

Solubilities of *n*-Butane Gas and Densities for Acetone–Methanol, Acetone–Ethanol, and Acetone–Propanol Solvent Solutions

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Solubilities of *n*-butane gas are reported for atmospheric pressure and 298.15 K in the mixed solvent solutions composed of acetone–methanol, acetone–ethanol, and acetone–1-propanol. These solubilities are compared with the solubility of *n*-butane in acetone–1-butanol mixed solvent solutions reported earlier. The densities and excess volumes for the complete composition range of the *n*-butane-free, mixed solvent solutions are also reported.

Introduction

In this paper the results of a systematic study of the solubility behavior of a gas in two-component, polar and associating solvent solutions are reported. It is considered that only a relatively few such experimental studies have been made for nonaqueous solvent solutions. Such information may be of theoretical as well as practical usefulness. Various kinds of complex solubility behavior may be found in mixed solvent solutions in which some degree of molecular association occurs. For example, a distinct maximum in the solubility–concentration curve for acetylene is observed in butanol–ethylene glycol solutions at 298.15 K as previously reported (1). In contrast the solubility of the same gas, acetylene, is essentially linear when plotted as a function of solvent concentration for the nonpolar solvent solutions composed of *n*-hexane and *n*-hexadecane (1). An equation for gas solubility in ideal mixed solvent solutions based on the development of Hildebrand et al. (2) is as follows:

$$\ln x_{1,\text{ideal mix}} = \phi_2 \ln x_{12} + \phi_3 \ln x_{13} \quad (1)$$

One may then consider that deviations from ideality are expressed by

$$\Delta \ln x_{1,\text{mix}} = \ln x_{1,\text{mix}} - \phi_2 \ln x_{12} - \phi_3 \ln x_{13} \quad (2)$$

Hence, it is possible to determine some measure of the direction and extent of deviation of the solubility from ideal behavior.

In this work solubilities of the highly soluble gas, *n*-butane, are reported for 298.15 K and 101.325 kPa pressure in the mixed solvent solutions of acetone–methanol, acetone–ethanol, and acetone–1-propanol; data for the solubilities of *n*-butane in acetone–1-butanol solutions were recently reported (3). Strong molecular interactions may be expected for these solvent solutions; an azeotrope is observed for an acetone–methanol solution (4), although, to our knowledge, none have been reported for solutions of the higher alkanols and acetone. In certain cases density or volume measurements for liquid solutions may be used to indicate the degree of molecular interaction. For example, the decrease in volume when specific volumes of ethanol and water are mixed may be considered to indicate that a strong attraction between the two types of molecules exists. It is of interest to test whether acetone–alkanol solutions have strong molecular interactions which can be detected by accurate density measurements. To this end

we have measured the densities of the acetone–alkanol solutions at 298.15 K for the complete concentration range from pure acetone to pure alcohol.

When two liquids are mixed an "ideal" specific volume is estimated on the basis that there is no volume change on mixing:

$$v_{\text{ideal}} = (\phi_2 \rho_2 + \phi_3 \rho_3)^{-1} \quad (3)$$

The deviation from the ideal solution volume, normally termed the excess volume, is then

$$V^E = v - (\phi_2 \rho_2 + \phi_3 \rho_3)^{-1} \quad (4)$$

When accurate densities are available for two pure liquids and for the solutions composed of these liquids, excess volumes can be calculated to express the deviations from ideal solution behavior. In turn, deviations from ideal solution behavior may be interpreted in terms of the intermolecular forces between the liquids concerned.

Experimental Section

The solubilities of *n*-butane were measured in the mixed solvent solutions by using a method previously described (3). It involved first charging a specific amount of the less volatile solvent component in the equilibration cell and degassing it, and then charging a specific volume of the (degassed) second, more volatile component, from a measuring buret. Finally it involved saturating the mixed solvent solution by exposure to *n*-butane gas supplied at constant pressure and by vigorous mechanical agitation of the equilibration cell. The quantity of each solvent component and of dissolved *n*-butane was accurately determined by weight. First the empty cell was weighed, then the cell and contents were weighed twice more after the addition of each solvent component, and finally yet a fourth time after equilibration was complete. Because the mass of each component in the cell could be accurately determined, accurate solubility determinations were possible. The actual quantity of dissolved *n*-butane in the cell ranged from 1 to 4 g in the Pyrex-glass cell whose volume was 70 mL. Further details of the equipment and procedure have been previously described (3).

