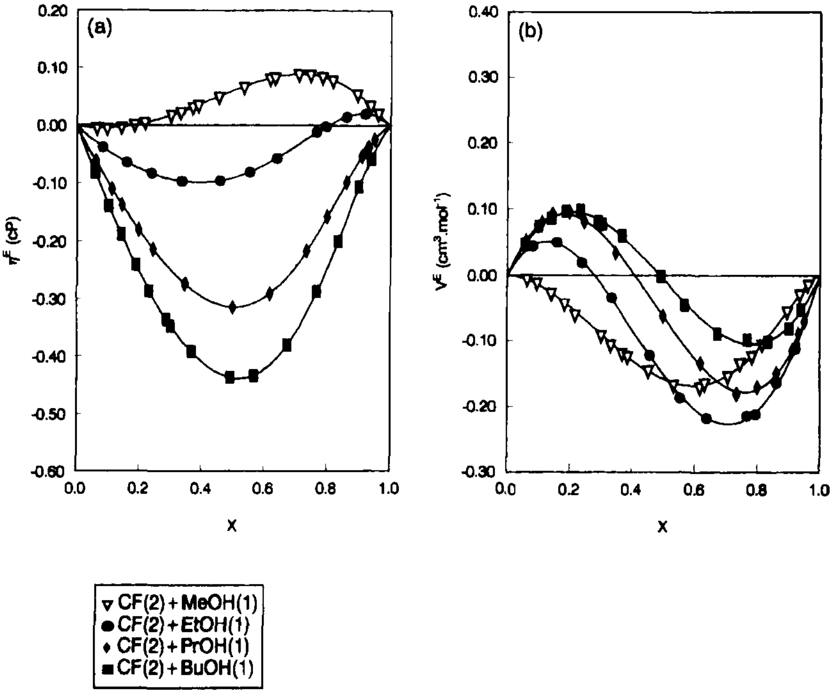

Figure 2 Excess viscosity and molar excess volume at 303.15 K for mixture of $(1-X)$ CF + XMeOH; + XEtOH; X1 − PrOH; X1 − BuOH.

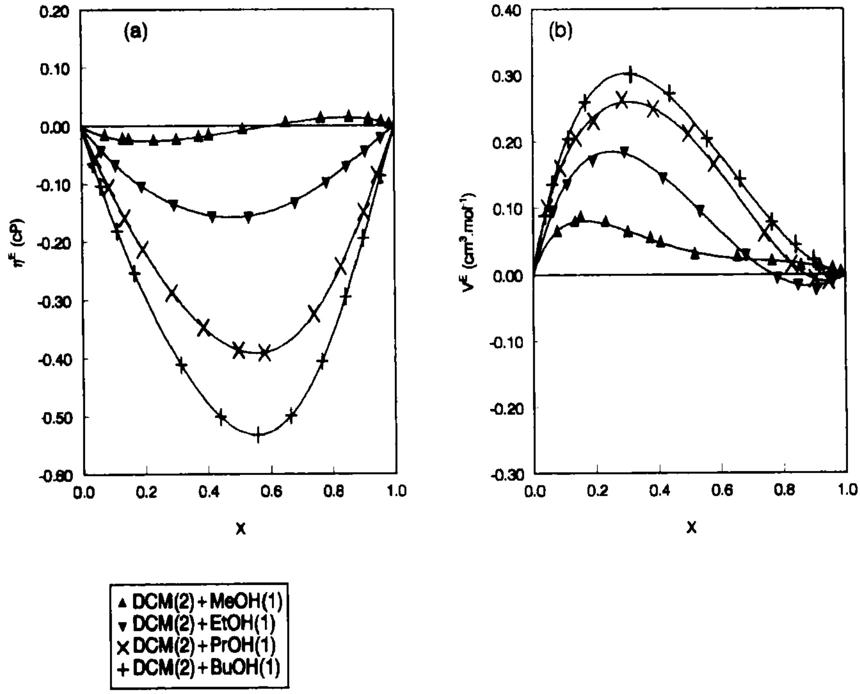

Figure 3 Excess viscosity and molar excess volume at 303.15 K for mixture of$(1-X)$ DCM + XMeOH; + XEtOH; X1 − PrOH; X1 − BuOH.

