The heat capacities and volumes of some low molecular weight amides, ketones, esters, and ethers in water over the whole solubility range

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The densities and heat capacities per unit volume of aqueous solutions of propionamide, methylacetate, ethylacetate, methylethylketone and diethylketone, and bis(2-ethoxyethyl)ether were measured over the whole solubility range with a flow densimeter and a flow microcalorimeter. Most systems were studied at 10, 25, and 40°C. Properties of the pure liquids were also measured whenever possible. The derived apparent molal volumes ϕ_V all decrease with concentration in the water-rich region, except with ethyl acetate which increases at high temperature. In general the more hydrophobic the solute the more negative the initial slope. All apparent molal heat capacities ϕ_C decrease as a function of concentration and the decrease is more important for more hydrophobic solutes. The apparent molal expansibilities ϕ_E are obtained from $\Delta\phi_V/\Delta T$. They are positive for all solutes but, at low concentrations, they are smaller than the corresponding molar value of the pure liquid. Various factors affecting hydrophobic interactions are examined.

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Les masses volumiques et capacités calorifiques des solutions aqueuses de proprionamide, d'acétates de méthyle et d'éthyle, des diéthyl et méthyléthyl cétone et du bis(2-éthoxy éthyl) éther ont été mesurées sur tout le domaine de solubilité avec un densimètre et un microcalorimètre à écoulement continu. La plupart des systèmes ont été étudiés à 10, 25 et 40°C. Lorsque possible les propriétés des liquides purs ont aussi été mesurées. A l'exception de l'acétate d'éthyle, les volumes molaires apparents ϕ_V décroissent avec la concentration dans la région riche en eau et en général les pentes initiales sont plus négatives les plus hydrophobes sont les solutés. Toutes les capacités calorifiques molaires apparentes décroissent en fonction de la concentration et l'effet augmente avec le caractère hydrophobe du soluté. Les expansibilités molaires apparentes ϕ_E, obtenues à partir de $d\phi_V/dT$, sont toutes positives mais sont aux basses concentrations inférieures aux valeurs molaires des liquides purs. Différents facteurs influençant les interactions hydrophobes sont discutés.

Introduction

Recent work in this laboratory (1–3) has been concerned with transitions in aqueous liquid mixtures. Through heat capacity measurements the apparent molal heat capacity ϕ_C of many simple liquids which are completely miscible in water, such as dimethylformamide (4), dimethylsulfoxide (5), and dioxane (6), decreases in a regular way from the standard (infinite dilution) partial molal heat capacity, $\phi_C{}^0 = \bar{C}_p{}^0$, to the molar heat capacity of the pure organic liquid $C_p{}^0$. On the other hand, with some liquids such as *tert*-butylalcohol (1), piperidine (6), triethylamine (7), and 2-*n*-butoxyethanol (3), ϕ_C goes through a maximum and then decreases sharply to $C_p{}^0$. The changes are much sharper if partial molal heat capacities $\bar{C}_p$ are plotted (2) and the concentration dependence of $\bar{C}_p$ suggests the existence of some pseudo-phase transition in the water region analogous to micellization.

The exact reason why some liquid mixtures show these sharp changes in ϕ_C and $\bar{C}_p$ is not clear and could be related to the hydrophobic character, the tendency of these systems to unmix, the geometry of the molecules, or the nature of the polar group on the molecule. The present study was undertaken to throw some light on the importance of some of these factors. Therefore amides, ketones, and esters of similar geometries were examined as a function of temperature and whenever possible over the whole solubility range. A polyether which unmixes at high temperatures was also investigated.

Heat capacities measured by flow microcalorimetry require the simultaneous determination of the solution densities. From the densities, obtained with a flow densimeter, apparent molal volumes ϕ_V were derived, and from their temperature dependence apparent molal expansibilities were calculated, $\phi_E = d\phi_V/dT$.

Experimental

The origin and purification procedure of the chemicals are as follows. Propionamide, from Baker Chemicals, was recrystallized from acetone and dried under vacuum over P_2O_5.

Methylacetate, from Baker Chemicals, ethylacetate and methylethylketone, both from Fisher Scientific (Certified A.C.S.), were used as such. Diethylketone, from Aldrich, was redistilled and the central fraction (30%) was collected. Bis(2-ethoxyethyl)ether, from Baker Chemicals and Eastman Kodak, was redistilled under vacuum with a fine stream of nitrogen.