The reproducibility of replicate solubility measurements was usually within 0.2%. It is considered that because the results were highly reproducible and the measurements involved were of high precision the accuracy of the measurements is at least 1%. Results obtained by using the same method were previously found to compare favorably with those of other workers (3). The amounts of each solvent, and of the dissolved gas were obtained to 0.1 mg, the temperature was measured to within 0.05 K, and the pressure was measured by manometer to 0.1 mm of mercury.

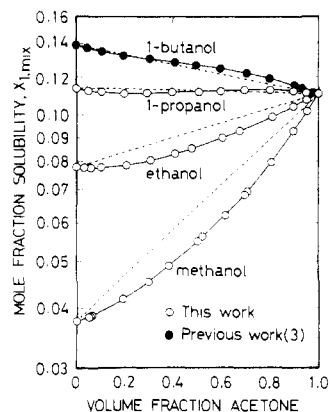
The *n*-butane gas, and solvents, were obtained from Chugoku Kasei and Nakarai Chemicals, respectively. The minimum purity of the *n*-butane was specified to be 99 vol % while the minimum purity for the solvents was 99.6 vol % for the methanol and 99.5 vol % for the remaining solvents. The properties of the solvents necessary for the calculation of solubilities were

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Table I. Solubility of *n*-Butane in Acetone-Alkanol Solutions at 298.15 K and a *n*-Butane Partial Pressure of 101.325 kPa

ϕ^a	$x_{1,mix}$	ϕ^a	$x_{1,mix}$	ϕ^a	$x_{1,mix}$
Methanol		Ethanol		1-Propanol	
0	0.037 63	0	0.078 25	0	0.1138
0.0508	0.038 38	0.0325	0.078 06	0.0503	0.1123
0.0565	0.038 49	0.0615	0.077 89	0.1052	0.1117
0.0653	0.038 63	0.1037	0.077 94	0.1983	0.1107
0.1905	0.041 79	0.2065	0.078 69	0.2915	0.1111
0.2949	0.045 31	0.3066	0.080 72	0.3959	0.1114
0.3829	0.048 89	0.4046	0.083 21	0.5043	0.1115
0.5000	0.054 86	0.4746	0.085 32	0.5972	0.1122
0.5202	0.056 17	0.6024	0.089 91	0.6933	0.1125
0.6146	0.062 04	0.6736	0.092 78	0.8002	0.1125
0.6912	0.068 46	0.8078	0.099 14	0.8975	0.1121
0.7059	0.069 94	0.8955	0.104 2	0.9498	0.1115
0.8031	0.080 04	0.9496	0.108 0	1	0.1108
0.8967	0.092 75	1	0.110 8		
0.9507	0.102 0				
1	0.110 8				

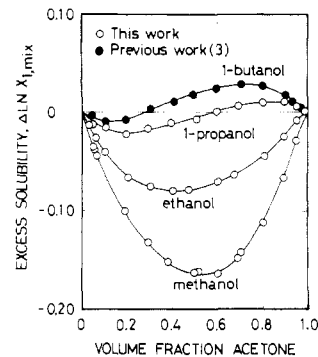
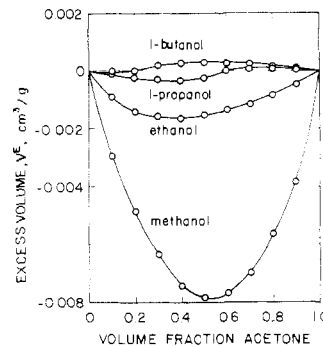
^a Volume fraction acetone, butane-free.**Figure 1.** Solubility of *n*-butane in acetone-alcohol mixtures at 298.15 K and 101.325 kPa.

obtained from literature sources (5–8).

