

- (11) Chen, C. T. A.; Chen, J. H.; Millero, F. J. *J. Chem. Eng. Data* **1980**, *25*, 307.
 (12) Correl, R. J.; Kestin, J. *J. Chem. Eng. Data* **1981**, *26*, 43.
 (13) Chen, C. T. A.; Millero, F. J. *J. Chem. Eng. Data* **1981**, *26*, 270.
 (14) Surdo, A. L.; Alzola, E. M.; Millero, F. J. *J. Chem. Thermodyn.* **1982**, *14*, 649.
 (15) Saluja, P. P. S. Canadian Atomic Energy Establishment, Manitoba, Canada, private communication.
 (16) Phutela, R. C.; Pitzer, K. S.; Saluja, P. P. S., University of California, Berkeley, unpublished results.
 (17) Rogers, P. S. Z.; Bradley, D. J.; Pitzer, K. S. *J. Chem. Eng. Data* **1982**, *27*, 47.
 (18) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables Hemisphere*: Washington, DC, 1985; *Proceedings of the Eighth Symposium on Thermophysical Properties* Senger, J. V., Ed.; A.S.M.E.: New York, 1981; Vol. 2, p 298.
 (19) Pitzer, K. S. *J. Phys. Chem.* **1973**, *77*, 268.
 (20) Pitzer, K. S. In *Activity Coefficients in Electrolyte Solutions*; Pytkowicz, R. M., Ed.; CRC Press: Boca Raton, FL, 1979; Chapter 7.
 (21) Pitzer, K. S.; Mayorga, G. J. *Solution Chem.* **1974**, *3*, 539.
 (22) Bradley, D. J.; Pitzer, K. S. *J. Phys. Chem.* **1979**, *83*, 1599; **1983**, *87*, 3798.

Received for review October 7, 1985. Accepted January 10, 1986. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering, and Geosciences of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

Ultrasonic Velocities in, and Adiabatic Compressibilities for, Binary Liquid Mixtures of 1,2-Dichloroethane with Benzene, Toluene, *p*-Xylene, Quinoline, and Cyclohexane

Jagan Nath* and Geeta Singh

Chemistry Department, Gorakhpur University, Gorakhpur 273 009, India

Measurements of ultrasonic velocities (u) and adiabatic compressibilities (k_s) have been made for mixtures of 1,2-dichloroethane ($\text{CH}_2\text{ClCH}_2\text{Cl}$) with benzene, toluene, and quinoline at 303.15 and 313.15 K, for mixtures of $\text{CH}_2\text{ClCH}_2\text{Cl}$ with *p*-xylene at 303.15 and 318.15 K, and for mixtures of $\text{CH}_2\text{ClCH}_2\text{Cl}$ with cyclohexane at 308.15 K. The values of the quantity Δk_s , which refers to the deviations of the experimental values of k_s for mixtures from the mole fraction mixture law values, have been found to be positive for $\text{CH}_2\text{ClCH}_2\text{Cl}$ -benzene, $\text{CH}_2\text{ClCH}_2\text{Cl}$ -toluene, $\text{CH}_2\text{ClCH}_2\text{Cl}$ -*p*-xylene, and $\text{CH}_2\text{ClCH}_2\text{Cl}$ -cyclohexane, and negative for $\text{CH}_2\text{ClCH}_2\text{Cl}$ -quinoline.

Introduction

Quite recently, Nath and Singh (1) made measurements of excess volumes for binary liquid mixtures of 1,2-dichloroethane ($\text{CH}_2\text{ClCH}_2\text{Cl}$) with benzene, toluene, *p*-xylene, quinoline, and cyclohexane at different temperatures, 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 of $\text{CH}_2\text{ClCH}_2\text{Cl}$ with the aromatic hydrocarbons and quinoline in the liquid state. Since the adiabatic compressibilities as obtained from ultrasonic velocities in binary liquid mixtures are known (2-5) 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 mixtures of $\text{CH}_2\text{ClCH}_2\text{Cl}$ with the aromatic hydrocarbons, and quinoline, from measurements of ultrasonic velocities. Hence, in the present program, we have made measurements of ultrasonic velocities in, and adiabatic compressibilities for, the binary liquid mixtures of $\text{CH}_2\text{ClCH}_2\text{Cl}$ with benzene, toluene, *p*-xylene, quinoline, and cyclohexane and the results obtained have been interpreted in this paper.