The purity of all chemicals was verified to be better than 99.8% with vapor phase chromatography on carbowax 20 M at 10% or SE 30 at 10%, and all liquids were kept over 4 Å molecular sieves. All solutions were prepared by weight with distilled deionized water (Continental Deionized Water System).

The densities d and heat capacities per unit volume σ of the solutions were measured relative to pure water, d_0 and σ_0, with a SODEV flow digital densimeter (8) and a Picker flow microcalorimeter (9, 10). Differences in densities $d - d_0$ were measured to $\pm 3 \times 10^{-6}$ g cm^{-3} and differences in heat capacities $\sigma - \sigma_0$ to $\pm 7 \times 10^{-5}$ J K^{-1} cm^{-3}. The flow rate in the microcalorimeter was maintained at about 0.45 cm^3 min^{-1} and the basic power at 21.5 mW causing an increase in temperature during the measurements of 0.7 K. The absolute temperature was determined to ± 0.01 K with a Hewlett-Packard quartz thermometer. The general procedure and uncertainties at other temperatures have been described elsewhere (1, 10).

Results

The apparent molal volumes and heat capacities are calculated in the usual way from the differences in densities $d - d_0$ and specific heat capacities $c_p - c_{p0}$;

$$[1] \qquad \phi_V = \frac{M}{d} - \frac{1000(d - d_0)}{mdd_0}$$

and

$$[2] \qquad \phi_C = Mc_p + \frac{1000(c_p - c_{p0})}{m}$$

where M is the solute molecular weight and m the molality. The data for pure water were taken from Kell (11) and Stimson (12). The difference $c_p - c_{p0}$ is calculated from

$$[3] \qquad c_p - c_{p0} = c_{p0} \left\{ \frac{\sigma - \sigma_0}{\sigma_0} + 1 \right\} \frac{d_0}{d} - c_{p0}$$

where $\sigma_0 = d_0 c_{p0}$.

The original data for Δd and $\Delta \sigma / \sigma_0$ and the derived values ϕ_V and ϕ_C are given elsewhere (13). The measurements were made over the whole mole fraction range whenever the liquids were completely miscible and up to saturation in the other cases. In the dilute range, the apparent molal quantities ϕ_Y can be fitted with an expression of the type

$$[4] \qquad \phi_Y = \phi_Y{}^\theta + A_Y m$$

where Y refers to V or C_p. The linear region where eq. [4] applies varies with the system and temperature. The values of $\bar{V}^\theta$, $\bar{C}_p{}^\theta$, A_V, and A_C, obtained from a least-squares analysis, and the concentration limit of the linear region are given in Table 1. Similar data for other related systems taken from the litera-

ture are also given. The molar values V^0 and $C_p{}^0$ for the pure liquids are also given whenever they were measured.

With bis(2-ethoxyethyl)ether two samples were used. The sample from Baker was taken in the measurements at 25°C and that from Eastman Kodak at 10 and 40°C. Some densities were also repeated at 25°C with the Eastman Kodak chemical and the ϕ_V fell on the same curve as the data obtained with the Baker sample.

Relatively few measurements of densities were made previously over the whole concentration range with the present aqueous systems. On the other hand some relatively good $\bar{V}^\theta$ and V^0 are available at 25°C in the literature and can be used to verify the accuracy of the present measurements.

For proprionamide $\bar{V}^\theta$ was determined by Herskowits and Kelly (14) as 70.9 cm^3 mol^{-1} and by Dunstan and Mussell (15) as 71 cm^3 mol^{-1}. Shahidi et al. (16) calculated $\bar{V}^\theta$ from the intrinsic volumes of the solute and interaction terms taking into account the geometry of the molecule and found, depending on the relation used, to be 72.0 or 71.3 cm^3 mol^{-1}. The present $\bar{V}^\theta$, 71.47 cm^3 mol^{-1}, agrees with these values.

For ethyl acetate Edwards et al. (17) obtained 88.8 $\pm$ 0.3 cm^3 mol^{-1} compared with the present 88.97 cm^3 mol^{-1}. The densities of pure ethyl acetate were also studied by various authors (18) and the present V^0 agrees inside the experimental uncertainty with these.