The mixed solvent solution densities were measured at 298.15 K by using a new model of an Anton Paar digital densitometer Model DMA 60 (Austria), capable of providing densities of high accuracy (9). The densities of distilled water and ethanol were used to calibrate the densitometer since two densities are required and these are known to a high accuracy. In the process of measuring the densities care was taken to ensure that no bubbles of gas were entrapped in the densitometer tube and that the temperature of the sample reached the control temperature of 298.15 ± 0.02 K. The compilation of Wilhoit and Zwolinski (10) was used as a source of density data for the alcohols. The density for acetone as obtained from the recent literature (11) was used for comparison. The solvents used for the density determinations were purchased from Aldrich Chemicals and had the following specified minimum purities: methanol 99.9%, ethanol 99.9% (absolute), 1-propanol 99.0%, 1-butanol 99.9%, and acetone 99.5%. The mixed solvent solutions were prepared by using a combination of two precision burets of small (10 mL) and large (25 mL) capacities for each solvent to permit accurate measurements of even small volumes of solvent. The burets and flasks used for storing the solvent solutions were sealed to avoid exposure to the air because of possible contamination with water vapor.

Results and Discussion

The solubilities of *n*-butane in the mixed solvent solutions of acetone-methanol, acetone-ethanol, and acetone-1-propanol are listed in Table I and shown in Figure 1 for a pressure of

**Figure 2.** Excess solubility of *n*-butane in acetone-alcohol mixtures at 298.15 K and 101.325 kPa.**Figure 3.** Excess volumes for acetone-alcohol solutions at 298.15 K and 101.325 kPa.

101.325 kPa and a temperature of 298.15 K. The solubilities of *n*-butane in the acetone-1-butanol solvent solutions as reported earlier (3) are also shown in Figure 1 for comparison. The order of solubilities in the alkanols was discussed earlier (3). The lowest solubility of *n*-butane was expected to occur for methanol, the most associated solvent while progressively increasing for the alkanols ethanol, 1-propanol, and 1-butanol as the associating tendency diminished. It may be observed from Figures 1 and 2 that a further reduction in solubility is observed especially for acetone-methanol, below that expected for an ideal mixed solution (dotted lines in Figure 1). Excess solubilities of *n*-butane, as defined by eq 2, are graphically represented in Figure 2. The reduction in solubility of *n*-butane in the methanol-acetone solvent solutions suggests that methanol and acetone may form association complexes in addition to those formed in the pure solvents to an extent that the solubility is inhibited in these solvent solutions. To a somewhat lesser extent a similar reduction in solubility of *n*-butane also occurs in ethanol-acetone solutions. Here also a degree of molecular association is considered to occur between the two solvent components. For the propanol-acetone and butanol-acetone solvents, however, a different phenomenon is observed. First of all, only a small effect on the solubility of *n*-butane is observed for these slightly associated solvents. Second, and of greater consequence, for the alcohol-rich solvent compositions a reduction in the solubility is observed while an increase is observed for the acetone-rich solvent compositions, when compared with expected solubilities in an ideal solvent mixture. One may consistently interpret the decrease in solubility in the alcohol-rich solvents as the result of an increase in the extent of molecular association and conversely, the slight increase in solubility in the acetone-rich solvents as the result of a decrease in the extent of molecular association. Usually such a hypothesis is difficult to substantiate in any way; in this instance, however, the accurate density measurements made for the solvent solutions have yielded results which are consistent with, and are considered to strongly support, the hypothesis made.

Table II. Densities and Excess Volumes at 298.15 K for Solutions of Acetone-Methanol, Acetone-Ethanol, Acetone-1-Propanol, and Acetone-1-Butanol

vol fraction acetone (ϕ)	acetone-methanol		acetone-ethanol	
	ρ , kg/m ³	V^E , m ³ /kg	ρ , kg/m ³	V^E , m ³ /kg
0.0	786.55	0	785.09	0
0.1	788.24	-2.94	785.64	-0.87
0.2	789.30	-4.87	785.98	-1.41
0.3	790.09	-6.35	786.09	-1.57
0.4	790.62	-7.42	786.14	-1.63
0.5	790.74	-7.83	786.08	-1.51
0.6	790.52	-7.70	785.99	-1.35
0.7	789.94	-6.99	785.87	-1.14
0.8	788.97	-5.65	785.69	-0.83
0.88	787.74	-3.84		
0.9	787.44	-3.40	785.49	-0.49
1.0	785.20	0	785.20	0

