°C are known (Table V), the single parameter used for (Na^+) represents the solubilities well up to about 1.5 M and within 10–15% at higher concentrations. Similarly, the data of Fedotieff (*10*) for solubility in aqueous $CuCl_2$ at 19 °C and those of Kreman (*11*) for solubility in aqueous $FeCl_2$ at 25 °C can be represented with similar precision for concentrations producing solubilities in the same range as for the complex mixtures, with deviations at higher and lower concentrations. The overall indications are that the parameters given could be applied successfully to any mixture where the concentration of ions falls in the ranges displayed in Table X, and probably to substantially wider ranges. The method itself should be applicable to a much wider range of solutions wherever experimental data are available for determination of the parameters required for other cations or anions.

General Discussion

The results presented in Tables IV and V for aqueous HCl and aqueous NaCl, respectively, should be as precise as any existing solubility data for CuCl in the temperature range 10–40 °C. The equilibrium constants, the heats of solution, and the virial parameters presented in Tables I and III will permit calculation of solubilities at concentrations not listed (up to 6 M) for this same temperature range. At temperatures below 10 °C or above 40 °C, the predictions become much less certain, because of uncertainties in the heats of solution and because of possible temperature dependence of the virial parameters. There is need for data of good precision above 35 °C on at least one system to settle the problem of temperature dependence. In using the parameters for calculation, no attempt should be made to extrapolate them beyond the range for which they were determined (to 6.5 M for HCl and 6.0 M for NaCl). The HCl parameters actually make fair predictions for solubility up to about 9 M but thereafter predict solubility to decrease with chloride concentrations. A more extensive set of parameters will certainly be needed to represent higher concentration ranges.

The data sets used for selection of the parameters for HCl and NaCl (*2*) contained solubilities for solutions in which the corresponding perchlorates were present. These solubilities were represented faithfully by the model, using virial coefficients for the perchlorates (*3*) along with those for the other species present. These solubilities were in general lower than those for the same chloride concentrations without perchlorate, primarily because of the increased ionic strength. It would be expected that the same technique would give reasonable results for solutions containing other "inert" materials, such as HNO_3, $NaNO_3$, etc. Such calculations should be treated with caution, however, since the virial parameters for the perchlorates are much more similar to those for the chlorides than are those for other salts of the same cation.

For prediction involving cations where solubility has not been determined, it would be desirable to correlate the virial parameters for ion pairs involving the complex species with those involving the corresponding chlorides. Inspection of Table III shows that for the monovalent cations the β's for the complex species decrease with those for the chlorides, with one exception. However, there is no obvious functional correlation, except that all β's decrease on going to systems where the solubility of CuCl increases. There is no obvious trend in the third virial coefficients, *C*.

As demonstrated earlier, it is frequently feasible to predict approximately the solubility of CuCl in a given medium from that in a reference system such as aqueous HCl or aqueous NaCl, given just a few determinations of solubility in the new system. Care should be exercised in doing so, since the dependence of relative solubility on concentration can vary widely, as comparison of the data in Tables IV–VII will demonstrate.

For mixtures in which two or more cations are present in variable concentrations, a very large number of data points may be required to obtain all parameters needed for detailed treatment of the solubility. In such cases a simpler parametric treatment (described above) following the same general lines of approach may well be sufficient for correlation within whatever ranges of concentration are observed.

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Excess Volumes and Isentropic Compressibilities of Binary Mixtures of a Ketone and Acetonitrile

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Excess volumes and isentropic compressibilities have been measured at 303.15 K for the binary systems of acetonitrile with methyl ethyl ketone, diethyl ketone, methyl propyl ketone, cyclopentanone, cyclohexanone, and 2-methylcyclohexanone. Excess volumes have been measured by the dilatometric method, and isentropic compressibilities have been calculated from densities and velocities of sound. The negative excess volumes and deviations in isentropic compressibilities were attributed to complex formation.

Introduction

As a part of studies of thermodynamic properties of binary liquid mixtures, we reported V^E values for mixtures of an alkanol with toluene (*1*), cyclohexylamine (*2*), and acetonitrile (*3*). Now we report the excess volumes and the isentropic compressibilities for the systems of acetonitrile with methyl ethyl ketone (MEK), diethyl ketone (DEK), methyl propyl ketone (MPK), cyclopentanone, cyclohexanone, and 2-methylcyclohexanone. The work has been taken up to study the molecular interactions, keeping in view the results reported by Narayanaswamy et al.