Methylethylketone was studied by Bøje and Hvidt (19) and by Edwards et al. (17). Their $\bar{V}^\theta$ values (82.5 and 82.9 cm^3 mol^{-1} respectively) are comparable with the present value of 82.52 cm^3 mol^{-1} Bøje and Hvidt also determined ϕ_V over the whole mole fraction range and their data, inside their quoted uncertainty, agree with ours. The suggested value for V^0, 90.14 cm^3 mol^{-1} is identical to ours.

Edwards et al. (17) obtained 165.0 $\pm$ 0.3 cm^3 mol^{-1} for $\bar{V}^\theta$ of bis(2-ethoxyethyl)ether which compares with the present value of 164.16 cm^3 mol^{-1}.

The precision of the $\bar{V}^\theta$ data is of the order of ± 0.05 cm^3 mol^{-1} and the generally good agreement with literature data fixes the accuracy at ± 0.5 cm^3 mol^{-1} or better.

To our knowledge there are no data in the literature on the heat capacities of the present organic aqueous mixtures. Pure methylethylketone was studied as a function of temperature by Sinke and Oetting (20) and by Andon et al. (21) and their $C_p{}^0$ are in good agreement with ours at 25°C but significant differences (a few percent) are observed at other temperatures. However, the generally good agreement of $\bar{V}^\theta$ and V^0 with the literature and the proven

TABLE 1. Apparent molal volumes and heat capacities of several solutes in water

Solute	T (°C)	$\bar{V}^{\theta}$ (cm³ mol⁻¹)	A_V (cm³ mol⁻² kg)	Max mol (mol kg⁻¹)	V^0 (cm³ mol⁻¹)	$\bar{C}_p^{\theta}$ (J K⁻¹ mol⁻¹)	A_C (J K⁻¹ mol⁻² kg)	Max mol (mol kg⁻¹)	C_p^0 (J K⁻¹ mol⁻¹)
Acetamide*	25	55.61	−0.12			162.4	−1.4		
Propionamide	25	71.47	−0.33	1		253.6	−4.5	2.5	
Methylacetate	25	72.46	−0.10	0.7	80.10	298.2	−15.5	1.2	
Ethylacetate	10	87.35	−0.60	0.6	96.53	409.6	−23.4	0.9	164.2
	25	88.97	+0.08	0.9	98.50	396.6	−22.1	0.9	169.5
	40	90.72	+0.46	0.8	100.58	390.9	−30.8	0.8	173.9
Acetone*	25	66.92	−0.37			240.5	−7.6		
Methylethylketone	4	80.83	−1.49	0.55	87.74	335.3	−17.5	1.5	152.8
	10	81.33	−1.41	0.55	88.40	335.8	−13.1	2.5	153.4
	25	82.52	−0.75	0.55	90.14	336.6	−10.4	2	158.4
	40	83.60	−0.11	1	91.95	335.1	−9.7	1	161.6
Diethylketone	25	98.08	−1.10	0.5	106.43	428.3	−18.0	0.5	
Bis(2-ethoxyethyl)- ether	10	162.72	−4.50	0.5	176.95	693.7	−39.2	2	344.7
	25	164.16	−2.21	0.6	179.59	697.8	−16.7	1.5	347.5
	40	166.49	−1.73	0.3	182.55	703.6	−8.5	1.3	352.0
2 Methoxyethanol†	25	75.11	−0.47	0.8	79.25	286.7	−8.7	4	176.4
2 Ethoxyethanol†	25	90.97	−0.86	0.6	97.15	383.5	−11.7	3.4	210.3

*Reference 31.
†Reference 3.

reliability of the flow microcalorimetric technique for the measurement of heat capacities lead us to believe that the present data on ϕ_C are accurate to 1 J K⁻¹ mol⁻¹ or better, at least in the water-rich region.

Discussion

Standard Quantities

The standard partial molal quantities $\bar{C}_p^{\theta}$ and $\bar{V}^{\theta}$ are useful in predicting the temperature and pressure dependence of equilibrium quantities and give information on solute–solvent interactions. For this purpose it is important to develop additivity schemes from which the properties of complex molecules can be predicted from those of simpler ones. Data exist in the literature on $\bar{V}^{\theta}$ of ketones, ethers, esters, and amides in water but little is known about their $\bar{C}_p^{\theta}$.

