Binary Systems of 1,2-Dichloroethane with Benzene, Toluene, *p*-Xylene, Quinoline, and Cyclohexane. 4. Viscosities at 303.15 K

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Kinematic viscosities (ν) have been measured for mixtures of 1,2-dichloroethane (CH_2ClCH_2Cl) with benzene, toluene, *p*-xylene, quinoline, and cyclohexane at 303.15 ± 0.01 K. McAllister's approach correlates the viscosity data with a significantly high degree of accuracy for all these systems. However, though the values of ν estimated according to Lobe's approach are of good accuracy for CH_2ClCH_2Cl–quinoline, the percent deviations of the experimental values of ν from those estimated according to this approach are quite high in the case of the other four systems. 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, η_A, and η_B refer to the dynamic viscosities of the mixture, component A, and component B, respectively, and x_A and x_B are the mole fractions of A and B in the mixture. The positive values of *d* for CH_2ClCH_2Cl–quinoline suggest that CH_2ClCH_2Cl forms an intermolecular complex with quinoline. The values of *d* for the systems of CH_2ClCH_2Cl with the aromatic hydrocarbons indicate the existence of a weak specific interaction between CH_2ClCH_2Cl and the aromatics.

Introduction

Binary systems of 1,2-dichloroethane (CH_2ClCH_2Cl) with benzene, toluene, *p*-xylene, quinoline, and cyclohexane are interesting from the viewpoint of the specific interaction between the components of the various binary systems in the liquid state. The specific interaction of CH_2ClCH_2Cl with aromatics and quinoline can be visualized to be on account of the presence of two Cl atoms and four H atoms in CH_2ClCH_2Cl due to which it can act as σ-acceptor toward and be involved in the formation of hydrogen bond with the aromatics and quinoline. The aromatic hydrocarbons in their interaction with CH_2ClCH_2Cl will act as π-donors, whereas quinoline will act as an n-donor. The system of CH_2ClCH_2Cl with cyclohexane, in which case only the dipolar, induction, and dispersion forces are believed to be present between the components, can be used as a reference system. Extensive studies concerning interactions between components of such systems have not been made. However, recently the measurements of excess volumes (*1*), and ultrasonic velocities and adiabatic compressibilities (*2*) for binary liquid mixtures of CH_2ClCH_2Cl with benzene, toluene, *p*-xylene, quinoline, and cyclohexane were carried out at different temperatures. Further, the measurements of dielectric constants and refractive indices for binary liquid mixtures of CH_2ClCH_2Cl with benzene, toluene, *p*-xylene, quinoline, and cyclohexane have also been made (*3*) at 303.15 K. The results of these measurements have indicated the existence of specific interaction of CH_2ClCH_2Cl with the aromatics and quinoline. Since, the measurements of viscosities for binary liquid mixtures are known (*4–6*) to shed light on the existence of a specific interaction between the components, it was thought worthwhile to get further information about the specific interaction of CH_2ClCH_2Cl with aromatics and quinoline from viscosity data. Further, there is a current interest (*7*) to know to what accuracy the approaches of McAllister (*8*) and Lobe (*9*) can predict the viscosities of binary liquid mixtures of components of varying complexity. Hence, in the present program, the measurements of kinematic viscosities of binary liquid mixtures of CH_2ClCH_2Cl with benzene, toluene, *p*-xylene, quinoline, and cyclohexane have been made at 303.15 K, and the results obtained have been interpreted in this paper.

Experimental Section

Materials. The methods of purification of the various liquids and checking their purity have been described earlier (*1*).

Method. The kinematic viscosities of the various pure liquids and their binary mixtures studied in the present program were measured at 303.15 ± 0.01 K by using kinematic viscometer of Tuan and Fuoss (*10*), as described earlier (*11*). The temperature of the water thermostat in which the viscometer was placed during the measurements was read with a two-junction copper–constantan thermopile, using a precision vernier potentiometer (Scientific Pye Instrument, England), and the flow times of the various pure liquids and their binary mixtures were noted with a stop watch which could read correct to ±0.1 s. The accuracy in the values of the kinematic viscosities ν obtained in this investigation is of the order of ±0.001 cSt.