that three main processes occur when CCl_4 mixes with alcohols. They are

(1) the ruptures of H—bonds in alcohols (mainly in region rich in CCl_4);

(2) CCl_4 molecules accommodate in the H—bonding networks of alcohols (mainly in region rich in alcohol);

(3) CCl_4 interacts with ROH with different degrees.

Going into somewhat more detail, we may consider that the interaction between Cl, atom in CCl_4 and (C—C) backbone of alcohols is much weaker than that between neighbouring (C—C) backbones or that CCl_4 screens the interaction between (C—C) backbones with a greater degree. Whether the existence of specific interaction, e.g., O—H···Cl—C type H—bond is right or not requires further analysis of the *d* parameter. It was noticed that the behaviour of η^E and V^E for systems containing chloroform is basically similar to those including carbon tetrachloride except that for system (MeOH + $CHCl_3$). This can be readily understood because of no (C—C) backbone in CH_3OH. Interacation between CH_3OH—$CHCl_3$ seems to be predominate over other interactions. The more negative η^E and V^E for systems including $CHCl_3$ than those containing CCl_4 suggests that the interaction of CCl_4—ROH is stronger than that of $CHCl_3$—ROH and the interstitial accommodation is still apparent for them.

According to the tendency of V^E in Figure 3, we suppose that $CHCl_3$ begins to interact with (C—C) backbone in ROH. In CH_2Cl_2 + ROH, the behaviour of η^E is similar to two other kinds of systems, and the η^E values become even more negative. At first appearance or from total effect, one is apt to think that the interaction of CH_2Cl_2—ROH becomes even weaker. If we take the abnormal tendency of V^E into consideration, new assumptions may be made:

(1) The excess volumes suddenly becomes especially positive. If the accommodation of CH_2Cl_2 in H-bonding networks of alcohols exists according to the traditional viewpoint, the V^E should be more negative because CH_2Cl_2 is smaller than CCl_4 or $CHCl_3$. If the accommodation hypothesis is correct, we have to accept the fact that the interaction of C—H···O—R is weaker than that of C—Cl···H—O—R.

(2) It is assumed that the interaction of C atom of CH_2Cl_2 with (C—C) backbone becomes stronger owing to its lacking two Cl atoms to screen it; so that the η^E becomes abnormally negative and V^E counter-directs towards positive values and ascends with increasing carbon chain length in ROH or being compared with CCl_4 and $CHCl_3$.

Certainly, the real structures are still open to question.

The following discussion is mainly based on d and Wvis results. In $CCl_4 + MeOH$, both d and η^E are slightly positive over almost all the region, so a fairly strong specific interaction is indicated. In $EtOH + CCl_4$, both d and η^E are negative below $x_{MeOH} = 0.6$ and positive above the composition. This suggests that only weak specific interaction exists between CCl_4 and EtOH in the region rich in ethanol. It is obvious that the dispersion force is dominant in systems of (CCl_4 + PrOH) and (CCl_4 + BuOH), because the d and η^E are negative with considerable magnitude over most of the composition range. This also confirms the preceding conclusion from analysis on V^E and η^E. The interaction energy W_{vis} of (CCl_4 + MeOH) changes enormously from a large positive value to a very low positive value over the whole composition range. This confirms that the interaction of MeOH—CCl_4 is stronger. In systems of CH_2Cl_2 + ROH there is no specific interactions between unlike molecules except that there may be only weak specific interaction between CH_2Cl_2—MeOH in the region rich in methanol. This tends to support our assumption that CH_2Cl_2 interacts mainly with the (C—C) backbone of ROH and that dispersion forces are dominant. Highly negative interaction energy W_{vis} for systems composed of CH_2Cl_2 also indicates this.