Various additivity schemes (16, 17, 22–25) have been proposed recently for $\bar{V}^{\theta}$ and $\bar{C}_p^{\theta}$. Nichols et al. (22) have made a fairly exhaustive study of $\bar{C}_p^{\theta}$ of molecules of biological interest and Perron and Desnoyers (23) made a similar study of aromatic molecules. The main difference in these two schemes lies in the value given to the H atom. The scheme of Perron and Desnoyers is an extension of the approach of Jolicoeur and Lacroix (24) and has the advantage of being applicable to $\bar{V}^{\theta}$ also. Recently Guthrie (25) has proposed a much more sophisticated group additivity scheme which can in principle yield a much better agreement between the predicted and experimental $\bar{C}_p^{\theta}$ but requires up to 49 parameters. With the present state of knowledge it is better to concentrate on the simpler additivity schemes of Nichols et al. and of Perron and Desnoyers. Also Edwards and co-workers (16, 17) have

proposed a relatively simple theory for the prediction of $\bar{V}^{\theta}$ from van der Waals volumes corrected for void space and interactions, but this is not, strictly speaking, an additivity scheme.

The main group contributions to $\bar{C}_p^{\theta}$ and $\bar{V}^{\theta}$ of Nichols et al. and Perron and Desnoyers are summarized in Table 2. Assuming these contributions correct, average values for the
$$\overset{O}{\underset{\|}{-C-}},\quad \overset{O}{\underset{\|}{-CO-}},\quad \text{and}$$
$$\overset{O}{\underset{\|}{-CNH_2}}$$
group were derived and are also given in Table 2. The average deviations between the calculated and measured $\bar{C}_p^{\theta}$ and $\bar{V}^{\theta}$ for the data in Table 1 are 5 J K⁻¹ mol⁻¹ for the $\bar{C}_p^{\theta}$ schemes of both Nichols et al. and Perron and Desnoyers and 0.5 cm³ mol⁻¹ for the $\bar{V}^{\theta}$ scheme of Perron and Desnoyers. The agreement is worse with the molecules which contain more than one polar group, e.g., with the polyether. This has been noted before (22, 26).

The expansibilities $\bar{E}^{\theta}$ can be estimated from $\Delta \bar{V}^{\theta}/\Delta T$ and for ethyl acetate, methylethylketone, and bis(2-ethoxyethyl)ether the values are found to be 0.112, 0.076, and 0.126 cm³ K⁻¹ mol⁻¹, respectively, at 25°C. On the other hand, if we calculate $\bar{E}^{\theta} - E^0$, the values are now −0.022, −0.046, and −0.060. This indicates that the expansibility of an organic molecule surrounded by water is less than that of an organic molecule surrounded by similar organic molecules. This is consistent with models which suggest that hydrophobic hydration occurs with a reduction of free space near the solute.

TABLE 2. Group contributions to $\bar{C}_p^\theta$ and $\bar{V}^\theta$ of aliphatic molecules at 25°C

Group	$\bar{C}_p^\theta$ (Wadsö) (J K^{-1} mol^{-1})	$\bar{C}_p^\theta$ (Perron) (J K^{-1} mol^{-1})	$\bar{V}^\theta$ (Perron) (cm^3 mol^{-1})
—CH$_3$	157	178	26.7
—CH$_2$	90	88	16.0
—H	67	90	10.7
$\overset{O}{\underset{\|}{—C—}}$	-67	-105	13.1
$\overset{O}{\underset{\|}{—CO—}}$	-10	-50	19.4
—OH	-4	12	12
—CONH$_2$	5	-14	28.8
—O—	-57	-72	4.1

Depending on the solute, the values of $\bar{C}_p^\theta$ increase or decrease with temperature. On the other hand $\bar{C}_p^\theta - C_p^0$ decreases with temperature with most systems suggesting that hydrophobic hydration is largest near the freezing temperature of water. Bis(2-ethoxyethyl)ether is an exception to this rule since $\bar{C}_p^\theta - C_p^0$ is approximately independent of T.

