THERMODYNAMIC STUDY OF MOLECULAR INTERACTIONS IN TERNARY LIQUID SYSTEMS

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ABSTRACT

Sound velocities in methanol, ethanol, *n*-propanol, *n*-butanol, acetonitrile, carbon tetrachloride and in their binary and ternary systems were measured in order to study the weak interaction between methanol, ethanol, *n*-propanol, *n*-butanol and acetonitrile in carbon tetrachloride. The association constants at 25°C and the heats of complexation of the above systems are 0.177, 0.286, 0.378 and 0.499 M^{-1} and 30.79, 23.3, 19.8 and 16.00 kJ mol^{-1} respectively.

INTRODUCTION

Although spectroscopic techniques are powerful tools for investigating the nature of molecular complexes and hydrogen bonding (by providing definite evidence relating to the formation of weak as well as strong bonds between molecules) these methods are subject to criticism, particularly in the case of weakly interacting systems as the valid separation of the equilibrium constant K and the extinction coefficient ϵ from the product $K\epsilon$ (obtained by using the Benesi–Hildebrand [1] and modified equations) may be difficult to attain, the error increasing with the decrease in strength of the complexes [2–6]. Therefore, if accurate values of K, ϵ and $K\epsilon$ are required which are essential in developing and testing the theories of electron donor–acceptor (or proton acceptor–donor) interactions, the results obtained by spectral methods have to be supplemented with results obtained by non-spectral methods. Recently, we have begun to explore the possibility of using non-spectral methods, such as refractive index measurements [5], viscosity measurements [7], the constant activity method [8], ultrasonic velocity measurements [9] etc., to study the interaction between the molecules and to obtain the equilibrium constant independently. It is interesting to note that

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although measurements of various thermodynamic excess functions of binary solutions have been the subject of many investigations, hardly any reports on the use of ultrasonic velocity measurements to study the interaction between the molecules in ternary systems and to obtain equilibrium constants and other thermodynamic parameters are available [10,11]. It was, therefore, felt worthwhile to study the interaction between proton donors and acceptors in suitable media using ultrasonic velocity measurements and hence to determine the association constants independently. The systems chosen for such study are: methanol, ethanol, n-propanol, n-butanol (proton donors), acetonitrile (proton acceptor) and carbon tetrachloride (a relatively non-interacting solvent).

MATERIALS AND METHOD

Acetonitrile, carbon tetrachloride, methanol, ethanol, n-propanol and n-butanol were purified by standard procedures. The densities and corrected boiling points agreed well with the literature values [12].

The densities and ultrasonic velocities of/in methanol, ethanol, n-propanol, n-butanol, acetonitrile, carbon tetrachloride and their binary mixtures of varying compositions were determined at 25, 30 35, and 40°C ($\pm 0.01°$) using a pyknometer and a Mittal M-82 multifrequency ultrasonic interferometer at a fixed frequency of 0.8 MHz respectively. Similarly, the densities and ultrasonic velocities of/in alcohol–acetonitrile–carbon tetrachloride ternary systems were determined at the above-mentioned temperatures. Duplicate experiments for each of the systems were carried out and the densities (ρ) and compressibility factors (k_s) were reproducible within the experimental error of ± 0.0003 g cm^{-3} and $\pm 0.13 \times 10^{-12}$ cm^2 dyne^{-1} respectively. The apparent stoichiometries (i.e. the composition at the maximum deviation) of the complexes were determined by Job's method [13].

In liquid mixtures, deviations from ideal behaviour can be interpreted in terms of intermolecular forces operating within the mixtures. Therefore, if we can assume that the deviation is entirely due to the "complex" alone, then the deviation should be proportional to the concentration of the complex. The equilibrium constant K can be obtained by modifying the procedure of Yoshida and Osawa [14]:

$$K = \frac{2\sqrt{k}\left[\sqrt{k}\,(C + C') - (C + kC')\right]}{(C - kC')^2} \tag{1}$$

where k is the ratio of the maximum deviation in any of the physical properties of the systems (in the present case, ultrasonic velocity) for the total concentration of C and C' in two different sets of experiments. (The detailed derivation is given elsewhere [9].) The heat of formation of complexes was obtained from van 't Hoff's equation.