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Table I. Densities of Pure Substances at 303.15 K

substance	ρ, g cm^{-3} present work	ρ, g cm^{-3} lit.
acetonitrile	0.771 29	0.771 25
MEK	0.794 45	0.794 52
DEK	0.804 55	0.804 50
MPK	0.796 60	0.796 56
cyclopentanone	0.938 98	0.939 02
cyclohexanone	0.937 57	0.937 61
2-methylcyclohexanone	0.916 25	0.916 32

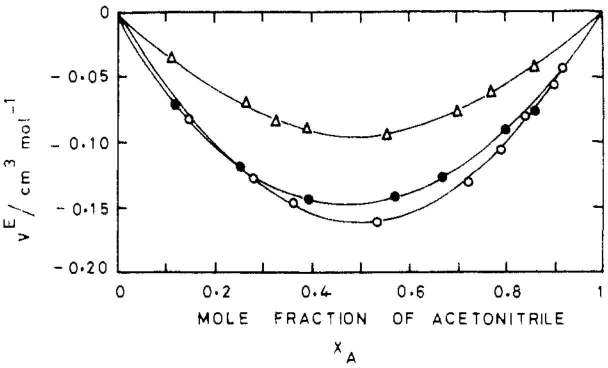

Figure 1. Excess volume (V^E) as a function of mole fraction (X_A) for the systems of acetonitrile with (○) methyl ethyl ketone, (●) diethyl ketone, and (△) methyl propyl ketone.

(*3*), Brown and Smith (*4*), and Lorimer and Jones (*5*).

Experimental Section

Purification of Materials. Acetonitrile (BDH) was purified as described by Putnam et al. (*6*). MEK (BDH), DEK (Riedel), and MPK (BDH) were purified as given by Naidu (*7*). Cyclopentanone (Riedel), cyclohexanone (BDH), and 2-methylcyclohexanone (BDH) were dried over anhydrous sodium sulfate for 2 days and then fractionally distilled. The purities of the final samples were checked by comparing measured densities at 303.15 K with those reported in the literature (*8*). The data are given in Table I. The agreement was within 5 × 10^{-5} g cm^{-3} except for MEK and 2-methylcyclohexanone.

Procedure. Excess volumes were determined directly by the use of a dilatometer as in our earlier work (*1*). Isentropic compressibilities were calculated from precise densities and velocities of sound determined at 303.15 K. Densities were measured by using a bicapillary pycnometer (*9*), which were accurate to 5 × 10^{-5} g cm^{-3}. Ultrasonic velocities of sound were measured with a single-crystal interferometer at a frequency of 2 MHz and were accurate to ±0.15%. The measurements were made at 303.15 K, and the temperature was controlled to ±0.01 K with a thermostatic bath.

Results

Excess volumes at 303.15 K for the six binary systems are presented in Table II and are graphically shown in Figures 1 and 2. The experimental excess volumes may be expressed by the equation

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = X_A(1 - X_A)\{a_0 + a_1(2X_A - 1) + a_2(2X_A - 1)^2\} \quad (1)$$

where X_A is the mole fraction of acetonitrile. The parameters a_0, a_1, and a_2 are evaluated by the method of least squares and are given in Table III along with the standard deviations $\sigma(V^E)$.

Table II. Excess Volumes, V^E (in cm^3 mol^{-1}), for the Six Systems at 303.15 K[a]