Concentration Dependence

The main objective of the present study was to examine some of the factors that could influence the concentration dependence of ϕ_C and ϕ_V of organic molecules in water. Some amines and alcohols show anomalous ϕ_C or $\bar{C}_p$ which suggests the existence of transitions similar to micellization although molecules like *tert*-butylalcohol and triethylamine could hardly be considered surfactants. The maximum observed in the ϕ_C of these molecules occurs around 0.05 mole fraction and is very temperature dependent. Unfortunately much of the data in the literature were aimed at deriving additivity schemes and were limited to 25°C and low concentrations or else were aimed at the measurement of excess functions and only mole fractions between 0.1 and 0.9 were considered. In order to throw some light on this problem ϕ_C and ϕ_V of a series of ketones, esters, amides, and ethers of similar geometries and sizes are compared in Fig. 1. The initial slopes are given in Table 1. With all these solutes A_C is negative and the order is very nearly inversely proportional to the value of $\bar{C}_p^\theta$. In none of these systems do we observe maxima in ϕ_C as in the case of alcohols (1), some amines (6, 7), and larger alkoxyethanols (3). It would therefore appear that with the present system the leading effect giving the sign and magnitude of A_C is the reduction of hydrophobic hydration as the concentration increases. This is consistent with the destructive co-sphere overlap models (7).

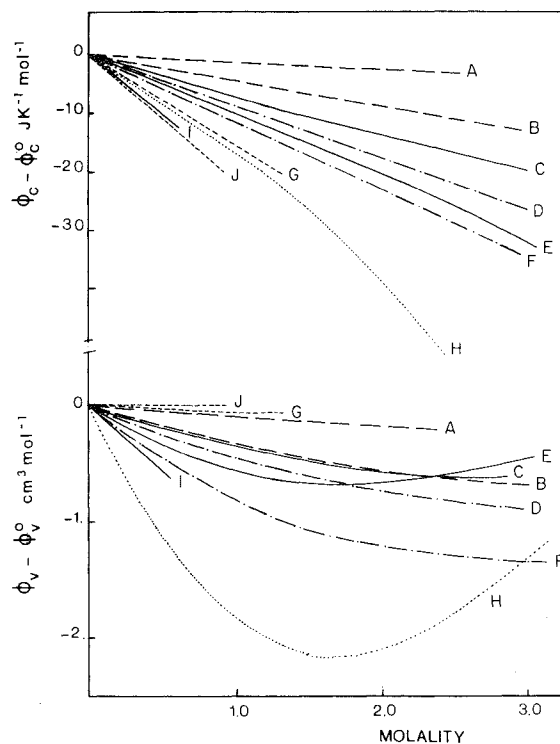The parameter A_V follows the same order as A_C

FIG. 1. Apparent molal heat capacities and volumes of various polar solutes in water in the water-rich region at 25°C: A, acetamide; B, propionamide; C, acetone; D, 2-methoxy-ethanol; E, methylethylketone; F, 2-ethoxyethanol; G, methyl-acetate; H, bis(2-ethoxyethyl)ether; I, diethylketone; J, ethyl acetate.

with the exception of the two esters. The volumes have the general trends of most organic liquids in water; ϕ_V decreases with concentration and, if the solubility is high enough, goes through a minimum and reaches a value V^0 which is larger than $\bar{V}^\theta$. The temperature dependence of ϕ_C and ϕ_V of ethyl acetate is shown in Fig. 2. As seen the initial slope A_V is even positive at 40°C. At present we have no explanation for the anomalous concentration dependences of ϕ_V of the esters.

The concentration dependence of ϕ_C and ϕ_V of methylethylketone at various temperatures is given in Fig. 3. Here the trends are fairly typical of this class of solutes except for 40°C. A_C and A_V are negative and become less negative as the temperature increases. Also, except at high temperature, ϕ_V goes through a minimum.

