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Binary Systems of Acetone with Tetrachloroethylene, Trichloroethylene, Methylene Chloride, 1,2-Dichloroethane, and Cyclohexane. 2. Viscosities at 303.15 K

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Measurements of kinematic viscosities, which are accurate to ±0.001 cSt, have been made for binary liquid mixtures of acetone with tetrachloroethylene (C_2Cl_4), trichloroethylene (C_2HCl_3), methylene chloride (CH_2Cl_2), 1,2-dichloroethane (CH_2ClCH_2Cl), and cyclohexane (c-C_6H_{12}) at 303.15 ± 0.01 K. McAllister's approach of the liquid-mixture viscosity has been found to correlate the liquid-mixture viscosity data throughout the whole range of concentration with a significantly high degree of accuracy in the case of all the systems. On the other hand, the analysis has shown that, although the values of the kinematic viscosities estimated according to Lobe's approach are of good accuracy for mixtures of acetone with CH_2Cl_2 and C_2HCl_3, the percentage errors in the values of the kinematic viscosities estimated according to this approach are quite high in the case of the mixtures of acetone with C_2Cl_4, CH_2ClCH_2Cl, and c-C_6H_{12}. Also the values of the parameter d have been calculated from the equation $\ln \eta = x_A \ln \eta_A + x_B \ln \eta_B + x_A x_B d$, where η_A and η_B refer to the dynamic viscosities of the two pure liquids A and B whose mole fractions in the mixture are x_A and x_B, respectively, and η is the dynamic viscosity of the mixture. The values of d suggest that acetone forms electron donor–acceptor complexes with C_2Cl_4, C_2HCl_3, CH_2Cl_2, and CH_2ClCH_2Cl.

Introduction

Quite recently (*1*), the measurements of ultrasonic velocities in, and adiabatic compressibilities and excess volumes for, binary liquid mixtures of acetone with tetrachloroethylene (C_2Cl_4), trichloroethylene (C_2HCl_3), methylene chloride (CH_2Cl_2), 1,2-dichloroethane (CH_2ClCH_2Cl), and cyclohexane (c-C_6H_{12}) have been made, and the results obtained have been discussed from the viewpoint of the existence of specific interaction between the components of the various mixtures. It has been indicated (*1*) that there exists specific interaction leading to the formation of molecular complexes between the components of the binary mixtures of acetone with C_2Cl_4, C_2HCl_3, CH_2Cl_2, and CH_2ClCH_2Cl. Since the viscosity data for binary liquid mixtures are known (*2–4*) to shed light on the existence of specific interaction between the components, it was thought worthwhile to get further information concerning the formation of adducts between the components of the binary liquid mixtures of acetone with C_2Cl_4, C_2HCl_3, CH_2Cl_2, and CH_2ClCH_2Cl, from viscosity data. Further, there is a current interest (*5*) to know to what accuracy the approaches of McAllister (*6*) and Lobe (*7*) can predict the viscosities of binary liquid mixtures of components of varying complexity. Hence, in the present program, the measurements of viscosities of binary liquid mixtures of acetone with C_2Cl_4, C_2HCl_3, CH_2Cl_2, CH_2ClCH_2Cl, and c-C_6H_{12} have been made at 303.15 K, and the results obtained have been interpreted in this paper.

Experimental Section

Materials. 1,2-Dichloroethane (BDH) was purified by the method described by Foster and Fyfe (*8*), and electronic-grade acetone (BDH) and reagent-grade cyclohexane (BDH) were purified in a manner similar to that described earlier (*9*). Spectral-grade tetrachloroethylene (E. Merck, Darmstadt), electronic-grade trichloroethylene (S. Merck), and methylene chloride (E. Merck, Darmstadt) of GR quality were placed over anhydrous calcium chloride overnight and then subjected to fractional distillations. The densities of the purified components measured at 303.15 K were found to be in good agreement with the available data (*10*, *11*).