X_A	V^E	X_A	V^E
	A + MEK (B)		
0.1461	−0.082	0.7226	−0.128
0.2802	−0.128	0.7865	−0.105
0.3621	−0.138	0.8391	−0.083
0.5346	−0.161	0.8999	−0.055
	A + DEK (B)		
0.1200	−0.071	0.6652	−0.128
0.2541	−0.118	0.8001	−0.091
0.3973	−0.146	0.8614	−0.075
0.5694	−0.144	0.8843	−0.042
	A + MPK (B)		
0.1104	−0.035	0.5575	−0.092
0.2678	−0.073	0.7000	−0.075
0.3273	−0.082	0.7786	−0.062
0.3902	−0.090	0.8636	−0.041
	A + Cyclopentanone (B)		
0.1201	−0.053	0.6450	−0.118
0.1988	−0.083	0.7649	−0.091
0.3461	−0.127	0.8203	−0.080
0.4947	−0.130	0.9163	−0.043
	A + Cyclohexanone (B)		
0.1199	−0.015	0.5288	−0.045
0.2241	−0.024	0.6200	−0.051
0.2999	−0.035	0.7351	−0.047
0.3688	−0.040	0.8608	−0.026
	A + 2-Methylcyclohexanone (B)		
0.1660	−0.067	0.5677	−0.093
0.2442	−0.085	0.6671	−0.080
0.3364	−0.095	0.7351	−0.071
0.4183	−0.094	0.8823	−0.038

[a] A denotes the common component, acetonitrile. X_A is the mole fraction of acetonitrile.

Table III. Values of Parameters in Eq 1 and the Standard Deviations σ of V^E (in cm^3 mol^{-1})

system	a_1	a_2	a_0	$\sigma(V^E)$
A + MEK (B)	0.016	−0.006	−0.628	0.004
A + DEK (B)	0.083	0.006	−0.600	0.004
A + MPK (B)	0.010	0.040	−0.375	0.001
A + cyclopentanone (B)	−0.014	−0.008	−0.525	0.005
A + cyclohexanone (B)	−0.066	0.016	−0.192	0.003
A + 2-methylcyclohexanone (B)	0.080	−0.095	−0.382	0.002

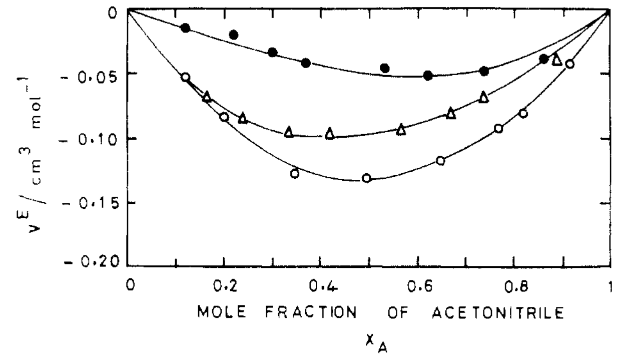

Figure 2. Excess volume (V^E) against mole fraction (X_A) for the systems of acetonitrile with (○) cyclopentanone, (●) cyclohexanone, and (△) methyl cyclohexanone.

Isentropic compressibilities k_s were calculated from

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

where u and ρ denotes the velocity of sound and the density. The values of k_s were accurate to ±2 TPa^{-1}. The deviations

Table IV. Volume Fractions (ϕ_A) of Acetonitrile, Densities (ρ), Sound Velocities (u), Isentropic Compressibilities (k_S) Calculated from u and ρ, and K_S Computed from Eq 3