The present investigation therefore shows that the maximum in ϕ_C is not a general effect since most types of molecules do not show any anomalous concentration dependence. With alcohols, amines and amine salts (27) additional interactions, such as hydrogen bonding, could be responsible for the positive contribution to ϕ_C.
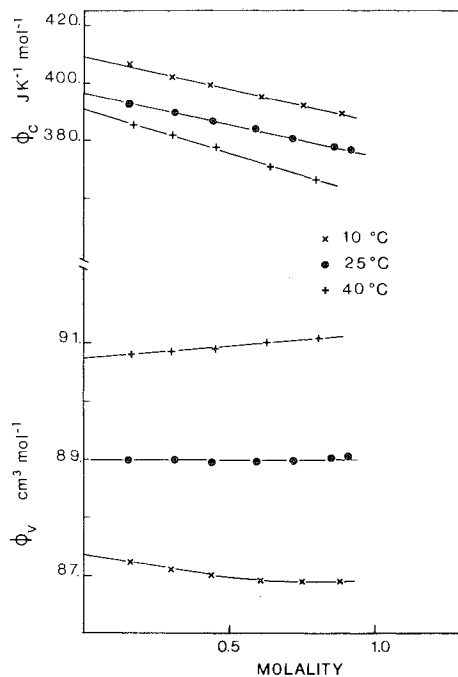
FIG. 2. Apparent molal heat capacities and volumes of ethyl acetate at various temperatures.
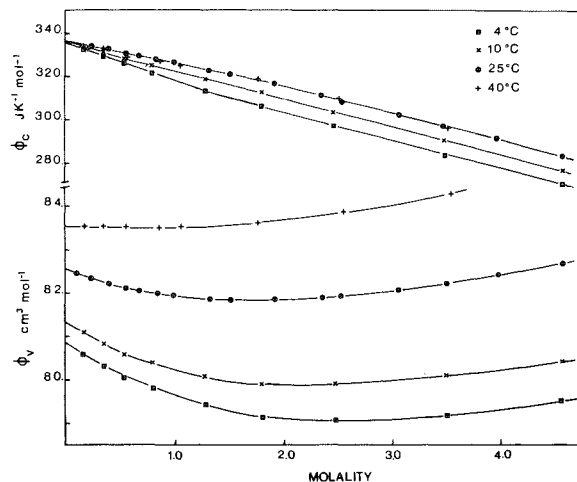

FIG. 3. Apparent molal heat capacities and volumes of methylethylketone at various temperatures.
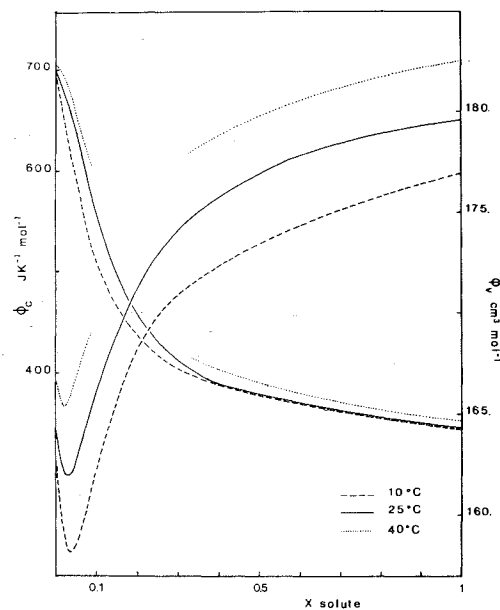
FIG. 4. Apparent molal heat capacities and volumes of bis(2-ethoxyethyl)ether at various temperatures.

The ϕ_C and ϕ_V of bis(2-ethoxyethyl)ether was investigated since this aqueous system shows a lower critical solution temperature at 28°C (28, 29). It is therefore possible to study its properties very close to the unmixing region. The ϕ_C and ϕ_V are plotted against the mole fraction at temperatures above and below the critical solution temperature in Fig. 4. Although the initial slopes A_V and A_C fall in a general pattern with the other liquid mixtures (Fig. 1), the large drop in ϕ_C and large increase in ϕ_V beyond the minimum suggests that a transition is occurring beyond 0.05 mole fraction. In this respect this ether resembles alcohols, etheralcohols, amines, and carboxylic acids at high concentration. The $\bar{C}_p$ and $\bar{V}$ rapidly tend to the values of C_p^0 and V^0 beyond 0.1 mole fractions indicating that an additional molecule will only see other ether molecules when added to the solution. On the other hand there is no anomaly in ϕ_C in the water-rich region contrary to alcohols and amines. ϕ_C decreases in a regular way to C_p^0. The slight hump in the concentration dependence of ϕ_C at high temperature does not appear very significant. On the other hand, if ϕ_C is plotted against the volume fraction X_V (Fig. 5), a different picture emerges. It was shown that with liquids such as dimethylformamide (7) ϕ_C is nearly linear in volume fraction. Therefore, if we consider the straight line between $\phi_C - \phi_C^\theta$ and C_p^0 as the ideal behavior, then it seems that the anomalies occur

mainly in the water-rich region and increase with temperature.