Table I. Values of Ultrasonic Velocities in, and Adiabatic Compressibilities^a for, Various Pure Liquids at 303.15 K

liquid	u , m s ⁻¹			$10^{12}k_s$, Pa ⁻¹		
	this work	lit.	ref	this work	lit.	ref
benzene	1278	1278	8	705	705	8
toluene	1284	1284.5	8	707	706.6	8
<i>p</i> -xylene	1289	1288	3	706	707	3
1,2-dichloroethane	1175	1175 ^b	5	585	585	5

^a Values of k_s calculated from eq 1, by using densities obtained from the data reported in ref 7. ^b Value obtained by interpolation.

Experimental Section

Materials. The methods of purifying the various components and checking their purity have been described earlier (1).

Method. The ultrasonic velocities, u , in pure liquids and their binary mixtures were measured with a single-crystal interferometer (supplied by Mittal Enterprises, New Delhi) at a frequency of 2 MHz s⁻¹. The accuracy in the values of u is of the order of ± 1.0 m s⁻¹. The adiabatic compressibilities, k_s , were calculated from the relation (3-6)

$$k_s = u^{-2}\rho^{-1} \quad (1)$$

where ρ refers to the density. The densities used to calculate k_s for pure liquids at various temperatures were obtained from the data reported by Timmermans (7), whereas the densities used to calculate k_s for mixtures were estimated from the densities of pure liquids, and the data on excess volumes for the various mixtures, as reported earlier (1). The accuracy in the values of $10^{12}k_s$ is of the order of ± 1.0 Pa⁻¹.

The working of the interferometer was tested by making measurements for pure liquids benzene, toluene, *p*-xylene, and 1,2-dichloroethane at 303.15 K. Table I shows that present values of u and k_s for these liquids are in good agreement with the data available in literature (3, 5, 8).

Results and Discussion

The experimental values of ultrasonic velocities in, and adi-

Table II. Experimental Values of Ultrasonic Velocities in, and Adiabatic Compressibilities for, the Various Systems of CH₂ClCH₂Cl at Different Temperatures