RESULTS AND DISCUSSION

The ultrasonic velocities and densities of methanol, ethanol, n-propanol, n-butanol, acetonitrile and carbon tetrachloride and their binary mixtures were determined at 25, 30, 35 and 40 °C. For the sake of brevity, only the data for methanol–carbon tetrachloride at one temperature only are given in Table 1. The excess compressibility Δk_s for each of the mixtures (e.g. methanol–carbon tetrachloride) was fitted to a smooth equation

$$\Delta k_s = X_1(1 - X_1)\left[A + B(2X_1 - 1) + C(2X_1 - 1)^2\right] \qquad (2)$$

where X_1 is the mole fraction of carbon tetrachloride and A, B and C are fitting parameters (e.g., $A = -24.39$, $B = -32.10$ and $C = -13.74$). It can be seen from the table that the observed velocities (in mixtures) are lower than the calculated (expected) velocities and this deviation indicates that carbon tetrachloride is not an "inert" solvent for alcohol (and acetonitrile). The negative values of Δk_s show that hydrogen-bonded materials are less compressible than their counterparts. This observation goes in parallel with the earlier observations made by spectral and other methods [15]. The deviation ΔV, which is negative, increases in magnitude with an increase in the concentration of methanol up to about 0.66 mole fraction of methanol (i.e. the maximum deviation is at a stoichiometry of 3:2) which is temperature independent (this is the case in other alcohol–carbon tetrachloride systems also). Our present observations (i.e., the apparent stoichiometry) agree well with those of Franks and Ives [16] as well as with those of Matteoli and Lepori [17], who had come to similar conclusions from

TABLE 1

Ultrasonic velocity and related properties in binary liquid mixtures of methanol–carbon tetrachloride at 25 °C

Methanol X_1	CCl$_4$ X_2	ρ [a] (g cm^{-3})	V_{obs} [b] (m s^{-1})	V_{cal} (m s^{-1})	ΔV (m s^{-1})	$k_s \times 10^{-12}$ (cm^2 dyne^{-1})	$\Delta k_s \times 10^{-12}$ (cm^2 dyne^{-1})	Degree of molecular interaction ξ
0.955	0.045	0.8671	1079	1100	−21	99.25	−2.81	0.007
0.905	0.095	0.9481	1052	1090	−38	95.30	−5.10	0.011
0.847	0.153	1.0378	1025	1079	−54	91.71	−7.02	0.018
0.781	0.219	1.1168	1002	1067	−65	89.18	−7.63	0.020
0.704	0.296	1.1946	984	1053	−69	86.45	−8.12	0.025
0.614	0.386	1.2800	966	1036	−70	83.72	−8.21	0.026
0.504	0.496	1.3482	949	1017	−68	82.35	−6.59	0.016
0.374	0.626	1.4337	930	991	−61	80.64	−3.06	0.010
0.209	0.791	1.5217	918	960	−42	77.98	−2.19	0.008

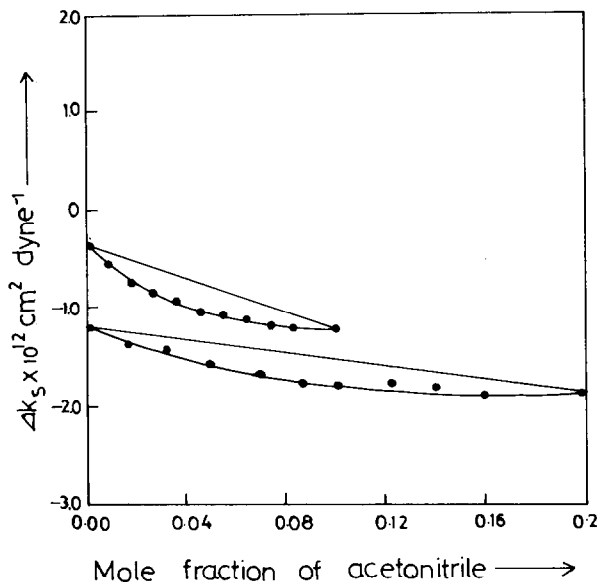[a] Error limit, ± 0.0003.
[b] Error limit, ± 0.5.