The most interesting feature of bis(2-ethoxyethyl)-ether is that data were obtained very close to the phase separation region. At 25°C we are at 3° from the lower critical solution temperature and at 40°C measurements were made on both sides of the phase diagram. All these data near the two phase region are qualitatively very similar to the data at lower temperatures and a smooth curve can be drawn joining the data points at 40°C (see Figs. 4 and 5). This was also observed with 2-butoxyethanol (3).
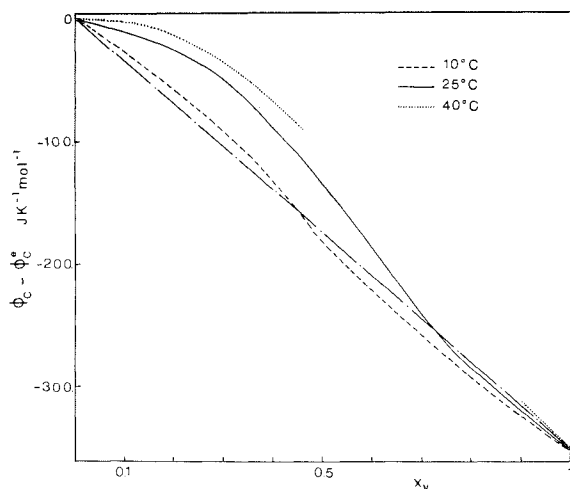
FIG. 5. Apparent molal heat capacities of bis(2-ethoxy-ethyl)ether as a function of volume fraction at various temperatures.

The positive deviation observed in Fig. 5 at high temperature might be due to anomalous energy fluctuations near the two phase region but these deviations are certainly small compared with those observed with alcohols, etheralcohols, and amines (1–3, 6, 7). This does not rule out the possibility that pseudo-transitions in aqueous organic mixtures may be related to the existence of an *upper* critical solution temperature since recent studies (30) suggest that 2-butoxyethanol has such a critical temperature below 0°C and the anomalies in ϕ_C are largest at the lowest temperature investigated (2, 3).

Since ϕ_V data are available as a function of temperature and concentration it is possible to calculate ϕ_E as a function of concentration. This was done in Fig. 6 for bis(2-ethoxyethyl)ether and methylethyl-
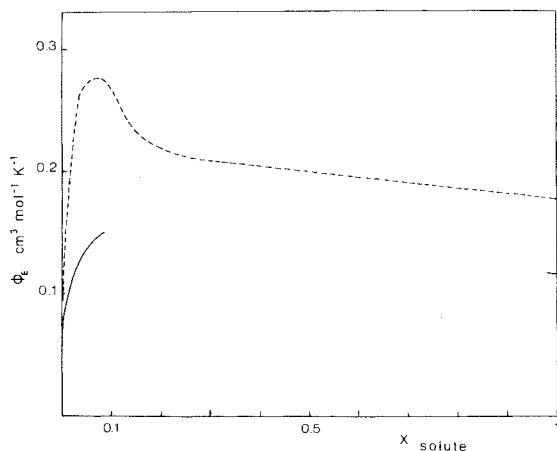

FIG. 6. Apparent molal expansibilities of bis(2-ethoxy-ethyl)ether (---) and methylethylketone at 17.5°C.

ketone at 17.5°C. These have the same general shape as alcohols in water (1, 3) although the maximum is not quite as sharp.

The present study eliminates some of the possible factors that could be responsible for the anomalous concentration dependence of ϕ_C of some organic molecules or ions in water. Polar molecules which do not contain alcohol or amine (and possibly carboxyl) groups show little anomaly. Also there is no increase in anomaly near the lower critical solution temperature. The hydrophobic character certainly plays an important role in this non-ideality and it is quite possible that the existence of strong hydrogen bonding or ionizing groups like alcohols and amines enhances the solubility of hydrophobic molecules more than other polar groups. On the other hand bis(2-ethoxyethyl)ether appears to be more hydrophobic than *tert*-butylalcohol or butoxyethanol but its non-ideality is much smaller.

The geometry of the molecules probably has some influence on the non-ideality but this effect has not been properly investigated yet.

Finally the maximum and the large decrease in ϕ_C is certainly related to some structural changes taking place in the solution. Heat capacity is related to the shift in equilibrium of the system during a unit increase in temperature. This shift in equilibrium contribution to ϕ_C will probably be larger if the corresponding changes in enthalpies are large. For example, current work on the enthalpy of dilution of 2-butoxyethanol in water indicates that the increase in relative enthalpy is very large with this system in the region where ϕ_C shows extrema. Unfortunately not sufficient data are available at present on the enthalpy of other organic aqueous mixtures in the water-rich region to establish such a correspondence.

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