temp, K	x_1	u , m s ⁻¹	$10^{12}k_s$, Pa ⁻¹	$10^{12}\Delta k_s$, Pa ⁻¹	temp, K	x_1	u , m s ⁻¹	$10^{12}k_s$, Pa ⁻¹	$10^{12}\Delta k_s$, Pa ⁻¹	temp, K	x_1	u , m s ⁻¹	$10^{12}k_s$, Pa ⁻¹	$10^{12}\Delta k_s$, Pa ⁻¹
CH₂ClCH₂Cl-Benzene														
303.15	0.0000	1278	705			0.9334	1176	600	7		0.2558	1463	419	-18
	0.0860	1262	701	6	313.15	1.0000	1175	585			0.4287	1402	447	-24
	0.1524	1251	696	9		0.0000	1242	764			0.4327	1401	447	-25
	0.2142	1242	690	11		0.0600	1233	760	4		0.4817	1382	457	-25
	0.3270	1227	679	13		0.2677	1202	746	17		0.6368	1324	488	-25
	0.3273	1227	679	13		0.3013	1198	743	18		0.7591	1273	518	-19
	0.3337	1225	680	15		0.5282	1169	719	24		0.8522	1235	543	-13
	0.4348	1214	668	15		0.6674	1156	699	22		0.9297	1203	565	-6
	0.5800	1198	652	17		0.7593	1148	684	19		0.9793	1183	579	-2
	0.6180	1196	645	14		0.8313	1143	670	15	313.15	1.0000	1513	405	
	0.7173	1189	630	11		0.8854	1141	658	10		0.0694	1490	415	-6
	0.7789	1184	622	10		0.9034	1140	655	9		0.1244	1474	421	-12
	0.8453	1180	612	8		1.0000	1136	633			0.1751	1455	430	-15
	0.9529	1177	593	2		CH₂ClCH₂Cl-<i>p</i>-Xylene					0.2115	1443	436	-17
	1.0000	1175	585		303.15	0.0000	1289	706			0.3336	1398	458	-23
313.15	0.0000	1230	771			0.0560	1281	704	5		0.3906	1380	467	-27
	0.0595	1220	766	3		0.1194	1270	702	10		0.4686	1350	484	-28
	0.1473	1206	759	8		0.1795	1262	699	15		0.5960	1302	512	-29
	0.3786	1178	732	13		0.2547	1250	695	20		0.6368	1285	522	-28
	0.4918	1167	717	14		0.3708	1232	689	28		0.7033	1260	539	-26
	0.4991	1166	716	14		0.4954	1216	677	31		0.8027	1219	567	-21
	0.5920	1157	704	15		0.5672	1206	670	33		0.8657	1192	588	-14
	0.5981	1157	703	15		0.7004	1193	650	29		0.9059	1176	600	-12
	0.6011	1157	702	14		0.7890	1183	637	26		1.0000	1136	633	
	0.7137	1149	684	11		0.8970	1178	612	15		CH₂ClCH₂Cl-Cyclohexane			
	0.7499	1147	678	10		0.9818	1175	590	3	308.15	0.0000	1206	899	
	0.7792	1145	673	10		1.0000	1175	585			0.0437	1197	897	11
	0.8547	1141	660	7	318.15	0.0000	1229	789			0.2582	1158	875	51
	1.0000	1136	633			0.1441	1207	784	14		0.3047	1153	865	55
CH₂ClCH₂Cl-Toluene														
303.15	0.0000	1284	707			0.3200	1181	775	28		0.4166	1141	840	62
	0.0642	1274	703	4		0.3776	1173	771	32		0.4203	1141	838	61
	0.1575	1258	699	11		0.5130	1156	757	36		0.5346	1134	804	61
	0.2529	1246	690	14		0.6894	1136	732	34		0.6704	1132	755	51
	0.3362	1234	684	18		0.7850	1127	715	30		0.6818	1132	751	50
	0.4530	1218	673	21		0.8761	1121	694	21		0.7159	1132	738	47
	0.5349	1208	664	22		1.0000	1119	657			0.7213	1132	736	47
	0.5708	1204	660	23		CH₂ClCH₂Cl-Quinoline					0.8187	1137	694	33
	0.7101	1191	640	20	303.15	0.0000	1545	386			0.8971	1144	657	19
	0.7238	1189	639	20		0.0316	1537	389	-3		0.8982	1144	657	19
	0.8853	1177	611	12		0.1068	1514	397	-10		0.9480	1149	633	10
						0.1666	1493	406	-13		0.9500	1150	632	9
											1.0000	1156	608	

Table III. Values of the Constants A_0 , A_1 , and A_2 of Eq 2, and the Standard Deviations $\delta(\Delta k_s)$ for the Various Systems of CH₂ClCH₂Cl at Different Temperatures

system	T , K	$10^{12}A_0$, Pa ⁻¹	$10^{12}A_1$, Pa ⁻¹	$10^{12}A_2$, Pa ⁻¹	$10^{12}\delta(\Delta k_s)$, Pa ⁻¹
CH ₂ ClCH ₂ Cl-benzene	303.15	61.83	-10.72	-0.40	1.19
	313.15	58.31	-1.57	-3.39	0.56
CH ₂ ClCH ₂ Cl-toluene	303.15	87.90	25.59	7.82	0.38
	313.15	96.03	18.01	-11.97	0.17
CH ₂ ClCH ₂ Cl- <i>p</i> -xylene	303.15	126.73	41.14	3.20	0.43
	318.15	142.73	51.30	17.05	0.72
CH ₂ ClCH ₂ Cl-quinoline	303.15	-101.52	-0.92	4.61	0.66
	313.15	-115.06	-20.90	-2.81	0.57
CH ₂ ClCH ₂ Cl-cyclohexane	308.15	249.39	-36.42	-22.55	0.41