vol fraction acetone (ϕ)	acetone-1-propanol		acetone-1-butanol	
	ρ , kg/m ³	V^E , m ³ /kg	ρ , kg/m ³	V^E , m ³ /kg
0.0	799.62	0	805.70	0
0.1	798.23	-0.08	803.62	-0.05
0.2	796.85	-0.18	801.53	0.11
0.3	795.43	-0.22	799.32	0.36
0.4	794.00	-0.24	797.21	0.46
0.5	792.49	-0.13	795.14	0.49
0.6	790.90	0.11	793.10	0.48
0.7	789.44	0.14	791.08	0.43
0.8	788.00	0.14	789.10	0.32
0.9	786.59	0.08	787.14	0.18
1.0	785.20	0	785.20	0

The results for the density measurements for the acetone-alkanol solutions for a temperature of 298.15 K are given in Table II. The excess volumes based on eq 4 are shown graphically in Figure 3. It was possible to determine excess volumes with some degree of accuracy because the densities were determined to a precision of five figures and with an accuracy of at least 0.01%. The resulting similarity between the excess volume diagram (Figure 3) and the excess solubility diagram (Figure 2) is most striking. Such a surprising similarity suggests that the same factors which contribute to a reduction in solvent solution volume (or increase in solution density) also contribute to a reduction in gas solubility in the mixed solvent solutions. Hence the hypothesis that a high degree of molecular association in the mixed solvent solutions results in a reduced solubility of *n*-butane as well as a solution of higher density appears to have strong support from the density measurements. It is not usually possible to observe a measurable effect of molecular association in a solution; however, when there is a change in the degree of association with composition in a two-component solvent solution as in this case, it becomes possible to measure the effect of such a change. It was with great interest and anticipation therefore that we measured the mixed solvent solution densities. The results seem to strongly support the hypothesis, first, that molecular association occurs to a varying degree in acetone-propanol and acetone-butanol solutions, and next, that the molecular association in the solvents has a direct effect on the solubility of gases in them.

It is expected that, because they are relatively simple to perform, accurate density measurements will be used more frequently in the future to indicate changes in certain solution properties such as the degree of molecular association. It was initially considered that the azeotropic composition for a solution of acetone and methanol might have been indicated by density measurements for the solution; however, no significant density

changes were observed in the density-composition relation.

Finally, it is noted that the density of acetone at 298.15 K as reported here (785.20) is slightly lower than that reported earlier (785.30 (1)). It is also noted that the densities of propanol and butanol as reported here (799.62 and 805.70, respectively) are also slightly lower than those reported by Wilhoit and Zwolinski (10) (799.75 and 806.0). In these experiments using solvents of relatively high purity for the density measurements it was found that the densities progressively *increased* on exposure to air, and equalled or exceeded the higher densities previously reported on exposure to air from 1 to 3 h. It appears possible that the slightly higher densities previously obtained are the result of absorption of water vapor from the air. In addition, a lower purity of butanol whose density was measured (99.0%) yielded a density of 806.0, suggesting that the impurity may have been of a higher density than that for the butanol itself.

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Glossary

V_{ideal}	volume of solution formed with no volume change on mixing, m ³ /kg
v	actual volume of solution, m ³ /kg
V^E	excess volume, $v_{\text{real}} - v_{\text{ideal}}$, defined by eq 4, m ³ /kg
X_{12}	mole fraction solubility of butane in one pure solvent component
X_{13}	mole fraction solubility of butane in a second pure solvent component
$X_{1,\text{ideal mix}}$	mole fraction solubility of butane in an ideal mixed solvent solution containing two solvent components
$\Delta \ln X_{1,\text{mix}}$	excess solubility of butane in a mixed solvent solution defined by eq 2
ρ_i	density of one of two solvent components, kg/m ³
ϕ_i	volume fraction of a solvent component in a butane-free solvent solution

Subscript

i one of two solvent components, 1 or 2

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; acetone, 67-64-1; *n*-butane, 106-97-8.

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