Method. The flow times of pure liquids and their binary mixtures were measured at 303.15 ± 0.01 K by using the kinematic viscometer described by Tuan and Fuoss (*12*). The viscometer was first calibrated by making measurements for liquids of known viscosities at 303.15 ± 0.01 K, and the measurements of kinematic viscosities, ν, were then made for pure liquids and their mixtures studied in the present program. The values of ν thus obtained are accurate to ±0.001 cSt.

Results and Discussion

The experimental values of the kinematic viscosities, ν, for the various pure liquids and the binary mixtures of acetone with C_2HCl_3, CH_2Cl_2, CH_2ClCH_2Cl, C_2Cl_4, and c-C_6H_{12} at 303.15 K are given in Table I, where x_1 refers to the mole fraction of acetone. The present values of ν for C_2Cl_4, C_2HCl_3, CH_2Cl_2, CH_2ClCH_2Cl, and acetone at 303.15 K have been found to be 0.498, 0.355, 0.303, 0.588, and 0.377 cSt, respectively, which are in excellent agreement with the corresponding literature values (*10*, *11*) (obtained from the dynamic viscosities η by making use of the density data) 0.497, 0.356, 0.301, 0.590, and 0.379 cSt, respectively, for the various liquids in the same order.

We shall now analyze our viscosity data for the various mixtures in the light of the various theories of liquid-mixture viscosity. The various theories for accurate estimations of viscosities of liquid mixtures have been discussed by Reid, Prausnitz, and Sherwood (*5*). One of the approaches for estimation of liquid-mixture viscosity is that of McAllister (*6*), who has adopted the Eyring approach (*13*, *14*) and has considered the interaction between layers of molecules in the velocity gradient to involve activated jumps of molecules between layers. In this picture, the motion of the molecule has been treated as if the molecule were undergoing a chemical reaction and has to overcome a potential energy barrier in this process. For a binary mixture of A and B in which case molecular interactions of A-A-A, B-B-B, A-B-A, B-A-B, A-A-B, and A-B-B types can be visualized, McAllister's approach yields the equation (*5*)

$$\ln \nu = x_A^3 \ln \nu_A + 3x_A^2 x_B \ln \nu_{AB} + 3x_A x_B^2 \ln \nu_{BA} + x_B^3 \ln \nu_B + R^0 \quad (1)$$

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Table I. Values of the Experimental and Calculated Kinematic Viscosities and the Parameter d for the Various Systems of Acetone at 303.15 K