Fig. 1. Plot of Δk_s vs. concentration of acetonitrile in the methanol–acetonitrile system (solvent, carbon tetrachloride).

calorimetric studies, but differ from those of Fletcher [18] obtained by a spectral method. Ultrasonic velocity measurements, like calorimetry, require relatively concentrated solutions which may exhibit self-association as well as the formation of more than one hydrogen-bonded species between donor and acceptor molecules. Moreover, the deviation includes a contribution from other intermolecular interactions in solutions. In spectral methods, the concentration of alcohol is very low (mostly monomers). As mentioned above, from the present data (Job's plot), we may be tempted to infer that the stoichiometry of the methanol–carbon tetrachloride "associated species" is 3:2. Here, a word of caution is necessary: the continuous variation method generally gives the correct stoichiometry of the "associated species" formed from the "unassociated species". In the present case, alcohols are dimerized (and also trimerized) and in such cases, the maximum deviation (which is actually at $0.5X$) will not occur at $0.5X$ but at about $0.66X$ [15]. It is quite interesting to note that the deviation in ultrasonic sound velocities ΔV, the excess adiabatic compressibility Δk_s, and the degree of molecular interaction ξ (calculated by the Van Dael method [19,20]) for alcohols and carbon tetrachloride vary in the order, methanol–carbon tetrachloride < ethanol–carbon tetrachloride < n-propanol–carbon tetrachloride < n-butanol–carbon tetrachloride (9:10:11:13). Methanol is a strongly hydrogen-bonded system and the interaction between the alcohol molecules decreases with the increase in alkyl chain length. The solvent, carbon tetrachloride, breaks the self-associated hydrogen bonds and forms a new bond with

TABLE 2

Ultrasonic velocities and adiabatic compressibilities in methanol–acetonitrile of different compositions in carbon tetrachloride at 25 °C (total concentration, $0.1X$) [a]

Methanol	Acetonitrile	ρ [b] $(g\ cm^{-3})$	V_{obs} [c] $(m\ s^{-1})$	V_{cal} $(m\ s^{-1})$	$k_s \times 10^{-12}$ $(cm^2\ dyne^{-1})$	$\Delta k_s \times 10^{-12}$ $(cm^2\ dyne^{-1})$	Degree of molecular interaction ξ
0.100	0.000	1.5581	916	938	76.49	− 0.34	–
0.091	0.009	1.5568	919	940	76.05	− 0.54	− 0.059
0.082	0.018	1.5561	922	941	75.57	− 0.74	− 0.083
0.073	0.027	1.5557	924	943	75.28	− 0.82	− 0.097
0.064	0.036	1.5554	926	945	74.97	− 0.90	− 0.103
0.054	0.046	1.5549	929	946	74.51	− 1.02	− 0.108
0.045	0.055	1.5520	931	948	74.33	− 1.05	− 0.111
0.036	0.064	1.5519	933	950	74.02	− 1.13	− 0.118
0.026	0.074	1.5510	935	952	73.75	− 1.16	− 0.133
0.017	0.083	1.5504	937	954	73.46	− 1.21	− 0.156
0.000	0.100	1.5492	939	955	73.20	− 1.20	− 0.230

[a] $0.9X$ carbon tetrachloride.
[b] Error limit $\pm 0.0003\ g\ cm^{-3}$.
[c] Error limit $\pm 0.5\ M\ s^{-1}$.

alcohol. The extent of new hydrogen-bond formation depends on the relative proton donor–receptor strengths of the competing species. As n-butanol is less self-associated compared with methanol, a n-butanol–carbon tetrachloride "complex" will be formed more easily than a methanol–carbon tetrachloride system. Therefore the interaction between alcohols and carbon tetrachloride (determined from the deviation in k etc.), should increase from methanol–carbon tetrachloride to n-butanol–carbon tetrachloride, and this increase is indeed observed. As the degree of interaction (and the deviation in k_s) decreases with an increase in temperature, we are tempted to conclude that the so-called "sociation constant" between alcohol and carbon tetrachloride decreases with an increase in temperature. The acetonitrile–carbon tetrachloride system also behaves in a similar way.