Results and Discussion

The experimental values of the kinematic viscosities, ν, for the various pure liquids and the binary mixtures of CH_2ClCH_2Cl with benzene, toluene, *p*-xylene, quinoline, and cyclohexane at 303.15 K are given in Table I, where x_1 refers to the mole fraction of CH_2ClCH_2Cl. The present experimental values of ν for benzene, toluene, *p*-xylene, quinoline, and CH_2ClCH_2Cl at 303.15 K have been found to be 0.647, 0.611, 0.663, 2.756, and 0.590 cSt, respectively, which are in excellent agreement with the corresponding literature values (*12*) (obtained from the dynamic viscosities η by making use of the density data) 0.652, 0.613, 0.666, 2.760, and 0.590 cSt, respectively, for the various liquids in the same order.

We shall analyze below our kinematic viscosity data for the various liquid mixtures in light of the various theories of liquid-mixture viscosity. The various approaches for accurate estimation of viscosities of liquid mixtures have been discussed by Reid, Prausnitz, and Sherwood (*7*). One approach for estimation of liquid-mixture viscosity is due to McAllister (*8*), 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 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 (*8*)

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

where

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Table I. Values of the Experimental and Estimated Kinematic Viscosities and the Parameter *d* for the Various Systems of 1,2-Dichloroethane at 303.15 K

x_1	ν_{exptl}, cSt	ν_{estd}, cSt eq 1	ν_{estd}, cSt eq 3	d
	CH_2ClCH_2Cl–Benzene			
0.0000	0.647			
0.0280	0.640	0.639	0.650	−0.27
0.2755	0.583	0.587	0.661	−0.38
0.3664	0.573	0.576	0.661	−0.37
0.4263	0.570	0.571	0.660	−0.35
0.4477	0.567	0.569	0.659	−0.36
0.4874	0.565	0.567	0.657	−0.35
0.5259	0.563	0.565	0.655	−0.35
0.6982	0.563	0.565	0.639	−0.34
0.8533	0.576	0.574	0.617	−0.29
0.9588	0.585	0.585	0.598	−0.32
1.0000	0.590			
	CH_2ClCH_2Cl–Toluene			
0.0000	0.611			
0.1754	0.595	0.594	0.621	−0.18
0.2900	0.584	0.585	0.625	−0.22
0.4478	0.577	0.576	0.628	−0.21
0.5599	0.570	0.572	0.627	−0.25
0.6742	0.570	0.572	0.623	−0.26
0.7344	0.572	0.573	0.619	−0.26
0.7771	0.574	0.574	0.616	−0.26
0.8593	0.579	0.578	0.608	−0.26
1.0000	0.590			
	CH_2ClCH_2Cl-*p*-Xylene			
0.0000	0.663			
0.1381	0.650	0.646	0.671	−0.12
0.1456	0.649	0.646	0.671	−0.13
0.2064	0.634	0.638	0.673	−0.22
0.2657	0.626	0.631	0.675	−0.23
0.2778	0.625	0.630	0.675	−0.23
0.3773	0.621	0.619	0.675	−0.19
0.5237	0.608	0.605	0.671	−0.21
0.6171	0.599	0.598	0.664	−0.24
0.7575	0.591	0.590	0.646	−0.27
0.8687	0.588	0.588	0.625	−0.29
0.9077	0.588	0.588	0.616	−0.30
1.0000	0.590			
	CH_2ClCH_2Cl–Quinoline			
0.0000	2.756			
0.2601	1.867	1.867	1.848	0.025
0.2811	1.808	1.809	1.789	0.024
0.4360	1.429	1.431	1.414	0.026
0.5464	1.208	1.208	1.198	0.031
0.7044	0.947	0.946	0.946	0.044
0.8480	0.755	0.754	0.758	0.046
0.9360	0.654	0.655	0.658	0.021
1.0000	0.590			
	CH_2ClCH_2Cl–Cyclohexane			
0.0000	1.066			
0.1889	0.841	0.844	0.995	−0.89
0.3111	0.753	0.753	0.944	−0.84
0.4999	0.669	0.663	0.856	−0.76
0.5514	0.650	0.647	0.831	−0.76
0.6372	0.626	0.625	0.787	−0.76
0.7536	0.603	0.605	0.726	−0.75
0.9732	0.590	0.590	0.605	−0.70
1.0000	0.590			