		ν_{estd}, cSt		
x_1	ν_{exptl}, cSt	eq 1	eq 3	d
	Acetone–C_2HCl_3			
0.0000	0.355			
0.0736	0.362	0.363	0.360	0.46
0.0847	0.363	0.365	0.361	0.46
0.1657	0.369	0.371	0.367	0.46
0.2468	0.378	0.375	0.372	0.52
0.2811	0.381	0.377	0.374	0.54
0.3331	0.382	0.378	0.376	0.53
0.3664	0.385	0.378	0.378	0.54
0.4367	0.384	0.378	0.381	0.51
0.4926	0.377	0.378	0.383	0.43
0.5007	0.375	0.378	0.383	0.41
0.6497	0.375	0.375	0.387	0.40
0.8029	0.368	0.372	0.386	0.29
1.0000	0.377			
	Acetone–CH_2ClCH_2Cl			
0.0000	0.588			
0.0858	0.566	0.567	0.577	0.11
0.1744	0.542	0.544	0.563	0.10
0.2092	0.536	0.536	0.557	0.12
0.3260	0.514	0.508	0.535	0.17
0.3706	0.499	0.498	0.526	0.13
0.4000	0.493	0.491	0.520	0.14
0.5274	0.465	0.462	0.492	0.13
0.5737	0.448	0.453	0.481	0.08
0.6139	0.443	0.444	0.472	0.11
0.6471	0.436	0.438	0.464	0.10
0.6802	0.428	0.431	0.456	0.08
0.6871	0.427	0.430	0.454	0.08
0.8127	0.410	0.407	0.423	0.16
1.0000	0.377			
	Acetone–CH_2Cl_2			
0.0000	0.303			
0.0891	0.315	0.314	0.316	0.27
0.1092	0.317	0.317	0.319	0.26
0.1893	0.325	0.326	0.330	0.24
0.2068	0.328	0.327	0.333	0.24
0.2251	0.328	0.329	0.335	0.23
0.2344	0.329	0.330	0.336	0.22
0.4015	0.343	0.344	0.354	0.21
0.4426	0.348	0.347	0.358	0.21
0.4856	0.351	0.350	0.362	0.21
0.5241	0.354	0.352	0.365	0.22
0.6139	0.359	0.357	0.371	0.20
0.7779	0.365	0.366	0.377	0.16
0.8313	0.368	0.368	0.378	0.15
1.0000	0.377			
	Acetone–C_2Cl_4			
0.0000	0.498			
0.1503	0.466	0.463	0.496	0.18
0.2872	0.440	0.440	0.490	0.19
0.3989	0.423	0.424	0.482	0.22
0.4450	0.416	0.418	0.477	0.22
0.4578	0.415	0.416	0.476	0.23
0.4798	0.413	0.413	0.474	0.24
0.5601	0.403	0.404	0.464	0.27
0.6432	0.395	0.395	0.452	0.30
0.7021	0.390	0.389	0.442	0.31
0.7230	0.388	0.388	0.438	0.31
1.0000	0.377			
	Acetone–c-C_6H_{12}			
0.0000	1.073			
0.1690	0.844	0.843	0.923	−0.50
0.4246	0.615	0.613	0.725	−0.51
0.6848	0.480	0.471	0.553	−0.47
0.7400	0.443	0.450	0.520	−0.64
0.7543	0.440	0.444	0.512	−0.62
0.7746	0.434	0.437	0.500	−0.62
0.8232	0.418	0.421	0.472	−0.63
0.8515	0.414	0.413	0.456	−0.54
0.8939	0.406	0.401	0.433	−0.46
0.9266	0.393	0.393	0.415	−0.62
1.0000	0.377			

where

$$R^0 = x_B^3 \ln \frac{M_B}{M_A} + 3x_Ax_B^2 \ln \frac{1 + 2M_B/M_A}{3} + 3x_A^2x_B \ln \frac{2 + M_B/M_A}{3} - \ln (x_A + x_BM_B/M_A) \qquad (2)$$

In eq 1, ν refers to the kinematic viscosity of the mixture of components A and B having mole fractions x_A and x_B, respectively, and ν_A and ν_B refer to the kinematic viscosities of pure components A and B, respectively. ν_{AB} and ν_{BA} are the two undetermined parameters which are characteristic of a system. In eq 2, M_A and M_B are the molecular weights of the components A and B, respectively. Taking A for acetone and B for the other component in the various systems, we have determined the values of the parameters ν_{AB} and ν_{BA} by the method of least squares from the viscosity data for the various systems, as described by Reid, Prausnitz, and Sherwood (*5*). The values of the parameters ν_{AB} and ν_{BA}, along with those of the standard deviations, $\delta(\nu)$, for the various systems are given in Table II. The values of the kinematic viscosities, ν_{estd}, of the various mixtures, as estimated from eq 1 by using the values of the parameters ν_{AB} and ν_{BA}, are given in Table I. The values of the average percent deviations, $(\Delta\%)_{av}$, and the maximum percent deviations, $(\Delta\%)_{max}$, of the experimental values of kinematic viscosities from those estimated for the various mixtures from eq 1, are given in Table II. Tables I and II show that McAllister's eq 1 correlates the liquid-mixture viscosity data to significantly high degree of accuracy in the case of all the systems.