The ultrasonic velocities and densities of ternary systems, namely, alcohol–acetonitrile–carbon tetrachloride of different compositions (the mole fractions of the alcohol and acetonitrile were varied, keeping the total concentration of them to $0.1X/0.2X$ and that of carbon tetrachloride to $0.9X/0.8X$) were determined at 25, 30, 35 and 40 °C. However, for the sake of brevity, data for only one such ternary system, methanol–acetonitrile–carbon tetrachloride at one temperature, are given in Tables 2 and 3. The non-linear plots of Δk_s vs. the composition of methanol (and the other alcohols) X indicate that alcohols do interact with acetonitrile and the apparent stoichiometry of the "mixed systems" seems to be $1:1$. Loewenstein and Margalit [21] had also arrived at the same conclusion. The

TABLE 3

Ultrasonic velocities and adiabatic compressibilities in methanol–acetonitrile systems of different compositions in carbon tetrachloride at 25°C (total concentration, 0.2X)[a]

Methanol	Acetonitrile	ρ[a] $(g\ cm^{-3})$	V_{obs}[a] $(m\ s^{-1})$	V_{cal} $(m\ s^{-1})$	$k_s \times 10^{-12}$ $(cm^2\ dyne^{-1})$	$\Delta k_s \times 10^{-12}$ $(cm^2\ dyne^{-1})$	Degree of molecular interaction ξ
0.200	0.000	1.5267	916	953	78.06	−1.16	–
0.183	0.017	1.5258	920	957	77.43	−1.34	−0.87
0.166	0.034	1.5238	924	959	76.86	−1.37	−0.103
0.148	0.052	1.5214	928	963	76.32	−1.54	−0.123
0.131	0.069	1.5197	932	966	75.75	−1.65	−0.146
0.113	0.087	1.5169	936	970	75.52	−1.73	−0.170
0.095	0.105	1.5145	940	973	74.72	−1.76	−0.195
0.077	0.123	1.5137	943	977	74.29	−1.75	−0.213
0.059	0.141	1.5112	947	980	73.78	−1.78	−0.256
0.041	0.159	1.5099	951	984	73.23	−1.87	−0.280
0.000	0.200	1.5060	955	987	72.80	−1.89	−0.301

[a] Error limits as in Table 2.

equilibrium constants for methanol–acetonitrile, ethanol–acetonitrile, n-propanol–acetonitrile and n-butanol–acetonitrile in carbon tetrachloride at 25°C (calculated using eq. (1)) are 0.177 M^{-1}, 0.286 M^{-1}, 0.379 M^{-1} and 0.499 M^{-1} respectively. The trend, i.e. the increase in K with the increase in the number of CH_2 groups in the alcohol, is as expected. However, our present values for methanol–acetonitrile in carbon tetrachloride are much lower than the literature data of 1.2 (at 28°C) [22] and 3.0 (at 30°C) [21]. Emslie et al. [2] have rightly pointed out that the effect of a relatively large concentration of D on the absorption of the complex [AD], when [A] ≪ [D] may have its counterparts when [A] ≫ [D]. Thus, for obtaining K by an optical method, the favourable condition should be [A] = [D], which is very rarely met. Person [23], however, has pointed out that for weak complexes, reliable equilibrium constants can be obtained only when the equilibrium concentration of the complex is of the same order of magnitude as the equilibrium concentration of the most dilute component (i.e. the concentration range should be 0.1–9.0 K^{-1}). Unfortunately, in all the spectroscopic methods a very small concentration of donor (but [D] ≫ [A]) has to be used in order to keep the absorbance within the measurable ranges. Takahashi et al. [24] attempted to introduce a "correction term" (due to solvent–solute interaction) in the Benesi–Hildebrand [1] equation which reduces the K values considerably. Thus, it is difficult to compare the equilibrium constants and the other derived thermodynamic parameters obtained by spectroscopic methods with those obtained by non-spectral methods as the former deal with the concentration whereas the latter deal with activities of