ϕ_A	ρ, g cm^{-3}	u, m s^{-1}	k_S, TPa^{-1}	K_S, TPa^{-1}
		A + MEK (B)		
0.0000	0.794 45	1170	920	
0.1448	0.791 88	1192	889	−17
0.2497	0.790 08	1202	876	−18
0.4025	0.786 94	1214	862	−17
0.5549	0.783 25	1226	849	−14
0.6043	0.782 04	1230	845	−13
0.6512	0.780 77	1233	842	−11
0.7536	0.778 09	1242	833	−9
0.9098	0.773 79	1253	823	−3
1.0000	0.771 29	1260	817	
		A + DEK (B)		
0.0000	0.804 55	1197	867	
0.1448	0.800 75	1207	857	−3
0.2468	0.797 71	1214	850	−5
0.3070	0.795 80	1212	855	−6
0.3966	0.792 85	1223	843	−4
0.4805	0.790 01	1228	839	−4
0.7157	0.781 75	1242	829	−2
0.7555	0.780 39	1244	828	−1
0.9393	0.773 52	1256	819	−1
1.0000	0.771 29	1260	817	
		A + MPK (B)		
0.0000	0.796 60	1200	872	
0.1525	0.793 31	1206	867	3
0.2429	0.791 26	1210	862	5
0.3816	0.787 87	1222	850	−1
0.4195	0.786 92	1225	847	−2
0.4779	0.785 41	1229	843	−3
0.6338	0.781 30	1239	834	−3
0.7570	0.777 82	1244	829	−1
0.9507	0.772 62	1256	820	−1
1.0000	0.771 29	1260	817	
		A + Cyclopentanone (B)		
0.0000	0.938 98	1374	564	
0.1285	0.918 36	1359	589	−7
0.2392	0.900 35	1344	615	−9
0.3677	0.878 91	1325	648	−9
0.4217	0.869 86	1319	661	−10
0.5088	0.855 20	1308	683	−10
0.6343	0.833 91	1296	714	−8
0.7306	0.817 56	1264	741	−8
0.9666	0.777 03	1264	805	−3
1.0000	0.771 29	1260	817	
		A + Cyclohexanone (B)		
0.0000	0.937 57	1388	554	
0.1531	0.912 43	1363	590	−4
0.2290	0.899 93	1349	610	−4
0.3633	0.877 67	1332	642	−7
0.4158	0.869 04	1324	656	−7
0.5194	0.851 81	1311	683	−7
0.5856	0.840 82	1302	701	−7
0.7587	0.811 78	1282	749	−4
0.9306	0.782 99	1266	796	−3
1.0000	0.771 29	1260	817	
		A + 2-Methylcyclohexanone (B)		
0.0000	0.916 25	1346	602	
0.1231	0.899 12	1334	625	−3
0.1692	0.892 56	1327	636	−2
0.2382	0.882 61	1320	650	−3
0.2906	0.875 08	1315	661	−3
0.3634	0.864 53	1304	680	0
0.4348	0.854 13	1300	693	0
0.7652	0.805 82	1270	769	−3
0.9527	0.778 29	1262	807	0
1.0000	0.771 29	1260	817	

Table V. Values of Parameters in Eq 4 and Standard Deviations σ of K_S (in TPa^{-1})

system	b_1	b_2	b_0	σ-(K_S)
A + methyl ethyl ketone (B)	62.42	−45.59	−62.14	1
A + cyclopentanone (B)	−4.33	−56.37	−36.43	1
A + cyclohexanone (B)	−4.59	−15.29	−26.11	1

in isentropic compressibilities, K_s, have been calculated from

$$K_s = k_s - \phi_A k_{s,A} - \phi_B k_{s,B} \tag{3}$$

where k_s, $k_{s,A}$, and $k_{s,B}$ are the isentropic compressibilities of the mixture and the pure components and ϕ_A and ϕ_B are the volume fractions. The values of K_s are given in Table IV. Experimental K_s values may be represented by the equation

$$K_s = \phi_A(1 - \phi_A)\{b_0 + b_1(2\phi_A - 1) + b_2(2\phi_A - 1)^2\} \tag{4}$$

where ϕ_A is the volume fraction of acetonitrile. The values of the parameters b_0, b_1 and b_2 are given in Table V along with the standard deviations $\sigma(K_s)$ for the systems of acetonitrile with MEK, cyclopentanone, and cyclohexanone. For the remaining systems the method of least squares has not been used because of low values of K_s.

Discussion

The excess volumes for all of the systems studied are negative at all compositions. Acetonitrile is a polar solvent and has the ability to form complexes. Lorimer and Jones (*5*) have reported negative V^E values for acetonitrile + trichloromethane and attributed them to complex formation. The values of V^E reported here suggest the complex formation between acetonitrile and ketones. This contention is supported by the work of Brown and Smith (*4*). The negative V^E values for the three aliphatic ketones fall in the order MEK > DEK > MPK. This order shows that the increase in chain length of an alkyl group attached to the carbonyl function decreases the interaction between unlike molecules. The order for alicyclic ketones: cyclopentanone > 2-methylcyclohexanone > cyclohexanone suggests that an increase in cyclic structure hinders the interaction. The higher values for methylcyclohexanone solutions than cyclohexanone solutions may be due to the presence of the methyl group which increases the negative charge on the oxygen atom of the carbonyl group.

The deviations in isentropic compressibilities, K_s, are 2–3 times the experimental error in all of the systems except for the systems acetonitrile + MEK and acetonitrile + cyclopentanone. However, the negative values in all of the cases support the complex formation (*10*). The order of values of K_s is almost similar to that observed with respect to excess volumes.

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