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

In eq 1, ν_A and ν_B refer to the kinematic viscosities of the pure components A and B, respectively, and ν refers to the kinematic viscosity of the mixture of A and B having mole fractions x_A and x_B, respectively. ν_{AB} and ν_{BA} are the two undetermined parameters which are characteristic of a system of A and B. In eq 2, M_A and M_B refer to the molecular weights of the components A and B, respectively. Taking CH_2ClCH_2Cl as A and other component as B in the systems CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, CH_2ClCH_2Cl-*p*-xylene, CH_2ClCH_2Cl–quinoline, and CH_2ClCH_2Cl–cyclohexane, 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 (*7*). The values of the parameters ν_{AB} and ν_{BA}, along with the standard deviations $\delta(\nu)$ for the various systems, are given in Table II, whereas the values of the kinematic viscosities, ν_{estd}, of the various mixtures, as estimated from eq 1, using the values of the parameters ν_{AB} and ν_{BA}, are given in Table I. The values of the average percent deviations, $(\Delta\%)_{\text{av}}$, and the maximum percent deviations, $(\Delta\%)_{\text{max}}$, of the experimental values of ν from those estimated for the various mixtures by using eq 1 are given in Table II. It is seen from Tables I and II that McAllister's eq 1 correlates the liquid-mixture viscosity data for the present mixtures to a significantly high degree of accuracy.

According to Lobe's approach (*7*, *9*), the kinematic viscosity ν of a binary mixture of A and B is given by

$$\nu = \phi_A\nu_A e^{\phi_B\alpha^*_B} + \phi_B\nu_B e^{\phi_A\alpha^*_A} \quad (3)$$

In eq 3, 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 refer to the kinematic viscosities of the two pure components 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 eq 4 and 5, respectively. The values of the kinematic viscosities,

$$\alpha^*_A = -1.7 \ln \frac{\nu_B}{\nu_A} \quad (4)$$

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

ν_{estd}, as estimated from eq 3 are also given in Table I. The values of the average percent deviations, $(\Delta\%)_{\text{av}}$, and those of maximum percent deviations, $(\Delta\%)_{\text{max}}$, of the experimental values of ν from those obtained from eq 3 are recorded in Table II. Tables I and II show that eq 3 estimates kinematic viscosities to a good degree of accuracy for mixtures of CH_2ClCH_2Cl with quinoline. Tables I and II, however, show that the

Table II. Values of the Parameters ν_{AB} and ν_{BA} of Eq 1, the Standard Deviations, $\delta(\nu)$, Average Percent Deviations, $(\Delta\%)_{\text{av}}$, and the Maximum Percent Deviations, $(\Delta\%)_{\text{max}}$, for the Various Systems of 1,2-Dichloroethane at 303.15 K

system	ν_{AB}, cSt	ν_{BA}, cSt	$\delta(\nu)$,[a] cSt	$(\Delta\%)_{\text{av}}$ eq 1	$(\Delta\%)_{\text{av}}$ eq 3	$(\Delta\%)_{\text{max}}$ eq 1	$(\Delta\%)_{\text{max}}$ eq 3
CH_2ClCH_2Cl–benzene	0.547	0.557	0.0024	0.33	11.78	0.69	16.3
CH_2ClCH_2Cl–toluene	0.554	0.577	0.0015	0.20	7.5	0.35	10.0
CH_2ClCH_2Cl-*p*-xylene	0.578	0.625	0.0034	0.40	7.2	0.80	10.9
CH_2ClCH_2Cl–quinoline	1.021	1.681	0.0013	0.08	0.72	0.15	1.05
CH_2ClCH_2Cl–cyclohexane	0.591	0.663	0.0034	0.32	21.2	0.90	28.0

[a] Equation 1.

values of ν estimated from eq 3 exhibit large percent deviations from the experimental values of ν in the case of the mixtures of CH_2ClCH_2Cl with benzene, toluene, *p*-xylene, and cyclohexane.