Due to the large changes of d and W_{vis} with mole fractions in all the mixtures studied. Equation (4) and Eq. (5) can not really represent these systems with constant parameters.

It is concluded that

(1) there is almost no specific interaction or these is only rather weak specific interaction between chlorinated methanes and alcohols except for methanol.

(2) The interaction of chlorinated methanes with alcohols falls in the order
$CCl_4 > CHCl_3 > CH_2Cl_2$

(3) The tendency of chloromethane interacting with (C—C) backbone in ROH ascends in the order
$CCl_4 \ll CHCl_3 \ll CH_2Cl_2$

(4) The H—bond of C—Cl···H—O, if truly existing, is much weaker than that of O—H···O—H but stronger than the interactiaon of C—Cl with (C—C) backbone in ROH.

All the arguments have been based on macrochemical properties, and clearly further investigations are called for.

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References

1. L. Grunberg, and A. H. Nissan, *Nature* (London), **164**, 799 (1949).
2. P. K. Katti and M. M. Chaudhri, *J. Chem. Eng. data*, **9**, 442 (1964).
3. P. P. Singh, *Indian J. Chem.*, **27A**, 469 (1988).
4. P. P. Singh, Bhatia and S. Maken, *Indian J. Chem.*, **29A**, 263 (1990).
5. P. P. Singh, B. R. Sharma and K. S. Sidhu, *Can. J. Chem.*, **56**, 2127 (1978).
6. V. J. Pardo, V. Rodriguez, C. Lafuente, F. M. Royo and J. S. Urieta, *J. Chem. Thermodyn.*, **25**, 373 (1993).
7. G. C. Paraskevopoulos and R. W. Nissan, *Trans. Faraday. Soc.*, **58**, 869 (1962).
8. A. J. Easteal and L. A. Woolf, *J. Chem. Thermody.*, **16**, 391 (1984).
9. G. Scatchard, S. E. Wood and J. M. Mochel, *J. Amer. Chem. Soc.*, **68**, 1960 (1946).
10. K. N. Marsh and C. Burfitt, *J. Chem. Thermodyn.*, **7**, 955 (1975).
11. M. H. Brusset *et al.*, C. R. Acad. Sc. Parisa, **266**, (serie)1 (1968).
12. A. M. Crabtree and J. F. O' Brien, *J. Chem. Eng. Data*, **36**, 140 (1991).
13. Wilhoit and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **2**, suppl.1 (1973).
14. G. C. Benson and O. Kiyhara, *J. Soln. Chem.*, **10**, 791 (1980).
15. J. L. Hales and J. H. Eilender, *J. Chem. Thermodyn.*, **8**, 1177 (1976).
16. J. I. Riddick, N. B. Bunger and T. Sakano, *Organic Solvents*, 4th edn., Wiley, New York (1986).
17. I. L. Acevedo and M. Katza, *J. Soln. Chem.*, **19**, 1041 (1990).
18. A. Weissberger, J. A. Riddick and W. B. Bunger, Techniques of Chemistry; Organic Solvents 3th edn., Wiley, New York (1970).
19. L. Pikkarainen, *J. Chem. Eng. Data*, **33**, 299 (1988).
20. R. H. Stokes and R. Mills, Viscosity of Electrolytes and Related Properties, Pergamon Press, New York (1965).
21. M. Takenaka and G. C. Benson *et al.*, *J. Chem. Thermodyn.*, **12**, 849 (1980).
22. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, **62**, 1112 (1966).
23. V. K. Rattan and B. P. Ssethi *et al.*, *Indian J. Tech.*, **26**, 197 (1988).
24. R. K. Nigam and B. S. Mahl, *Indian J. Chem.*, **9**, 1255 (1971).
25. R. K. Nigam and P. P. Singh, *Indian J. Chem.*, **9**, 691 (1971).
26. R. Battino, *Chem. Rev.*, **71**, 5 (1971).