adiabatic compressibilities for, binary liquid mixtures of CH₂ClCH₂Cl with benzene, toluene, *p*-xylene, quinoline, and cyclohexane at various temperatures are given in Table II, where x_1 refers to the mole fraction of CH₂ClCH₂Cl. The values of the quantity Δk_s , which refers to the deviations of the experimental values of k_s for the various mixtures from the mole fraction mixture law values, are also given in Table II and have been fitted by the method of least squares to the equation

$$\Delta k_s = x_1 x_2 [A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \quad (2)$$

In eq 2, x_1 refers to the mole fraction of CH₂ClCH₂Cl, x_2 refers

to the mole fraction of the aromatic hydrocarbon, quinoline or cyclohexane, and A_0 , A_1 , and A_2 are constants characteristic of a system at a given temperature. The values of the constants A_0 , A_1 , and A_2 along with the standard deviations $\delta(\Delta k_s)$ are given in Table III.

The data show that throughout the whole range of composition, the values of Δk_s are positive for CH₂ClCH₂Cl-benzene, CH₂ClCH₂Cl-toluene, CH₂ClCH₂Cl-*p*-xylene, and CH₂ClCH₂Cl-cyclohexane, and negative for CH₂ClCH₂Cl-quinoline. At $x_1 = 0.5$, Δk_s for the various systems has the sequence

$$(\Delta k_s)_{\text{cyclohexane}} > (\Delta k_s)_{\text{p-xylene}} > (\Delta k_s)_{\text{toluene}} > (\Delta k_s)_{\text{benzene}} > (\Delta k_s)_{\text{quinoline}}$$

The data show that the values of the temperature coefficient $\delta(\Delta k_s)/\delta T$ are positive for CH₂ClCH₂Cl-toluene and CH₂ClCH₂Cl-*p*-xylene, and negative for CH₂ClCH₂Cl-benzene and CH₂ClCH₂Cl-quinoline. The negative values of Δk_s for CH₂ClCH₂Cl-quinoline indicate the existence of specific interaction leading to the formation of adducts between CH₂ClCH₂Cl and quinoline in the liquid state. Further, the positive values of $\delta(\Delta k_s)/\delta T$ for the systems CH₂ClCH₂Cl-toluene and CH₂ClCH₂Cl-*p*-xylene also indicate the existence of specific interaction between CH₂ClCH₂Cl and the aromatic hydrocarbons. The negative values of $\delta(\Delta k_s)/\delta T$ for the system CH₂ClCH₂Cl-quinoline can be explained to be due to the self-association (9) of the quinoline molecules through hydrogen

bonding, whereas the negative values of $\delta(\Delta k_s)/\delta T$ for the system $\text{CH}_2\text{ClCH}_2\text{Cl}$ -benzene can be visualized to be due to the predominance of the contributions to Δk_s from nonspecific interactions over those from specific interactions.

Acknowledgment

We are extremely grateful to Professor S. C. Tripathi, Head of the Chemistry Department, Gorakhpur University, Gorakhpur, for encouragement during the course of this investigation.

Registry No. $\text{CH}_2\text{ClCH}_2\text{Cl}$, 107-06-2; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; quinoline, 91-22-5; cyclohexane, 110-82-7.

Literature Cited

- (1) Nath, J.; Singh, G. *J. Chem. Eng. Data* **1986**, *31*, 115-116.
- (2) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1965**, *61*, 2102-2111.
- (3) Nath, J.; Narain, B. *J. Chem. Eng. Data* **1982**, *27*, 308-312.
- (4) Nath, J.; Tripathi, A. D. *J. Chem. Eng. Data* **1983**, *28*, 263-266.
- (5) Nath, J.; Dixit, A. P. *J. Chem. Eng. Data* **1984**, *29*, 313-316.
- (6) Nath, J.; Dixit, A. P. *J. Chem. Eng. Data* **1984**, *29*, 320-321.
- (7) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1950.
- (8) Preyer, E. B.; Hubbard, J. C.; Andrews, J. H. *J. Am. Chem. Soc.* **1929**, *51*, 759-770.
- (9) Morcom, K. W.; Travers, D. N. *Trans. Faraday Soc.* **1966**, *62*, 2063-2068.