According to Lobe's approach (*5*, *7*), the kinematic viscosity, ν, of a binary mixture of components A and B is given by the equation

$$\nu = \phi_A\nu_A e^{\phi_B\alpha_B^*} + \phi_B\nu_B e^{\phi_A\alpha_A^*} \qquad (3)$$

where ϕ_A and ϕ_B refer to the volume fractions of the components A and B, respectively, in the mixture, and ν_A and ν_B are the kinematic viscosities of the pure liquids A and B, respectively. Lobe has suggested that if A is chosen as the component with lesser pure-liquid viscosity and if the kinematic viscosity of the mixture varies monotonically with composition, then the values of α_A^* and α_B^* are given by the equations

Table II. Values of the Parameters ν_{AB} and ν_{BA} of Eq 1, the Standard Deviations, $\delta(\nu)$, Average Percent Deviations, $(\Delta\%)_{av}$, and the Maximum Percent Deviations, $(\Delta\%)_{max}$, for the Various Systems of Acetone at 303.15 K

				$(\Delta\%)_{av}$		$(\Delta\%)_{max}$	
system	ν_{AB}, cSt	ν_{BA}, cSt	$\delta(\nu)$,[a] cSt	eq 1	eq 3	eq 1	eq 3
acetone–C_2Cl_4	0.421	0.433	0.0014	0.21	13.2	0.64	15.1
acetone–CH_2Cl_2	0.362	0.354	0.0012	0.29	2.30	0.56	3.34
acetone–C_2HCl_3	0.382	0.409	0.0040	0.82	1.75	1.82	4.89
acetone–CH_2ClCH_2Cl	0.437	0.516	0.0032	0.53	5.15	1.17	7.4
acetone–c-C_6H_{12}	0.454	0.657	0.0049	0.77	12.7	1.87	17.9

[a] Equation 1.

$$\alpha_A^* = -1.7 \ln \frac{\nu_B}{\nu_A} \qquad (4)$$

$$\alpha_B^* = 0.27 \ln \frac{\nu_B}{\nu_A} + \left(1.3 \ln \frac{\nu_B}{\nu_A}\right)^{1/2} \qquad (5)$$

The values of the kinematic viscosities, ν_{estd}, as estimated from eq 3, using the values of α_A^* and α_B^* given by eq 4 and eq 5, respectively, are also given in Table I, whereas the average percent deviations, $(\Delta\%)_{av}$, and the maximum percent deviations, $(\Delta\%)_{max}$, of the experimental values of the kinematic viscosities from those estimated for the various mixtures from eq 3 are given in Table II. Tables I and II show that although eq 3 estimates viscosities of binary liquid mixtures to a good degree of accuracy in the case of mixtures of acetone with CH_2Cl_2 and C_2HCl_3, the percentage errors are quite high in the case of mixtures of acetone with C_2Cl_4, CH_2ClCH_2Cl, and c-C_6H_{12}.

Earlier attempts have been made to describe the dynamic viscosities, η, of binary liquid mixtures in terms of the dynamic viscosities of the pure components and a parameter attributed to the intermolecular interaction between the components. According to Grunberg and Nissan (*2*), the dynamic viscosity η of a binary mixture of components A and B is given by

$$\ln \eta = x_A \ln \eta_A + x_B \ln \eta_B + x_A x_B d \qquad (6)$$

where x_A and x_B are the mole fractions of the components A and B, respectively, η_A and η_B refer to the dynamic viscosities of the pure components A and B, and d is a parameter which can be regarded as a measure of the strength of interaction between the components. The values of d, as estimated from eq 6, by taking η, η_A, and η_B in millipoise, are given in Table I, which shows that the variation of d with composition is not large. The values of d suggest that acetone forms electron donor–acceptor complexes with CH_2Cl_2, CH_2ClCH_2Cl, C_2HCl_3, and C_2Cl_4.

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Registry No. C_2Cl_4, 127-18-4; C_2HCl_3, 79-01-6; CH_2Cl_2, 75-09-2; CH_2ClCH_2Cl, 107-06-2; c-C_6H_{12}, 110-82-7; acetone, 67-64-1.

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