TABLE 4

Equilibrium constant K and the other thermodynamic parameters of alcohol–acetonitrile systems in carbon tetrachloride at 25 °C

System	$K_{25 °C}$ [a] (dm^3 mol^{-1})	$-\Delta H°$ [b] (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})	$-\Delta S°$ (kJ mol^{-1})
Methanol–acetonitrile	0.177 (1.2[28 °C]) [c] (3.0[30 °C]) [d]	30.8	4.289	0.117
Ethanol–acetonitrile	0.286	23.6	3.101	0.089
n-Propanol–acetonitrile	0.379	19.8	2.405	0.074
n-Butanol–acetonitrile	0.499	16.0 (10.5) [e]	1.724	0.054

[a] Error limit, ±0.005.
[b] Error limit, ±0.12.
[c] Literature value, see ref. 22.
[d] Literature value, see ref. 23.
[e] Literature value, see ref. 25.

the species. In our investigations, we have varied the concentration of D as well as that of A (i.e. at one stage [D] = [A] and the concentration ranges chosen meet the requirements) and we feel that our values of K obtained by ultrasonic velocity measurements are reasonable.

The heat of formation of the complexes were calculated using the van 't Hoff equation and the results are summarized in table 4. The heat of formation $-\Delta H°$ decreases from methanol–acetonitrile to n-butano–aceto-nitrile, even though the association constant increases in the opposite directions; such trends were reported earlier when an aliphatic alcohol was one of the components in the mixed system [26]. The present values of the heat of formation seem to be a little higher even though they are comparable with the values reported by Touhara and Nakanishi [27] for similar systems. Nagata [28] as well as Murthy et al. [29] had predicted (on the basis of calculation) such high values for the energy of interaction. Here it is to be noted that the heat of complexation must be considered as a composite result for alcohol–acetonitrile–carbon tetrachloride systems of different alcohol aggregates [30]. We do not have any definite model to explain these higher values of $\Delta H°$. However, one possible reason for the high values of $\Delta H°$ is probably the specific and non-specific interactions between the solvent carbon tetrachloride and the donor and acceptor. Touhara and Nakanishi [27] have tried to explain the higher value of $\Delta H°$ for alcohol-pyridine–cyclohexanes in terms of "correction terms" arising from the difference in dipolar stabilization energies. The temperature dependence of the equilibrium constant between donor and acceptor may not be the same as that between donor and solvent and acceptor and solvent owing to the change in solvation number. Carter et al. [31] are of the opinion that the

solvent S has to be included in the association constant

$$(AS_n) + (DS_m) \rightleftarrows (DA \cdot S_p) + qS \tag{3}$$

when n, m and p are the numbers of solvent molecules S around the respective species and q (where $q = n + m - p$) is the number of solvent molecules that are squeezed out on complexation and returned to the bulk solvent. As the temperature is increased, the values of n, m and p will not remain the same and thus will alter the values of K, i.e. the observed decrease in K with increase in temperature is much higher. Therefore, it is not a surprise if we observe higher values of ΔH° from the van 't Hoff plot. The free energy ΔG° in the present case is positive ($K < 1$) and the entropy ΔS° is small and negative. The negative entropy shows that the "complex" is more ordered compared with the free components.

From the present observations, it appears that ultrasonic velocity measurements can be used not only to detect the formation of molecular complexes and hydrogen bonding but can also be used to determine the equilibrium constants even in the case of weakly interacting systems. However, the present procedure, as mentioned earlier, demands very careful measurements of velocities to realize significant differences between the solvent and dilute solutions. In addition, the measurements are very time consuming. However, the method is useful when no alternative is available.

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