Earlier attempts have been made to describe the dynamic viscosities, η, of binary liquid mixtures in terms of the dynamic viscosities of pure components and a parameter attributed to the intermolecular interactions between the components. According to Grunberg and Nissan (*4*), the dynamic viscosity of a binary mixture of components A and B is given by the equation

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

where η_A and η_B refer to the dynamic viscosities of the pure liquid components A and B, respectively, x_A and x_B are the mole fractions of the components A and B, respectively, in the mixture, and d is a parameter which is regarded as a measure of the strength of interaction between the two components. In order to calculate d from eq 6, the measured values of ν were converted to dynamic viscosities η by using densities which for pure liquids were those available in literature (*12*). The densities of the mixtures were obtained from the densities of pure components and the measurements on excess volumes (*1*) for the various binary mixtures. The values of d for the various binary mixtures are given in Table I which shows that the variation of the parameter d with composition of a particular mixture is not large. The values of d are positive for CH_2ClCH_2Cl–quinoline, and negative for CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, CH_2ClCH_2Cl–*p*-xylene, and CH_2ClCH_2Cl–cyclohexane. The mean values of d for the systems CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, CH_2ClCH_2Cl–*p*-xylene, CH_2ClCH_2Cl–quinoline, and CH_2ClCH_2Cl–cyclohexane have been found to be −0.34, −0.24, −0.22, +0.031, and −0.78, respectively. The positive values of d for CH_2ClCH_2Cl–quinoline show that CH_2ClCH_2Cl forms an intermolecular complex with quinoline in the liquid, which gives evidence in favor of our earlier conclusions (*1–3*). The values of d, which are slightly negative for CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, and CH_2ClCH_2Cl–*p*-xylene, as compared with d for CH_2ClCH_2Cl–cyclohexane, indicate the existence of a weak specific interaction between CH_2ClCH_2Cl and the aromatic hydrocarbons.

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Registry No. CH_2ClCH_2Cl, 107-06-2; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; quinoline, 91-22-5; cyclohexane, 110-82-7.

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Heterogeneous Equilibrium in the Quinary System $NaCl–KCl–MgCl_2–CaCl_2–H_2O$ in the 0–50 °C Temperature Range

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The quinary system $NaCl–KCl–MgCl_2–CaCl_2–H_2O$ was experimentally investigated in the 0–50 °C temperature range in a condition of equilibrium with three solid phases: sodium chloride (NaCl), carnallite ($KCl·MgCl_2·6H_2O$), and bischofite ($MgCl_2·6H_2O$). A correlation was established between magnesium chloride concentration and the two independent variables, i.e., temperature and calcium chloride concentration. The solubilities of sodium chloride and potassium chloride were found to be low, less than 0.6 wt % NaCl and less than 0.4 wt % KCl.

Introduction

Many natural brines, such as seawater or the brines of the Dead Sea in Israel, contain sodium, potassium, calcium, and magnesium chlorides. The aqueous solubilities of these minerals are thus of great importance from both industrial and geological points of view. A large amount of experimental work has been done on binary, ternary, and quarternary subsystems of the quinary system $NaCl–KCl–MgCl_2–CaCl_2–H_2O$, and most of the results have been summarized by Linke and Seidell (*1*). However, very few equilibrium data have been published on this quinary system.

The experimental determination of the phase diagram of the quinary system $NaCl–KCl–MgCl_2–CaCl_2–H_2O$ is somewhat complicated, because a number of solid phases may appear at the various equilibria. The magnesium and calcium chlorides crystallize in a variety of hydrate forms: $MgCl_2·12H_2O$, $MgCl_2·4H_2O$, $MgCl_2·2H_2O$, $CaCl_2·6H_2O$, $CaCl_2·4H_2O$, and $CaCl_2·2H_2O$. In addition, salt pairs may precipitate, such as $CaCl_2·2MgCl_2·12H_2O$, $2CaCl_2·MgCl_2·12H_2O$, and $KCl·MgCl_2·6H_2O$.

For the quinary system, the Gibbs phase rule shows that at constant pressure and temperature there are four degrees of freedom. Hence, it is important that the phase diagram range

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