Received for review September 13, 1985. Accepted January 16, 1986. Thanks are due to the Council of Scientific and Industrial Research, New Delhi, for financial assistance.

Solubility and Metastable Zone Width of Sodium Chloride in Water-Diethylene Glycol Mixtures

Angelo Chianese,[†] Sergio Di Cave,* and Barbara Mazzarotta

Dipartimento di Ingegneria Chimica, Università di Roma, 00184 Roma, Italy

The solubility of sodium chloride in aqueous diethylene glycol (DEG) was determined in the range of 0-100% DEG concentration and 10-90 °C. The temperature-solubility relationships can be expressed by straight lines, whose parameters are functions of the solvent composition and can be predicted by second-order expressions. The temperature coefficient of the solubility varies progressively, being negative for solutions 100-74 wt % of DEG, and positive for solutions 74-0 wt % of DEG. The metastability range in 0-100% aqueous DEG was also determined: it becomes wider on increasing the DEG content in the solvent.

Introduction

During the dehydration of crude natural gas, usually performed with concentrated solutions of ethylene glycols, significant amounts of salts may accumulate in the liquid phase. In order to prevent excessive scaling over the heat-transfer surfaces of the dehydration loop, it is very important to know the solubility characteristics of these salts in the particular solvent. The predominant salt is sodium chloride: its solubilities in mixtures of water-diethylene glycol (DEG) are reported in some published papers (1-6). However, the data are not complete, being limited either to a partial range of solvent compositions (mixtures rich of DEG) (1-4), or to room temperature alone (5, 6). Moreover, while the dependence of the temperature-solubility coefficient on the solvent composition is qualitatively confirmed, from the quantitative point of view significant discrepancies appear; in fact for 80 wt % of DEG both negative (1-3) and positive (4) values are reported. Finally, no data seem to be available about the metastability range. In this work the solubility of sodium chloride in aqueous solutions of DEG has been investigated for water/DEG ratios 0-100% and

in a wide interval of temperatures (10-90 °C); in addition the metastability range width has been determined.

Experimental Method

All the chemicals were Farmitalia Carlo Erba with the following purities: sodium chloride >99.5%, diethylene glycol >99.5%, and water bidistilled grade.

The experimental apparatus was a 250-mL cylindrical jacketed glass cell, connected to a thermostatic bath and magnetically stirred. Temperature was maintained and read with a precision of ± 0.1 °C.

(1) **Solubility.** The two methods commonly adopted (7) to determine solubility data have been used. The first, which consists of increasing and decreasing the temperature of a solution prepared from weighed amounts of salt and solvent till nucleation or dissolution take place, has been found unsuitable, especially for solvent compositions in the range 80-50 wt % of DEG where the temperature exhibits little or no influence over sodium chloride solubility: measurements were carried out according to this first method only for 100% DEG solvent.

The second method consists of maintaining at a fixed temperature a stirred solution containing some excess of salt till equilibrium conditions are reached, and afterwards measuring the concentration of the saturated solution. In the present case the salt content was determined by applying the gravimetric method to samples (about 10 mL each) withdrawn from the solution. The precision of the gravimetric method was tested by determining the solids recovery with water-DEG solutions containing weighed amounts of sodium chloride: the standard deviation obtained was <0.04 g of NaCl/100 g of solvent.

Liquid and solid phases were assumed to be in equilibrium when the differences between the salt content of the liquid determined in three consecutive samples withdrawn at about 6-h intervals was within 0.08 g of NaCl/100 g solvent. The sampling procedure was as follows. Stirring was stopped and the crystals were allowed to settle for 15-30 min, depending on the viscosity of the solution, which is principally affected by the DEG concentration; three samples were withdrawn by

[†] Dipartimento di Ingegneria Chimica, Università de L'Aquila Monteluco-Rojo, 67100 L'Aquila, Italy.